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Blue Thermally Activated Delayed Fluorescence OLEDs: towards improved performance

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Blue Thermally Activated Delayed Fluorescence OLEDs: towards improved performance

Kleitos Stavrou



A Thesis Presented for the Degree of Doctor of Philosophy

Organic Electroactive Research Group

Department of Physics

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Abstract

Organic molecules are inherently complex entities, their intricacies often veiled from direct observation. Both theoretical and experimental approaches tirelessly endeavour to illuminate their elusive 'dark' side, yet unveiling their mysteries remains a formidable challenge. This work specifically delves into organic light-emitting molecules, focusing on thermally activated delayed fluorescence (TADF) emitters. Light serves as the key tool to indirectly peek into their behaviour. By exciting these TADF molecules with light, time-resolved 'snapshots' of their relaxation from the excited to the ground state are obtained. Through analysis of these 'snapshots,' patterns emerge, holding valuable information such as molecular conformations, quantized energy (sub)levels in the excited and ground state(s), homo- and hetero-molecular interactions. Furthermore, this analysis facilitates the estimation of exciton kinetics within the studied system, whose aim is to efficiently harness its energy and release it in the form of light. This thesis integrates this experimental approach to explore fundamental aspects of TADF and multiple-resonance (MR)-TADF emitters in guest host systems, alongside organic light-emitting diode (OLED) fabrication and engineering. Its ultimate goal is to address the Achilles' heel of OLEDs by enhancing blue OLED performance.

Current OLED technologies predominantly rely on fluorescent and/or triplet fusion emitters for commercial blue OLED pixels. While these materials ensure acceptable device lifetimes, they often suffer from lower efficiency compared to blue phosphorescent or TADF emitters. However, all these emitter types share a common challenge: their relatively broad emission spectrum results in unnecessary energy losses to meet stringent emission colour standards. On the contrary, MR-TADF emitters, although encounter issues with relatively poor exciton harvesting efficiency, particularly for triplet excitons, offer a narrow emission spectrum.

Here, through an in-depth investigation of both TADF and MR-TADF emitters, key aspects of each emitter generation can be elucidated, enabling their integration into hyperfluorescence (HF) OLEDs. This innovative approach circumvents the limitations of TADF blue emitters by utilizing them as sensitizers for MR-TADF terminal emitters. The broad emission spectra and low radiative rates of a TADF sensitizer can be offset by the fast and narrowband emission from the terminal emitter while ensuring the utilization of 100% triplet excitons by the former. Through exploration of the essential requirements for efficient sensitization in HF OLEDs, by pushing the boundaries of sensitization, an unforeseen material combination emerged.

Surprisingly, greenish-emitting sensitizers were found capable of supporting blue HF-OLEDs. This discovery results in a reduction of both singlet and triplet energies for all materials within the emission layer, consequently enhancing device stability.

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List of Abbreviations

A - Electron accepting unit/molecule

CCD - Charge coupled device

CIE - Commission International D'Eclairage

CT - Charge transfer

D - Electron donating unit/molecule

DCM - Dichloromethane

DF - Delayed fluorescence

DOS – Density of States

EBL - Electron blocking layer

EIL - Electron injection layer

EML - Emissive layer

EQE - External quantum efficiency

ETL - Electron transporting layer

HBL - Hole blocking layer

HF - Hyperfluorescence

HIL - Hole injection layer

HOMO - Highest occupied molecular orbital

HTL - Hole transporting layer

ITO - Indium Tin oxide

LE - Locally excited

LUMO - Lowest unoccupied molecular orbital

MCH - Methyl Cyclohexane

MR – Multiple resonance

Nd:YAG - Neodymium doped Yttrium Aluminium Garnet

OD – Optical Density

OLED - Organic light emitting diode

PF - Prompt fluorescence

PH - Phosphorescence

PL - Photoluminescence

PLQY - Photoluminescence quantum yield

IC - Internal conversion

ISC - Intersystem crossing

rISC - Reverse intersystem crossing

RT - Room Temperature

RTP - Room temperature phosphorescence

SOC - Spin orbit coupling

TADF - Thermally activated delayed fluorescence

TCSPC - Time correlated single photon counting

TDDFT - Time-Dependent Density Functional Theory

TF - Tooling factor

TTA - Triplet-triplet annihilation

VTE - Vacuum thermal evaporation

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Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements.

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Kleitos Stavrou

April 2024

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1 Introduction

1.1 Motivation

Light has been essential for the evolution of life on earth, and more specifically for humankind itself. From the discovery of fire to the first artificial lighting source, science has taken a lot of steps forward to reach an optimised form of equipment for the daily use of light. The previous generation of light sources is light emitting diodes (LEDs) where inorganic materials are used to produce light. Towards that direction, organic light emitting diodes (OLEDs) were first reported in 1987 by Kodak researchers Tang and Van Slyke¹ and since then developed into an important part of everyday life. Compared to LED technologies, OLEDs use carbon-based materials to produce light, one of the most abundant elements in the world and the most chemically active element for molecular formation. Thus, the possible carbon combinations (many times also facilitating other atoms of the periodic Table) for light-emitting molecules are substantial. Since then, many companies, such as LG, Philips, Apple, Samsung and others, already offer lightning panels based on OLED technology, using a plethora of materials compared to the conventional materials used in LED technology. OLEDs are found mainly in luminescence displays, such as OLED TV's and smartphone screens.

The first report of OLED technology development traces back to the 1960s when the first organic molecule (eosin) was found to emit delayed fluorescence.² In the forthcoming years, numerous organic compounds having fluorescence emission have been reported but their application in OLEDs suffered low device efficiencies and high operating voltages. This problem was addressed by Tang et al. by building the first multilayer OLED operating at relatively low voltages.¹ Ten years later, Pioneer developed the first commercial OLED applied as a passive-matrix-driven display screen³ in-car audio systems. The breakthrough happened in 2007, when Sony released the world's first OLED display,⁴ while the first commercial OLED panels were developed in 2011 by Lumiotec.⁵ Since then, OLED displays have been established in the global market, competing with LED and LCD technologies while having the advantage of being used in applications such as flexible, bendable, and active-matrix (AMOLED)⁶ displays (**Figure 1.1**).

OLEDs, so far, were facilitated mainly using phosphorescence emitters^{7,8} for the red and green colours, having already achieved external quantum efficiencies (EQEs) above 20% and good

operational lifetimes, above 10,000 hours. For the blue colour, although phosphorescence emitters have been explored, they suffer poor device lifetimes and triplet-triplet annihilation (TTA)⁹ emitters are mainly used. The latter, because of their mechanism of harvesting triplet excitons, have limited maximum device performance but also experience poor device lifetimes, compared to the other, lower energy, colours.



Figure 1.1. OLED v. Zoom in: the individual pixels. Typically, the blue pixel has a bigger size to reduce the blue OLED lifetime problem.

Most recently, the last generation of OLEDs attracted the interest of industry and the scientific community, the thermally activated delayed fluorescence emitter (TADF).¹¹ With their unique ability to achieve 100 % internal quantum efficiency (IQE), TADF emitters are a promising generation of replacing the conventional OLED emitters. These emitters are divided into three subclasses; exciplex emitters¹² based on the intermolecular charge transfer effect; the conventional donor-acceptor type emitters¹³ based on the intramolecular charge transfer effect, and the latest generation, the multiple resonance (MR) TADF emitters,¹⁴ relying on the short-range charge transfer phenomenon. Although TADF emitters have many positive characteristics, they appear to also suffer from low device lifetime, especially in the blue region.

The blue OLED problem is not something new in the field of light-emitting diodes. Although for different reasons but also related to the relatively high energy of blue emission, the red and green inorganic LEDs were commercially available in the late 60s but it was not until 25 years

later when the persistence of the physics Nobel prize winner Shuji Nakamura (2014) led to the first ever efficient blue LED. In this context, this thesis aims to explore ways to improve the blue OLED efficiency and stability problem, focusing on donor-acceptor type and MR-TADF emitters.

1.2 Thesis Organization

Chapter 2 provides a foundational understanding of the pertinent theory. Beginning with an introduction about atoms and molecules, focusing on the organic molecules and their key properties for electronic applications. A concise overview of singlet and triplet states alongside their energy splitting dynamics and the process of intersystem crossing sets the stage. Subsequently, the discourse delves into the intricacies of electronic transitions within organic molecules, elucidating their photophysical properties. A thorough examination of the mechanisms underlying delayed fluorescence ensues, with particular emphasis on the TADF mechanism. Concluding the theoretical framework, attention shifts towards the design and operational principles of OLEDs, providing invaluable insights into their functionality.

Chapter 3 issues comprehensive insights into the organic materials utilized and the methodology employed for data acquisition. This segment encompasses a detailed description of the chemical structures of the studied molecules, elucidating their compositional details. Further, it outlines the sample preparation procedures undertaken, in conjunction with an overview of the optical measurements conducted, including steady-state and time-resolved measurements and analyses. Additionally, this section sheds light on the intricate process of device fabrication and subsequent testing, offering a holistic perspective on the experimental framework employed in this study.

Chapter 4 sets the beginning of the experimental results. In this chapter the impact of guest-host interactions on the well-known donor-acceptor (D-A) type TADF emitter DMAC-TRZ is explored. The inherent flexibility DMAC-TRZ, coupled with the sensitivity of its CT state to external factors, underscores the pivotal role of the environment in shaping the properties of such D-A type TADF emitters. Furthermore, the exploration extends to the concept of conformational homogeneity, introducing homogeneity plots as a tool to effectively illustrate the distinct conformational fingerprints of DMAC-TRZ across varying environments.

Chapter 5 delves into the forefront of TADF emitter innovation, specifically the multi-resonance (MR) TADF category exemplified by *v*-DABNA. The investigation focuses on the photophysical attributes of this structurally rigid emitter, highlighting its remarkable

insensitivity to environmental factors. Through comprehensive optical analyses, the study elucidates the potent intermolecular interactions, characteristic of this planar molecule, shedding light on the phenomenon of excimer formation that also underlies the pronounced concentration quenching effect observed in OLEDs employing MR-TADF molecules.

Chapter 6 offers insights into enhancing existing MR-TADF emitters tailored for hyperfluorescence applications. Through precise molecular adjustments, the near-UV emission of the MR-TADF emitter a-3BNOH undergoes conversion to deep blue (a-3BNMes), rendering it viable for utilization as a terminal emitter in HF-OLEDs. Consequently, the narrow emission spectrum of a-3BNMes, coupled with the triplet harvesting capabilities of a D-A type TADF sensitizer, yields highly efficient devices emitting deep blue light, aligning closely with the stringent emission colour standards.

Chapter 7 explores the boundaries of efficient energy transfer from the sensitizer to the terminal emitters in HF-OLEDs. While typically a high spectral overlap between the sensitizer's emission and the terminal emitters' absorption spectrum is necessary, this exploration investigates a scenario with minimal overlap. Remarkably, this allows HF-OLEDs to achieve blue emission utilizing a greenish sensitizer. Despite not achieving 100% energy transfer, the efficiency surpasses that of HF systems employing the same terminal emitters but with bluer sensitizers. This peculiarity is elucidated by the unexpected presence of a high-energy quasi-axial conformer of DMAC-TRZ, which directly transfers energy to the terminal emitter in HF-OLEDs, deviating from the behaviour observed in conventional TADF OLEDs where energy transfer typically occurs via the quasi-equatorial conformer.

Chapter 8 synthesizes the pivotal findings from preceding chapters to optimize energy transfer in HF-OLEDs. Initially, leveraging insights from Chapter 4, efforts focus on minimizing conformational inhomogeneity by integrating the rigid spiro-bridge ACRSA emitter as a sensitizer. Consequently, the undesirable energy transfer inefficiencies, from low energy conformers to the terminal emitter observed in Chapter 7 are mitigated, leading to nearly 100% energy transfer efficiency. A suite of crucial criteria for effective sensitizers is introduced, with many of these criteria met by ACRSA. This, results in the realization of blue HF-OLEDs, using ACRSA as the sensitizer, exhibiting nearly tripled EQE and enhanced device lifetime compared to their greenish/sky blue TADF OLED counterparts.

Finally, chapter 9 summarises the findings from chapters 4 to 8.

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2 Background Theory

This chapter provides a comprehensive overview of the theory pertinent to this thesis. It commences with an exploration of organic molecules and semiconductors, elucidating the distinctive characteristics that render them desirable for electronic applications. Following this, a concise overview of singlet and triplet states along with their relevant transitions is provided. The discussion then delves into the mechanisms underlying delayed fluorescence, with a particular focus on thermally activated delayed fluorescence (TADF). The significance of intermolecular interactions in organic systems is then outlined, and finally, the chapter examines the design and mechanism of OLEDs within the scope of the devices fabricated in this study.

2.1 Fundamentals

2.1.1 The history of the atom

Atoms have been considered at various times throughout history to be the fundamental elements that matter is consisted of. Initial theories from ancient Greece and India, and even Dalton's modern theory in the early 19th century, define atoms based on the terminology of its name. Atom (in Greek; $\alpha\tau\omicron\mu\omicron = \alpha + \tau\acute{\epsilon}\mu\nu\omega = \text{cannot} + \text{cut}$) means something that cannot be divided. As Dalton proposed, all compounds are combinations of different numbers and types of atoms. It was not until the end of the century when J.J Thomson discovered electrons in atoms, and the name has remained despite our understanding of atoms changing completely. Thomson proposed that electrons were embedded in a diffuse mass of positive charge to give internal structure to electrically neutral atoms. Almost ten years later, Ernest Rutherford, one of Thomson's students, refined this to a planetary model where electrons orbited around a small positive-charge nucleus. Niels Bohr was the first to grasp the inherently quantum nature of the atom, explaining the absorption and emission spectra of some light elements with electron orbits of fixed sizes and discrete energies. After, Louis de Broglie proposed the wavelike behaviour of moving particles (such as electrons within an atom), while Erwin Schrödinger extended this to demonstrate the impossibility of knowing the exact location or momentum of an electron. These developments led to the modern understanding of the atom, where electron wavefunctions determine the possible positions where it is more likely to find an electron. Since the mid-twentieth century many more subatomic particles were discovered, including the components of the nucleus (protons and neutrons), and even their own constituent particles (quarks and gluons).

2.1.2 From atoms to molecules

The concept of molecules can also be traced back to ancient Greece, with Democritus arguing that everything is made from atoms and voids. Empedocles introduced the concepts of fundamental elements and forces (analogous but significantly simpler compared to modern understanding) that lead to elemental interactions and the formation of matter. Since then, many scientists and philosophers have been puzzled about the micro-interactions within matter, and how these build from atoms up to our macroscale experience. The word molecule was itself introduced by Amedeo Avogadro who stated that: "The smallest particles of gases are not necessarily simple atoms but are made up of a certain number of atoms united by attractions to

form single molecules”.¹ From the latter, the molecule can be defined as a group of at least two atoms held together by attractive forces, now known as chemical bonds. This concept has survived to the modern day with surprisingly little modification and is the underpinning of modern chemistry.

2.2 Organic molecules

2.2.1 The importance of Carbon

Carbon is considered the fourth most abundant element in the universe by mass after hydrogen, helium, and oxygen. It is also the most common elements of all known life. This central position in living matter likely arises because carbon is arguably the most chemically “active” (or flexible) element in the periodic table, meaning that one can make more unique molecules based on carbon than from any other atom. This ubiquity makes carbon an ideal candidate for all material-based applications.

Organic materials are formally considered a class of materials based on carbon atoms. A key characteristic of carbon is that its 4 valence electrons allow the formation of up to 4 covalent chemical bonds for each atom, supporting the above-mentioned chemical flexibility. Carbon-carbon bonds are strong and stable and can be typically categorized into single (σ -bond), double (one σ - bond and a π -bond) and triple (one σ - bond and two π -bond) bonds. In many contexts (e.g. alternating single and multiple bonds, along with nitrogen, oxygen, boron etc.), conjugated systems can also be formed by the extension of p orbitals and π -bonds across multiple carbon atoms, leading to delocalized electrons and functional materials.

Formalising the above concepts, an atom consists of a centred nucleus and the surrounding electrons. The electrons have a set of well-defined allowed energies and spatial distributions around the nucleus, which are called atomic orbitals. In neutral carbon atom for example, which has six ground state electrons, two occupy the 1s orbital, two the 2s orbital, and the last two in two of the triply degenerate p orbitals (p_x , p_y and p_z) (**Figure 2.1a**). Molecules are a stable arrangement of atoms, with each electron interacting with multiple nuclei and the resulting attractive electrostatic forces forming the bonds that overcome inter-nuclear repulsions.

2.2.2 Molecular orbitals

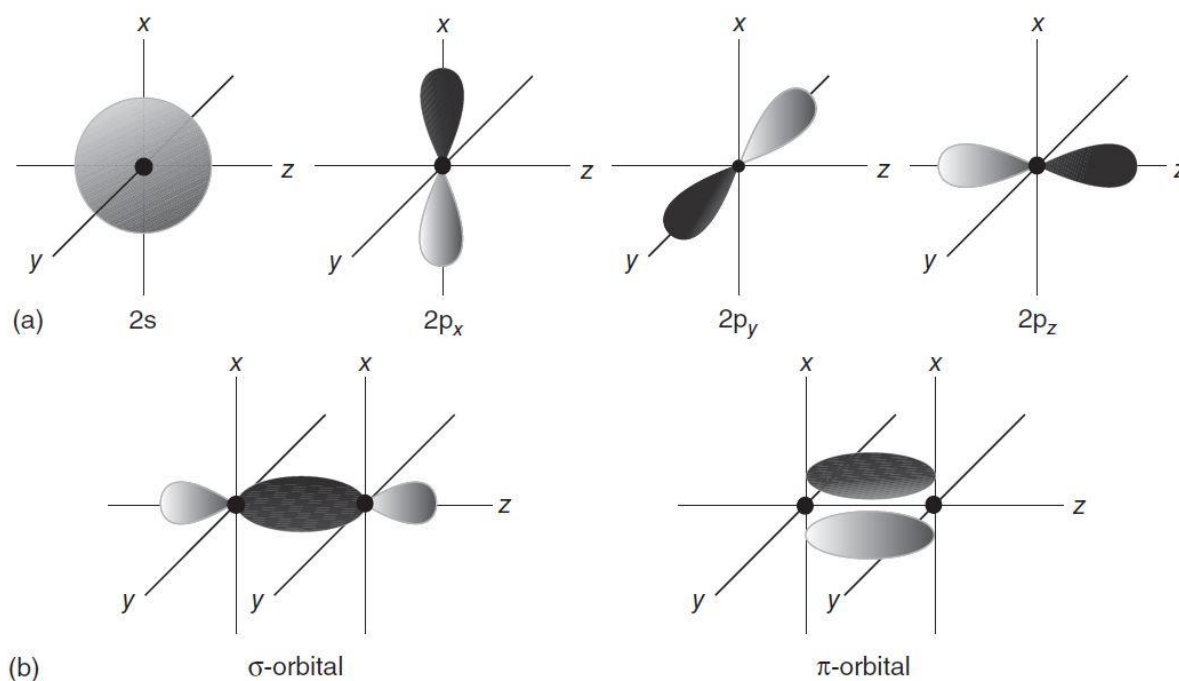


Figure 1. The (a) atomic and (b) molecular orbitals.

In molecules, the electrons instead occupy molecular orbitals (orbitals of the whole set of nuclei), a term used to describe the distributions and energies of electrons shared between atoms (**Figure 2.1b**). Combinations of the carbon atomic orbitals can be used as a reference to visualise and understand the molecular orbitals. Upon interaction with another atom like hydrogen or another carbon atom, new hybrid orbitals are formed from a linear combination of the 2s and 2p atomic orbitals. The hybrid carbon-centred orbitals in this case are named sp , sp^2 and sp^3 , with s and p^x referring to the type of involved orbitals, while x is the number of orbitals involved. For example, in **Figure 2.2a** six hydrogens bond to two carbons through interactions of the hydrogen s and carbon sp^3 hybrid orbitals (as shown to the left), meaning that three orbitals of both carbon systems are mixing. Additionally, the remaining sp^3 orbitals of each carbon atom interact with each other resulting in the formation of a σ -orbital (or σ -bond) carbon-carbon single bond in ethane. In ethene, the two carbons are instead sp^2 hybridized, with one unhybridized p orbital not involved in C-H bonding. Similarly as above, the remaining sp^3 orbitals form the σ -bond while the mixing of the atomic p orbitals forms an additional π -bond, that together form a double bond. Finally, for ethyne two p orbitals result in one σ - and two π -bonds in the carbon-carbon triple bond (**Figure 2.2**).

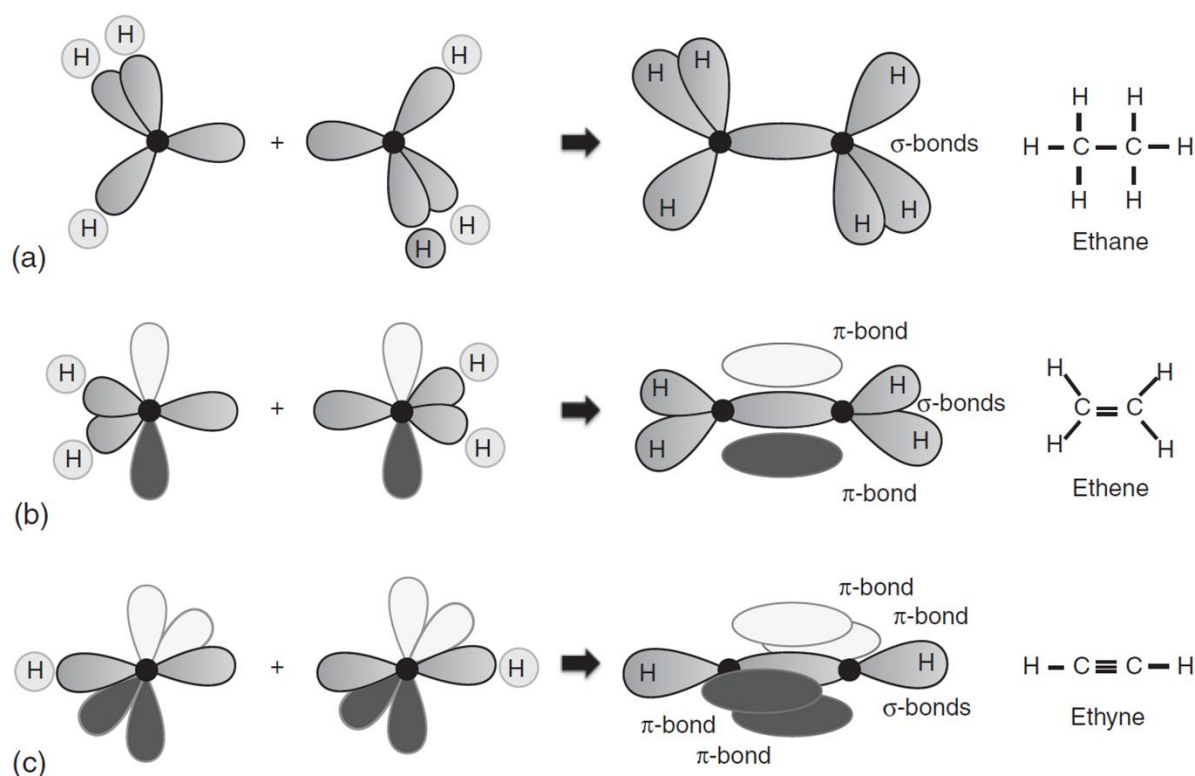


Figure 2.2. Illustration of (a) six hydrogen atoms and two sp^3 hybridized carbons to form the molecule ethane, (b) four hydrogen atoms and two sp^2 hybridized carbons to yield ethene, and (c) two hydrogen and two sp hybridized carbon atoms to form ethyne.²

As well as considering their new shapes, the altered energies of molecular orbitals are shown in **Figure 2.3**. In diatomic hydrogen, the lower energy “bonding” molecular orbital (σ orbital) is occupied by two electrons and gives a system lower in energy than the two singly occupied 1s atomic orbitals of the separated hydrogen atoms would have. This lower energy orbital is therefore responsible for keeping the molecule stable in the ground state and corresponds to the σ -bond. Out-of-phase combinations of the two atomic orbitals are also possible, leading to a higher energy “anti-bonding” molecular orbital (σ^*). In most cases, upon excitation with some form of energy, this orbital can be occupied by an electron, but the excited electron will relax back to the bonding molecular orbital, either through the release of heat or light. These sorts of transitions can occur between all types of orbitals, such as σ -, π - and n -orbitals (non-bonding), with specific rules about transitions and energetic requirements.

In the ground state of a molecule, the orbitals are filled with the available electrons from the lowest energy orbitals upwards (Aufbau principle). In larger molecules, the two main orbitals typically taking part in an electronic transition are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The example of formaldehyde

shows how all possible transitions from the HOMO to the LUMO can occur (**Figure 2.3b**), although the HOMO-LUMO transition will typically be the lowest in energy.

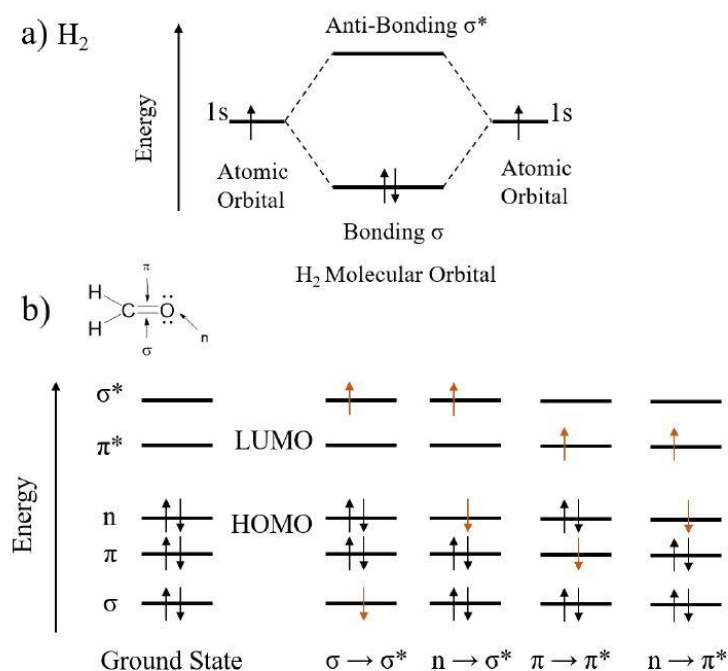


Figure 2.3. (a) Schematic of the hydrogen molecular orbital. (b) Energy levels of molecular orbitals in formaldehyde and all possible electronic transitions.³

2.2.3 Conjugated molecules

Extending the concept of π -bonds, conjugated systems have a region of overlapping p-orbitals (see above) between neighbouring sp^2 -hybridized atoms. As the electrons in such bonds are indistinguishable and feel attractions to all nuclei in the system, they are typically able to move within and extend throughout the conjugation system. In tandem, the associated molecular orbitals are found to extend across the entire π -system. This is in strong contrast to electrons in σ -bonds, which are tightly localised between the bonded atoms.

The most used π -conjugated systems for OLED applications are aromatic because they exhibit unusual stability and can emit light in the visible and near visible spectrum. According to Hückel theory, planar molecules with $4n + 2$ π -electrons are aromatic, where n is a natural number. A classic example of aromatic systems is benzene which has six σ - and π -bonds. The latter, consists of six molecular p-orbitals which are delocalized from the atoms (atomic p-orbitals) and thus the conjugated molecule is formed. Three orbitals have a bonding character and are occupied by six electrons, while the other three have an anti-bonding character and remain unoccupied. This can be presumed, in the simplest form, as two rings of π -electrons

above and below the σ -bonds. An important parameter for the π -conjugation to exist is the molecules to be planar, to allow the best possible overlap between the orbitals. When the orbitals are orthogonal, the overlap is broken and leads to no conjugation, and electron systems that are effectively separate are non-communicating. This is the case for many donor – acceptor TADF molecules, where the small degree of through-bond or through-space electronic communication between segments must be carefully managed.⁴

2.2.4 Excited π -conjugated molecules

Upon excitation, conjugated molecules absorb discrete amounts of energy and undergo a transition of a π -electron typically (although not always) from the HOMO to the LUMO. Such a transition has a π - π^* character (see above) unless a non-bonding electron pair (i.e., from an oxygen, nitrogen, sulphur etc.) moves to the antibonding π^* -orbital leading to an energetically lower n - π^* transition. In the excited state or the presence of an electron to the π^* -orbital, the molecules are not stable and tend to relax to the ground state. If the energy between HOMO and LUMO is within the visible region they can absorb or emit this energy in the form of visible light.

2.3 Excited states

Organic molecules, like atoms, can exist at least temporarily in excited electronic states. As shown in **Figure 2.3b**, the lowest energy ground and excited states can be correlated with HOMOs and LUMOs, respectively. Considering the number of molecular orbitals, defined as HOMO, HOMO-1, HOMO-2 etc., and LUMO, LUMO+1, LUMO+2 etc, a stable ground and excited state is a combination of the different HOMOs and LUMOs, respectively. When one electron is in the HOMO and one in the LUMO the molecule is in an excited state configuration and a further quantum property of the electrons comes into play. Both electrons have a property named spin (an intrinsic quantity of angular momentum) that can combine in different ways that will define the nature of the excited state (singlet, triplet, etc.), and thus also the energy and the overall wavefunctions of the two electrons. To explore this, one needs to follow a quantum mechanical approach. Accordingly, electron spin is a manifestation of their angular momentum, and spin angular momentum is a vector quantity that couples according to the rules of quantum mechanics. A specific spin state is given by the total spin, the sum of all electron spins in all orbitals. However, in doubly occupied orbitals the total spin is zero as electrons are paired with anti-parallel spin, and so typically only the electrons in singly occupied orbitals determine the overall spin.

2.3.1 Singlet and triplet states

In organic semiconductors, the unpaired electrons of an excited state configuration usually have one electron in a π -orbital and one in a π^* -orbital. The spin of the state is defined based on the two electrons' spin angular momentum. When the spin of the electron in the π -orbital and the one in the π^* -orbital are antiparallel they add up and the total spin is zero, and this is referred to as a singlet state. In the opposite case, where the two spins are parallel, the total spin is one in units of $\hbar$, and is called the triplet state (**Figure 2.4**). The wavefunction of the electron can be written as a product of the electronic wavefunction and depends only on the electron's spatial coordinates and on the spin wavefunction Ψ_{spin} . While the spin wavefunctions of a one-electron state have eigenvalues $S = \frac{1}{2}$, $M_s = \frac{1}{2}$ or $-\frac{1}{2}$ (to give two possible unique states), the spin wavefunctions of the two-particle system can be written as:

$$\Psi_{\text{spin}} : \left\{ \begin{array}{ll} \frac{1}{\sqrt{2}} \{ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \} & S = 0 \text{ and } M_s = 0 \\ |\uparrow\uparrow\rangle & S = 1 \text{ and } M_s = 1 \\ \frac{1}{\sqrt{2}} \{ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \} & S = 1 \text{ and } M_s = 0 \\ |\downarrow\downarrow\rangle & S = 1 \text{ and } M_s = -1 \end{array} \right.$$

The first spin wavefunction has $S = 0$ and spin multiplicity m equal to 1, where $m = 2S + 1$. This state has only a single possible value of its z-component, i.e. eigenvalue $M_s = 0$, and is therefore called a singlet. The next three spin wavefunctions have $S = 1$ and $m = 3$, and differ in the z-component of the spin which can take one of three eigenvalues ($M_s = 1, 0, -1$). This arrangement is therefore called triplet, and a vectorial representation is given in the **Figure 2.4c**. For the triplet wavefunctions, the spins are always in phase, while they are out of phase in the singlet state.^{2,5,6}

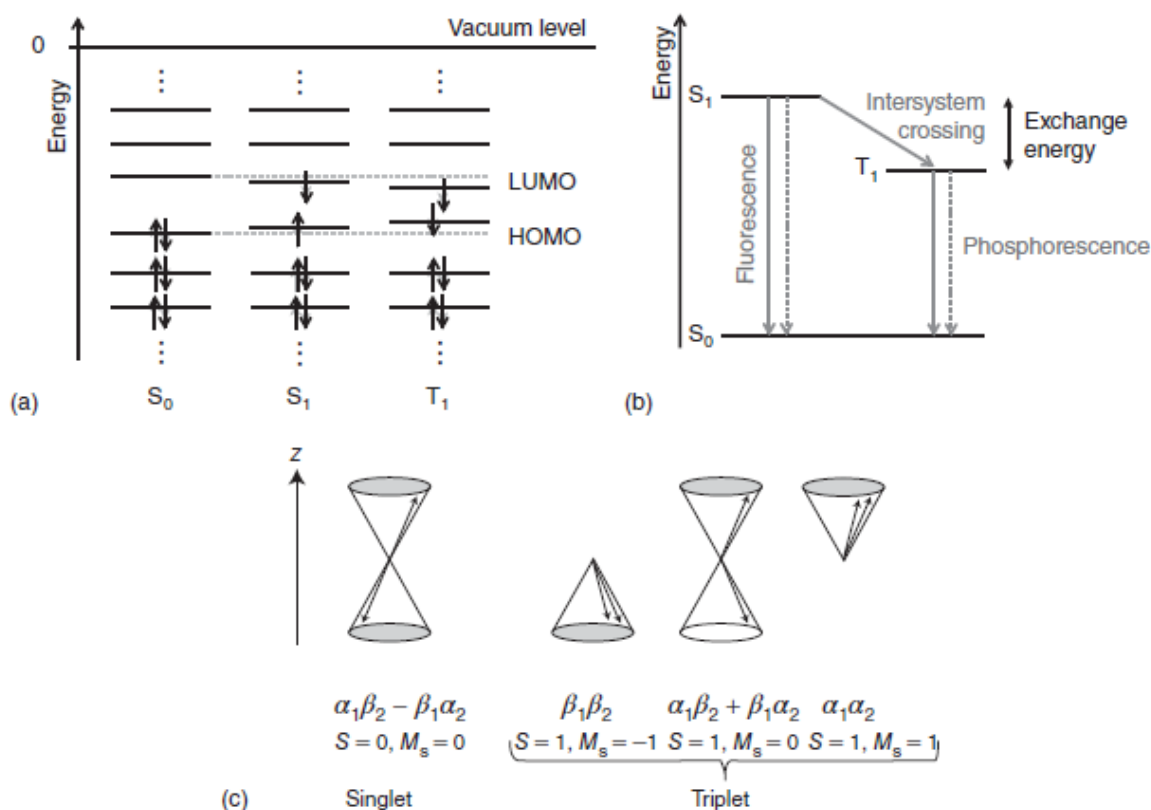


Figure 2.4. Singlet (S) and triplet (T) states in: (a) orbital configuration scheme. The scheme explicitly incorporates Coulomb and exchange energies into the positions of the frontier orbitals. For the triplet state, only a single spin configuration is presented, (b) a state diagram showing the states that arise from antisymmetric combinations of molecular orbitals. Solid and dotted lines represent radiative and nonradiative decay channels, respectively, and (c) vector diagram, illustrating the relative orientation of the two electron spins for each.²

2.3.2 Singlet and Triplet State Energies

The singlet and triplet state energies are defined in terms of the sum of the orbital energies (E_{orb}) associated with the one electron orbital for a fixed nuclear framework in the excited state, the Coulomb interaction integral (K , the first order Coulombic correction due to classical electron-electron correlation), and the exchange interaction integral (J , the first order quantum mechanical correction of the electron-electron repulsion energy due to the Pauli principle). This is described, for the case of singlet and triplet states, by the following equations:

$$E_S = E_{orb} + K + J \quad (2.2)$$

$$E_T = E_{orb} + K - J \quad (2.3)$$

Based on these equations, the energies of the excited singlet and triplet states differ by twice the exchange energy, which itself depends largely on the wavefunction overlap between the electron in the HOMO (Φ_H) and that in the LUMO (Ψ_L), integrated over the possible electron's position (r_1 and r_2). From this the singlet-triplet energy gap (ΔE_{ST}) is also provided:

$$\Delta E_{ST} = E_{S1} - E_{T1} = 2J = 2 \iint \Phi_H(r_1)\Psi_L(r_2) \left(\frac{e^2}{r_1 - r_2} \right) \Phi_H(r_2)\Psi_L(r_1) dr_1 dr_2 \quad (2.4)$$

If the overlap between these orbitals is significant, as in the case of fluorescence molecules, the exchange energy is large. Conversely, when the HOMO and LUMO are located in different parts of the molecule, as in TADF molecules, the integral and exchange energy is small. This criterion holds considerable importance for TADF emitters and will be explored further in this chapter.

According to equations 2.2 and 2.3 the triplet state will always exhibit lower energy compared to the corresponding singlet derived from the same transition. This lower energy arises from the Pauli principle, which dictates that orbitally unpaired electrons with parallel spins cannot simultaneously occupy the same space. Consequently, electron-electron repulsion is reduced in the triplet state, leading to lower energy levels compared to the singlet state. However, recent studies have revealed exceptions to this rule, particularly in heptazine systems where the first singlet state energy may be lower than its corresponding triplet.⁷ The underlying reasons for this phenomenon are at the forefront of modern organic electronics research.

2.4 Transitions Between Molecular States

Up to this point, the atomic nuclei within the molecule have been treated as stationary entities, occupying fixed positions in both the ground and excited molecular states. However, in reality, the nuclei in molecules undergo oscillations around an equilibrium position with specific vibrational frequencies (ω). These oscillations are described by the nuclear vibrational wavefunction, which, together with the electronic and spin wavefunctions, defines the total wavefunction of a molecular state.

Molecules, comprised of various oscillating atoms, can be conceptualized as systems of coupled oscillators, akin to the mechanical analogy of spheres connected by springs. This perspective transforms the electronic excited states illustrated in **Figure 2.4b** into vibrational potential energy surfaces, as depicted in **Figure 2.5**. On these surfaces, the quantized molecular

vibrational modes are represented by different energy level lines, with a range of nuclear coordinates that can be explored in each vibrational sublevel.

The specific energies of these vibrational modes can be indirectly monitored through experimental techniques such as Raman spectroscopy or Fourier transform infrared spectroscopy. While electronic and vibrational excitations are typically independent of each other (Born-Oppenheimer approximation), understanding these vibrational modes is crucial as they are now known to promote the otherwise forbidden coupling of excited states with different multiplicities in TADF materials. **Figure 2.5** provides a visual representation of vibronic (vibrational + electronic) excited states, and the potential energy surfaces of nuclear coordinates that exist for each individual electronic state.

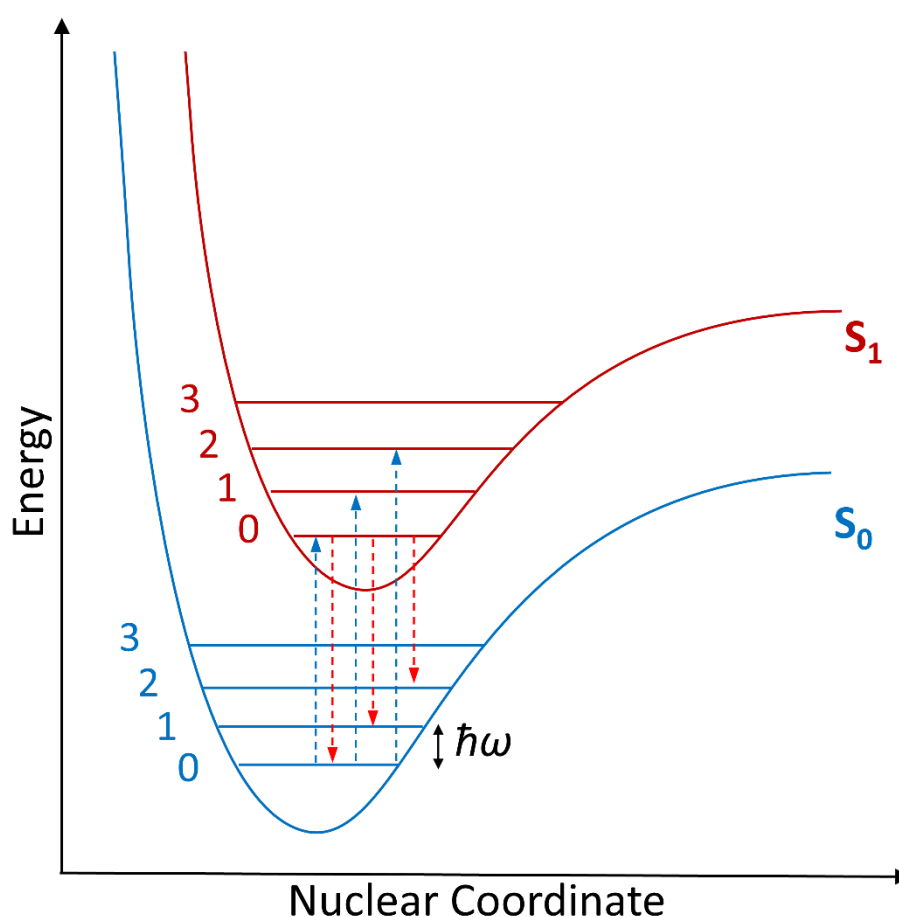


Figure 2.5. Potential energy surface as a function of nuclear displacement, showing representative vibronic states. S_0 and S_1 represent the ground and first excited state respectively. Horizontal lines represent the energies of vibrational modes for each state, and vertical lines transitions between these.

In **Figure 2.5**, the blue dashed arrows represent transitions from the base of the ground electronic state to the excited state (absorption), while the red dashed arrows represent

transitions from the base of the excited state to the ground state (emission, in molecules with the ability to emit light) both sets connecting different vibrational sublevels. Similar to how vibration modes can be experimentally observed with infrared spectroscopy, higher energy transitions between molecular vibronic states with different electronic character can be detected using absorption (UV-Vis) and fluorescence spectrometry with higher energy visible or UV photons.

2.4.1 Jablonski diagram

Once a molecule in the ground state (electron in the HOMO) absorbs energy, a series of potential transitions can occur. Some transitions are universal, while others are contingent upon the specific molecule's properties and electronic system. One way to visualize these transitions is through the Jablonski diagram (**Figure 2.6**). In this diagram, the black horizontal lines represent the electronic states, while the grey horizontal lines represent the vibrational sublevels of each electronic state.

When a ground state molecule absorbs a photon, it becomes excited to a specific singlet state ($S_1, S_2, \dots S_n$) at a particular vibrational level (0, 1, ... n), depending on the energy of the incident photon, which must be equal to the energy difference between the two states. Typically, only singlet states are optically accessible, as this transition must preserve the total spin of the molecule ($M_s=0$ in the ground state) and (0 spin) photon before and after excitation. If the excited molecule resides in an upper singlet state beyond S_1 , it typically relaxes to its lowest vibrational level and then undergoes internal conversion (IC) toward the lowest excited singlet state. This vibrational relaxation and IC can occur iteratively until the base of the S_1 state is reached, at which point the increased energy gaps between S_1 and S_0 vibronic states slow or prevent further rapid non-radiative relaxation. From there, the excited molecule can undergo a variety of radiative and non-radiative transitions based on its individual properties (**Figure 2.6**). A detailed explanation of these transitions is provided below.

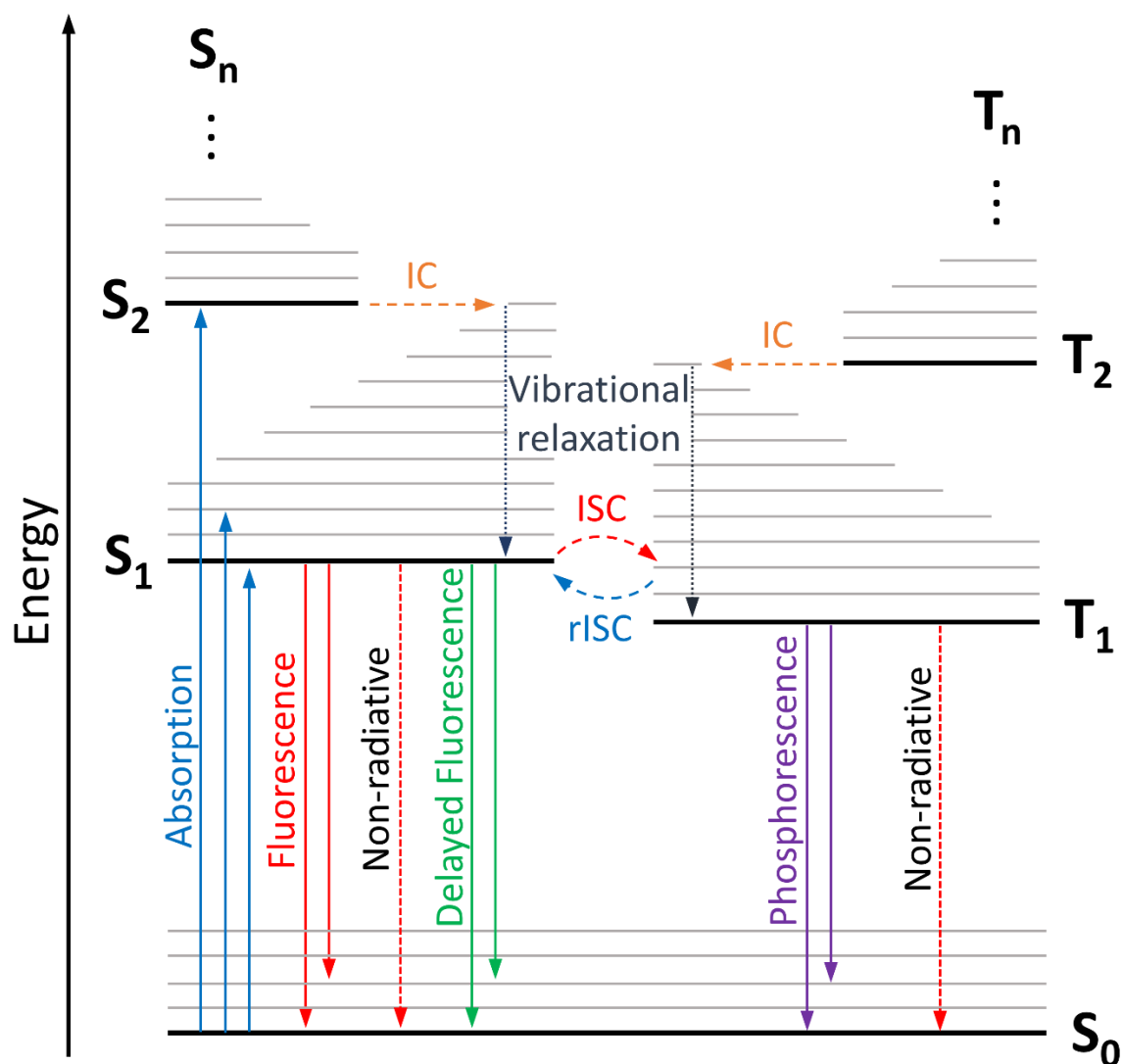


Figure 2.6. Jablonski diagram representing the main transitions between molecular states.

2.4.2 Key Molecular State Transitions

In organic photoactive molecules, their molecular electronic and vibronic transitions determine their semiconductor properties and applications. For instance, the absorption energies of a molecule determine the energies needed to transition a ground-state molecule to an excited state. This process can generate mobile (less bound) charges, albeit temporarily, which partly define the electrical properties of the molecule or molecular system.

- a) *Absorption:* This process occurs for photons whose energy matches the gaps between molecular vibronic states, giving a spectrum of photon transmission that is as unique to each molecule as a fingerprint is to a human (although sometimes the differences may be minor, depending on the molecular structure). Absorption energies can vary widely, particularly in organic light-emitting molecules, ranging from UV (>3.3 eV) to IR (<1.6

eV), typically correlated with their molecular size and conjugation length. In practical terms, a molecule that absorbs only in the UV or IR and does not fluoresce appears transparent, while a material that strongly absorbs across the entire visible region appears black to the human eye.

Absorption occurs within a few femtoseconds (faster than typical molecular vibrations) and so is considered a practically instantaneous process. Absorption intensity is determined by the fraction of photons absorbed by a material at a specific wavelength. Experimentally, this is typically measured in solution or solid films and is defined as the base-10 logarithm of the incident light intensity over the transmitted light (for further details, refer to chapter 3.4.1).

Once normalized for sample dimensions and concentration, the intrinsic strength of a transition, also known as the oscillator strength (f), depends on the type of transition. For most molecules investigated in this thesis, the intense transitions observed were between orbitals of the same type within a molecule (e.g. $\pi\pi^*$ transition), occurring due to improved orbital overlap between initial and final states. Molecules with HOMO and LUMO located in different parts of the molecule and/or having limited orbital overlap ($n\pi^*$ and CT transitions) typically exhibit weak absorption (low oscillator strength). Generally, a higher oscillator strength for a transition within a molecule indicates a greater likelihood of improved quantum efficiency, as the radiative rates exceed the non-radiative rates. In the absorption of a molecule, only spin-allowed transitions can be observed, hence transitions between singlet ground states and triplet excited states cannot usually be observed.

- b) *Fluorescence*: This is typically the event following absorption in organic light-emitting molecules. Once a molecule transitions to the excited state, which is inherently unstable, it tends to relax back to the ground state of the same spin multiplicity and release excess energy as a photon (the inverse of the absorption process). Fluorescence represents a spin-allowed radiative transition and, as a result, can occur relatively fast, typically within the nanosecond regime. However, as discussed below, changes in nuclear coordinate between the excited and ground state lead to lower orbital overlap and slower emission processes compared to absorptive ones (in which the molecule nuclear coordinates are initially identical). Delayed fluorescence, conversely, involves interactions between singlet and triplet excited states and will be elaborated on in detail later in this chapter. It's essential to differentiate here fluorescence from photoluminescence (PL), the latter of which is a broader term that encompasses all emissive mechanisms.

c) *Phosphorescence*: This entails a radiative transition from an excited triplet state to the singlet ground state, requiring a change in spin multiplicity. Although typically a spin-forbidden (and therefore very slow) transition, phosphorescence may occur under certain conditions, where the triplet state wavefunction acquires contribution from a singlet state wavefunction and vice versa. This perturbation is facilitated by spin-orbit coupling (SOC). Conservation of total angular momentum (the sum of spin and orbital angular momentum) during an optical transition does not formally require spin (a subcategory of angular momentum) to be individually conserved. Thus, for triplet states coupled with ground singlet state, the required forbidden spin flip can occur if accompanied by a change in associated orbital angular momentum. This change in angular momentum may arise through the use of heavy atoms (atoms with high mass) in organic molecules, which enhance SOC and consequently the interaction between orbitals (**Figure 2.7**). This phenomenon is observed in organometallic complexes, such as Iridium complexes commonly utilized in red and green phosphorescent OLEDs. Purely organic molecules may also exhibit phosphorescence emission due to vibrations, which can alter the orbital angular momentum to make an otherwise forbidden transition weakly allowed. Vibrations can also mix states to give singlet character, i.e. vibronic coupling. Overall, vibration-induced SOC is weaker compared to heavy atom-induced SOC, resulting in phosphorescence lifetimes of seconds and microseconds, respectively. Practically, phosphorescence can often be enhanced by measuring at low temperatures, with the inhibition of molecular vibrations also slowing non-radiative triplet decay mechanisms and allowing the slow phosphorescence channel to yield detectable emission.

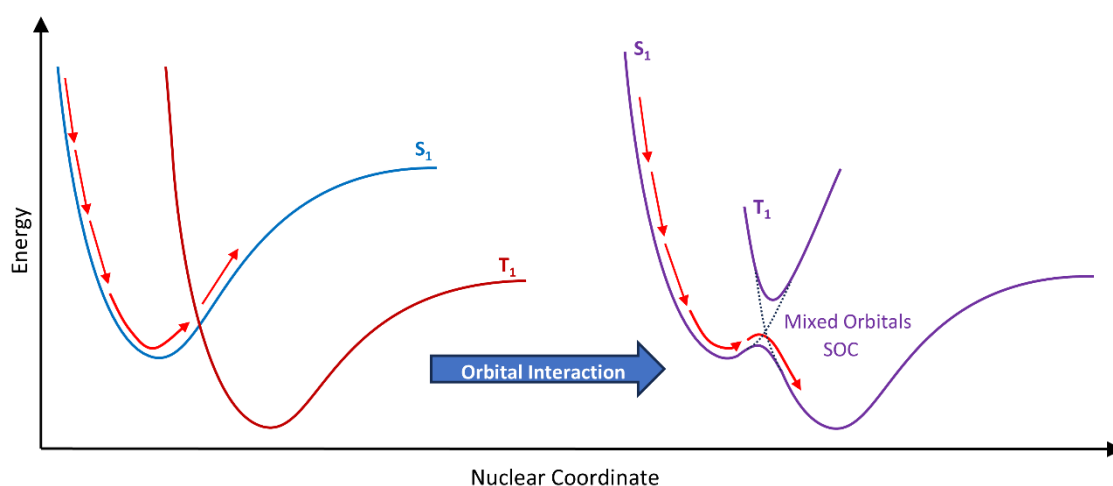


Figure 2.7. Singlet and triplet state interaction. Left, discrete S_1 and T_1 states, with no or limited interaction. Right, S_1 and T_1 state mixing due to spin orbit coupling, enabling ISC and rISC.

- d) *Intersystem Crossing (ISC)*: This is a non-radiative transition yielding a change in excited state multiplicity, for example moving from the first excited singlet state to the first excited triplet state or, in certain cases, to a higher excited triplet state, contingent upon the energy difference between these states.⁸ The timescale at which ISC occurs is termed the ISC rate (k_{ISC}), usually around $10^{7(\pm 1)} \text{ s}^{-1}$ in TADF emitters. Similar to the previous paragraph, SOC facilitates spin inversion through orbital interactions, achieved by mixing the involved singlet and triplet states (**Figure 2.7**). Notably, the El-Sayed rule stipulates that for rapid ISC, the radiationless transition should involve a change in the involved molecular orbital types.⁹ For instance, a $\pi\pi^*$ singlet strongly couples with an $n\pi^*$ triplet, and vice versa, whereas transitions between states with the same character ($\pi\pi^*$ or $n\pi^*$) are weakly coupled. As with phosphorescence, this change in orbital type allows the total angular momentum of the transition to be conserved, converting a spin-forbidden transition into a weakly allowed one.
- e) *reverse Intersystem Crossing (rISC)*: Although there is no defined direction for ISC, in typical optical measurements it involves the conversion of optically prepared singlet states into triplet states. In recent times and in the context of TADF materials the convention of labelling the reverse process (itself also a type of ISC) has emerged, denoting the analogous transition from T_1 (or T_n) to S_1 . When the energy difference between the two states is minimal, thermal activation of the involved triplet state to a vibrational level isoenergetic with the singlet state triggers rISC. The emitted light from the rISC-populated singlet state is termed thermally activated delayed fluorescence (TADF), elucidated in detail later in this chapter.
- f) *Internal Conversion (IC)*: This transition, also non-radiative, occurs between states within the same spin manifold (e.g., S_n to S_1 , T_n to T_1) and is typically followed by vibrational relaxation down to the base vibrational level of the corresponding electronic state, followed by the release of thermal energy. The lifetime of IC typically falls within the (sub)picosecond regime, as at energies above the base of the S_1 state the density of vibronic states can be very high, accelerating this process.

2.4.3 Franck-Condon Principle

The Franck-Condon factor influences rates of individual absorption and emission transitions in a molecular system, and hence the overall spectral shape. Absorption occurs instantaneously (at around 10^{-15} s), without atomic nuclei displacement being possible. This near-instantaneous electron rearrangement alters the electric potential experienced by the nuclei, leading to slower subsequent nuclear displacement. Through such nuclear displacements the molecule will relax to the lowest vibrational level of the lowest excited state, followed by an emissive decay (in light-emitting molecules) to the ground state.

If the nuclear geometry remains relatively unchanged and the vibronic levels of the excited states closely resemble those of the ground state, the absorption and emission spectra exhibit similarity, with maximum overlap between the two base vibronic states transitions (**Figure 2.8a**). Conversely, if the molecular geometry changes in the excited state, the potential wells of the ground and excited states shift relative to each other. This diminishes the wavefunction overlap between the two states, resulting in a redshifted emission spectrum. In practice, the observed redshift reflects a redistribution of orbital overlap due to nuclear reconfiguration and manifests as a phenomenon akin to a Stokes shift.

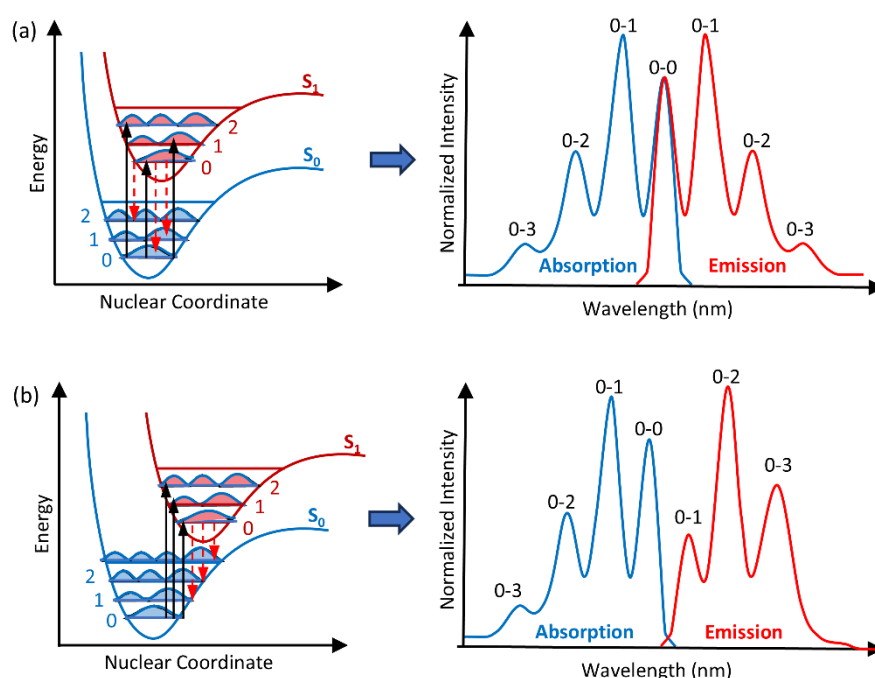


Figure 2.8. Franck-Condon principle. (a) Negligible nuclear displacement (identical excited and ground state geometries and vibrational states) leads to strong 0-0 transition overlap in absorption and emission. (b) Significant nuclear displacement (excited state geometry is shifted

compared to the ground state geometry), red shifting the onset of the emission spectrum due to negligible overlap between the ground and excited state 0-0 transition.

2.4.4 Stoke Shift

The Stokes shift arises from vibrational relaxation and solvent reorganisation effects on the molecular dipole. The latter, often referred to as solvatochromism, is discussed in subsection 2.6.1. The energetic difference between the two 0-0 transitions is defined as the Stokes shift, representing the number of vibrational quanta dissipated during relaxation. In thermally activated delayed fluorescence (TADF) molecules, this principle is strongly influenced by their CT character. The lower energy CT state, formed between the donor and acceptor unit, typically exhibits a redshifted and broad emission, giving rise to large Stokes shifts.

2.5 Delayed Fluorescence Mechanisms

As discussed in section 2.4.2, following the excitation of a ground-state electron and relaxation to the lowest vibrational level of the first excited state, several transitions can occur, including ISC. Once some excited singlet molecules ISC to populate the triplet state, they can return to the singlet excited state through three distinct mechanisms: Triplet-Triplet Annihilation (TTA), hot exciton upper state crossing (hrISC), or Thermally Activated Delayed Fluorescence (TADF). Among these mechanisms, TADF is currently of keen interest worldwide for OLED applications, as TTA can at best convert pairs of triplet excitons back into singlets, while the design rules for hrISC are not currently understood (**Figure 2.9**).

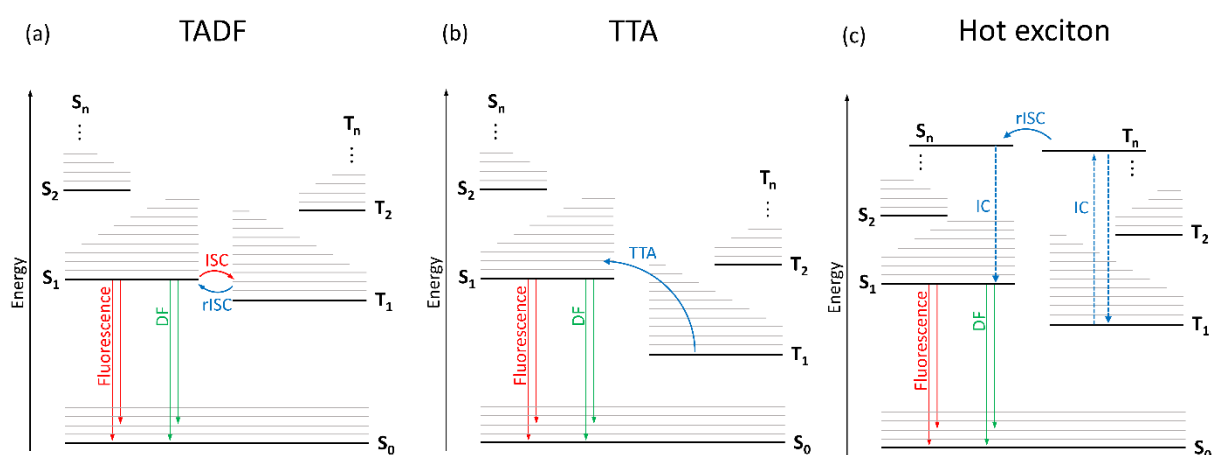


Figure 2.9. Representations of the molecular states involved in (a) TADF, (b) TTA, and (c) hot exciton upper state crossing.

2.5.1 Triplet-Triplet Annihilation

TTA is a bimolecular process, necessitating the proximity of two molecules so that their triplet excitons can interact and annihilate to form a single exciton in the lowest singlet state (**Figure 2.9b**). For TTA emitters to achieve high quantum efficiency, suitable energy state alignment is essential between the lowest triplet and singlet states, typically requiring the singlet state to be equal or more than double in energy compared to the triplet state.^{10,11} However, even under optimal conditions, the internal quantum efficiency (IQE) of TTA emitters is limited to 62.5%.¹¹ In this thesis, TTA has been occasionally encountered and investigated solely as a potential competing delayed fluorescence mechanism in some molecules that already exhibit TADF. Experimentally, discernment is achievable by measuring the delayed fluorescence intensity as a function of excitation dose. With an increased excitation dose, the triplet population increases, thus quadratically increasing the possibility of (bimolecular) triplet exciton collision. TTA can hence be identified from the double logarithmic plot of integrated delayed intensity at different excitation doses. A slope of two at low excitation doses, turning to one at high excitation doses indicates TTA, with the changeover indicating a high-efficiency regime in which triplet density is high enough that all additional excitons are likely to find a TTA partner within their decay lifetime.¹² A constant slope of one signifies a mono-excitonic process such as TADF, phosphorescence or rISC, while an intermediate slope implies inefficient TTA or mixed triplet harvesting mechanisms.¹³

2.5.2 Hot Exciton upper state crossing

The Hot Exciton mechanism, more correctly known as Upper-state Triplet Crossing, has been recently proposed for TADF.¹⁴ This mechanism necessitates an excess of energy in the populated triplet excited state to generate upper-state vibrationally excited excitons or hot (non-thermally-relaxed) excitons, which subsequently interconvert to higher-lying singlet states due to very small energy gaps at these high energies (**Figure 2.9c**). With appropriate excited state mixing, upper triplet crossing can occur via rISC to an energetically proximate upper singlet state.¹⁵ While this mechanism holds the potential to harvest 100% of triplet excitons, it encounters numerous challenges depending on the unpredictable energetic alignment of the interacting triplet and singlet states. Additionally, typically internal conversion greatly outcompetes rISC, leading to a decrease in triplet harvesting efficiency as triplet excitons cannot remain unthermalised for significant durations. Although this mechanism has not been the focus of this thesis, its introduction provides valuable insights into different delayed

fluorescence mechanisms, while also offering useful insight towards the triplet harvesting mechanism in multiple resonance TADF emitters (as discussed further below).

2.5.3 Thermally Activated Delayed Fluorescence

Thermally Activated Delayed Fluorescence (TADF),¹⁶ also known as E-type delayed fluorescence, derives its name from the compound Eosin,^{17,18} one of the first substances where this phenomenon was explored. TADF relies on the presence of a small energy gap (typically less than 200 meV) between the first singlet and triplet states, facilitating ISC between them. Subsequently, rISC occurs from the triplet to the singlet state, relying on ambient thermal energy and with the rate of rISC being temperature dependent. Emission originates from the same singlet state as fluorescence, although the excursion of excitons through and back from the triplet manifold causes this fluorescence to be significantly delayed relative to excitation (microsecond-millisecond lifetimes) compared to typical fluorescence (nanosecond lifetimes). These two features – thermal activation, and delayed emission from singlet states – give the phenomenon its name.

Adachi *et al.*¹⁹ successfully demonstrated this mechanism in 2009 using Sn(IV)-Porphyrin complexes characterized by a small singlet-triplet energy gap (ΔE_{ST}), albeit with low photoluminescence efficiency. It wasn't until three years later that the same group introduced the first series of efficient TADF emitters based on carbazolyl dicyanobenzene (CDCB), featuring carbazole as a donor (D) and dicyanobenzene as an electron acceptor (A) unit. These D-A structures exhibited highly decoupled HOMO and LUMO, localized in the D and A units, respectively, resulting in minimal ΔE_{ST} . Notably, the exemplary molecule 4CzIPN (a green emitter) achieved nearly 20% External Quantum Efficiency (EQE) OLEDs,²⁰ rivalling the performance of state-of-the-art phosphorescent OLEDs but without the requirement of heavy metal ions. Consequently, both academia and industry have allocated substantial resources to investigate the TADF mechanism, leading to the discovery of numerous novel emitting materials and surpassing the device efficiency of competing organic light-emitting technologies such as Fluorescence, TTA, and Phosphorescence.

2.5.3.1 Donor-Acceptor Molecules

As previously mentioned, a critical requirement for TADF is a small ΔE_{ST} between the lowest singlet and triplet states. Achieving this necessitates a reduced overlap between the HOMO and LUMO, typically facilitated by a highly twisted structure, and thus electronically decoupled D-A molecule (**Figure 2.10a**). The HOMO becomes localized on the electron donor

unit, while the LUMO resides on the acceptor unit (**Figure 2.10b**), also resulting in prominent Charge Transfer (CT) states between the two. Locally excited (LE) states associated with the donor and acceptor units themselves also possess individual singlet and triplet states interleaved with those of the CT manifold. Notably, the CT singlet (^1CT) state is usually lower than the equivalent LE singlet (^1LE) state(s). Conversely, the energy of the CT triplet state (^3CT), which is energetically proximate to the ^1CT state, can be higher, similar, or lower compared to the LE triplet (^3LE) state(s) (**Figure 2.10c**). This ordering of excited states holds crucial importance in the design of TADF molecules, as the relative position and spacing of the ^3CT with respect to the ^3LE dictates the type of TADF and consequently, the rate of reverse intersystem crossing (k_{rISC}), as discussed below.

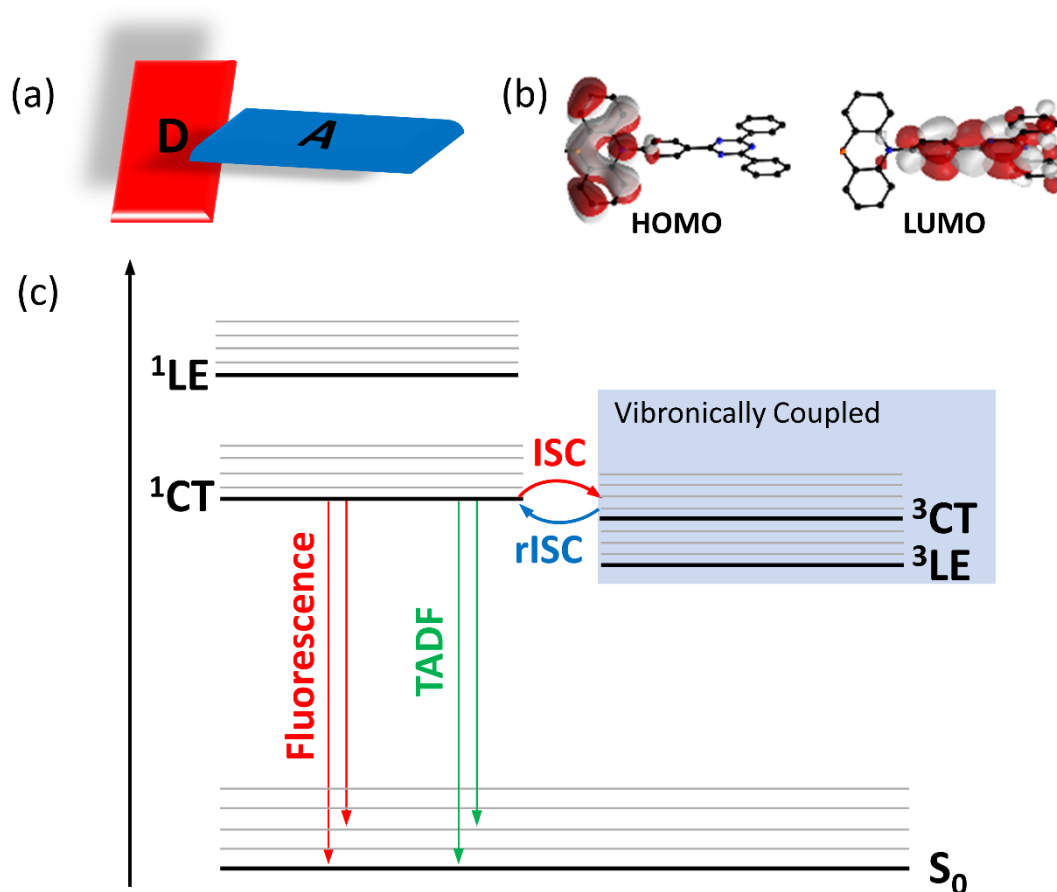


Figure 2.10. (a) Illustration of a highly twisted D-A molecule, leading to (b) HOMO-LUMO separation (the HOMO is localized in the donor unit and the LUMO is localized in the acceptor unit). (c) Schematic representation of the molecular energy levels and key transitions involved in the TADF mechanism under the vibronic coupling model.

The core of understanding the TADF mechanism lies in comprehending how singlet and triplet states interact and facilitate channels for (r)ISC. Contrary to initial interpretations of the

process, transitions between the ^1CT and ^3CT states via SOC are forbidden. This is due to the fact that SOC between singlet and triplet states with identical orbital distributions is zero,²¹ as any change in electron spin cannot be offset by a corresponding change in (unchanging) orbital angular momentum (see the converse of El-Sayed rule discussed above, in subsection 2.4.2 d). Alternatively, Ogiwara *et al.*²¹ proposed, using electron paramagnetic resonance (EPR) spectroscopy, that rISC is driven by hyperfine-coupling-induced ISC. This mechanism arises from interactions between an electron's spin and nuclear spins, making it entirely local and unaffected by electron-hole separation and electronic orbital character as in SOC. However, due to the limited overlap between relatively large electron and relatively tiny nuclear wavefunctions (required for angular momentum exchange), hyperfine coupling constants are exceedingly small, resulting in estimated rISC rates approximately five orders of magnitude smaller than experimentally obtained rates. Similarly to ^1CT - ^3CT SOC and hyperfine coupling, 'El-Sayed allowed' SOC between ^1CT and nearby ^3LE states also cannot explain the anomalously large experimental rISC rates.

The disagreement between theoretical predictions and experimental observations concerning k_{rISC} and the associated excited states was effectively bridged in 2016, with the introduction of the most precise model of the TADF mechanism to date. The groundbreaking theoretical work by Penfold *et al.*,²² building upon earlier investigations by Chen *et al.*²³ and Marian *et al.*²⁴, alongside the experimental contributions of Monkman *et al.*²⁵, emphasized the significance of vibronic coupling between the lowest ^3CT and ^3LE states, typically originating from the triplet states of either the donor or acceptor unit. This vibronic coupling mediates the SOC and, consequently, facilitates rISC between singlet and triplet states. The non-adiabatic coupling between the lowest triplet states (illustrated as mixed states similar to Figure 2.7) is notably larger than typical spin-orbit coupling, resulting in the rapid establishment of equilibrium between the two triplet states via reverse internal conversion (rIC). Subsequently, the ^3CT state can become coupled to the singlet charge-transfer (^1CT) state (by default El-Sayed forbidden) via coupling elements derived from second-order perturbation theory, mediated by the ^3LE state:

$$k_{\text{rISC}} = \left(\frac{2\pi}{\hbar} \right) \left| \frac{\langle ^1\Psi_{\text{CT}} | \hat{H}_{\text{SOC}} | ^3\Psi_{\text{LE}} \rangle \langle ^3\Psi_{\text{LE}} | \hat{H}_{\text{vib}} | ^3\Psi_{\text{CT}} \rangle}{\delta(^3E_{\text{LE}} - ^3E_{\text{CT}})} \right|^2 \delta(^3E_{\text{CT}} - ^1E_{\text{CT}}) \quad (2.5)$$

Hence, the vibronic coupling between the lowest ^3CT and ^3LE states plays a pivotal role in determining the otherwise unexplained efficiency of rISC and TADF. In instances where the

two triplet states are uncoupled, the rate of reverse intersystem crossing (k_{rISC}) tends to be poor, approaching zero, especially when the ΔE_{ST} is substantial. Conversely, in the presence of coupled triplet states, the relative positions of ^3CT with respect to ^3LE delineate the three types of TADF (**Figure 2.11**), with type II TADF considered the most efficient and appealing approach.

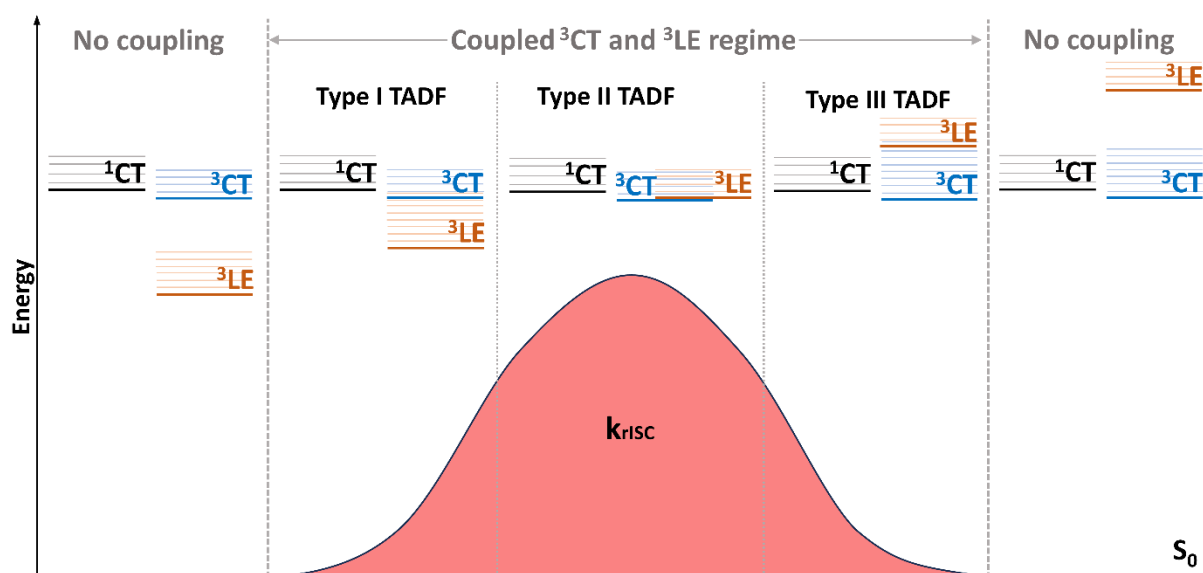


Figure 2.11. TADF types, based on the energy levels of relevant electronic states, and the effect of vibronic coupling between ^3CT and ^3LE on k_{rISC} . The red curve indicates trends in the magnitude of k_{rISC} as the ^3LE is raised in energy from left to right.

2.5.3.2 Multiple-Resonance Type

Multiple-resonance (MR) TADF emerged as a new generation of TADF emitters, introduced in 2016 by Hatakeyama *et al.*²⁶ Unlike conventional D-A type TADF molecules, MR-TADF emitters feature a planar molecular geometry and necessitate at least one electron-donating atom (typically nitrogen or oxygen) with electron-deficient atoms (such as boron) positioned within a fused polycyclic framework (**Figure 2.12b**). As previously mentioned, TADF requires the separation of HOMO and LUMO, achieved through perpendicular segments in D-A molecules. In fully planar MR-TADF molecules, this separation instead occurs through the complementary resonance effect of electron-donating and accepting atoms. The electron-rich regions predominantly reside on the donor atoms and the carbon atoms positioned ortho and para to them, while electron-deficient regions are concentrated on the acceptor atoms and their ortho and para-positioned carbon atoms (**Figure 2.12b**). This structural arrangement results in the formation of short-range CT states, with HOMO and LUMO interpenetrating each other, but never directly overlapping. This arrangement of orbitals facilitates active triplet harvesting

channels, while the rigid planar structure supports narrow emission and high PLQY that often eludes D-A materials (**Figure 2.12**).

The triplet harvesting mechanism in MR-TADF emitters, as elucidated by Penfold *et al.*,²⁷ shares similarities with typical D-A type TADF emitters, involving a second-order spin-vibronic coupling. However, a key distinction lies in the nonadiabatic coupling between higher vibrational sublevels of the first singlet state and higher-lying singlet states (in contrast to the nonadiabatic coupling between triplet states in D-A type TADF emitters), which mediates spin-orbit coupling (SOC) with these higher-lying triplet states (e.g., T_2 , T_3 , ... T_n). This divergence arises due to the relatively large energy gaps (ΔE_{ST}) between the S_1 and T_1 states, and their correspondingly small SOC elements. Consequently, the higher-lying singlet state(s) interacts analogously to the ^3LE state in D-A type TADF systems, albeit without necessitating significant charge population from S_1 via rIC. (r)ISC takes place between S_1 and this higher-lying triplet state, analogous to the hot exciton upper state crossing triplet harvesting mechanisms discussed earlier. Numerous strategies have been proposed to enhance the reverse intersystem crossing rate of MR-TADF emitters, including reducing ΔE_{ST} through π -extension of the multiresonance skeleton^{28–31} or augmenting SOC by incorporating heavy atoms.³²

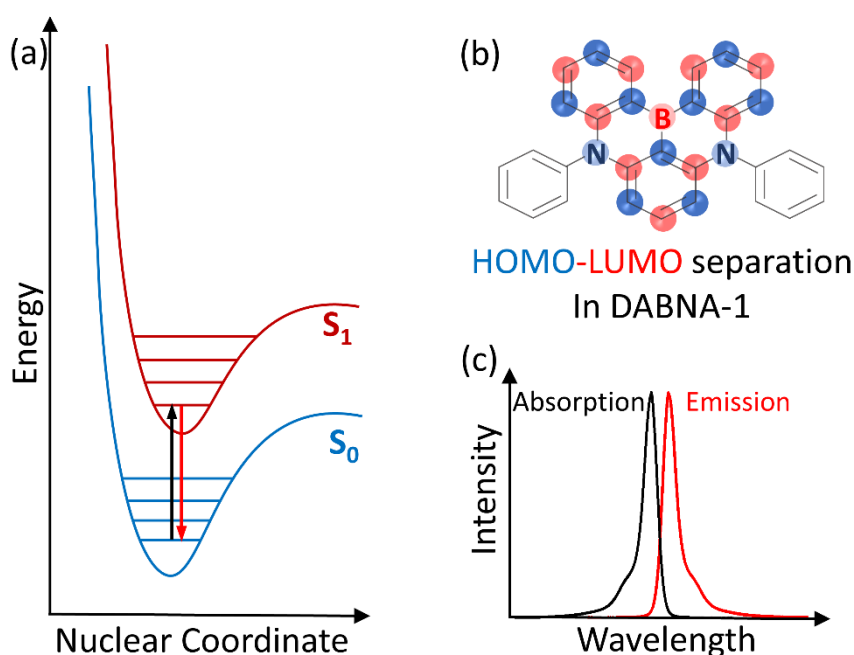


Figure 2.12. (a) Sliced potential energy surface of an MR-TADF emitter. Because of the similar ground and excited state geometries and vibrational levels (c) narrow emission, FWHM, and small Stoke shift are observed. (b) HOMO (blue) and LUMO (red) localization

of the MR-TADF DABNA-1, demonstrating the multiple resonance effect that establishes non-overlapping but interpenetrating molecular orbitals.

This thesis explores several novel MR-TADF emitters, with a primary focus on their application as efficient terminal emitters in hyperfluorescence (HF) OLEDs. To achieve this objective, an extended molecular version of DABNA-1 (depicted in Figure 2.12b), namely v-DABNA,³¹ is utilized due to its acceptable triplet harvesting efficiency and narrow blue emission.

2.6 Molecular Interactions

So far in this chapter molecular properties and mechanisms have been explored purely in isolation without considering interactions between molecules or their surroundings, with the exception of bi-excitonic TTA mechanism, which involves a bimolecular process. However, in condensed matter applications molecules are rarely isolated, and especially so in organic thin films used in devices like OLEDs. These films typically consist of multiple co-deposited molecules sandwiched between two electrodes. Even when a thin film contains only one material, its molecular properties are influenced by interactions with neighboring molecules (homo-molecular interactions, such as dimer or excimer formation). Conversely, in films with multiple materials, interactions between the same and/or different molecules occur (hetero-molecular or host-guest interactions). Often in fundamental optical studies, materials are dissolved and studied in solvents, where interactions between the solvent and solute molecules impact their properties. These interactions are primarily mediated by the ground and excited state dipole moments of the solute and solvent. D-A type TADF molecules tend to have large dipole moments, making them highly sensitive to solvent-solute interactions in particular.

2.6.1 Dipole Moment

A molecule exhibits a permanent dipole moment when it possesses an asymmetric charge distribution resulting from differences in electronegativity within its structure. This asymmetry leads to the formation of polar bonds and, in some cases, polar molecules. For example, water (H₂O) displays a polar bond between hydrogen and oxygen due to the electronegativity difference, with the positive pole on hydrogen and the negative pole on oxygen. The bent V-shape of the water molecule ensures that these bond dipoles do not cancel out, resulting in a net molecular dipole. In contrast, carbon dioxide (CO₂) also contains polar C-O bonds with a positive pole on carbon and negative poles on oxygen. However, the linear geometry of CO₂

causes the dipoles to cancel each other, leaving the molecule nonpolar. The strength of the interaction between a charge distribution and an external electric field depends on the dipole moment, with stronger dipoles exhibiting greater interactions.

For molecular transitions, the transition dipole moment rather than the permanent dipole moment determines the interaction strength with an electric field. This transition dipole moment is evaluated using an integral that involves the wavefunctions of the initial and final states involved in the transition. Unlike the permanent dipole moment, which is determined by a single state, the transition dipole moment reflects the interaction that drives changes between two states under an electric field. Its magnitude provides insight into the strength of coupling between the states and the probability of transitions, forming a fundamental basis for understanding spectroscopic and photophysical processes.

2.6.2 Solvatochromism

Solvatochromism describes the phenomenon wherein the emission colour of a material (solute) changes in solvents of varying dielectric constants (or polarities).³³ This pronounced colour change, observed in the photoluminescence spectrum, stems from the excited state molecular dipole interacting with solvent molecules, which form a thin shell around the solute. Upon excitation of the solute, it undergoes some near-instantaneous change in electronic distribution and therefore electric dipole moment, although solvent molecules will initially maintain their orientation as determined by the ground-state solute charge distribution. Typically, within picoseconds the solvent dipoles will gradually reorient to align their dipole moments with that of the solute, thus minimizing the system's total electrical potential energy through the intramolecular Coulomb interaction. This relaxation reduces the energy of the excited CT state, and so causes changes in the emission spectrum of the solute in terms of position, intensity, and band shape. Negative solvatochromism refers to a shift to higher emission energies (blueshift) with increasing solvent polarity, usually associated with $n\pi^*$ transitions, while positive solvatochromism results in shifts to lower energies, as is often the case for most TADF emitters. Identifying positive solvatochromism serves as a means to experimentally confirm a strong CT state. Conversely, LE states, lacking considerable change in dipole moment between ground and excited states, are insensitive to changes in environmental polarity. This insensitivity also extends to Multiple-Resonance (MR) TADF molecules with short-range CT emissive states, that screen each other from external perturbation and for which the photoluminescence spectrum only experiences slight broadening in high dielectric solvents.

In the context of D-A type TADF emitters, knowing the value of the lowest ^3LE state of a TADF molecule allows for the selection of solvents with suitable dielectric constants to minimize the energy splitting between the polarity-sensitive ^1CT and the polarity-insensitive ^3LE , and thus dramatically increases the triplet harvesting rate. Additionally, at low temperatures (below the solvent's freezing point), the solvent shell becomes unable to reorient effectively and relax the Coulomb energy. Consequently, the emission colour of a solute in high-polarity frozen solvents can become similar to that observed in low-polarity solvents at room temperature. Unable to reorient, the solvent loses its ability to impact the solute through dipole alignment.^{34,35}

2.6.3 Solid State Effects

Analogous effects also exist when an emitter is incorporated into a solid host matrix. Depending on the dielectric constant of the host material, the emitter's CT state can be tuned, albeit to a lesser extent compared to the solution state.³⁶ This diminished tuning capability arises from the inability of 'solute' and 'solvent' molecules to rotate freely within the solid-state matrix (steric effects), which limits the dipole reorientation of host molecules around the emitter. While solid state effects may modestly adjust the energy of the emitter ^1CT state, they typically cannot enhance the efficiency of weakly TADF-active emitters to the larger extent observed in well-matched solvents.

Steric effects in the solid state can also hinder the emitter's conformational relaxation. This phenomenon, proposed by Dias *et al.*,³⁵ suggests the presence of conformational heterogeneity in the films, wherein a distribution of CT states emits at different energies and exhibits distinct decay kinetics. This aspect is thoroughly investigated in chapter 4.

Another distinction between solution and solid states is the spacing between emitter molecules. In solution, the solute-to-solvent ratio remains minimal, even in nearly saturated solutions, resulting in emitter molecules being tens of nanometers apart. In contrast, in the solid state, the emitter-to-host ratio is significantly higher (especially in OLEDs), leading to much smaller intermolecular distances, exposing the emitter molecules to prevalent intermolecular interactions in the form of dimer formation and aggregation.

2.6.3.1 Homo-molecular Interactions

Emitter molecules, when in close proximity, can interact and form aggregates. Depending on the nature of the interaction, individual molecules (monomers) can combine to form dimers, trimers, and higher-order aggregates, depending on the number of involved monomers. Due to

interactions of the comprised molecules' electronic systems (analogous to solvatochromic effects discussed above), the formed species have altered ground and excited states that are typically lower in energy compared to the isolated monomer. Such homo-molecular species can often be detected via absorption spectroscopy, as the newly formed ground state typically exhibits lower energy absorption bands compared to the monomer. Additionally, some monomers interact only in the excited state, leading to the formation of excimers (excited-state dimers, which have no ground state). In this scenario, the monomer's ground state (and absorption spectrum) remains unaffected, and the effect can only be observed using photoluminescence techniques.

2.6.3.2 Hetero-molecular Interactions

As mentioned earlier, emitter molecules can also interact with host molecules. Depending on the energies of the HOMO and LUMO of the involved molecules, new complex species can be formed. If the interaction occurs in the excited state, the resulting species is termed an exciplex, characterized by a strong CT character and possessing a large dipole moment akin to that of D-A TADF molecules. The energy of the exciplex's first excited state is determined by the energetic difference between the higher LUMO and the lower HOMO of the bimolecular system, as illustrated in **Figure 2.13**.

Exciplex species typically form between two different host or electron/hole transport molecules. This generates a CT species occasionally with TADF properties, as the HOMO and LUMO of the excited state are well-separated across different molecules. Such exciplexes find widespread application in OLEDs due to their ability to offer better control over the charge transport properties within the emissive layer. Additionally, through TADF they can provide extra triplet harvesting channels in some cases.

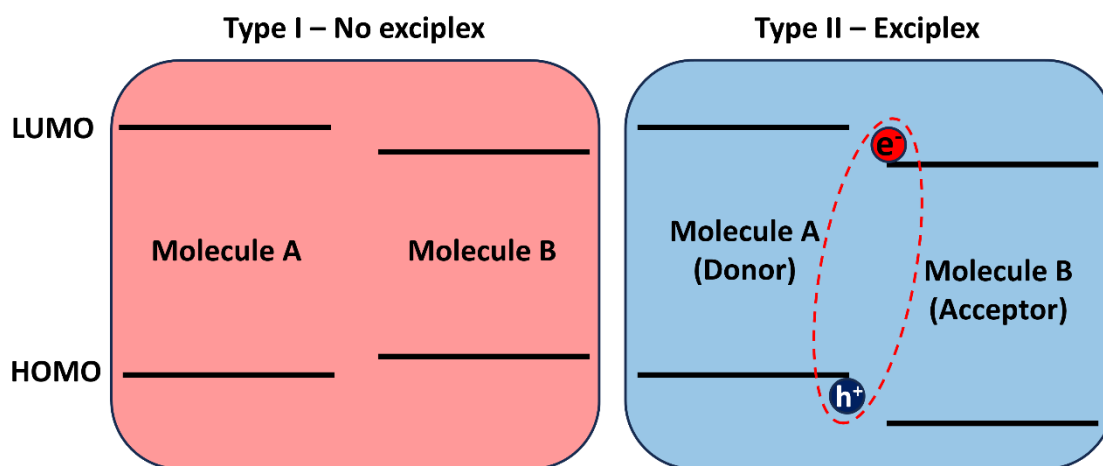


Figure 2.13. Illustration of conditions and molecular orbitals involved in exciplex formation. Left, no CT formation and energy transfer from molecule A to B occurs. Right, suitable energy level combination between the two molecules to promote CT and exciplex formation.

2.7 Energy Transfer

Analogous to how excitons can relax to lower excited states within a molecule through IC, when two molecules with differing excited state energies interact, the excitation of the higher-energy molecule can, in some cases, be transferred to the lower-energy one. Depending on the involved states, distinct mechanisms control the energy transfer process.

2.7.1 Förster Resonance Energy Transfer

In the case of energy transfer from a singlet or triplet state of an excited molecule to the singlet state of another (relaxed) molecule, Förster resonance energy transfer (FRET)³⁷ is usually the dominant pathway. An important requirement is the emission spectrum of the higher energy (donor or sensitiser) molecule to overlap with the absorption spectrum of the lower energy (acceptor or terminal emitter) molecule, thus giving intermolecular dipole-dipole coupling (**Figure 2.14b**). This leads to a non-radiative energy transfer from the donor chromophore to the acceptor chromophore (**Figure 2.14a**). The efficiency of this energy transfer is inversely proportional to the sixth power of the distance between the donor and acceptor, making FRET highly sensitive to even small changes in intermolecular distance.³⁸

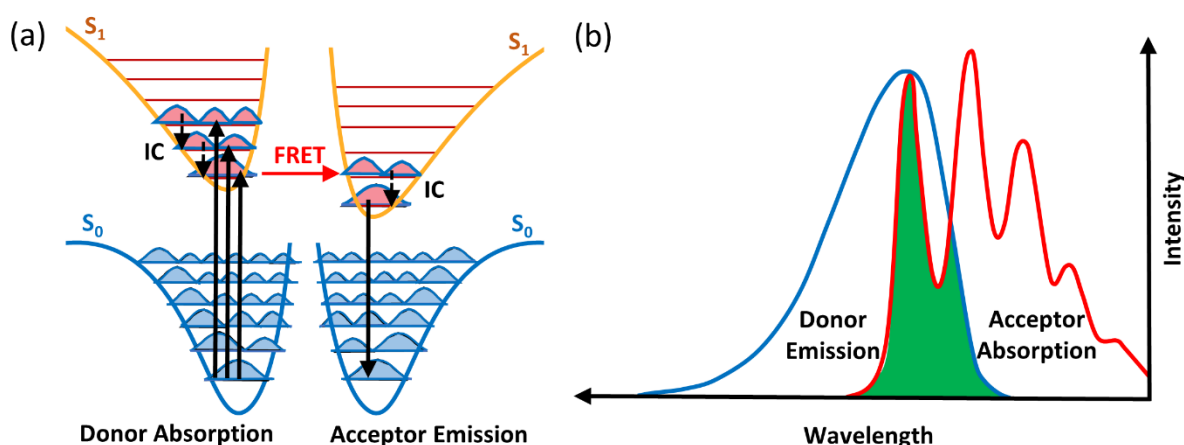


Figure 2.14. (a) FRET between an excited donor to an acceptor molecule. (b) Acceptor's absorption and donor's emission spectral overlap (green area).

Consequently, measurements of FRET efficiency offer a valuable means to determine the proximity of two fluorophores, providing accurate assessments of molecular distance within

the range of 1 to 10 nm. Efficient energy transfer is achieved when the donor and acceptor molecules are positioned within the Förster radius (R_0), representing the distance at which energy transfer from the donor to the acceptor represents a 50% likelihood out of all competing deactivation processes. A detailed mathematical analysis of the FRET model is presented in sub-section 3.7.4.

2.7.2 Dexter Energy Transfer

In contrast, triplet-to-triplet state energy transfer occurs via the Dexter³⁹ mechanism. This transfer mechanism requires two simultaneous spin flips to proceed, and so would typically be expected to be strictly forbidden. However, wavefunction overlap between the donor and acceptor molecules at short distances (typically below 1 nm) can instead allow this outcome to arise through simultaneous bidirectional transfer of electrons with paired spins. The net result is that the molecule with the lower-energy triplet excited state gains both energy and unpaired spin from the electron it receives, while the higher-energy donor returns to its S_0 ground state with now-paired electron spins. However, as the triplet excitons relevant to Dexter transfer are not directly detectable through emission, the kinetics of this process remain difficult to quantify.⁴⁰

2.8 Organic Light Emitting Diodes

An OLED is a stack of organic thin films sandwiched between electrodes in which the emissive layer (the layer which incorporates an efficient emissive molecule) emits light in response to an electric current. A brief history of OLEDs and the different OLED categories have been discussed in chapter 1.

2.8.1 Mechanism

In OLEDs operating under forward bias, charges are injected from the anode (holes) and cathode electrodes (electrons). At the metal-organic interface, charges accumulate and overcome interface barriers to enter the organic semiconductors. Holes are injected from the anode's Fermi level into the HOMO level of the hole transport layer (HTL), while electrons are injected from the cathode's Fermi level into the LUMO energy level of the electron transport layer (ETL). Due to the low charge carrier concentration within the transport layers and under applied voltage, the HOMO and LUMO energy levels develop a slope across the device, necessary to facilitate the injection of charge carriers and their transport across the device (**Figure 2.15**). These charges then traverse the bulk of the organic semiconductor layers by

hopping from one molecule's LUMO to the LUMO of an adjacent molecule for electrons, and from one molecule's HOMO to the HOMO of an adjacent molecule for holes. This charge transport process is not entirely barrier-free though, as molecules polarize upon charging, resulting in a polaron binding energy, necessitating very thin organic layers within devices. When electrons and holes come in close proximity, they experience mutual Coulomb attraction forming a bound state known as an exciton. Upon this formation through recombination, excitons may either decay radiatively or non-radiatively, generating heat. Ideally excitons are formed in the emissive layers (EML), and light emission occurs when the excited molecules transition electronically from their excited states to the ground state. The choice of materials in the EML can itself significantly alter the relaxation processes of the excitons formed there, for example through the radiative decay of triplet excitons enabled by phosphorescent dopants.

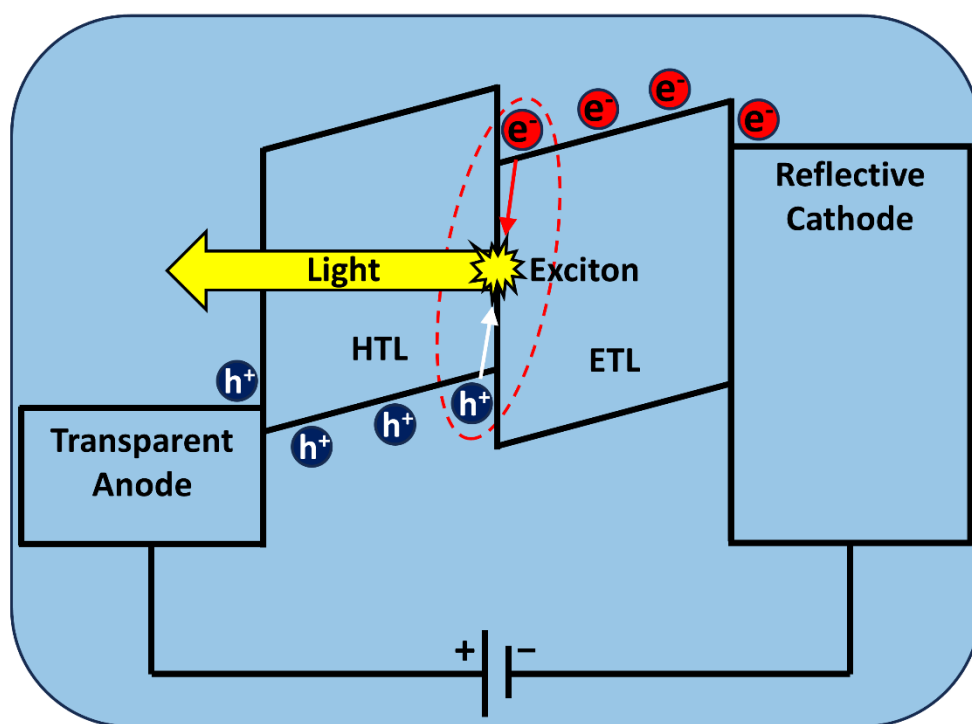


Figure 2.15. General operation principle of an OLED. For simplicity, a two-layer device is shown. In principle, OLED is a multilayer stack as shown in Figure 2.16.

2.8.1.1 Charge Transport Mechanism

Charge transport in disordered systems, such as organic semiconductors, is predominantly governed by a hopping mechanism. In these systems, charge carriers move between states via hopping, as the wavefunction overlap between adjacent sites is insufficient for coherent band-like transport. The high disorder that is found in amorphous thin organic films makes the

charges to be localized; therefore, they can be transported through the film by hopping among molecules. These molecules have a distribution of energy states. This distribution is caused by the random orientation of the deposited molecules in the amorphous phase. Between these energy states there is a small energy barrier for hopping from one molecule to another; this renders the hopping process as thermally activated. The rate of hopping depends on the energetic and spatial proximity of localized states, as well as the thermal energy available to overcome energy barriers between them.

2.8.1.2 Density of States (DoS) and Disorder

The distribution of localized states, represented by the density of states (DoS), plays a critical role in determining transport properties. In disordered materials, the DoS is typically characterized by a broad distribution, such as an exponential or Gaussian shape, reflecting the inherent energetic and structural disorder. This disorder creates an uneven landscape of trap states, leading to mobility that is strongly temperature- and field-dependent.

Energetic disorder, arising from variations in molecular orientations, electronic couplings, and local dielectric environments, can significantly impede charge transport by increasing the likelihood of carrier trapping in deeper localized states. Structural disorder, on the other hand, impacts the spatial connectivity between hopping sites, further reducing mobility. The interplay between these forms of disorder governs the overall efficiency of charge transport.

To improve charge transport, doping is commonly employed to increase the number of available charge carriers or modifying the material's energy landscape. In this process, electron donors (n-type doping) or acceptors (p-type doping) dopants introduce additional charge carriers into the material. These dopants interact with the host material to either inject electrons into the conduction band or create holes in the valence band, thereby increasing the carrier density.

2.8.2 Structure

The organic emitting molecules, whose properties have been thoroughly examined (*vide supra*), constitute just one component of the overall OLED structure. Their primary function is to convert all injected charges into photons efficiently, and in some cases control the wavelength of these emitted photons. Although only singlet excitons are optically generated (initially), under electrical excitation, the random recombination of spin-up or spin-down charge carriers leads to 25% of excitons exhibiting singlet character and 75% having triplet

character. This imbalance underscores the importance of TADF emitters, prized primarily for their triplet harvesting efficiency. As well as being intrinsically non-emissive, triplet excitons also often possess longer excited state lifetimes than singlets, rendering them susceptible to and responsible for triplet quenching phenomena in a device. Therefore, an ideal TADF emitter should have rapid rISC and short excited-state lifetimes, minimizing the buildup of triplet exciton population.

Achieving optimal performance in multilayer OLEDs necessitates a delicate balance between the optical and electrical parameters of the organic layers involved. Any imbalance for example in the recombination zone location and width, may undermine efficient emission properties of the organic emitters, with a plethora of possible quenching channels that must be managed and minimized. It is noteworthy that this balance varies between top and bottom-emitting OLEDs, although the focus here is on the latter throughout. To support the fine-tuning of optical and electrical parameters, OLEDs have evolved into complex structures sometimes comprising more than ten organic layers (**Figure 2.16**). Details of the layers relevant to this thesis include:

- a) *Anode*: Serving as the transparent electrode in bottom-emitting OLEDs, this layer requires high transparency and ideally a low refractive index to prevent waveguided trapping of generated photons. Electrically, it necessitates a high work function and a Fermi energy level close to the HOMO of common HTL materials (around 5 eV). Furthermore, good conductivity and low roughness are crucial for hole mobility and film uniformity in subsequent layer(s). Indium Tin Oxide (ITO), a ternary composition of Indium, Tin, and Oxygen, is the most commonly used anode material that adequately achieves all of these properties.
- b) *Hole injection layer (HIL)*: This material, with high hole mobility, bridges the inorganic anode and the organic HTL by lowering the hole injection energy barrier. Common materials are HATCN (structure in chapter 3) and MoO₃.
- c) *Hole transport layer*: Responsible for hole conduction, this layer transports holes towards the EML. Most HTL materials are carbazole or other aromatic amine based, and can in many cases also perform the role of electron blocking layer.
- d) *Electron blocking layer (EBL)*: Acting as a thin hole-conducting material, similar to HTL but with a shallow LUMO, it is not conducive to electrons and instead confines them in the EML (**Figure 2.16**).
- e) *Emissive layer (EML)*: Located in the middle of the device where electron-hole recombination occurs, this layer typically comprises a host material and the organic

emitting material as a dopant. In some cases, a second host (for improved charge balance) and/or emitter material (in hyperfluorescence OLEDs) are utilized, and conduction of electrons and holes can be supported by both the host(s) and guest(s).

- f) *Hole blocking layer (HBL)*: Similar to EBL but for holes, this electron transporting material has a deeper HOMO level than the EML to prevent holes escaping the EML.
- g) *Electron transport layer*: Comprising an electron-conducting material, that provides a pathway from the cathode to the emissive layer.
- h) *Electron injection layer (EIL)*: A material with high electron mobility. It bridges the inorganic cathode and the organic ETL by lowering the electron injection energy barrier. Common materials are LiF and Liq.
- i) *Cathode*: Consisting of a low-work function material, with a Fermi energy close to the ETL's HOMO energy value. Aluminum (Al) and Silver (Ag) are widely used materials as they are relatively cheap and durable, having replaced electrically superior but air-sensitive materials like Calcium (Ca) in recent decades.

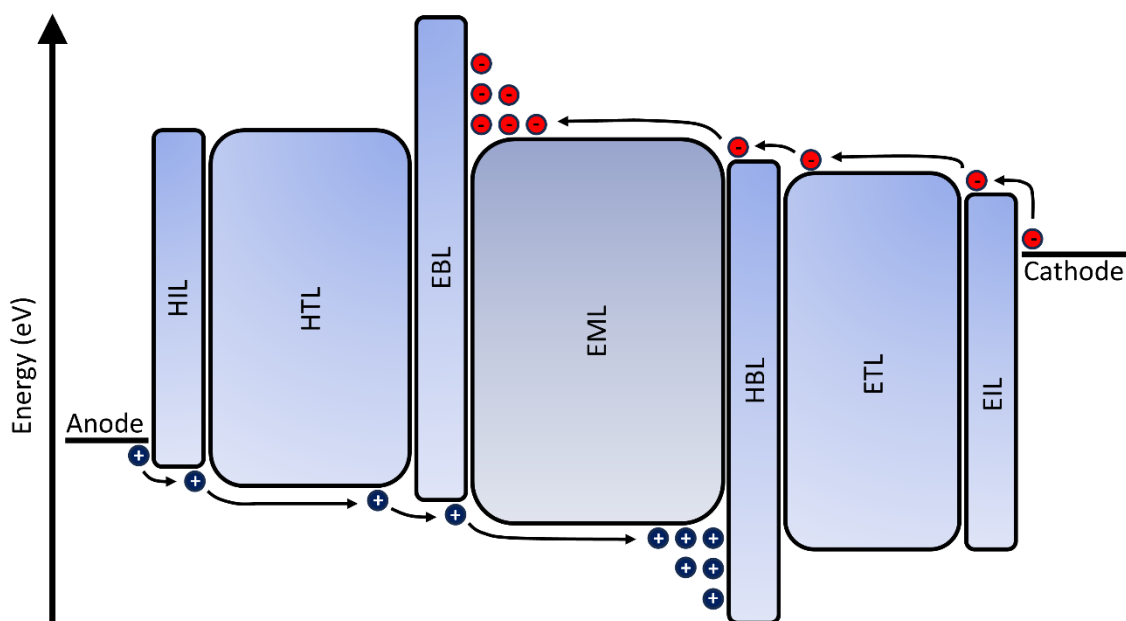


Figure 2.16. OLED structure. Red and blue circles represent electrons and holes respectively.

Although they serve different functions, certain properties such as low refractive index, optical transparency, and electrical conductivity, are essential for all layers. Additionally, controlling the mobility of injected electrons and holes to ensure similar mobilities (and balanced rates of injection) towards the EML is crucial. This fine-tuning influences the position of the recombination zone, ideally preventing interface charge recombination but also crucial for

optimizing cavity effects on the emitted photons.⁴¹ Unfortunately, optimizing cavity modes often involves a trade-off between improved radiance and an enhanced electroluminescence spectrum. While both are typically desirable, prioritizing improved radiance often comes at the expense of sacrificing the device's colour coordinates. A detailed explanation of OLED efficiency parameters is provided in sub-section 3.6.3.

2.8.3 Stability and Device Lifetime

The failure mechanisms encountered in OLED devices can be broadly classified into two categories: intrinsic and extrinsic. Intrinsic degradation pertains to challenges inherent to the materials and device structure, such as the stability of organic thin films, interfaces between anodes and organic layers, excited state molecular stability, movement of ionic impurities, diffusion of transparent electrode metals into the active layers, cation instability, large energy barriers for charge carriers, positive charge accumulation, and the width of recombination zones.⁴² Conversely, extrinsic deterioration includes factors unrelated to materials or device structure, such as environmental influences like atmospheric oxygen and moisture. Appropriate encapsulation techniques can mitigate extrinsic degradation by effectively isolating the devices from the surrounding environment, and while optional in a research context is required for all commercial applications of OLEDs.

Intrinsic degradation is commonly followed by trap formation within the bulk material,⁴³ which has dual effects: firstly, the traps serve as non-radiative recombination centers, and secondly, they impede carrier mobility, leading to an increase in the operating voltage.⁴⁴ Especially blue OLEDs suffer from intrinsic degradation processes, as discussed in chapter 1. These effects accumulate over time, ultimately resulting in significant cumulative and irreversible degradation of device performance, observed as a loss of luminance efficiency and sometimes uniformity during operation. This performance loss can be directly monitored with OLED lifetime measurements, discussed in sub-section 3.6.4.

2.8.4 TADF OLEDs

While there may be variations in device structure, the underlying principles discussed above apply for all classes of OLEDs, including for TADF and MR-TADF devices. Specific to TADF though, D-A emitters typically exhibit a broad emission spectrum, whereas MR-TADF emitters enjoy narrow emission but experience poor device efficiency roll-off (decrease of efficiency with increasing current density/luminance).

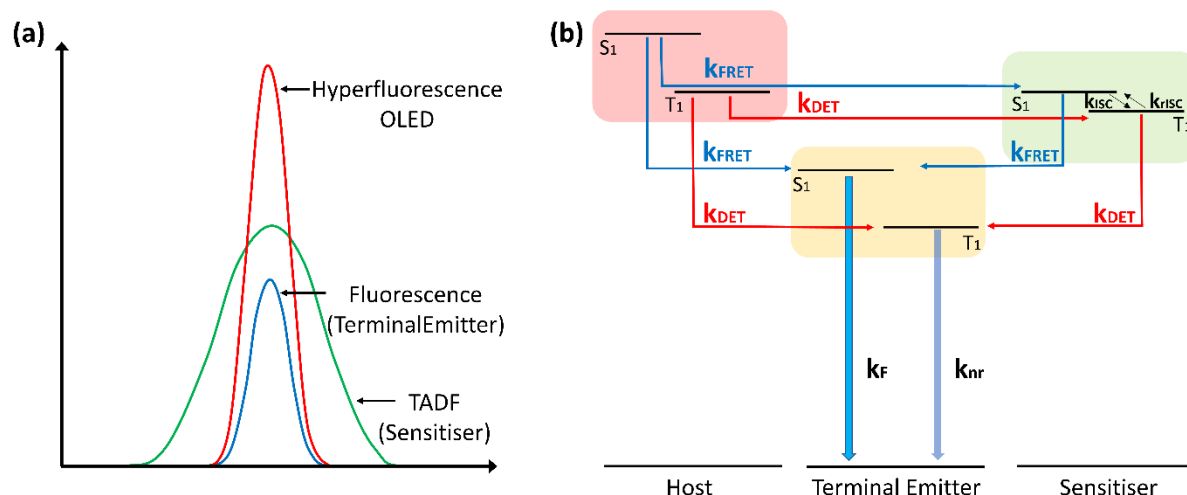


Figure 2.17. Hyperfluorescence approach. (a) Illustration of the relative electroluminescence spectra for a TADF (green), fluorescence (or MR-TADF, blue), and hyperfluorescence (red) OLED. (a) Energy transfer process between the different materials and exciton types in a host:sensitizer:terminal emitter HF-OLED.

A recent innovative approach known as hyperfluorescence (HF)⁴⁵ addresses these challenges by combining the narrow emission spectrum of an energy-acceptor molecule, referred to as the terminal emitter, with the superior triplet harvesting efficiency of an energy-donor molecule known as the sensitizer. This approach enables the emission spectrum of the D-A TADF sensitizer to become narrow while preserving its high-performance characteristics (**Figure 2.17a**). This phenomenon is facilitated through FRET from the TADF sensitizer to the terminal emitter, as illustrated in **Figure 2.17b**.

In this thesis, this specific approach is employed in various projects to address the stability issues of blue OLEDs, utilizing an MR-TADF molecule as the terminal emitter.

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3 Materials, Systems and Experimental Methods

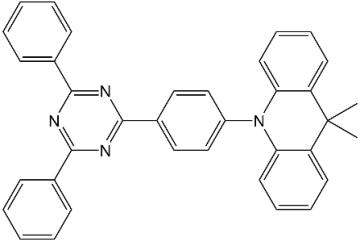
This chapter aims to provide the necessary background information required for the upcoming chapters. This includes the organic materials used, sample preparation, optical measurements, device fabrication and testing, and data analysis protocols.

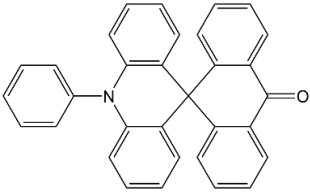
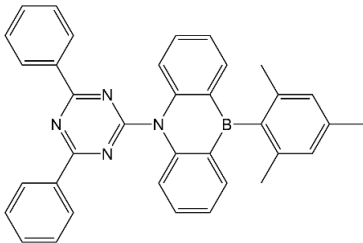
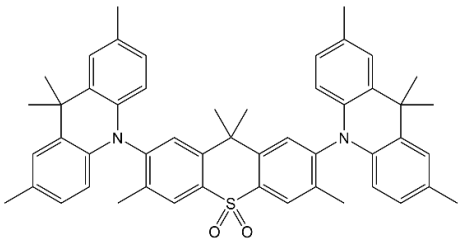
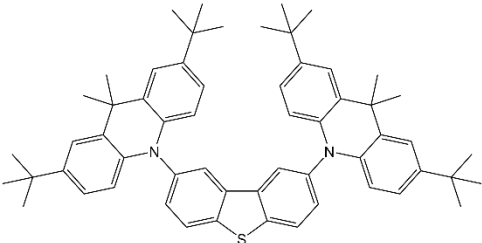
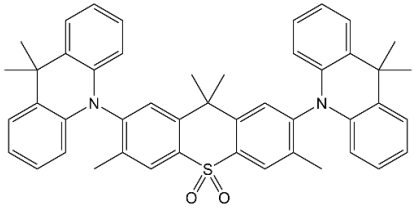
3.1 Organic Materials Used

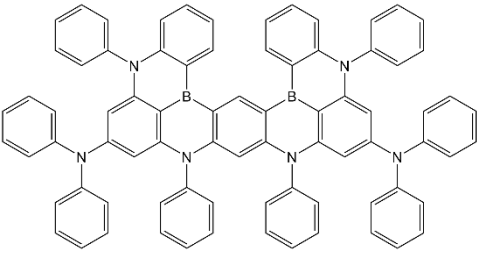
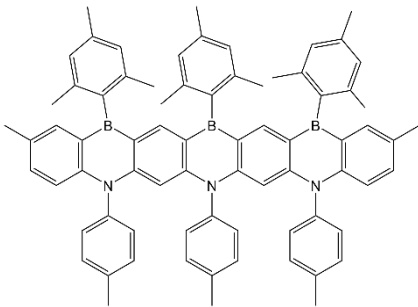
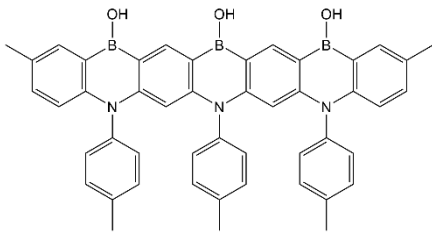
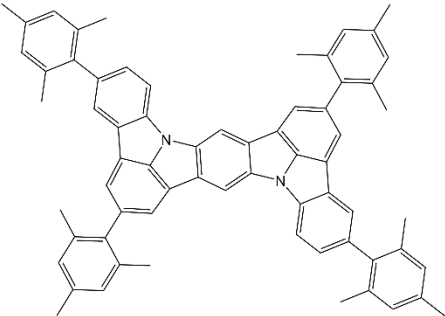
In this thesis, a large number of emitters, sensitisers, hosts, carrier transport layer and carrier injection materials were used for optical measurements and OLEDs fabrication. The D-A-D type TADF molecules (DTMA-TTXO₂, DtBuAc-DBT and DDMA-TTXO₂) were synthesized at Durham University, Chemistry Department, Prof. Martin R. Bryce Group. The α -3BNMes, α -3BNOH, DiICzMes₄, and AZB-TRZ emitters were synthesized at St Andrews University, Chemistry Department, Prof. Eli Zysman-Colman Group. v-DABNA was synthesised at Kwansei Gakuin University, Department of Chemistry, Prof. Takuji Hatakeyama Group.

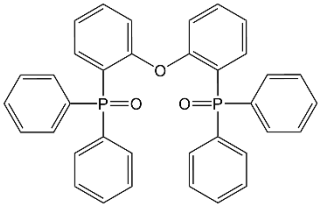
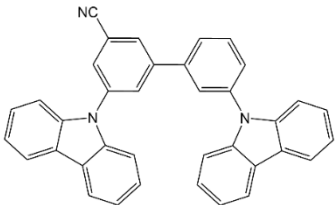
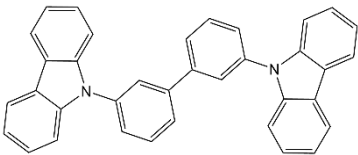
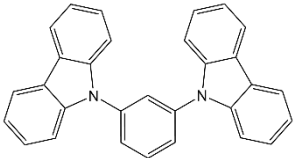
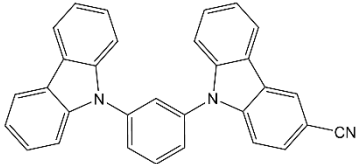
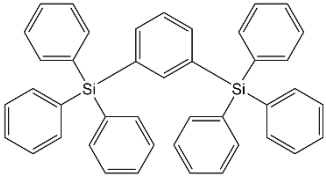
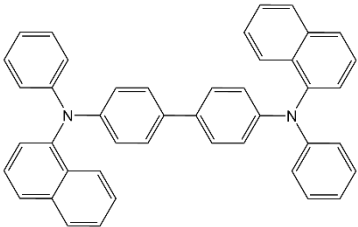
The D-A TADF emitters (DMAC-TRZ and ACRSA) were purchased from Ossila. The host and transport layer materials were purchased from Ossila, Sigma Aldrich and Lumtec. Zeonex was purchased from Zeon. PS and PMMA were purchased from Sigma Aldrich. **Table 3.1** summarises all chemical structures, chemical names, and abbreviations of the compounds used in every chapter. For photophysical studies, the compounds were used as purchased (considering a maximum impurity percentage below 2%). For device fabrication, all compounds were first purified by vacuum train sublimation (for more information see chapter 3.3), under a temperature gradient,¹ by myself, unless the synthesised samples were sublimed by the corresponding group. This is considered the most effective method for the separation of impurities from the synthesised conjugated organic molecules and depends on the different molecular weights of the different molecules. For this method to work successfully, the impurities need to have a sufficiently different vapour pressure (depending on their molecular weight) compared to the desirable final product, which is the case for most molecules.

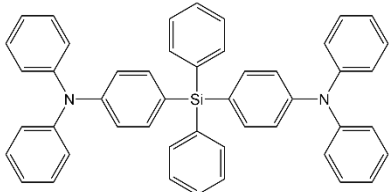
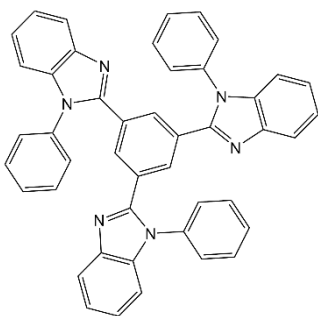
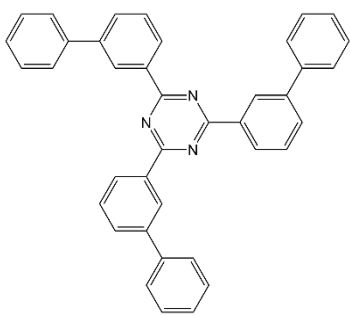
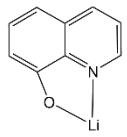
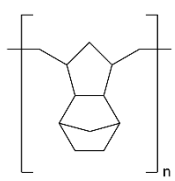
Table 3.1. Information on the materials used in this thesis.

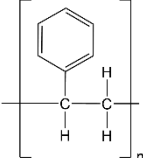
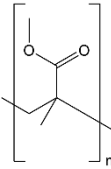
Chemical Structure	Chemical Name	Abbreviation	Chapter
Donor-Acceptor(-Donor) Type TADF emitters			
	9,10-Dihydro-9,9-dimethyl-10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)acridine	DMAC-TRZ	4,7,8

	10-phenyl-10H,10'H-spiro[acridine-9,9'-anthracen]-10'-one	ACRSA	8
	5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-10-mesityl-5,10dihydrodibenzo[b,e][1,4]azaborinine	AZB-TRZ	8
	2,7-Bis(2,7,9,9-tetramethyl-acridin-10-yl)3,6,9,9-tetramethylthioxanthene-S,Sdioxide	DTMA-TTXO ₂	5
	2,8-bis(2,7-di(tert-butyl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[b,d]thiophene	DtBuAc-DBT	6
	2,7-bis(9,9-dimethylacridin-10-yl)-3,6,9,9-tetramethylthioxanthene-S,S-dioxide	DDMA-TTXO ₂	6
MR-TADF emitters			

	$N^7, N^7, N^{13}, N^{13}, 5, 9, 11, 11$ 5-octaphenyl- 5,9,11,15 -tetrahydro- 5,9,11,15-tetraaza- 19b,20b- diboradinaphtho[3,2,1- de:1',2',3'- jk]pentacene-7,13- diamine	v-DABNA	5,7,8
	-	α-3BNMes	6
	-	α-3BNOH	6
	-	DiICzMes ₄	6
OLED host, injection and transport layer materials			

	Bis[2-(diphenylphosphino)phenyl]ether oxide	DPEPO	4, 5, 6, 7
	3,3'-di(carbazol-9-yl)-5-cyano-1,1'-biphenyl	mCBPCN	4, 7, 8
	3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl	mCBP	6, 7 8
	1,3-Bis(N-carbazolyl)benzene	mCP	5, 6
	9-(3-(9H-Carbazol-9-yl)phenyl)-9H-carbazole-3-carbonitrile	mCPCN	4
	1,3-bis(triphenylsilyl)benzene	UGH-3	4, 5, 6, 8
	N,N' -Bis(naphthalen-1-yl)-N,N' -bis(phenyl)-benzidine	NPB	5, 6, 7, 8

2.6  2.	4,4'- (Diphenylsilanediyl)bis(N,N-diphenylaniline)	TSBPA	5, 6
	2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1H-benzimidazole)	TBPi	5, 6
	2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine	T2T	6, 7, 8
-	Lithium fluoride	LiF	5, 6
	8-Hydroxyquinolinolato-lithium	Liq	6, 7, 8
Polymer Hosts			
	-	Zeonex	4, 5, 6, 7, 8

	Polystyrene	PS	7
	Poly(methyl methacrylate)	PMMA	6, 7

3.2 Sample Preparation

3.2.1 Solution

Solution samples were prepared dissolving the materials in different polarity solvents typically at $2 \times 10^{-5} \mu\text{M}$ concentration for solution measurements and stirred over night to ensure fully dissolved solutions with no intermolecular interactions. The molecules with poor solubility were stirred at higher temperatures (between 50°C and 100°C) depending on the solvent's evaporation temperature and the material's degradation temperature. For the extinction coefficient measurements, the concentration of the emitter in the solvent was determined based on the absorption coefficient of the emitter's low energy bands (typically optical density below 0.2). Then different concentrations of emitter were used to get an average extinction coefficient value, minimising the measurement error. For O_2 free measurements, the solutions were placed in degassing quartz cuvettes with a path length of 1 cm. Depending on the solvent, three to five pump freezing-thawing cycles were enough for complete O_2 removal. This step is critical to explore the triplet state contribution in the overall PL emission, as triplet states are efficiently quenched by O_2 . The quenching mechanism results in an oxygen molecule in an excited singlet state and the emitting molecule in the ground state. Room temperature and low temperature measurements of solutions were performed using a liquid nitrogen cryostat. To explore the triplet harvesting quenching and triplet energy level, low temperatures were achieved with liquid nitrogen reaching as low as 78 K, which is the boiling point of the nitrogen.

3.2.2 Films

Solid-state samples were prepared using either solution process techniques (drop-casting and spin-coating) or thermal evaporation. Drop-casted films were prepared in a small vacuum

chamber using solutions with different wt% concentration ratios of guest and host molecules and casted onto either quartz or sapphire substrates. The substrates were left under vacuum until dry. This technique requires small amounts of material and provides thick films with strong photoluminescence signal, which is important for low quantum efficiency emitters. However, the films are typically less uniform and depending on the solvents evaporation rate can sometimes form aggregates. Spin-coated films were made with similarly prepared solutions to the drop-casting technique but using higher guest-host concentrations to maximize the film thickness. The solutions were casted on a spinning substrate using the dynamic spin-coating technique and were then annealed close to the solvent's evaporation temperature but below the glass transition temperature of the molecules.² These films are typically more uniform but less thick compared to drop-casted films. Evaporated films were fabricated similarly to OLED fabrication with a Kurt J. Lesker Super Spectros deposition chamber (**Figure 3.4**), at pressures below 10^{-7} mbar. Detailed description of the system and the evaporation process can be found in section 3.6.2. This technique provides uniform films, with similar morphology to the emissive layer of a working OLED but cannot be always used because the material quantity requirements are at least 200 mg which is sometimes not the case with some studied materials. The thickness of the films were measured using an Ellipsometer (J Woollam, JAW5964), which is a known accurate technique used to measure thickness and refractive indexes of thin films on solid surfaces.

3.3 Film Thickness Measurement

Prior to OLED fabrication, precise measurement of all deposited films thicknesses is of utmost importance. Each new material used for thermal evaporation requires its individual tooling factor for accurate control of its evaporation rate during deposition, and the tooling factor value is extracted from the film thickness measurement using the following equation:

$$\text{Tooling factor} = \frac{\text{Measured Thickness}}{\text{Estimated Thickness}} TF \quad (3.1)$$

where TF represents the initial (estimated) tooling factor utilized during the film deposition process, which will subsequently be substituted with the actual tooling factor obtained from the equation. 3.1. The technique used in here to accurately measure the film thickness is spectroscopic ellipsometry (J.A. Woollam VASE ellipsometer), in Durham University, Physics Department.

3.3.1 Ellipsometry

Spectroscopic ellipsometry is an optical technique that examines the polarization change of light when it interacts with a thin film (or multi-layer structures) at different angles and a range of wavelengths. When the polarized light hits the thin film at an angle, the light's polarization state changes as it reflects off the film surface. Ellipsometry measures these changes in terms of complex amplitude ratios of the reflected light's electric field component. By employing a model-based approach, ellipsometry can determine essential thin film properties (i.e. refractive index, extinction coefficient, anisotropy etc.), including the film thickness.³

In this study, the films were deposited on silicon substrates that were 1 mm thick and coated with a thin layer of silicon oxide (SiO₂) of known thickness. This choice of substrate serves two primary purposes: firstly, the highly reflective SiO₂ surface ensures an optimal reflectance signal for the measurements; secondly, SiO₂ is a widely used standard material in ellipsometry, allowing its properties to be reliably fitted in the modeling software. As a result, the sample model only needs to focus on fitting the organic film thickness to match the simulated and actual data, streamlining the analysis process. The measurements were conducted within the wavelength range where the films are transparent, typically spanning from 500 nm to 1100 nm. The collected data were then subjected to numerical fitting to accurately estimate the film thickness.

3.4 Steady State Measurements

3.4.1 Absorption

The absorption spectra of a molecule represent the probability of a photon being absorbed by a molecule over different wavelengths. The UV-Vis absorption spectra were obtained using a Shimadzu model UV-3600 double beam spectrophotometer, which uses two samples (a reference/blank sample and the measured sample) and two identical beams, one for each sample. The measured absorption spectrum represents the optical density (OD) as a function of wavelength and is defined by the equation below:

$$OD = \log \frac{I_0}{I} \quad (3.2)$$

where I_0 is the intensity of the incident light (or the reference sample transmitted light intensity) and I the intensity of the transmitted light through the measured sample. I_0 is always greater than I as the light intensity always decreases through the measured sample when photons are absorbed.

The molar extinction coefficient (ϵ) of the measured material provides information about the oscillator strength of each transition, which can help differentiate the type of the transition (e.g. strong $\pi\pi^*$, weak $n\pi^*$, etc), and can then be estimated by the Beer-Lambert law⁴ and the following equation:

$$\epsilon = \frac{\log(I_0/I)}{lc} \quad (3.2)$$

where c is the concentration of the sample and l is the distance, the incident beam needs to travel through the sample (typically is the length of the cuvette).

3.4.2 Photoluminescence

Photoluminescence is the process in which a molecule is excited at a specific wavelength (typically at wavelengths where its absorption spectrum has positive values) and the absorbed energy converts a ground state electron to an excited state electron and then followed by the opposite transition (excited state electron converted to a ground state electron) which is usually accompanied with the emission of light, in fluorescent molecules (see Jablonski diagram in subsection 2.4.1). Steady state photoluminescence spectra were recorded using Jobin Yvon Horiba Fluorolog spectrometer or a matrix spectrometer QePro (Ocean Optics). Solution and solid-state samples can be measured both at room and low temperatures (using liquid nitrogen).

3.4.3 Photoluminescence Quantum Yield

Photoluminescence quantum yield (PLQY) is an intrinsic property of a material and is defined by the following equation:

$$\Phi_{PLQY} = \frac{\text{Photons Emitted}}{\text{Photons Absorbed}} \quad (3.3)$$

Thus, a combination of the two previous steady-state measurements can provide the PLQY of a material.⁵ Here, PLQY was acquired using a Horiba Jobin Yvon SPEX Fluorolog 3 equipped with an integrating sphere, which is based in the Chemistry Department at Durham University. Usually, two measurements are needed, one with the samples in the integrated sphere and one

with a blank sample in the sphere. This measurement can be done in ambient conditions, to estimate the oxygen quenched PLQY (no exciton harvesting from the triplet states), or under N₂ atmosphere to estimate the overall PLQY. The latter is sometimes crucial in TADF molecules. Samples with high PLQY values can be measured with accuracies close to $\pm 5\%$. Instead, for weaker emitting samples (or samples with low absorbance values at the excitation wavelength) the accuracy of the measurement is typically lower, and the error can even exceed $\pm 20\%$, depending on the measured sample properties.

3.5 Time-resolved Measurements

3.5.1 Time-resolved Photoluminescence Spectroscopy

Time-resolved photoluminescence spectroscopy is a critical tool to explore the properties of TADF molecules because it provides insights about both the singlet and triplet states response over time. Complicated TADF molecules can sometimes have photoluminescence emission from more than one states, thus a tool capable of distinguishing the different states is required. This tool is the time gated acquisition setup which can measure simultaneously the time-resolved decays and time-resolved spectra using a sensitive gated intensified charge coupled device (iCCD) camera (Stanford Computer Optics, 4Picos) with 200 ps resolution. A pulsed Nd:YAG laser emitting at 355 nm (150 ps FWHM) or a nitrogen laser emitting at 337 nm (3 ns FWHM) is the excitation source and the excitation beam path is shown in **Figure 3.1**. Once the sample is excited, promoting electrons to higher energy states, it then emits photoluminescence as the excited carriers relax back to the ground state. The emitted photons are focused into a spectrograph equipped with a 300 lines/mm grating and imaged onto the iCCD camera which is synchronised with the laser in use. For the Nd:YAG laser, the trigger is an electrical (TTL) pulse sent from the laser directly to the iCCD. For the nitrogen laser, the excitation beam is split in two, one part is directed towards the sample and the other to a photodiode which then sends electrical pulses to the iCCD (**Figure 3.1**). Once the photons reach the camera, they interact with a photocathode which converts them into photoelectrons that are multiplied in the MCP. They then hit a phosphor screen that generates photons. These photons are then focused onto the CCD chip and are converted into electrical signal.

The iCCD camera features an image intensifier to amplify weak photoluminescence signals and a fast gating mechanism that provides nanosecond-scale resolution by controlling the

temporal window of sensitivity. Its gating capability, coupled with precise synchronization with the excitation pulse, allows the capture of ultrafast photoluminescence decays. The temporal resolution, determined by the minimum gate width of 200 ps, synchronization accuracy, and the laser pulse duration, is optimized to capture specific decay dynamics with high precision.

The temporal resolution of an iCCD camera is a critical parameter in TRPL experiments, as it determines the ability to resolve fast photoluminescence decay dynamics. Important parameters are:

Gate Width: The temporal resolution is primarily governed by the minimum gate width of the intensifier. Modern iCCD cameras can achieve gate widths as short as a few hundred picoseconds (e.g., 200 ps), enabling the capture of ultrafast luminescence events.

Synchronization Accuracy: Precise synchronization between the camera gating and the excitation pulse is essential. Jitter in synchronization introduces temporal smearing, reducing effective resolution.

Pulse Duration of the Excitation Source: The excitation pulse duration sets a fundamental limit on the system's temporal resolution. For ultrafast dynamics, femtosecond or picosecond lasers are typically used.

Signal-to-Noise Ratio (SNR): While shorter gate widths improve temporal resolution, they also reduce the signal intensity. Optimizing SNR is crucial for accurate measurements.

Decay Time Range: iCCD cameras are versatile and can be used to study a wide range of decay times, from ultrafast processes (picoseconds) to longer timescales (microseconds to milliseconds) by adjusting the gate delay. The setup is controlled by the 4 Picos software and its main parameters are the chosen time delay (time after the trigger pulse at which the camera starts collecting) and integration time (the time window during which the camera is collecting). The setup can use delay times from 0.2 ns – 99 ms, if the laser pulse frequency is 10 Hz, and up to 1 s if the pulse frequency is 1 Hz. The latter is important for long lived species and is typically used for low temperature triplet state measurements. Considering the first case (10 Hz pulse frequency), during the 0.2 ns – 99 ms window the camera collects multiple delay times, each one having a specific integration time, and both values are determined by the user according to the studied material properties (for most TADF materials both time values increase exponentially). Each camera delay time measurement corresponds to one time-resolved spectrum which has a specific integration time. Dividing all the spectra with their

individual integration times and integrating the products over the wavelength provides the integrated intensity values. As shown in **Figure 3.1b**, each point is on integrated spectrum with a specific delay time (shown in the x-axis) and the gap between each point is the integration time. More information can be found in section 3.7.

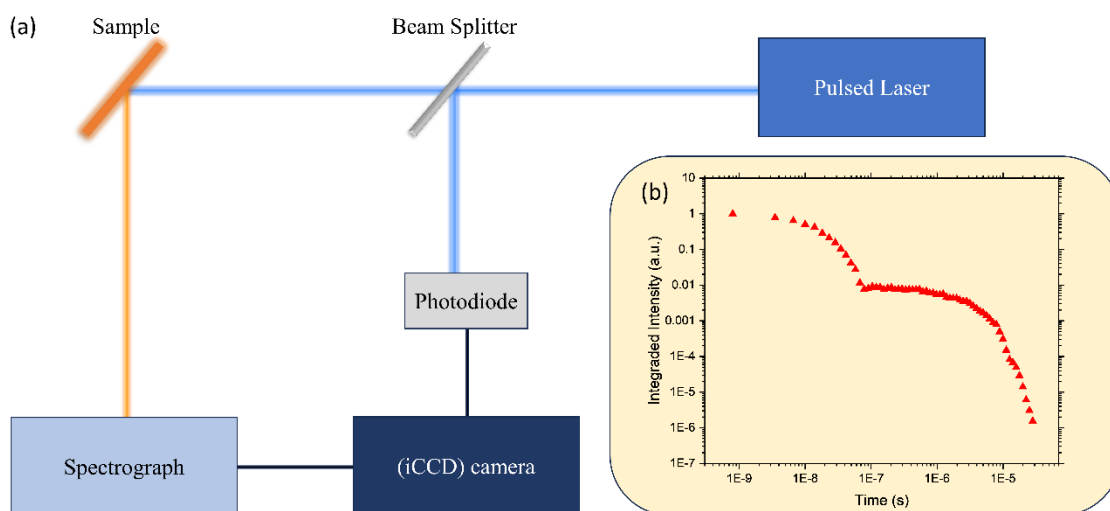


Figure 3.1. a) Simplified Time-resolved Photoluminescence setup. When the Nd:YAG laser is used the beam splitter and photodiode are not part of the setup (laser triggers directly the iCCD. More optical parts (i.e. lenses, filters, irises) exist in the actual setup but are not shown for simplicity reasons. b) Example of an obtained time-resolved decay curve.

The time-resolved photoluminescence response of organic molecules can be measured under vacuum and at different temperatures as the sample is placed either in a liquid N₂ cryostat or a Helium cryostat, both of which are connected to a roughing pump. Both cryostats have a temperature controller but different temperature ranges, starting from 80 K and 20 K for N₂ and Helium cryostats respectively, and going up to 330 K.

3.5.2 Time Correlated Single Photon Counting

Time-correlated single photon counting (TCSPC) is employed to estimate excited state lifetimes with a temporal resolution of 5 picoseconds.⁶ This technique relies on detecting single photons using low excitation intensities and acquiring numerous excitation-decay events to obtain high-resolution decay curves. Each event is counted as the time between the excitation pulse and the detection of the photon emitted by the sample. To achieve this, part of the excitation pulse triggers a fast photodiode, generating a "start or stop" signal for the timer,

while the other part excites the sample, leading to the detection of emitted photons and generating a second "stop or start" signal for the timer.

The TCSPC setup can operate in either forward mode or reverse mode. In the forward mode, the photodiode signal acts as the "start", and the sample signal acts as the "stop", however this mode can result in numerous Time-to-Amplitude converter circles, necessitating periodic resets to avoid overloading the electronics. In contrast, the reverse mode utilized here, connects the high-count rate signal from the light source to the "stop" input and the low rate to the "start" input. This mode reverses the time axis of the memory histogram, displaying photon events with longer retardation times on the right side of the time axis (**Figure 3.2a**).

During data acquisition, the instrument response function (IRF) is initially collected, using a Ludox solution and monitoring the laser/diode emission, representing the temporal response of the system. Then, emission from the sample is collected, and each event's delta time (between start + stop) is stored in a histogram, forming the decay curve waveform (**Figure 3.2b**). The decay rate of the excited-state population is determined by the radiative and non-radiative processes given by the following equation:

$$\frac{dn(t)}{dt} = -(K_r + K_{nr})n(t) \quad (3.4)$$

Where $n(t)$ is the number of excited molecules at time t , K_r is the emissive rate, and K_{nr} is the non-radiative decay rate. Throughout emission each excited fluorophore has the same probability of emitting in a given period, resulting in an exponential decay of the excited state population. This population is proportional to the time-dependent fluorescence intensity $I(t)$ and can be expressed as:

$$I(t) = I_0 e^{(-\frac{t}{\tau})} \quad (3.5)$$

where I_0 is the intensity at time (t) zero (beginning of the decay), and τ is the lifetime. Thus, in the give histogram the slop of the fluorescence decay is the fluorescence lifetime. TADF systems, especially in solid-state films, are typically expressed with multiple exponential decay components and can be expresses as a series of mono exponential decays.

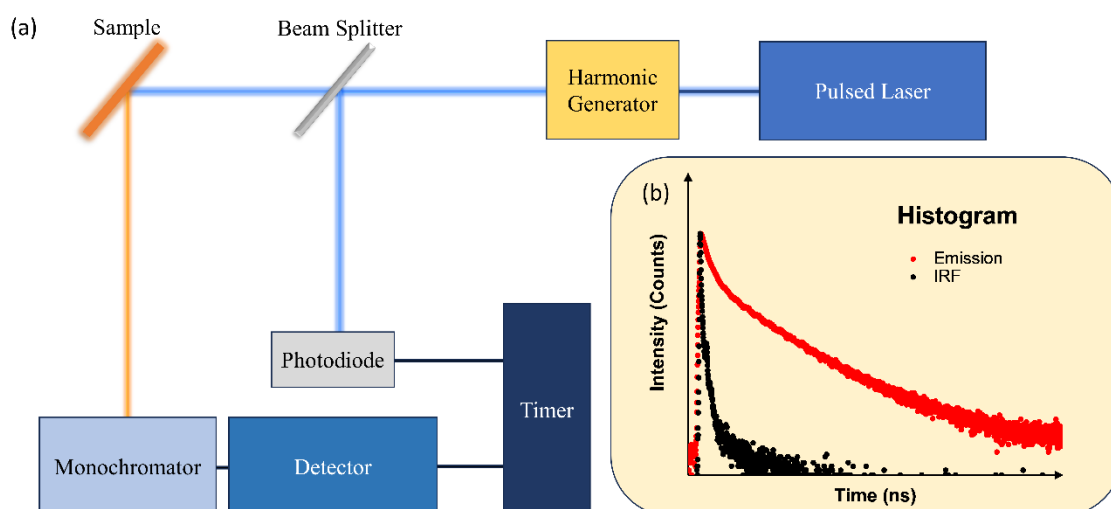


Figure 3.2. (a) Time-correlated single photon counting (TCSPC) setup. Please note that the diagram omits some other optics like filters, lenses, and polarizers that are typically part of the TCSPC system. (b) Example histogram obtained from the TCSPC technique. The histogram consists of two curves: a black curve representing the Instrument Response Function (IRF) of the system and a red curve representing the decay curve of the emitter.

The TCSPC system utilized here involves a Ti: Sapphire (Coherent Mira 900) pulsed laser tuned at 864 nm, pumping a commercial harmonic generator (Harmonixx, Photonic Solutions) from which the 2nd or 3rd harmonic can be generated producing 432 nm and 288 nm, respectively. Part of the excitation beam is directed to a fast photodiode (Becker & Hickl GmbH) while the other part excites the sample. The emitted light from the sample is directed through a subtractive double monochromator (Acton Research Corporation 2400s) with 4 nm spectral resolution. The instrument response function (IRF) has a resolution of approximately 27 ps. All the decay lifetimes in this study were estimated using exponential functions in OriginPro9.

3.6 Organic Light Emitting Diodes

3.6.1 Substrate Preparation

OLEDs were fabricated on glass substrates with dimensions of 2.5 cm × 2.5 cm × 0.1 cm, featuring patterned Indium Tin Oxide (ITO) pre-sputtered by VisionTek Systems on the top surface (**Figure 3.3**). The ITO has a custom-made pattern with two different width ITO contacts. The thicker contact has a width of 0.4 cm, while the thinner one has a width of 0.2

cm. Prior to thermal evaporation, the substrates underwent cleaning in sonication baths containing acetone and then isopropyl alcohol (IPA) for 15 minutes each. Following this, the substrates were dried using pressurized nitrogen gas before being subjected to oxygen plasma treatment for 15 minutes. Subsequently, the ITO substrates were loaded into the vacuum chamber for thermal evaporation of the organic layers and inorganic electrode. All the organic materials were deposited on the centre of the substrate using a square patterned mask. Meanwhile, the inorganic top electrode was deposited in a pattern similar to that of the ITO (see **Figure 3.3** right side). The area where the bottom ITO anode and the top inorganic cathode overlap constitutes the OLED. As a result, this substrate configuration leads to four different pixels, each having active areas of 4 mm², 8 mm² (two pixels), and 16 mm².



Figure 3.3. OLED substrates with patterned ITO. Blank substrate (left side) and fully evaporated OLED (right side).

3.6.2 Fabrication

OLED fabrication was performed with vacuum thermal evaporation (VTE), a versatile technique employed for depositing thin films from a wide range of materials, providing precise control over the deposited thickness. The principle involves heating the material in a high vacuum environment to generate vapour pressure. Even with relatively low vapour pressure, the high vacuum conditions (10^{-7} mbar) create a gas cloud inside the chamber, enabling an even and uniform deposition onto a rotating (10 rpm) substrate. The ultra-high vacuum is achieved with the use of a Helium cryopump system.

The evaporation system, specifically the Lesker Super-Spectros 200, comprises a side chamber utilized for loading substrates, which can then be transferred to the main chamber using a

robotic arm (see **Figure 3.4a**). The main chamber is equipped with 14 thermal sources, as depicted in **Figure 3.4b**. Among these sources, three high-temperature sources are positioned in the center of the chamber and are used for evaporating materials with high evaporation temperatures, such as Aluminium, Silver, and Lithium Fluoride. The remaining eleven side sources offer better control over temperatures ranging from 100°C to 350°C, and these are dedicated for evaporating the organic materials.

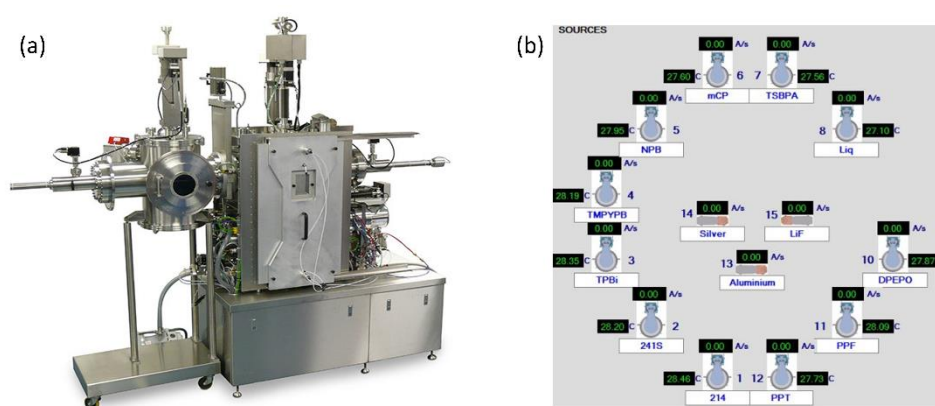


Figure 3.4. (a) Lesker Super-Spectros 200 setup. (b) Representation of the 14 sources in the vacuum chamber from the Eclipse software.

The working principle of all sources is the same and illustrated in **Figure 3.5a**. The crucible, heated by a coil surrounding it, is controlled by an external controller that monitors the sensor's temperature and the driving current of the heater. Once the material reaches its evaporation temperature, it vapourizes and emerges from the crucible, forming a conical shape of vapour. For organic materials, the vapour consists of millions of molecules, similar to the representation shown in **Figure 3.5a**. During the initial stages of the evaporation process, a thickness sensor comprising a Quartz Crystal Microbalance (QCM) device monitors the vapor deposition rate. Typically, the first evaporation run of a material is used to calculate the material's tooling factor, as described in chapter 3.3. The tooling factor serves as a correction factor, accounting for the relative orientation of the evaporation source with respect to the thickness monitor and the chamber's geometry.

For OLED fabrication, the process may involve both single and co-evaporation of materials, as depicted in **Figure 3.5b**. Generally, most transport layers necessitate single evaporation, unless they are doped with an additional hole or electron transport material to enhance charge transport properties. On the other hand, the emissive layer typically requires at least two

materials, namely the host and the emitter. Having eleven organic sources allows the theoretical co-evaporation of up to six materials simultaneously (each two sources share the same thickness sensor). However, for the purpose of this study, the maximum number of materials evaporated simultaneously was limited to four. Once all the organic materials are deposited on the substrate, a robotic arm transfers the substrate holder to an inorganic mask for the cathode (typically Aluminium) deposition. This step is essential to create the pattern as shown in **Figure 3.3**, defining the OLED's structure.

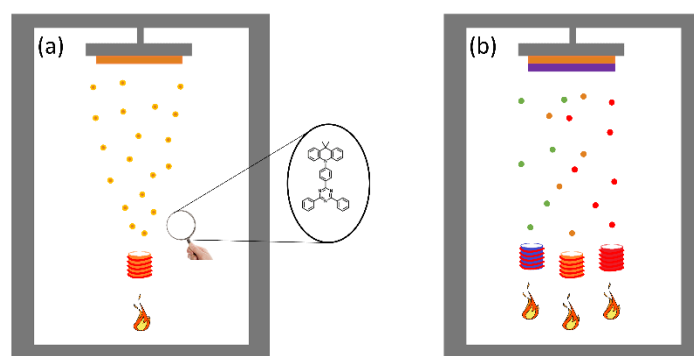


Figure 3.5. Illustration of Vapour Thermal Evaporation technique. (a) single evaporation and (b) co-evaporation. Each dot represents an evaporated molecule (or cluster of evaporated molecules, depending on the evaporation conditions). The fire icons illustrate the high temperature of the thermal source.

After deposition, the substrates are transferred to a glovebox under an inert atmosphere. They can either be directly measured or undergo encapsulation before being taken out into ambient conditions. The encapsulation process is carried out using a robotic setup, which applies a UV-curable epoxy (DELO Katiobond) along the outer edges of the active area. Subsequently, the device is manually sealed with an oxygen plasma-cleaned glass coverslip, ensuring effective encapsulation to protect the OLED structure.

3.6.3 OLED performance measurement

To evaluate the performance of an OLED, both electrical and optical characterizations are essential. These characterizations provide crucial information about various parameters, including the overall device efficiency, power consumption, and colour characteristics. Electrical characterization of devices is performed using a Keithley 2400 sourcemeter. The optoelectrical performance of OLEDs is measured in a 10" integrating sphere (Labsphere) in

ambient conditions or a 6" integrating sphere in the glovebox, both coated with a highly reflective material (Spectralon) (**Figure 3.6a**). The integrating sphere is connected to a calibrated fiber coupled device Ocean Optics USB4000 spectrometer and is calibrated using a reference lamp with a known power spectrum output ($P_{cal}(\lambda)$ in W/nm), to determine the accurate and standardized device efficiency, taking into account the response of the entire measurement system. To characterize the OLED, an in-house software (Python) performs all the necessary calculations using as input the active area of the device. The software stores/calculates parameters such as applied voltage (V), current (mA), current density (mA/cm²), luminous flux (lm), brightness or luminance (cd/m²), external quantum efficiency (%), current efficiency (cd/A), power efficiency (lm/W), Commission Internationale de l'Eclairage (CIE) coordinates, and electroluminescence spectra (EL). These characterizations provide comprehensive insights into the OLEDs performance and help assess its efficiency and optical properties.⁷

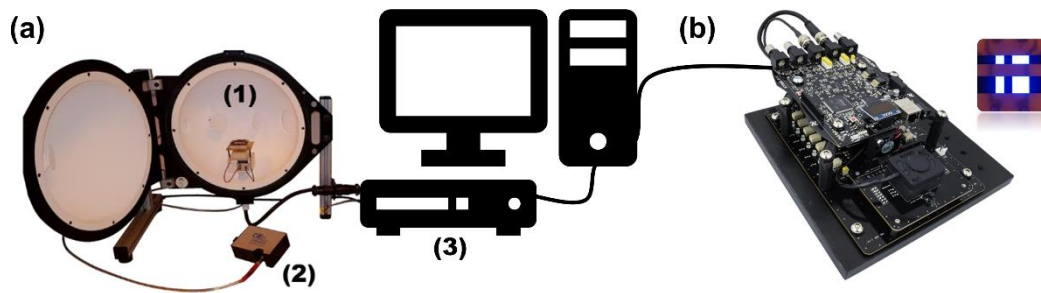


Figure 3.6. (a) Picture of the OLED testing system, where 1 is the 10" integrating sphere with OLED mounting stage, 2 is the Ocean Optics USB4000 spectrometer connected with an optical fibre cable, and 3 is the Keithley 2400 sourcemeter unit. (b) Picture of the OLED lifetime testing system and a picture of how the OLED pixels are in the OLED holder.

In an operating device, the flow of electrical charge carriers is characterized by the current observed at different applied voltages. This parameter can also be analyzed in terms of current density, which represents the current per unit area. The luminous flux (Φ_v), on the other hand, refers to the amount of light that can sensitize the human and is given by the equation:

$$\Phi_v = 683.002(lm/W) \int \tilde{y}(\lambda) \Phi_{e,\lambda}(\lambda) d\lambda \quad (3.6)$$

where $\Phi_{e,\lambda}$ is the spectral radiant flux, $y(\lambda)$ is the luminosity function (also called eye sensitivity function $V(\lambda)$), and λ is the wavelength. It is standardized with the eye's maximum sensitivity

at 555 nm, assuming normal lighting conditions (**Figure 3.7**). To account for both the colour and direction of light, luminous intensity is used, measured in candela (cd). Brightness or luminance is the luminous intensity per unit of area. For mobile displays, typical brightness levels range between 100-400 cd/m². For general illumination purposes, higher values of around 5000 cd/m² are typically required.

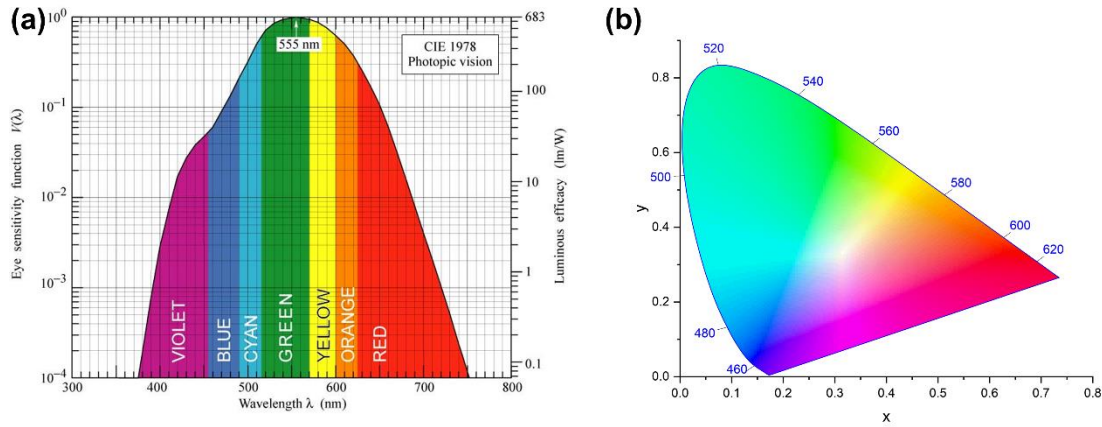


Figure 3.7. (a) Eye response curve. Eye sensitivity function (left axis) and luminous efficiency (right axis) per wavelength.⁸ (b) Commission Internationale de l'éclairage (CIE) 1931 chromaticity coordinates plot.

An important reference metric for OLED devices is the external quantum efficiency (EQE), which defines the ratio between the number of photons (n_{ph}) that escape the surface of the OLED and the number of electrons injected into it (n_e). The total radiant flux (W) emitted from the device in Watts is measured by integrating the calibrated electroluminescence (EL) spectrum, obtained using a spectrometer. The n_{ph} is then determined by the equation:

$$n_{ph} = \int \frac{W(\lambda)}{E_{ph}} d\lambda \quad (3.7)$$

where E_{ph} is the energy of the photon at a given wavelength and expresses by the equation:

$$E_{ph} = \frac{hc}{\lambda} \quad (3.8)$$

where λ is the wavelength, h is the Plank constant, and c is the speed of light. The n_e is then calculated from the device current (I) and the following equation:

$$n_e = \frac{I}{e} \quad (3.9)$$

where e is the elementary charge. The EQE can be finally determined from the equation:

$$EQE = \frac{n_{ph}}{n_e} \quad (3.10)$$

The EQE of an OLED can also be described as the product between the charge balance factor (γ), the fraction of spin-allowed excitons (η_{ST}), the photoluminescence quantum yield (Φ_{PL}) and the outcoupling efficiency (η_{out}). The last factor is the reason why OLED performance is typically limited below 30 %.⁹ The EQE equation can thus be expressed as:

$$EQE = \Phi_{PL} \cdot \gamma \cdot \eta_{ST} \cdot \eta_{out} \quad (3.11)$$

and is used to estimate the maximum theoretical EQE of an OLED with a specific emitter in the emissive layer (EML). For this estimation, γ is assumed to be 100% when the excitons are well confined within the EML. For TADF molecules η_{ST} is also considered to be 100%. The Φ_{PL} is a distinctive property of the emitter, and more specifically the EML. Thus, it is always measured in the host system used in the device. Finally, η_{out} express the percentage of photons that can escape the device surface depending on factors such as the total internal reflection, internal losses at the cathode, and anisotropy. The typical value of η_{out} for a randomly oriented emitter lies between 0.25 and 0.3 and is the primary reason why OLED performance is typically limited to below 35 %.

The current efficiency (CE) is defined as the amount of current flowing through the device with an emissive area (A) necessary to produce a certain luminance (L), given by:

$$CE = \frac{LA}{I} = \frac{L}{J} \quad (3.12)$$

The power efficiency (PE), also known as luminous efficacy, represents the ratio between the luminous flux emitted by the device and the electrical power, calculated as the product of the voltage (V) applied to the device and the measured current (I) that flows through it and is expresses as:

$$PE = \frac{Lum}{I \cdot V} \quad (3.13)$$

Lastly, the emitted colour of the device is assessed using the CIE chromaticity coordinates and the electroluminescence spectrum. The CIE system relates the distribution of wavelengths in the visible spectrum to the physiological perception of colours in human vision.¹⁰ It visually

represents this relationship through a chromaticity diagram with coordinates X and Y (see **Figure 3.7b**).

3.6.4 OLED Lifetime

Prior to OLED lifetime testing, devices require isolation from atmospheric conditions to minimize extrinsic degradation mechanisms, ensuring that only intrinsic factors determine degradation. To achieve this, two approaches have been explored: device encapsulation or lifetime measurements in a controlled environment (nitrogen filled glovebox). Both approaches led to devices with minimum moisture and oxygen interaction, which adversely affect the organic layers, metals, and organic-inorganic interfaces. The controlled environment measurements were preferred because of the reduced consumption of materials (i.e. getters, UV-curable resin, encapsulation glasses).

The OLED luminance is commonly used to assess their stability by monitoring the luminance decay over time, at a constant current.¹¹ The operational lifetime can be defined as the time taken for the luminance to decrease to a predefined percentage of its initial value (L_0). Typically, for industrial standards, a target value of 90 or 95% is used, denoted as LT_{90} and LT_{95} , respectively. This translates to a 10 and 5% decrease of initial luminance, respectively. For academic standards, the LT value ranges from 50 to 90% (LT_{50} to LT_{90}) because the OLED fabrication standards are less optimized.

To characterize the lifetime of an OLED, initially, its J-V-L (current density-voltage-luminance relationship) is determined. Based on this data, the necessary current (I_0) required to initiate the lifetime test at the desired L_0 is determined. I_0 is then kept constant while the voltage typically increases gradually to maintain the constant current. The increase in voltage is correlated to the decrease of L_0 (recorded over time using a photodetector) as both depend on quenching/degradation sites within the operating OLED. These sites typically act as traps, requiring higher voltage to generate the same device current while they also act as exciton quenchers.

These measurements are conducted using the Ossila OLED Lifetime system (**Figure 3.6b**), which employs a Si photodiode to measure the relative luminance decay and an Ossila X100 source measure unit to drive the OLED at a constant current and measure the current variation in the photodiode.

3.7 Data Analysis

3.7.1 Time-resolved Decay

The time-resolved raw data were processed using a Python script following the method described by Niels *et al.*¹² Both the raw and processed data were subsequently analyzed in OriginPro9.

In section 3.5, a comprehensive explanation of the operating principle of time-resolved spectroscopy was presented. For TADF molecules, different time delay regimes describe the involvement of various states in the time-resolved emission. During the PF regime, singlet states predominantly emit, while triplet harvesting through rISC occurs in the DF regime (**Figure 3.7a**). By analyzing the PF regime and the fluorescence spectrum, the singlet state energy can be determined (**Figure 3.7b**).

Throughout the decay process, different species with distinct photoluminescence spectra are observed, mainly towards the end of both the PF and DF regimes. One critical parameter for TADF molecules is the lowest lying triplet energy, as it is typically the state involved in triplet harvesting through rISC. However, directly observing the triplet energy at room temperature is challenging (as it is a forbidden transition). To address this, the temperature is reduced to 80 K (or sometimes even 20 K), allowing the observation of the lowest triplet energy in the form of a phosphorescence spectrum, which typically exhibits structured emission associated with a local state. The ΔE_{ST} can be determined from the energetic difference between the energy onsets ($E = h\nu/\lambda$) of the fluorescence and phosphorescence spectrum.

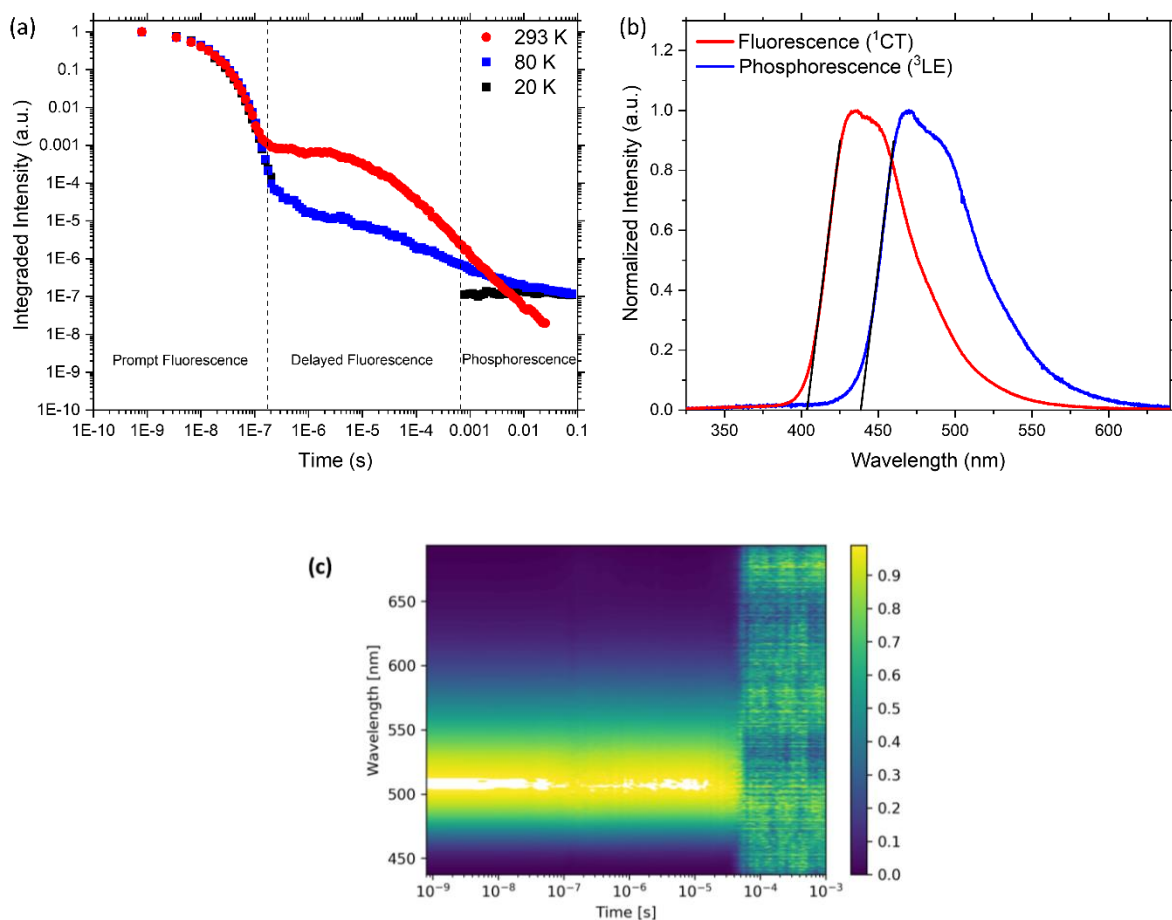


Figure 3.7. (a) Different delay time regimes of time-resolved photoluminescence decays, at different temperatures. (The phosphorescence regime is typically observed at low temperature measurements). (b) Estimation of the energy onset and ΔE_{ST} from the time-resolved spectra, at low temperature. (c) Contour plot of the RT TRPL spectra.

In some cases, when the signal-to-noise ratio is poor, the collected data are removed from the time-resolved decay. This is observed in Figure 3.7, at the 20 K decay, where the DF is suppressed/quenched but phosphorescence emission could be observed earlier but could not be detected. The same phenomenon is observed in the contour plots (Figure 3.7c), at the end of the decay ($t > 10^{-4}$ s).

3.7.2 Decay Kinetics

Rate constants calculations require some input parameters (depending on the used method) which can be extracted from the time-resolved decay analysis. The input parameters from the time-resolved decays are the amplitude (A) and lifetime (τ) of the PF and DF components and can be fitted using exponential functions according to equation 3.14.

$$y(t) = \sum_{i=1}^n A_{PFi} e^{-\frac{t}{\tau_{PFi}}} + \sum_{i=1}^n A_{DFi} e^{-\frac{t}{\tau_{DFi}}} \quad (3.14)$$

where i is the number of exponentials used to fit each component. In **Figure 3.8a** a single exponential was used for each component.

In all section of this thesis, the method previously presented by Dias *et al.*¹³ was used which considers the total fluorescence yield (Φ_F) of a TADF emitter as the sum of the prompt fluorescence (Φ_{PF}) and delayed fluorescence (Φ_{DF}) yield and can be expressed with the following equation:

$$\Phi_F = \Phi_{PF} + \Phi_{DF} = \sum_{i=0}^n \Phi_{PF} (\Phi_{ISC} \Phi_{rISC})^i = \Phi_{PF} \frac{1}{1 - \Phi_{ISC} \Phi_{rISC}} \quad (3.15)$$

where Φ_{ISC} and Φ_{rISC} are the ISC and rISC yields, respectively. From the equation 3.15 is concluded that the Φ_{rISC} can be 100% if the ratio between DF and PF (Φ_{DF}/Φ_{PF}) is around or above 4, which is the case in all efficient TADF emitters. This ratio can be experimentally determined according to the equation 3.16.

$$\frac{\Phi_{DF}}{\Phi_{PF}} = \frac{\int I_{DF}(t)dt}{\int I_{PF}(t)dt} = \frac{A_{DF}/\tau_{DF}}{A_{PF}/\tau_{PF}} \quad (3.16)$$

where $\int I_{DF}(t)dt$ and $\int I_{PF}(t)dt$ are the integrated areas of the time-resolved decay in the PF and PF regime respectively (**Figure 3.8a**). Thus, TADF emitters who meet the $\Phi_{DF}/\Phi_{PF} \geq 4$ criterion can use the following simplified equation to calculate the triplet formation yield:

$$\Phi_{ISC} = \frac{\Phi_{DF}/\Phi_{PF}}{1 + \Phi_{DF}/\Phi_{PF}} = \frac{\Phi_{DF}}{\Phi_{PF} + \Phi_{DF}} \quad (3.17)$$

The necessary rate constants can be calculated using the following simplified equations:

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_{PF}} = \frac{1}{\tau_{PF}} \frac{\Phi_{DF}}{\Phi_{PF} + \Phi_{DF}} \quad (3.18)$$

$$k_{rISC} = \frac{1}{\tau_{PF}} \frac{1}{(1 - \Phi_{ISC})} = \frac{1}{\tau_{PF}} (1 + \Phi_{DF}/\Phi_{PF}) \quad (3.19)$$

In chapter 8, a second method of kinetic analysis¹⁴ was also used to estimate the rate constants because in some films more than one species were involved in the time-resolved decay, and the non-radiative rates were high.

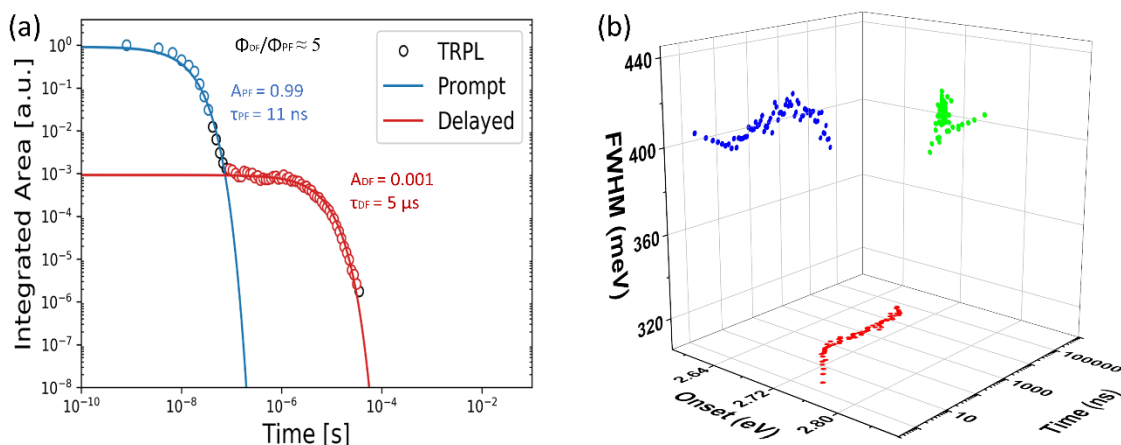


Figure 3.8. (a) Example of exponential fitting and DF/PF ratio estimated from TADF emitter v-DABNA's time-resolved photoluminescence decay. (b) Homogeneity plot of TADF emitter DMAC-TRZ in solid state.

3.7.3 Homogeneity

The homogeneity plots (**Figure 3.8**) are introduced in chapter four. An in-home algorithm was applied on the raw data of the time-resolved photoluminescence measurement to extract the energy onset (obtained according to **Figure 3.7b**) and full width half maximum (FWHM) from each time-resolved spectrum. The generated files were then plotted in a three-dimensional graph (**Figure 3.7b**). The bottom and left side represent the energy onset and FWHM, respectively, of the time-resolved spectra over time. The right side combines the FWHM with the onset energy and describes the dispersion of dihedral angles in a solid state system (see next chapter).

3.7.4 FRET Calculations

The FRET¹⁵ radius (R_0) corresponds to the effective separation between energy donor and energy acceptor at which FRET becomes 50% efficient and was estimated using the following equation:

$$R_0 = \left(\frac{9(\ln 10)\kappa^2\Phi_D}{128\pi^5 N_A n^4} J \right)^{1/6} \quad (3.20)$$

Where Φ_D is the PLQY of the sensitiser (Donor), κ^2 is the dipole-dipole interaction (in our study 2/3 was used which is the value for a random distribution), N_A is the Avogadro constant, n is the refractive index of the film and J is the spectra overlap between the terminal emitter's (Acceptor) extinction coefficient and the sensitiser's (Donor) area-normalized photoluminescence spectrum and is calculated using the following equation:

$$J = \int \bar{I}_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (3.21)$$

Where $\bar{I}_D(\lambda)$ is the area-normalized PL spectrum of the sensitiser in the host, $\epsilon_A(\lambda)$ is the extinction coefficient of the terminal emitter and λ is the corresponding wavelength.

FRET efficiency was estimated using the following equation:

$$n_{FRET} = 1 - \frac{\tau_{DA}}{\tau_D} \quad (3.22)$$

Where τ_{DA} and τ_D are the prompt lifetimes of the sensitiser emission quenched by the terminal emitter in the hyperfluorescence film (host, sensitiser and terminal emitter) and the prompt lifetime of the sensitiser in the TADF film (host and sensitiser), respectively. In the hyperfluorescence systems the direct excitation followed by fluorescence emission of the terminal emitter is not taken into consideration in the τ_{DA} lifetime.

FRET rate is then estimated with the following equation:

$$k_{FRET} = \frac{n_{FRET}}{\tau_{DA}} \quad (3.23)$$

And the average Donor-Acceptor distance by the equation:

$$r = R_0 \left(\frac{\tau_{DA}}{\tau_D - \tau_{DA}} \right)^{1/6} \quad (3.24)$$

3.7.5 Jacobian Conversion

Photoluminescence spectroscopy is a widely used technique for studying the optical properties of materials. Spectra are typically presented as a function of wavelength (λ), yet a representation as a function of energy (E) can yield superior physical understanding. The conversion from wavelength to energy is governed by the equation:

$$E = \frac{hc}{\lambda} \quad (3.25)$$

where E represents the photon energy (in eV), h is the Plank constant, c is the speed of light in vacuum, and λ is the photon wavelength (in nm).

The theoretical conversion from wavelength to energy appears straightforward. However, the practical application reveals complications due to the nature of recorded data intervals. Spectrometers record signal values per unit wavelength, resulting in intervals $d\lambda$ that are not uniformly distributed when converted to energy. This disparity arises from the inverse relationship between wavelength and energy, causing uniformly spaced wavelength data to appear unevenly spaced in energy.¹⁶

To address this, the conservation of energy is considered and treat the recorded signals as a function $f(\lambda)$. The transformation of the recorded signal values necessitates a scaling adjustment, derived from the following relationship:

$$f(E) = \frac{f(\lambda)d\lambda}{dE} \quad (3.26)$$

Combining this with equation 3.25, the signal values can be scaled using the following evaluation:

$$f(E) = \frac{f(\lambda)d}{dE} \left(\frac{hc}{E} \right) = -\frac{f(\lambda)hc}{E^2} \quad (3.27)$$

The scaling of signal values, known as the Jacobian transformation, is crucial for accurate representation. The negative sign in the transformation can be disregarded as it merely reflects the opposite directions of integration in wavelength and energy domains.

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4 Interactions in TADF guest-host systems.

DMAC-TRZ is used as a TADF emitter ‘probe’ to differentiate the environmental effects in a range of solid-state host materials. A variety of well-known TADF OLED hosts with different characteristics were studied. Using time-resolved photoluminescence measurements, the charge transfer state energy distribution is introduced and explored in different permanent dipole moment environments. From the time-resolved response of the photoluminescence FWHM and the apparent dynamic redshift of CT emission onset, the disorder-induced heterogeneity of D-A dihedral angles is introduced. Concentration dependence studies show how intermolecular interactions affect/interact with the heterogeneity phenomenon but also how aggregation formation quenches the photoluminescence quantum yield (PLQY). This study provides new principles on both TADF emitters and hosts design parameters.

The work presented in this chapter was published in ACS Applied Electronic Materials: Stavrou, K.; Franca, L. G.; Monkman, A. P. Photophysics of TADF Guest–Host Systems: Introducing the Idea of Hosting Potential. ACS Appl. Electron. Mater. 2020, 2 (9), 2868–2881.

4.1 Introduction

In OLEDs, the emissive layer incorporates one or more host molecules to control electrical transport properties and prevent emitter self-quenching.¹ Emitters often tend to aggregate, forming dimers and other species, which contribute to non-radiative losses.²⁻⁴ Selecting a suitable host molecule for a specific emitter requires consideration of several properties, such as ensuring that the host's triplet energy is higher than that of the emitter to prevent triplet quenching and degradation of TADF.⁵⁻⁷ Additionally, host molecules must exhibit favourable energy transfer properties and balanced bipolar charge transport.^{8,9} Beyond these primary considerations, factors such as the host's permanent dipole moment, polarizability, and molecular packing also play critical roles. Unlike LE states, which are relatively insensitive to environmental factors, CT states with large dipole moments interact strongly with the host, causing shifts in their energy levels..^{3,10} In rigid host matrices, solvatochromism, as observed in solutions, is absent due to the lack of solvent shell rearrangement. Consequently, these interactions affect the energy landscape and molecular conformations, which, in turn, influence the photophysical behavior of the emitter-host system..

It is important to note that the energy difference between singlet and triplet states (ΔE_{ST}) is directly affected by the dihedral angles between donor and acceptor units of the emitter, i.e. different conformations.¹¹ Some host molecular structures favor stacking, forming compacted matrices, while others with greater free volume may allow slight motion of the guest within the matrix. This variability results in a distribution of D–A bridge dihedral angles and, consequently, a distribution of CT state energies.^{10,12} These parameters must be optimized for each specific emitter-host combination to achieve efficient emission.

In this chapter, a detailed investigation of the guest-host interactions of various host materials is demonstrated to explore their influence on the photophysical properties of the well-known TADF emitter DMAC-TRZ (see chapter 2.2). This emitter exhibits efficient TADF mechanisms with high photoluminescence quantum yield, even in neat films,,¹³ resulting in the fabrication of efficient doped and non-doped OLEDs. The effect of host permanent dipole moments and guest concentrations (up to neat films) on triplet harvesting mechanisms and conformational homogeneity is explored in detail. A novel homogeneity plot is introduced, providing a tool to assess the conformational uniformity of emitters within specific

environments using time-resolved spectroscopy. These insights allow us to identify new design parameters for further optimizing TADF efficiency and OLED performance.

4.2 Collaborator contributions

The solution-casted films were fabricated by myself and Larissa Gomes Franca, while the evaporated films by myself. The experimental measurements in this chapter were made and analyzed by myself and Larissa Gomes Franca. The novel homogeneity plots were analyzed and introduced by myself.

4.3 Experimental methods

4.3.1 Sample preparation

Photophysical characterization of solutions was performed in three different solvents: methylcyclohexane (MCH), toluene (PhMe), and dichloromethane (DCM). All solutions were prepared at a concentration of 20 μM and degassed by five freeze–pump–thaw cycles. Solid-state samples were fabricated by drop-casting and evaporation methods onto quartz and transparent sapphire substrates. All host–guest drop-cast films were produced at 1 wt% DMAC–TRZ doping in the host matrix. The hosts used were: zeonex, UGH-3, DPEPO, mCPCN, and mCBPCN (see chapter 2.2). For neat drop-cast films, a solution of 1 mg/mL was added dropwise onto the substrate. Host–guest evaporated films were made by co-evaporation deposition at an evaporation rate of 0.9 $\text{\AA}/\text{s}$ for the host and 0.1 $\text{\AA}/\text{s}$ for DMAC–TRZ materials. For neat evaporated films, the evaporation deposition was performed at a rate of 0.5 $\text{\AA}/\text{s}$. All evaporated films were prepared using a Kurt J. Lesker Super-Spectros 200 deposition system under vacuum, 10^{-7} mbar, and a final thickness of 100 nm was obtained.

4.4 Result and Discussion

The absorption spectra of DMAC-TRZ exhibit two low-energy bands in MCH, with peak maximums at 370 nm and 410 nm, respectively (**Figure 4.1a**). With increasing solvent polarity, a decrease in oscillator strength and a redshift were observed for the 410 nm band towards 450 nm, indicative of a direct CT transition. The 370 nm band appeared unaffected by the solvent polarity, only a small decrease in oscillator strength was observed. This indicates that this low extinction coefficient transition (in the order of $10^3 \text{ M}^{-1}\text{cm}^{-1}$), has a mixed CT/LE character. Photoluminescence spectra (**Figure 4.1b**) showed a large bathochromic shift in emission by increasing solvent polarity even moderately. In a lower polarity solvent, MCH, a structured

spectrum with vibronic character was observed. With increasing polarity, the emission spectrum redshifted and became structureless and Gaussian-shaped. This is a clear indication of a strong low-energy intramolecular CT excited state.

The time-resolved photoluminescence decay of DMAC-TRZ in toluene solution is shown in **Figure 4.1a**, having two clear decay regimes, the prompt (0 – 100 ns) and the delayed fluorescence (0.1 – 30 μ s). The decay was fitted with two exponentials providing lifetimes of 27 ns and 5.50 μ s for prompt and delayed emission, respectively. Using kinetic modelling,¹⁵ the radiative decay rate ($k_F = (1.50 \pm 0.08) \times 10^7 \text{ s}^{-1}$), intersystem crossing rate ($k_{ISC} = (2.50 \pm 0.08) \times 10^7 \text{ s}^{-1}$) and reverse intersystem crossing rate ($k_{rISC} = (5.1 \pm 0.2) \times 10^5 \text{ s}^{-1}$) were calculated. The emission spectra at different delayed times, from these two regimes, are also shown in **Figure 4.1b**. The same Gaussian band shape emission spectrum is observed throughout from a single CT state, with energy onset at 2.73 eV. In **Figure 4.1c**, a three-axis representation of the energy onset and FWHM of the emission spectrum over time is shown (explained in detail in subsection 3.7.3), indicating the DMAC-TRZ CT states distributions over time. The third trace, FWHM over energy onset, acts as a homogeneity indicator (“fingerprint”) of the studied system. DMAC-TRZ in toluene, has all the data points concentrated, with minimum scattering, forming a ‘green dot’. The latter translates to a homogeneous system where all the molecules have almost the same conformation and thus a similar CT state emission profile. This occurs due to the fast molecular relaxation/reorganization, something expected in solution environments.

Five commercially available hosts that satisfy the requirement of having their singlet (S_1) and triplet (T_1) energies^{10,14} higher than the S_1 and T_1 energies of DMAC-TRZ ($T_1 = 2.75 \text{ eV}$) were chosen for solid-state measurements. Zeonex, UGH-3, DPEPO, mCPCN, and mCBPCN with neat film T_1 values of 3.5, 3.5, 3.1, 2.86, and 2.82 eV respectively (mCPCN and mCBPCN values were obtained experimentally by me using low-temperature time-resolved PL measurements, while the rest were obtained from literature^{10,14}). Thus, singlet and triplet energy transfer from the host to the guest can be achieved, via Förster Resonance and Dexter energy transfer, respectively, whilst preventing quenching of delayed fluorescence by the host. Initially, all samples were fabricated by a solution-processed method.^{16–18} Evaporated samples were also studied to identify potential differences in the photophysical properties of DMAC-TRZ between the two methods. To compare the emissive behaviour between solution and solid-state environments the neutral polymer zeonex was chosen as a host matrix, because of its large free volume and low dielectric value, similar to MCH. Small molecule rigid hosts, UGH with

considerably low dielectric constant, mCBPCN, mCPCN and DPEPO with respectively increasing dielectric constant, are expected to have a larger impact on the emitter's behaviour.

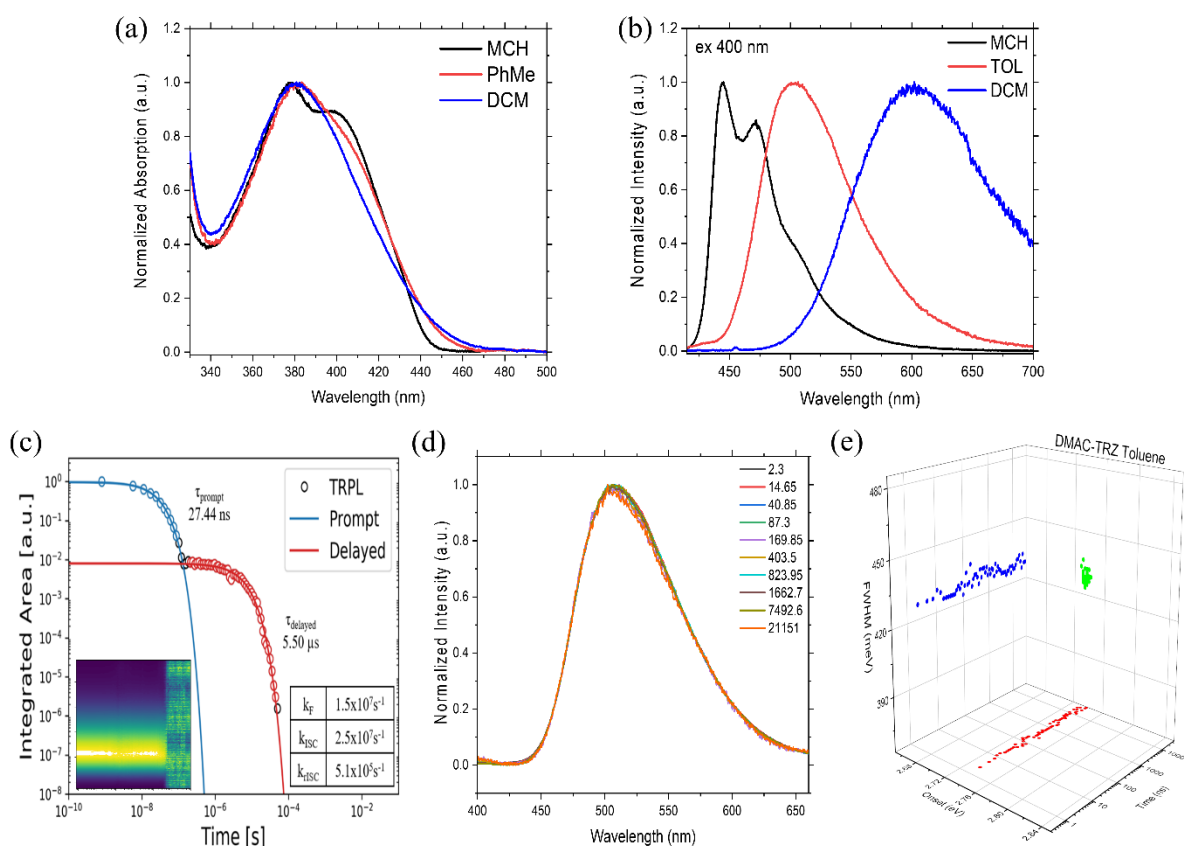


Figure 4.1. Normalized (a) absorption spectra and (b) normalized photoluminescence spectra of DMAC-TRZ in different solvents. Time-Resolved PL (c) decay (Inset: Contour plot, explained in subsection 3.7.1), (d) spectra, and (e) onset energies (bottom), FWHM (left) and FWHM over onset energies (right) of 20 μ M DMAC-TRZ solution in toluene, at 298 K.

The absorption spectrum of DMAC-TRZ in zeonex is shown in **Figure 4.2a**, having the CT band maximum at 410 nm, similar to MCH. The neat DMAC-TRZ film absorption spectrum is structurally similar to the one in zeonex but with a redshifted onset energy, presumably due to the enhanced intermolecular interactions. In all other hosts, the ground state band has a similar shape, however, due to the low film thickness and concentration of emitter the low energy bands have lower intensity compared to zeonex and neat film, respectively. From the PL spectra, the effect of each host on the emitter is more apparent. In zeonex the spectrum is energetically similar to that observed in non-polar MCH solvent (**Figure 4.1a**), with an energy onset at 427 nm, whilst as the host dielectric constant increases, the CT spectrum appears to

redshift with DPEPO having a maximum at 507 nm along with a highly broadened spectral band shape.

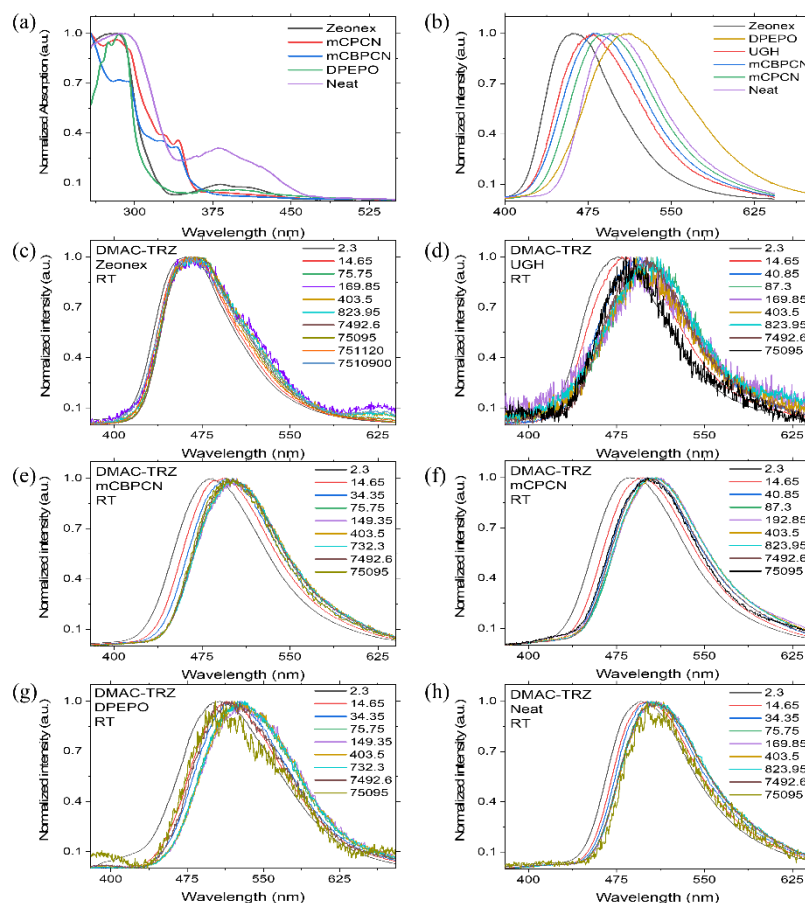


Figure 4.2. Normalized absorption (a) and PL (b) spectra of 1 wt% DMAC-TRZ in different hosts. Time-resolved PL spectra, of 1 wt% DMAC-TRZ in (c) Zeonex, (d) UGH, (e) mCBPCN, (f) mCPCN, (g) DPEPO host, and (h) neat film, at 298 K. Times given on each plot are in ns, unless stated.

To understand the effect of the solid-state environment on DMAC-TRZ, time-resolved PL measurements are shown in **Figure 4.2c-h**. In solution, all molecules (emitter and solvent) have the freedom to reorganize and reach an equilibrium. This includes the stabilization of the dihedral angle between the emitter's donor and acceptor units according to the polarity and reorganization of the surrounding solvent molecules. In solid-state, the emitter molecules are locked in by the neighbouring host molecules during the formation of a rigid film (limited empty space). As a result, instead of having a single 'equilibrium' ^1CT state energy (**Figure 4.1b, c**), there is a distribution of different CT states depending on the emitter's conformation (different D-A dihedral angles), dictated by host packing and guest host interactions, including the host permanent dipole moment and polarizability effects. An apparent time-dependent

spectral redshift of the emission band is observed during the prompt period (i.e. the first 5-100 ns, which is orders of magnitude slower than typical solution state solvatochromic shifts) and up to the beginning of the delayed emission. At later delay times (late delayed emission > 10 μ s), a blue shift of the time-resolved emission can also be observed in most cases (**Figure 4.3**).

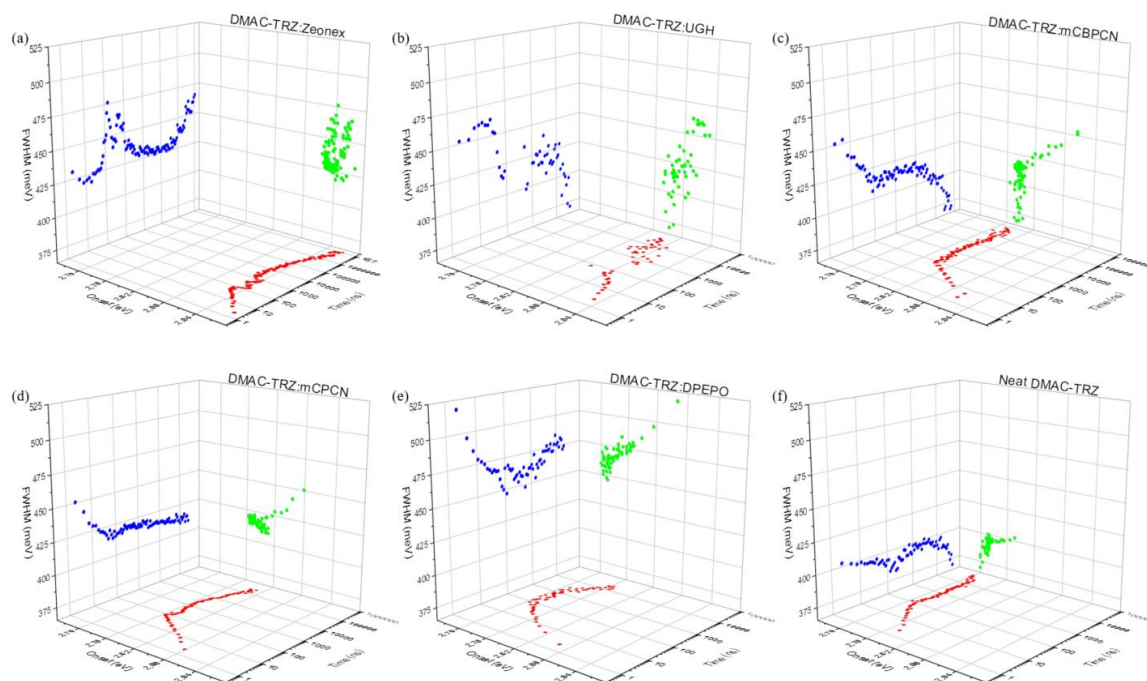


Figure 4.3. Time-resolved onset energy and FWHM of 1 wt% DMAC-TRZ in (a) Zeonex, (b) UGH, (c) mCBPCN, (d) mCPCN, (e) DPEPO and (f) neat film, at room temperature.

This individual molecular behaviour, in all hosts, can be observed by the homogeneity ‘fingerprint’ plot in **Figure 4.3** (FWHM vs. Onset). Similar to solution state, the narrower the distribution of the points, the more homogeneous the system is. Neat film is the most homogeneous solid environment overall. DMAC-TRZ in zeonex host has the highest homogeneity of prompt CT state distribution, while in mCPCN and mCBPCN hosts have the most stable DF emission. Recent work by Dias *et al.* and Penfold *et al.* have shown that the prompt CT emission of TADF molecules undergoes apparent dynamic redshift over the first few hundred nanoseconds arising from the heterogeneity of dihedral angles leading to a dispersion in CT energy (**Figure 4.9c**).^{1,19} The most planar D-A molecules (reduced dihedral angle) have the more LE character and strongest excited state coupling to the ground state, so emit to the blue at an energy close to the local donor (or acceptor) state with faster radiative rate. The most orthogonal D-A molecules have the strongest CT character and therefore emit

to the red at lower energy with a slower radiative rate (weak ground state coupling). In the delayed region the opposite is observed if the rISC mediating local triplet state is lower in energy than the ^3CT . The most orthogonal D-A have the highest rISC rate, as a result decay faster while the planar are slower and is assigned to the late time blue shift of the emission. Introducing rigidity as a parameter, the less rigid (higher free space) the host, i.e. zeonex, the smaller the distribution of CT state energies should be, and so the smaller apparent red shift in time. Dispersion was found to increase with increasing host rigidity as shown in **Figure 4.3**.

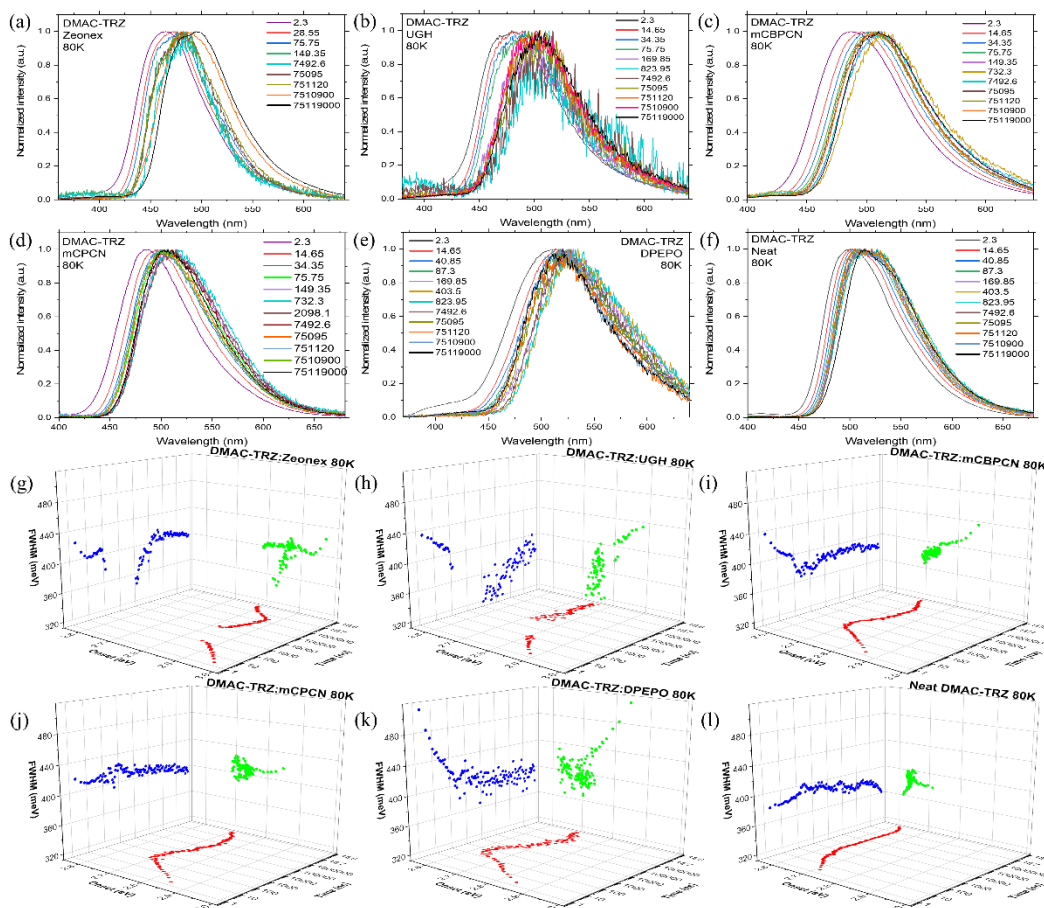


Figure 4.4. Time-resolved PL spectra of 1 wt% DMAC-TRZ in (a) Zeonex, (b) UGH, (c) mCBPCN, (d) mCPCN, (e) DPEPO host, and (f) neat film. Time-resolved onset energy and FWHM of 1wt% DMAC-TRZ in (g) Zeonex, (h) UGH, (i) mCBPCN, (j) mCPCN, (k) DPEPO and (l) neat film, at 80 K. Times given on each plot are in ns, unless stated.

The same behaviour was observed in low-temperature measurements, at 80 K (**Figure 4.4**). Rigid hosts had similar CT distributions as observed in room temperature measurements whereas in zeonex the dispersion increases greatly, similar to a rigid host at room temperature (**Figure 4.4a, g**). The low temperature prevents the zeonex chain motion thus freezing in DMAC-TRZ conformational heterogeneity. It is pointed out that even at low temperatures,

phosphorescence emission only becomes the dominant delayed emission mechanism after 10 ms and is not responsible for the μ s blue shift.

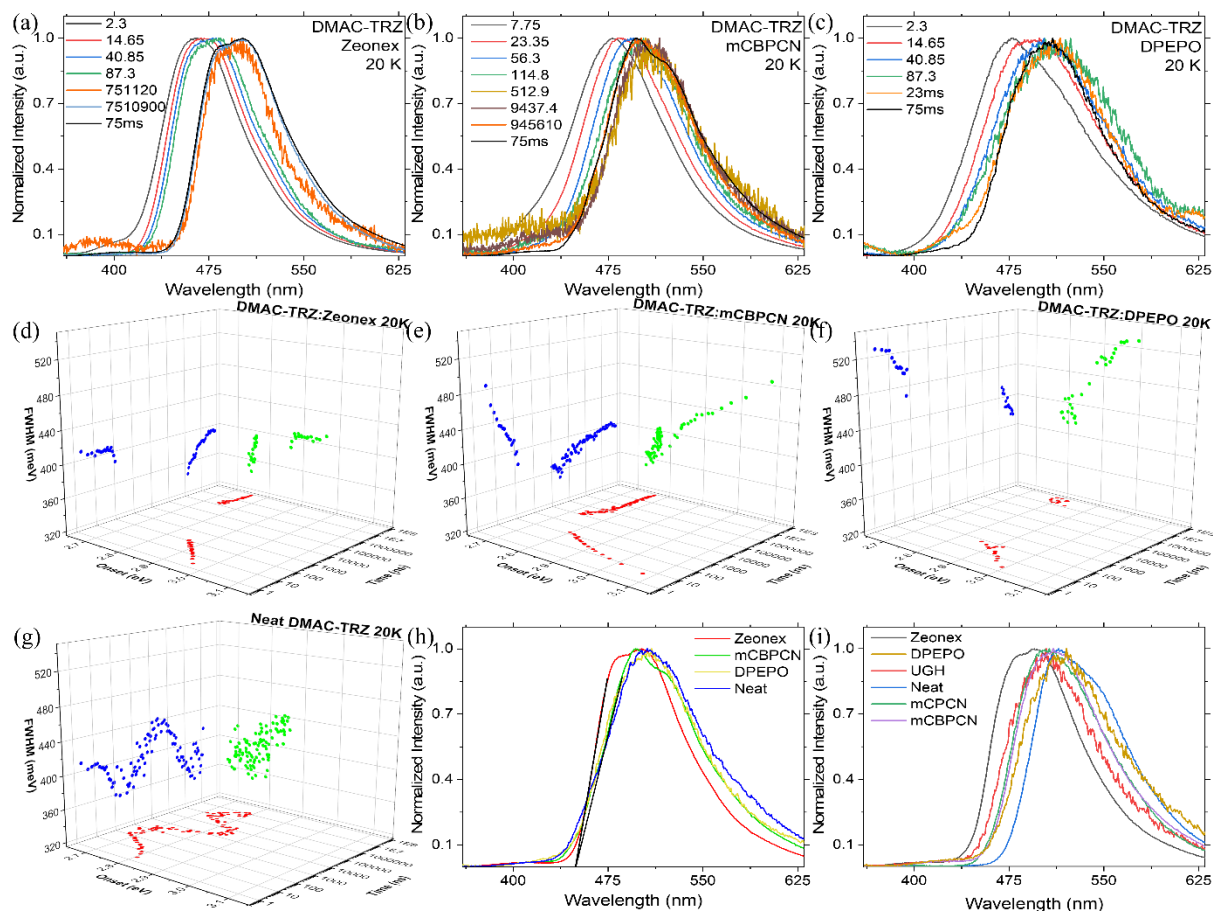


Figure 4.5. Time-resolved PL spectra of 1 wt% DMAC-TRZ in (a) Zeonex, (b) mCBPCN and (c) DPEPO host, at 20 K. Time-resolved onset energy and FWHM of 1 wt% DMAC-TRZ in (d) zeonex, (e) mCBPCN, (f) DPEPO host, and (g) neat film, at 20 K. Phosphorescence spectra of 1 wt% DMAC-TRZ in different hosts at (h) 20 K and (i) 80 K (time delay at 75 ms). Times given on each plot are in ns, unless stated.

Usually, 80 K time-resolved PL spectra (in the ms regime) are used to define the phosphorescence energy of various systems/molecules. Phosphorescence typically defines the lowest lying triplet state of any system, typically the (local) triplet state of the donor, and thus should be insensitive to the environment, i.e. host independent. On the contrary, phosphorescence was observed to be different in each host at 80 K (**Figure 4.5i**). At low temperatures, both non-radiative processes are suppressed, and delayed emission is minimized or quenched as there is little thermal energy to activate the TADF mechanism. However, in DMAC-TRZ, the lowest triplet state energy is energetically so close to the ^1CT that, even at 80 K, there is enough thermal energy in the system to activate rISC. Thus, delayed fluorescence

(DF) was observed even at 80 K. Further, because of the enhanced rISC rate dispersion at low temperatures, DF was observed even at ms times, originating from the conformers with larger HOMO-LUMO overlap. Consequently, the observed phosphorescence is not pure triplet state emission but a combination of both delayed fluorescence and phosphorescence emission. This introduced errors in the estimation of the lowest triplet state energy value, with the error value being host-dependent.

The latter was addressed with 20 K time-resolved PL measurements, which demonstrates the real lowest triplet energy value of DMAC-TRZ, at 2.75 eV (**Figure 4.5h**) in all hosts. Time-resolved PL spectra analysis at 20 K reveals spectral shifts mainly confined within the prompt time region confirming this to be an effect of inhomogeneity in the early times, as shown in **Figure 4.5d-g**. Based on the magnitude of the singlet triplet energy gap (ΔE_{ST}) there is a minor delayed CT contribution for a couple of hundred nanoseconds only.

Another indication that the real triplet energy value was measured at 20 K, is the vibronic structure of the phosphorescence emission in zeonex and mCBPCN, indicating that the emission originates from a locally excited triplet state (**Figure 4.5h**). Comparing the two spectra, zeonex has only prompt fluorescence emission followed by phosphorescence at ms due to its high ΔE_{ST} . mCBPCN on the other hand, has a small but observable delayed contribution for some μs (even at 20 K) as the gap in this case is much lower. Nevertheless, phosphorescence emission onset energy stabilizes close to 1 ms, while at 80 K the sample still shows a constant spectral shift even close to 100 ms. Similar behaviour with the latter is observed in DPEPO, although the phosphorescence spectrum is not structured the onset maintains the same value. On the contrary, neat DMAC-TRZ film has constant delayed emission, similar to the 80 K measurement, but different triplet energy onset over longer delays. Thus, at 20 K the temperature is low enough to minimize the rISC and prevent emission overlap between delayed fluorescence and phosphorescence over longer delay times except for neat film which must have other mechanisms contributing to the delayed part, for example dimer emission or triplet-triplet annihilation (TTA).

The above clarifies the apparent host dependency of the triplet energy, but the consistent spectral shift issue adds an extra dimension to the problem. In low dielectric/polarizability hosts the singlet triplet gap is high, as a result of the lowest-lying singlet CT state being well above the local lowest triplet state. Higher dielectric hosts minimize the singlet-triplet gap but can also cause the lowest-lying CT states to fall below the lowest local triplet state, as observed weakly in the cases of mCPCN/mCBPCN but more pronounced in DPEPO/neat film (**Figure**

4.3). At 80 K, the distribution of CT states is larger compared to room temperature, as can be seen in **Figure 4.4** by an increased distribution of onsets over time during the entire time region of analyses. In the delayed regime ($t > 100$ ns), the low temperature suppresses k_{rISC} , allowing rISC to repopulate the ^1CT states energetically close to the lowest ^3LE because of the minimal excess thermal energy within the system (**Figure 4.4**). This effect is also evident from the smaller time-resolved FWHM values in the 80 K measurements compared to room temperature.

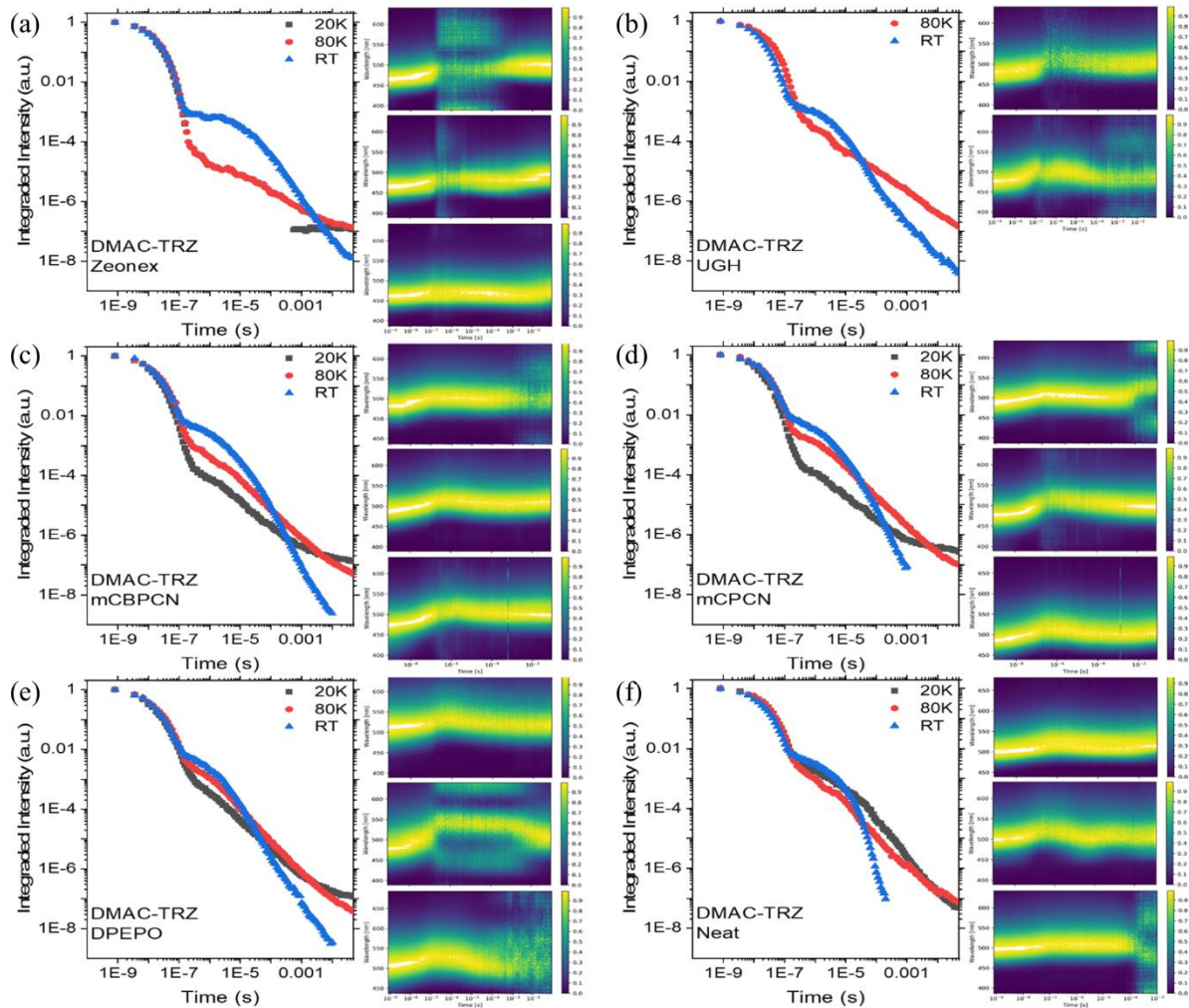


Figure 4.6. Time-resolved PL decays of 1% w/w DMAC-TRZ in (a) Zeonex, (b) UGH, (c) mCBPCN, (d) mCPCN and (e) DPEPO host. (f) Neat film of DMAC-TRZ, at room temperature (cyan), 80 K (red) and 20 K (grey). On the right side of each graph the contour plots of the PL over time at 298 K, 80 K and 20 K from top to bottom. Data points not plotted indicate a signal measured that is below the noise floor of the iCCD detector, there is no real measurable signal at these times.

From the temperature-dependent decay kinetics, **Figure 4.6**, an exponential dependence in DF intensity with the magnitude of ΔE_{ST} was observed.²⁰ In zeonex, where the gap is 170 meV (**Table 1**), the delayed contribution is minimized at 80 K (observed by the huge drop of the delayed regime at $t > 100$ ns) while at 20 K it is completely quenched and only phosphorescence emission was observed at longer delay times. In mCPCN and mCBPCN, with ΔE_{ST} at 12 and 24 meV respectively, the delayed emission quenching at 80 K is less compared to the one in zeonex host and is proportional to the ΔE_{ST} . At 20 K, both systems have similar behaviour and the delayed contribution is negligible. However, if there is a sizable population of CT states having a negative gap, as in DPEPO, then the delayed emission contribution decrease becomes even smaller at both 80 K and 20 K (**Figure 4.6e**), not following an exponential dependence on the singlet-triplet energy gap. Indeed, the delayed contribution to the overall emission is only slightly reduced and becomes longer lived with decreasing temperature. This is type III rISC (see subsection 2.5.3.1) where ^1CT and ^3CT are energetically below the coupling ^3LE state.²¹ Given that ^3CT must always be lower in energy than ^1CT , then for type III rISC the $^3LE - ^3CT$ gap is bigger than the $^3LE - ^1CT$ gap and so the non-adiabatic coupling (between ^3CT and ^3LE) will become less efficient, but conversely the $^3LE - ^1CT$ gap is smaller than for type I systems (CT states above ^3LE).²¹ In the case where $|\Delta E_{ST}| < 50$ meV then this can be a large effective change because the k_{rISC} depends exponentially on the $^3LE - ^1CT$ gap and quadratically on $^3LE - ^3CT$ gap²² so at lower temperatures, type III systems can display TADF whereas for type I it is quenched as the $^3LE - ^1CT$ gap dominates (**Figure 4.7**). This, I believe is also why the type III states decay more slowly, but as Penfold *et al* have calculated,²³ even at absolute zero, there is still non-adiabatic coupling overcoming large $^3LE - ^3CT$ gaps. Thus, for DPEPO, the DF temperature dependency departs from the expected exponential because the type III rISC contribution plays an important part in the overall DF of this system.

At this point it is worth mentioning that another way to conclude if there is pure phosphorescence emission at longer delays is by observing the slope of the time-resolved decay in the ms regime. As seen in all cases, the slope of the decay after 1ms gets closer to zero at 20 K while at 80 K the slope is still negative (**Figure 4.6**). The only film that doesn't follow this trend is neat, due to possible contribution from dimers or TTA. The neat film decay in both temperatures is similar but in 20 K it tends to reach a plateau at later times.

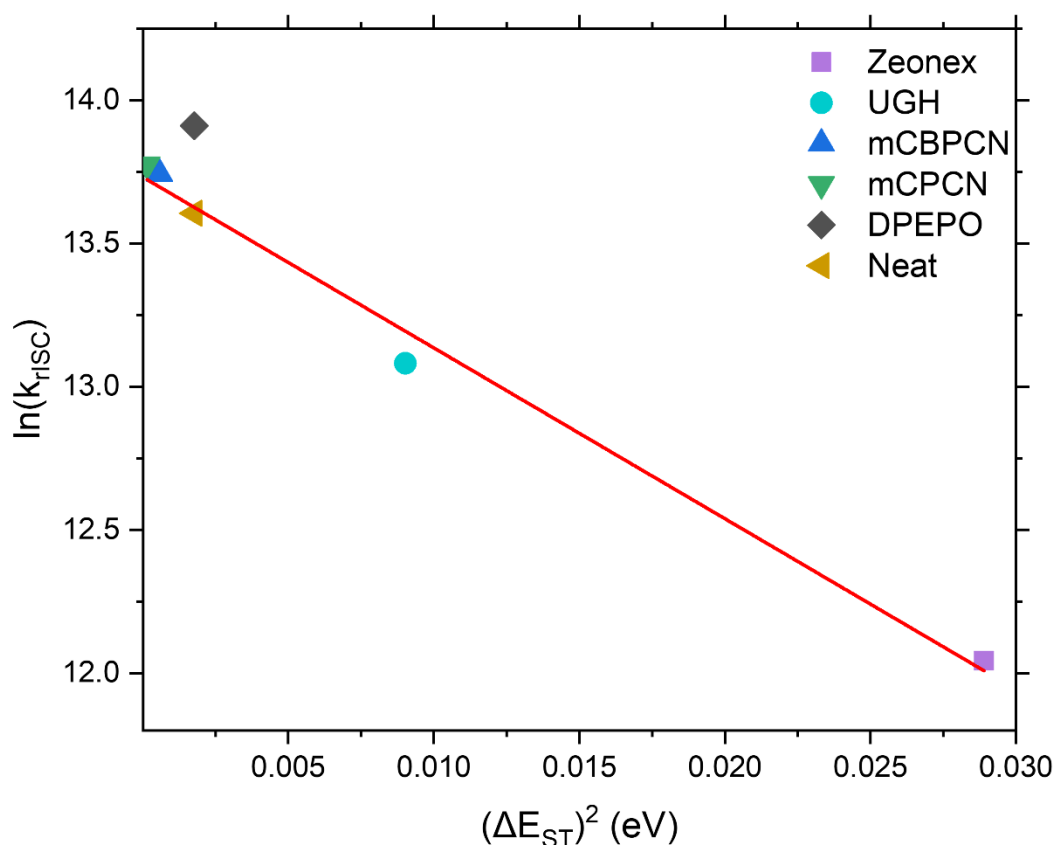


Figure 4.7. Linear relation between k_{rISC} and $(\Delta E_{ST})^2$

In **Figure 4.6**, the room temperature time-resolved PL decays show how the lifetime of the prompt and delayed emission depend on the host and its characteristics. The prompt lifetime is similar in all cases, between 15 to 19 ns (**Table 1**). For the delayed emission, neat film has similar behaviour to DMAC-TRZ in toluene (**Figure 4.1**), indicating low inhomogeneity (**Figure 4.3**). In DPEPO where the ^1CT , on average, lies below the lowest triplet state, a minor decrease in the intensity of the delayed component is observed (**Table 1**). mCPCN and mCBPCN with minimal ΔE_{ST} are very similar, whereas zeonex and UGH with large ΔE_{ST} show a longer delayed lifetimes as well as lower delayed contribution relative to the prompt. Further, in rigid hosts, with dispersive CT energies, the DF lifetime becomes bi-exponential relative to DMAC-TRZ in solution and zeonex film. DF lifetimes decrease with increasing host dielectric, with the additional fast DF lifetime component (compared to solution) having largest and the slower DF lifetime component having a smaller contribution to the overall DF regime (**Table 1**).

Another phenomenon appearing in all the guest-host films is the long delay time tail of the decay, having a linear instead of an exponential slope. Further, at long delay times (time delay $> 10 \mu s$), the time-resolved decay has increased lifetime (longer tail lifetime) compared to the

solution and neat film. Using diluted emitter in toluene as a reference (**Figure 4.1a**), which has no long-lived linear tail, and comparing with the neat film (**Figure 4.6f**), the long delay time decay is similar. The neat film, which has the smallest degree of inhomogeneous broadening also has a negligible non-exponential tail effect. This originates from the surpassed heterogeneity of DMAC-TRZ in both systems (solution and neat film). In solution, due to allowed relaxation pathways, only one molecular conformation is contributing to the DF regime (homogeneous system). In neat film, this is assumed to arise effectively through the ‘aggregated’ form of solid DMAC-TRZ giving a lower energy homogeneous environment. In guest host systems, the main introduced extra parameters (compared to solution and neat film) are: the guest’s reduced molecular rearrangement freedom, because of rigidity, the reduced homo-molecular interactions, due to higher average distances between the DMAC-TRZ molecules compared to neat film, and finally the host permanent dipole moment. The guest-host systems long delay time decay (tail) slope tends to decrease with increasing host dielectric, not always proportionally (**Figure 4.8a**). This means that the tail slope trend, thus the distribution of CT states based on the variety of molecular conformations, i.e. dihedral angles, and their corresponding k_{ISC} distribution is controlled by the host environment.

In zeonex the tail slope value is shallow (least homogeneous), whereas for higher dielectric hosts the slope becomes steeper and is steepest for neat film (most homogeneous in solid state). The high dielectric host (DPEPO) has only a slightly larger slope than mCPCN and mCBPCN. To understand this, a simple model is proposed based on a distribution of dihedral angle values, i.e. variety of molecular conformations (local environments) in each system giving a distribution of ΔE_{ST} , and thus k_{ISC} rates and DF lifetimes values (**Figure 4.9**). In mCBPCN, DMAC-TRZ has on average small ΔE_{ST} , thus faster k_{ISC} rate throughout the DF regime and the long delay time tail decays quickly, **Figure 4.9a**. The tail fitting with an arbitrary set of exponentials, thus DF decay times, represents the distribution of dihedral angles ($\theta_1 - \theta_8$). In zeonex, **Figure 4.9b**, DMAC-TRZ average ΔE_{ST} is much higher, thus k_{ISC} values are much smaller. Assuming that the distribution of angles is roughly the same in both hosts, so that the number of different ΔE_{ST} ’s is comparable, and starting from a large ΔE_{ST} (zeonex), with increasing ΔE_{ST} values a stronger effect on the tail phenomenon was observed. Starting from a smaller ΔE_{ST} (mCBPCN) with increasing ΔE_{ST} values the tail phenomenon impact appeared suppressed. In other words, if the inhomogeneity of a system is small it will have a smaller effect on the tail phenomenon and thus on the distribution of ΔE_{ST} ’s.

Table 1. Kinetic modelling results, time constants and decay rates, for solution processed DMAC-TRZ films in different hosts.

DMAC-TRZ 1% w/w in Host		Zeonex	UGH	mCBPCN	mCPCN	DPEPO	Neat Film
Spectral shift (nm)*	RT	8	12	17	18	19	9
	LT	21	26	28	24	21	14
ΔE_{ST} (meV)*		170	95	24	12	-42	-42
$\Delta E[T_H-T_G]$ (eV)***		>0.50	0.75	0.10	0.14	0.35	-
τ_{prompt} (ns)		18.5	15.7	15.8	18.4	15.7	18.5
$A_{delayed}$ (%)	A ₁	100	71.4	70.4	66.6	72.3	61.9
	A ₂	-	28.6	29.6	33.4	27.7	38.1
$\tau_{delayed}$ (μ s)	τ_1	6.27	1.59	0.86	0.61	0.6	0.69
	τ_2	-	9.19	5.62	4.42	3.56	5.71
k_F		3.3×10^7	3.8×10^7	3.0×10^7	2.6×10^7	2.9×10^7	2.5×10^7
k_{ISC}		2.1×10^7	1.3×10^7	2.0×10^7	1.8×10^7	1.8×10^7	1.8×10^7
k_{rISC}		1.7×10^5	4.8×10^5	9.3×10^5	9.6×10^5	1.1×10^6	8.1×10^5

*Data were extracted experimentally from the time-resolved spectra at room temperature (RT) and 80 K (LT). Spectral shift was measured by the onsets of first frame (2.3 ns) and energetically lowest lying CT frame. ΔE_{ST} was measured using the onset of the stabilized CT emission at room temperature and the onset of phosphorescence emission at 20 K.

**DMAC-TRZ in toluene solution for comparison, concentration 20 μ M.

***T_H, G: Triplet energy of Host (H), Guest (G) measured at 80 K and 20 K respectively, at 80 ms time delay. UGH and Zeonex triplet energy was taken from literature.

Considering the ΔE_{ST} value of DMAC-TRZ highly twisted conformer in zeonex being relatively large and the distribution of the more planar conformers having larger ΔE_{ST} values, each DF decay component assigned to a different conformation ($\theta_1 - \theta_8$) has longer delayed lifetimes compared to DMAC-TRZ in mCBPCN host, which has a much smaller relative ΔE_{ST} values for all its conformers. As shown in **Figure 4.9d**, the model approach is in good agreement with the experimental results (**Figure 4.8a**). In DPEPO, with type III TADF, the fastest k_{rISC} does not come from the lowest energy CT state which is below the ^3LE . As a result,

the effect of disorder is more complex on the distribution of decay times which explains why DPEPO film does not fully follow the described host dielectric-tail phenomenon relation.

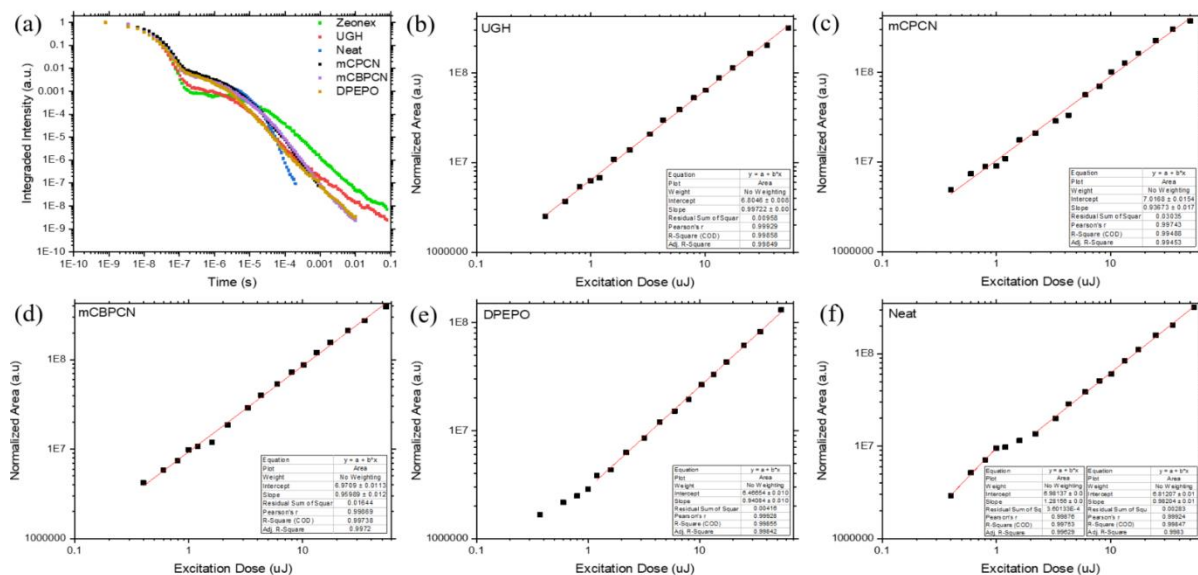


Figure 4.8. a) Time-Resolved PL decays of 1 wt% DMAC-TRZ in different hosts. Power dependence of 1 wt% DMAC-TRZ delayed fluorescence in (b) UGH, (c) mCPCN, (d) mCBPCN, (e) DPEPO, and (f) neat film. All measurements at 298 K.

To monitor the monomolecular nature of DMAC-TRZ's TADF in the different films, laser fluence measurements were conducted (**Figure 4.8**). The measurements were performed over a time range of 0.5 μ s to 10 μ s. In this regime the fast DF component (conformers) is dominant in all five systems. The gradient of the power dependence measurements is close to one in all systems, showing mono-excitonic TADF nature, except neat film which has a gradient of 1.3, at low excitation doses. This indicates the coexistence mono- and bi-excitonic TADF nature for the neat film with the contribution of a bi-molecular long lived triplet exciton harvesting mechanism, such as TTA.²⁴

From kinetic modelling, the fluorescence decay rate and k_{ISC} are similar in all cases (**Table 1**).¹⁵ The k_{ISC} is purely dependent on the host, and how it effects the ΔE_{ST} . The higher the singlet-triplet gap the slower the rate. Starting from zeonex with rate of $(1.7 \pm 0.1) \times 10^5 \text{ s}^{-1}$ the rate increases proportionally to the gap while DPEPO, with negative average ΔE_{ST} , has one order of magnitude higher rate than zeonex ($1.1 \times 10^6 \text{ s}^{-1}$). According to Gibson *et al.*,²³ by casting a semiclassical (Marcus-like) approach on the second-order perturbation theory, k_{ISC} is dependent of the nonadiabatic coupling, second order coupling connecting ^3LE and ^1CT via ^3CT and $\exp(\Delta E_{ST})^2$. Applying the calculated rates and ΔE_{ST} in our results, an excellent fit with theory as found, **Figure 4.7b**. DPEPO is the only host that does not follow the trend due to its

negative gap. In this type III case (**Figure 4.7a**), the second order coupling is affected as the ^1CT state is closer to the ^3LE than the ^3CT leading to $\Delta E_{\text{TT}} > \Delta E_{\text{ST}}$, (where T-T corresponds to $^3\text{LE} - ^3\text{CT}$) but the more temperature sensitive process of the rISC step, controlled by the $^1\text{CT} - ^3\text{LE}$ gap, is smaller in this case.

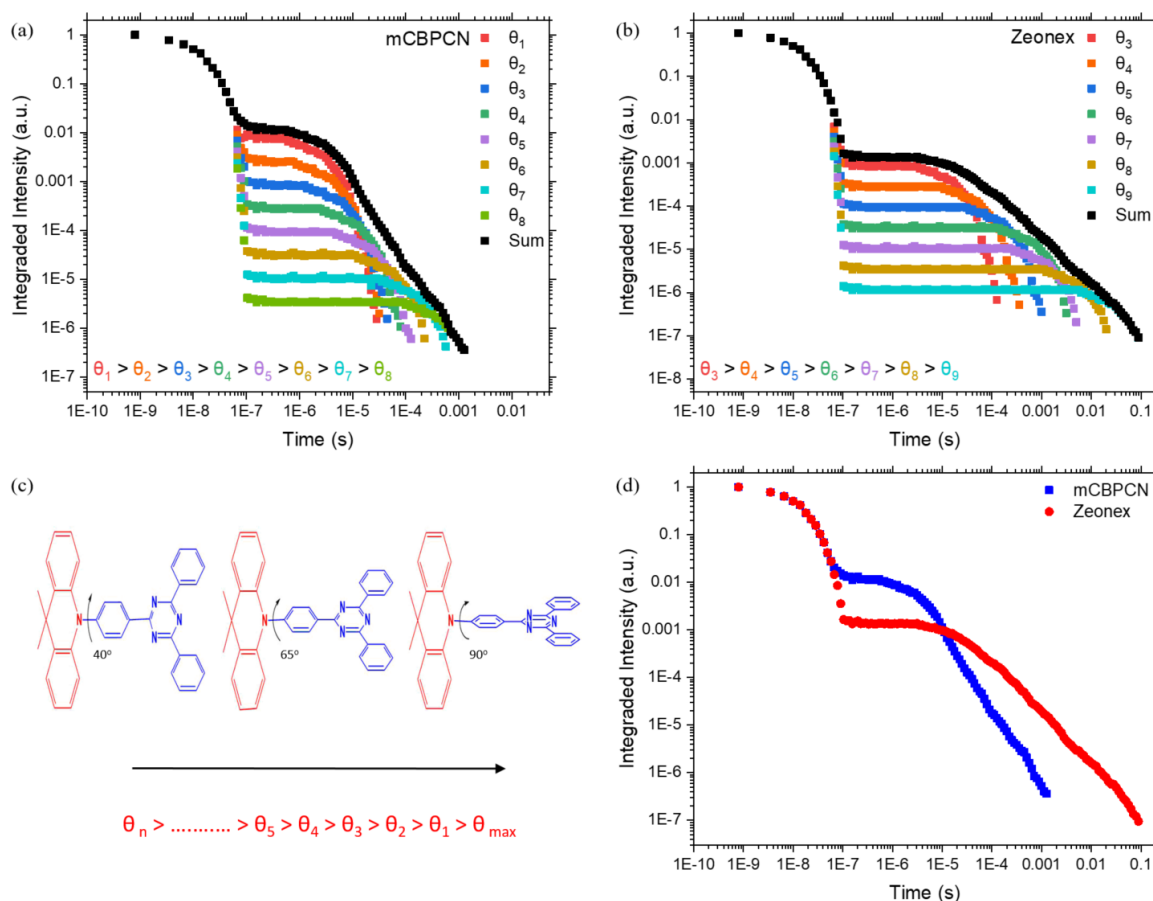


Figure 4.9. Theoretical approach of the CT distribution based on various dihedral angle molecules and the contribution to the tail phenomenon of the time-resolved PL decay for (a) mCBPCN and (b) Zeonex. (c) Schematic diagram of the hypothetical dihedral angle values. (d) Calculated theoretical time-resolved PL decays of mCBPCN and Zeonex, in good agreement with the experiment.

Evaporated films, with higher emitter concentrations (10 wt%), as typically used in OLEDs, were fabricated to study the photophysical properties and the molecular conformational distribution (inhomogeneity) differences compared to 1 wt% solution processed films (10 wt% solution processed films were tested and appeared to have similar behaviour with the evaporated films). mCBPCN and mCPCN were chosen as hosts because of their high enough but comparably smaller triplet value (desirable for devices), better stability, and positive effect on decreasing DMAC-TRZ's ΔE_{ST} . Steady state measurements as shown in **Figure 4.10**.

Photoluminescence excitation spectra have a band at 400 nm in both hosts, increasing in intensity with increasing concentration related to the increasing amount of DMAC-TRZ in the blended films. This band is also observed in DMAC-TRZ neat film. The concentration dependent photoluminescence spectra show a small bathochromic shift with increasing concentration towards the emission spectrum of DMAC-TRZ neat film, indicating the existence of stronger intermolecular interactions with increased concentration. Intermolecular interactions, such as dimer/aggregate formation in DMAC-TRZ neat film can result in higher wavelength emission compared to the host-guest blends.

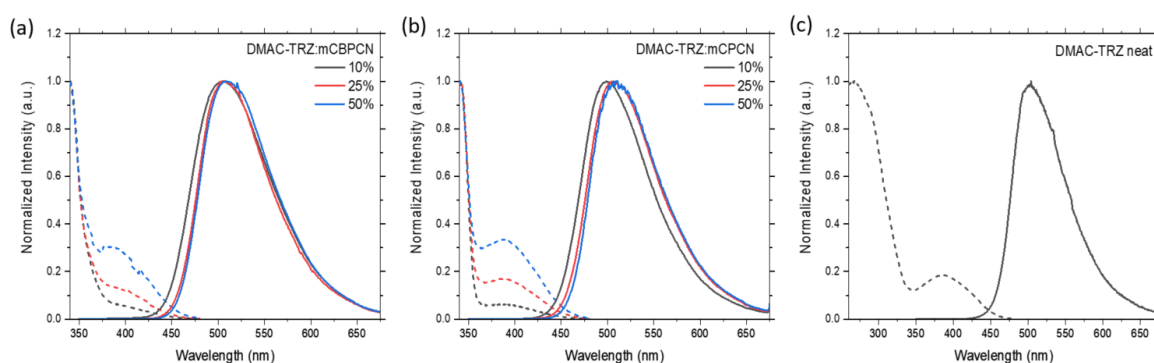


Figure 4.10. Photoluminescence, excited at 340 nm (solid line), and excitation spectra collected at 500 nm (dashed line) of (a) DMAC-TRZ:mCBPCN, (b) DMAC-TRZ:mCPCN, at various concentrations, and (c) DMAC-TRZ neat film.

Figure 4.11 shows the time-resolved emission spectra of the guest-host evaporated films at different guest concentrations. Similar to solution process films, the prompt emission has a CT character, with the higher energy CT states decaying faster, giving rise to an apparent dynamic red shift and stabilization of the emission energy onset at around 100 ns (**Figure 4.11a-f**). Further, smaller shifts are observed attributed to states of a small D-A dihedral angle distribution. These shifts of around 2 and 3 nm, indicate a far smaller distribution compared to 1 wt% solution processed films. This can also be attributed to stronger intermolecular interaction because of the higher emitter concentration, especially at higher doping levels. DMAC-TRZ:mCBPCN films PL spectra, subsequent to spectrum stabilisation (time delay > 100 ns), have the same time-resolved PL onset energy in all concentrations, at around 455 nm (**Figure 4.11g-i**). Contrary, in the mCPCN blends, the stabilised time-resolved PL onset energy decreases with increasing concentration (**Figure 4.11j-l**), which suggests the existence of a different packing mechanism in the two hosts. Presumably, the mCBPCN matrix generates different intermolecular interactions, insensitive to increasing concentration, while mCPCN leads to stronger aggregation with increasing concentrations.

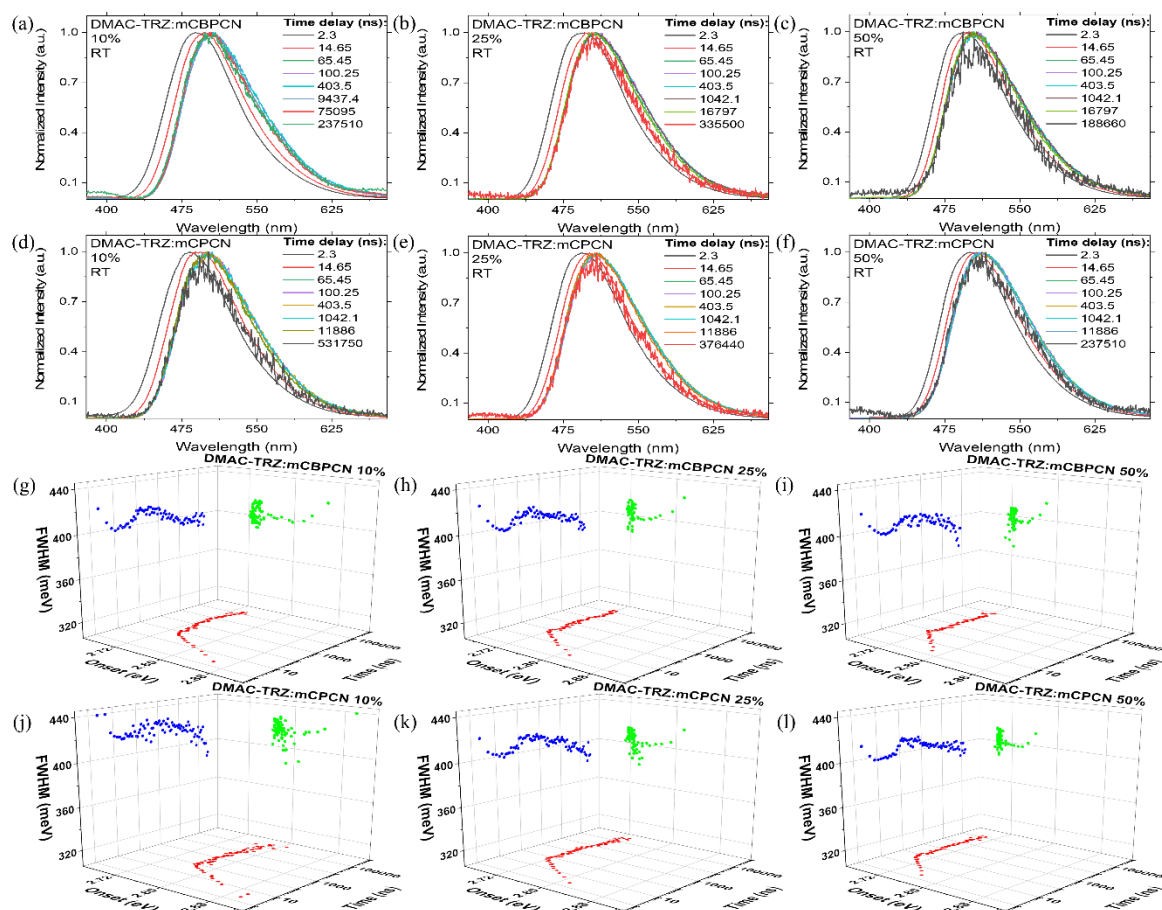


Figure 4.11. Time-Resolved normalized PL spectra of evaporated DMAC-TRZ at (a) 10, (b) 25, and (c) 50 wt% in mCBPCN and at (d) 10, (e) 25, and (f) 50 wt% in mCPCN. Time-Resolved onset energy and FWHM of (a) 10, (b) 25, and (c) 50 wt% evaporated DMAC-TRZ in mCBPCN and (d) 10, (e) 25, and (f) 50 wt% evaporated DMAC-TRZ in mCPCN host. Excitation wavelength at 355 nm. Times given on each plot are in ns, unless stated.

In neat film, the intermolecular interactions are considered the prevailing state. The time-resolved emission spectra of DMAC-TRZ neat film, at room temperature, revealed a prompt CT red shift during the first hundred ns (**Figure 4.12a, c**), followed by a stable CT emission up to 100 μ s. The energy onset is at 461 nm close to that observed in the 50% DMAC-TRZ:mCPCN film. This verifies that by increasing emitter concentration in the mCPCN blends approaches the behaviour of DMAC-TRZ neat film. At 80 K, spectral shift trends are very similar to room temperature, with slightly larger shifts, although the emission has longer lifetime (**Figure 4.12b**). After 100 μ s, the PL spectra presented vibronic structure, indicating phosphorescence emission. The neat film phosphorescence spectrum has onset wavelength at 472 nm, similar to the solution processed films at 80 K, but longer than what is observed at 20

K (onset 450 nm). This suggests thermally activated triplet migration to the low energy dimer/aggregate sites.

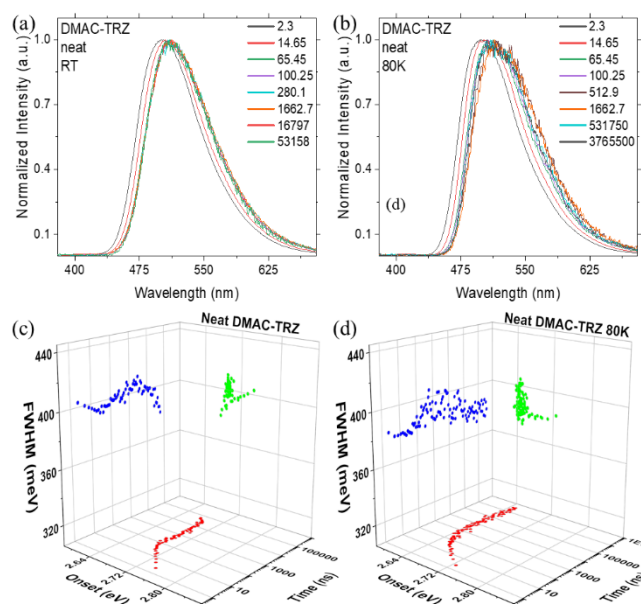


Figure 4.12. Time-Resolved normalized PL spectra of DMAC-TRZ neat film at (a) room temperature and (b) 80 K. Time-Resolved onset energy and FWHM at (c) room temperature and (d) 80 K. The curves were obtained with 355 nm excitation. Times given on each plot are.

Time-resolved decays of DMAC-TRZ evaporated films at room and low temperature are shown in **Figure 4.13**. At 10% concentration, in both hosts, a significant DF quenching was observed at 80 K compared to room temperature. With increasing concentration, the TADF quenching at low temperatures decreases in both systems. Focusing on DMAC-TRZ:mCPCN films, at room temperature, with increasing concentration the amplitude of the delayed regime (time delay > 100 ns) decreases (**Figure 4.13h**). This is attributed to stronger intermolecular interactions at higher concentrations leading to enhanced excited state quenching, similar to neat film (**Figure 4.13g**). Different behaviour is observed in DMAC-TRZ:mCBPCN films (**Figure 4.13i**). With increasing emitter concentration, a negligible change in the DF regime is observed (minor increase in amplitude). This unique behaviour points to the peculiarity of mCBPCN as a host. Based on our finding so far, increasing the concentration of DMAC-TRZ in any host, leads to aggregation/excimer formation which changes the systems behaviour and induces excited state quenching. On the other hand, in mCBPCN this effect is minimized which implies the existence of an optimized packing between DMAC-TRZ and mCBPCN even at higher concentrations. This is also observed by the stable time-resolved FWHM and delayed

emission onset energy even at long time delays, indicating a singular emitting species (**Figure 4.11**).

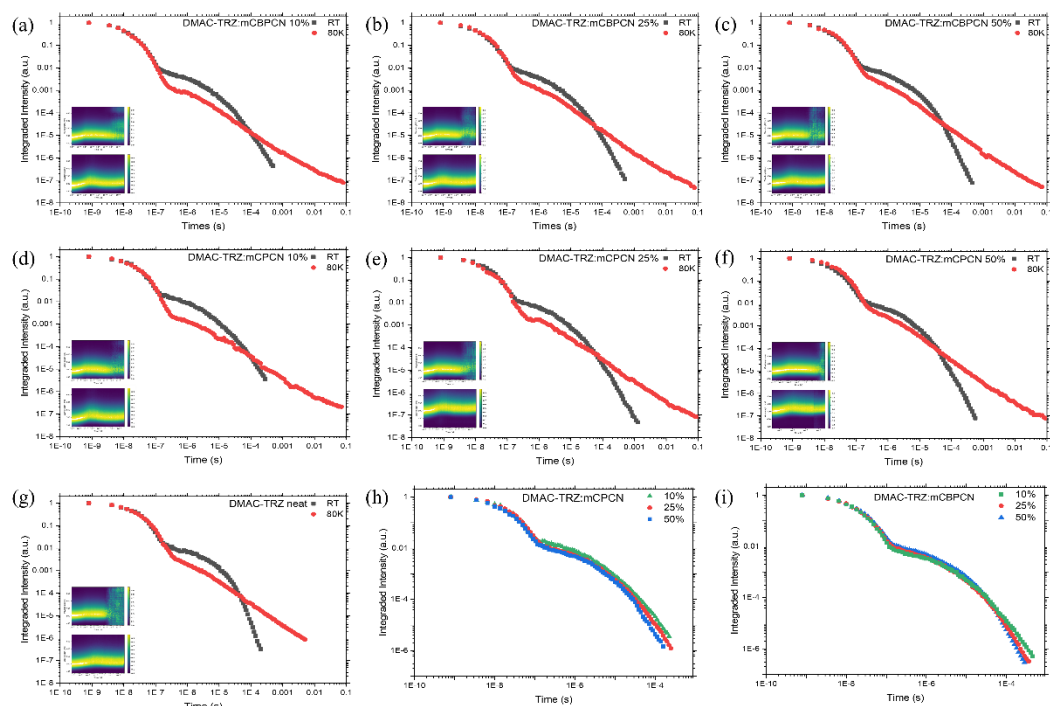


Figure 4.13. Time-Resolved PL decays of evaporated DMAC-TRZ films at (a) 10, (b) 25, and (c) 50 wt% in mCBPCN, at (d) 10, (e) 25, and (f) 50 wt% in mCPCN, and (g) neat film, at 298 K (grey) and 80 K (red). Inset: contour plots of time-resolved PL over time at 298 K (top) and 80 K (bottom). Time-Resolved PL decays of various concentrations of DMAC-TRZ in (h) mCPCN and (i) mCBPCN at 298 K.

The fitting parameters and kinetic modelling results of the decays are shown in **Table 2**. The prompt lifetime of mCBPCN is constant while for mCPCN decreases with increasing concentration. In the delayed regime, with increasing concentration the amplitude of the delayed component increases in mCBPCN and decreases in mCPCN (**Figure 4.13h, i**) but the ratio of the two fitting amplitude components (A_1 and A_2) remains constant in both systems. On the contrary, the DF lifetimes of DMAC-TRZ:mCBPCN decrease with increasing concentration whilst in mCPCN they remain constant. This implies that the lifetime quenching in mCPCN is controlled by excited state migration to quenching sites (aggregates) while in mCBPCN the aggregation quenching is suppressed.

The PLQY of all samples is given in **Table 2**. The integrating sphere measurement is sensitive to the sample's absorption coefficient, for this reason two different excitation wavelengths were used. At 370 nm the absorbance is high enough at all concentrations, but a local state and the host are also excited. At 400 nm the CT is directly excited (ideally a closer scenario to an operating OLED) but unfortunately has limited absorbance at low concentrations. In the DMAC-TRZ:mCBPCN films, with increased concentration a minor decrease in PLQY is observed at 370 nm excitation. With direct CT excitation, at 400 nm, a higher PLQY value is observed, verifying the existence of extrinsic losses using 370 nm excitation. Subsequently, PLQY values close to unity at 25% concentration film are found, while at 50% it is only slightly below 0.9. At 10% concentration the CT absorption is limited making the PLQY value unreliable, but following the trend seen with 370 nm excitation the value should be similar to

Table 2. Kinetic modelling results, time constants and decay rates, for various concentrations of evaporated DMAC-TRZ films diluted in mCBPCN, mCPCN hosts and neat film.

Host		mCBPCN			mCPCN			None
DMAC-TRZ Conc. (%)		10	25	50	10	25	50	100
Spectral shift (nm)*	RT	20	17	13	20	17	13	12
	LT	24	24	27	25	24	25	14
ΔE_{ST} (meV)*		-42	-42	-42	12	-42	-60	-60
PLQY (%)**	370	87	85	83	-	-	-	-
	400	-	98	87	-	90	80	75
τ_{prompt} (ns)		19	18	18	25	23	19	29
$A_{delayed}$ (%)	A ₁	75	77	75	79	80	81	69
	A ₂	25	23	25	21	20	19	31
$\tau_{delayed}$ (μ s)	τ_1	1.5	1.2	1.1	1.2	1.3	1.3	1.6
	τ_2	9.5	8.2	8.0	8.6	8.3	8.2	9.2
k_F (s ⁻¹)		2.2×10^7	2.1×10^7	1.8×10^7	1.2×10^7	1.7×10^7	1.8×10^7	1.2×10^7
k_{ISC} (s ⁻¹)		2.1×10^7	2.0×10^7	2.1×10^7	2.2×10^7	2.0×10^7	2.4×10^7	1.8×10^7
k_{rISC} (s ⁻¹)		7.3×10^5	8.3×10^5	9.0×10^5	9.0×10^5	8.8×10^5	8.6×10^5	5.8×10^5

* Data were extracted experimentally from the time-resolved spectra at room temperature (RT) and 80 K (LT). Spectral shift was measured by the onsets of first frame (2.3 ns) and energetically lowest lying CT frame. ΔE_{ST} was measured using the onset of the stabilized CT emission at room temperature and the onset of phosphorescence emission at 20 K.

the 25%film, ca. unity. In mCPCN, to measure the maximum PLQY values only the direct CT excitation PLQY's, at 400 nm, were obtained. Compared to mCBPCN, there is a reduction by around 10-15% at all concentrations due to possible dimer/excimer excitation. For comparison, in neat film, the PLQY is found to be only 0.75, close to the 50 wt% DMAC-TRZ:mCPCN film.

PLQY values combined with calculated ΔE_{ST} and kinetic rISC rates reveal the possible performance of the optimum emitter concentration in a device (**Table 2**). In the case of mCBPCN the ΔE_{ST} is constant, the PLQY decreases only at 50% concentration and the fluorescence rate follows the same trend. rISC increases slightly with increased concentration whereas intersystem crossing is stable.¹⁵ On the other hand, mCPCN has an increasingly negative ΔE_{ST} , a higher drop of PLQY values accompanied with an increasing fluorescence rate, slower k_{rISC} (moving toward the neat film rate), and a stable ISC with increasing concentration. Therefore, mCBPCN is the ideal host for DMAC-TRZ which has better performance in all concentrations compared to mCPCN and neat films. With the bi-phenyl linking group between the carbazole units, mCBPCN is sterically bulkier and so prevents DMAC-TRZ dimer/aggregate formation.

These results have catalyzed the commencement of additional studies regarding quest-host interactions and the dihedral angle distribution effects. Initially, a new fitting tool was introduced by us²⁵ to uncover the distribution of dihedral angles' effect, revealing the real kinetic properties of a quest host system using Laplace transform fitting. This tool provides the density of rates, depending on the homogeneity fingerprint of each quest host system (**Figure 4.14a**), and was published in the journal of Physical Chemistry Letters.

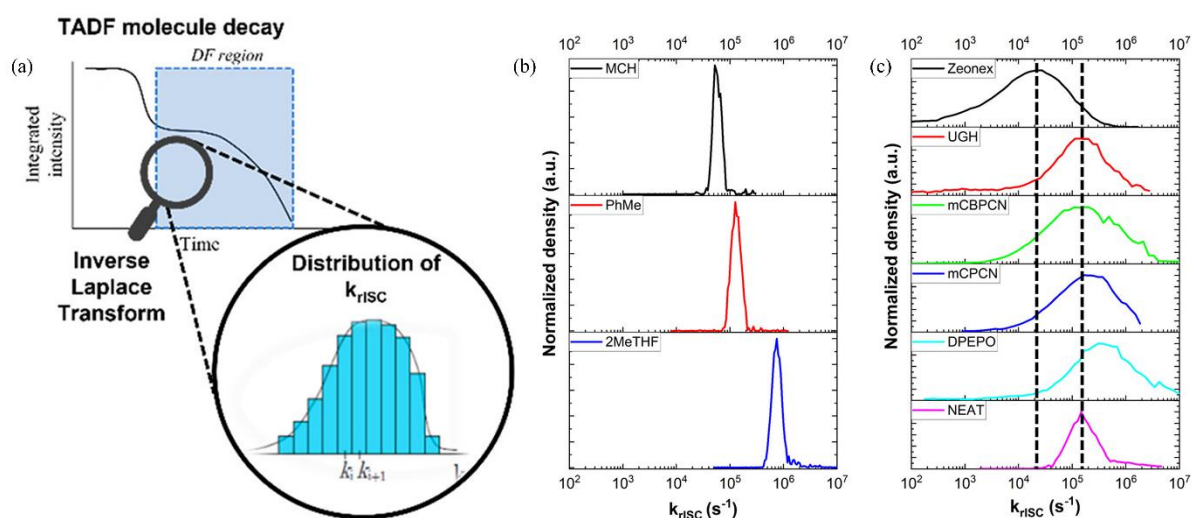


Figure 4.14. (a) Inverse Laplace transform multiple fitting model. Distribution of k_{rISC} rates of (b) DMAC-TRZ in solvents of increasing polarity at 0.8 mM concentration and (c) 1% loading drop casted films of DMAC-TRZ in different hosts at room temperature. λ_{exc} at 355 nm.

Figure 4.14b and **c** show the distribution of rISC rates, as extracted from the model, in solution and solid state environments, respectively. The narrow solution state distribution and the broad solid state distribution verify the results of this chapter and highlight their importance in the improvement of TADF mechanism understanding. Further, in collaboration with Prof. Anna Painelli's group, we published a theoretical study in the journal of the American Chemical Society about the effect of polarity, rigidity and disorder in the condensed phase.²⁶ Specifically, we adopted the essential state model proposed and parametrized *ab initio* for DMAC-TRZ. This model takes into account the anharmonic and nonadiabatic vibrational and conformational motions and is directly compared with the experimental data of this chapter.

4.5 Conclusion

An in depth photophysical analysis of DMAC-TRZ behaviour in a variety of hosts, in both solutions processed and evaporated films, has been presented. The good TADF performance of the emitter is reflected in solution measurements with strong TADF contribution and high k_{rISC} . The DMAC-TRZ CT state undergoes bathochromic shift with increasing solvent polarity and a rapidly diminishing oscillator strength. Similar behaviour was observed in solid state with some extra parameters effecting the emitter's performance. In solution processed film, host packing is the main factor that leads to dihedral angle inhomogeneity, thus dispersion of CT energy, ΔE_{ST} and k_{rISC} . In flexible zeonex matrix the packing effect is weaker, while in both low and high permanent dipole moment small molecule hosts the effect is dominant. In these rigid hosts an additional delayed lifetime component, which decrease with increasing host dielectric, is observed. At low temperature (80 K), the inhomogeneity is more obvious due to the reduced thermal energy which is required for rISC activation so that states with larger ΔE_{ST} have far longer delayed emission lifetimes. The presence of dimer/aggregate states is not observed in 1 wt% DMAC-TRZ films in different hosts, however, in neat DMAC-TRZ film, where intermolecular interactions are dominant, the smallest degree of inhomogeneity was found because the monomer emission is quenched. In addition, the phosphorescence energy is difficult to be measured especially when ΔE_{ST} is very small. This requires very low temperatures to complete quench the DF and minimise triplet migration to dimer/aggregates to

reveal the actual lowest lying triplet of the system. This way is shown that the triplet energy of the emitter does not dependent on the host matrix.

The DF tail phenomenon is introduced and explored showing a strong correlation with the guest host interactions. In DMAC-TRZ solution this phenomenon does not exist whereas in neat film is minimal. The guest host systems always present the tail phenomenon and is shown that with smaller average system's ΔE_{ST} there is a shorter tail lifetime. This verifies that the ΔE_{ST} inhomogeneity, introduced by packing on the D-A dihedral angle, is small when the average ΔE_{ST} distribution is small leading to a narrow distribution of k_{rISC} 's and a shorter tail. When the average ΔE_{ST} is large, the disorder induced energetic distribution is larger leading to a wide distribution of k_{rISC} and subsequently a longer tail.

The comparison between 1 wt% DMAC-TRZ solution processed, and 10 to 50 wt% evaporated films reveals the importance of concentration on packing and intermolecular interaction. Exploring two similar guest host systems, DMAC-TRZ in mCBPCN and mCPCN, a surprisingly inconsistent behaviour appears. mCBPCN presents a different packing of the DMAC-TRZ molecules reducing aggregation formation with the DF being unaffected by increased concentration. On the contrary, DMAC-TRZ:mCPCN showed stronger intermolecular interactions even in lower concentrations thus the DF contribution decreases with increasing concentration. A combination of parameters, such as the delayed emission contribution, higher PLQY value, novel packing mechanism, and higher k_{rISC} makes mCBPCN an ideal host of the DMAC-TRZ system.

This study provides new insights and understanding into the guest host effects on TADF emitters and promotes a deeper knowledge on how optimization on material design and proper combination of guest host characteristics can improve the overall performance of a TADF molecule.

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5 Exploring the Multiple Resonance TADF properties

Multiple resonance TADF emitters have emerged into a novel class of OLED emitters because of their unique narrowband emission accompanied by triplet harvesting properties. In this chapter the photophysics of the highly efficient multiple resonance TADF ν -DABNA is explored. Similar to the previous chapter, the quest host interaction have been explored showing that the triplet harvesting rate of ν -DABNA in solution and solid state (in a variety of hosts) remains constant ($k_{\text{rISC}} \sim 3\text{-}6 \times 10^5 \text{ s}^{-1}$) indicating a minor effect from the host permanent dipole moment on the SRCT, compared to the long range (D-A type) CT states, such a DMAC-TRZ in chapter 4. The ΔE_{ST} previously estimated by thermal estimations, was observed under specific conditions using optical measurements and is verified to be 70 meV, but the triplet energy is also found to be temperature dependent. A consistent increase of the exciton emission band FWHM with temperature reveals the role of hot transitions from vibrational excited states at room temperature. Combined with an observed temperature dependency of ΔE_{ST} is deduced that the rISC mechanism involves thermally activated rIC of T_1 to T_n ($n \geq 2$) followed by rapid (r)ISC to the S_1 state. Further, the effect of multiple resonance TADF emitter molecular geometry on intermolecular interaction formation is demonstrated, revealing a broad excimer band even at very low doping level. This species is responsible of quantum efficiency quenching verified by the decreased performance of the material in devices. By considering molecular alignment of the ν -DABNA emitter the potential for yet-greater OLED performance is identified, curtailed by excimer formation.

The work presented in this chapter was published in ACS Applied Materials & Interfaces: Stavrou, K.; Danos, A.; Hama, T.; Hatakeyama, T.; Monkman, A. P. Hot Vibrational States in a High-Performance Multiple Resonance Emitter and the Effect of Excimer Quenching on Organic Light-Emitting Diodes. ACS Appl. Mater. Interfaces 2021, 13, 7, 8643–8655.

5.1 Introduction

TADF materials¹⁻³ require a small ΔE_{ST} and a common strategy to reduce it is to use electronically decoupled donor and acceptor groups that give rise to spatial separation of the HOMO and the LUMO.³ However, D-A materials give rise to broadband charge transfer emission spectra with FWHM of 70–100 nm due to structural relaxation in S_1 , which has hampered the practical application of TADF materials in OLED displays. To overcome this drawback, an alternative strategy for HOMO-LUMO separation has been reported featuring multiple resonance (MR) effects of boron and nitrogen atoms.⁴⁻⁷ This effect localizes HOMOs and LUMOs on different atoms of a single aromatic system to realize not only small ΔE_{ST} (<200 meV), but also narrowband emission (FWHM of <30 nm) and high PLQY. These attractive characteristics have encouraged scientists to develop a variety of MR-TADF materials.⁸⁻¹⁷ However, these materials all exhibit relatively small rISC rates (k_{rISC} ; $\sim 10^4$ s⁻¹) and consequently suffer from efficiency roll-off at high luminance due to their slow spin upconversion mechanism.

Recently, a new MR-TADF material, v-DABNA, with a fully resonant extended π -framework has been developed (**Figure 5.1**).¹⁸ v-DABNA showed an increased k_{rISC} ($\sim 10^5$ s⁻¹), and thus allowed us to fabricate an OLED with an excellent external quantum efficiency (EQE) with minimal efficiency roll-off (34.4%/26.0% at 15/1000 cd m⁻²).¹⁸ Moreover, v-DABNA exhibited extremely narrower-band emission (FWHM of 14–18 nm), which is comparable to those of well-defined LEDs based on gallium nitrides and CdS/ZnS quantum dots. However, despite these notable properties, its photophysics has largely been unexplored so far. In this chapter, a detailed photophysical analysis of v-DABNA is reported based on steady-state and time-resolved photoluminescence (PL) measurements along with HF OLEDs fabrication. The underlying mechanisms of MR-TADF in the DABNA-type materials is elucidated, identifying both intrinsic and extrinsic factors that limit current emission linewidth and rISC performance.

5.2 Collaborator Contribution

All solution and film samples were made by myself. The steady state and Time-resolved PL measurements were done by myself. The OLEDs were fabricated by myself and Dr. Andrew Danos. The crystallographic data were collected by Toshiki Hama, from Prof. Takuji

Hatakayama's group at the Department of Chemistry, School of Science and Technology, Kwansei Gakuin University. Brief details of this work are given for completeness.

5.3 Experimental Methods

5.3.1 Sample preparation

Photophysical characterization of solutions was performed in five different solvents: toluene (PhMe), dichloromethane (DCM), chlorobenzene (CB), acetonitrile (MeCN) and 2-methyltetrahydrofuran (2-MeTHF). The solutions were prepared at concentration of 25 M, except MeCN and 2-MeTHF solutions at 0.25 μ M due to solubility reasons. In PhMe and DCM solutions, for the additional concentration study, a range of concentrations between 2.5 nM and 25 μ M was used. All solutions were degassed by five freeze-pump-thaw cycles. Solid state samples were fabricated by solution casting technique onto quartz and transparent sapphire substrates. All host-guest films were produced at a range of concentrations between 0.0001 and 10 wt% of ν -DABNA in different host matrices (zeonex, DPEPO, and UGH-3). For neat film, a solution of 0.1 mg/mL, in toluene, was used.

5.3.2 Crystallographic data collection and structure determination

The crystal data of ν -DABNA was collected on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using curved graphite monochromated Mo K α radiation ($\lambda = 0.71075$ Å). The reflection data for ν -DABNA was integrated, scaled, and averaged by using CrystalClear. Semi-empirical absorption correction was applied using the program of Abscor.¹⁹ The structures were solved by direct methods (SIR2014²⁰) and refined by full-matrix least square method on F^2 for all reflections (SHELXL-2014/7²¹). All hydrogen atoms were placed using AFIX instructions (C–H = 0.95 Å and O–H = 0.84 Å), while all other atoms were refined anisotropically. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$. All calculations were performed by using Yadokari-XG 2009²² and illustrations were drawn by using ORTEP-3.

5.4 Results and Discussion

5.4.1 Photophysics

The basic photophysical properties of v-DABNA in toluene solution were characterised. A multi-component, structured absorption spectrum of narrow bands is shown in **Figure 5.1**, dominated by the lower energy band. The energetic progression is not vibronic because there is no consistent energy separation between each band. Thus, these bands are assigned to higher energy electronic transitions, i.e. S_1 , S_2 , $S_3 \dots S_n$, with S_2 being only 250 meV above S_1 , **Figure 5.1a**. The absorption is mirrored by a sharp emission band (FWHM at 70 meV) with onset and peak energy of 2.75 eV and 2.66 eV, respectively. At higher emitter concentration (25 μM in toluene), the emission band red shifts by 40 meV and broadens towards 100 meV FWHM, primarily due to a shoulder on the red edge of the main emission peak, **Figure 5.1c, d**.

Table 5.1. Comparison of the two emission bands, S_1 - S_0 transition (1^{st}) and S_1 - S_0 vibrational mode/aggregation related band (2^{nd}), in different concentrations in PhMe.

v-DABNA:PhMe Concentration (μM)	0.0025		0.025		0.25		2.5		25	
Peak number	1^{st}	2^{nd}	1^{st}	2^{nd}	1^{st}	2^{nd}	1^{st}	2^{nd}	1^{st}	2^{nd}
Peak Wavelength (nm)	466	487	466	487	466	488	468	488	473	488
Peak intensity (counts)	8.5E5	1.2E5	4E6	5.4E5	3.8E7	5.4E6	1.6E8	3E7	3.9E8	1.5E8

These spectroscopic observations are consistent with the rigid π -conjugated, near planar molecular framework of v-DABNA,¹⁸ dominated by absorption and emission from the same lowest energy electronic transition. The true band shape of the narrow $S_0 \leftarrow S_1$ transition is represented by that observed in lower concentrations in toluene solution indicating a strong leading component and a weak vibronic side band, intensity ratio 1:0.14 and energy separation of *ca.* 120 meV (960 cm^{-1}), **Table 5.1**. This indicates that a vibrational mode strongly couples to the S_1 electronic transition. This analysis also confirms that the higher energy absorption bands are therefore not vibronic replicas of the lowest excited state. Excitation profiles (of film samples) reveal finer vibronic structure on the lowest energy absorption band, **Figure 5.1e**. The fitting of these features gave a consistent vibronic progression with an energy spacing of

ca. 285 cm⁻¹, consistent with coupling to stretching/scissoring modes of the peripheral phenylene rings.¹⁸

The emission and absorption spectra are only weakly affected by solvent polarity, **Figure 5.1f, g**. This lack of solvatochromic shift and no obvious change in line shape with increasing solvent polarity indicates no apparent (“long range”) CT character to the first excited state. Peak extinction coefficient at $3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and minimal Stokes shift (14 nm) indicate a local excitonic nature to this lowest energy excited state and is characteristic of the short-range charge transfer (SRCT) states. In toluene (**Figure 5.1f**), the main emission band was observed to start red shifting at concentrations above 2.5 μM , which is mainly ascribe to self-absorption and inner filter effect (no red shift of the absorption band was observed on the red side of the band). From 2.5 nM to 2.5 μM , the long wavelength side of the emission band also starts to increase in intensity, indicating the emergence of a new emission band. As a result, the emission spectrum FWHM also increases. The same phenomenon is observed in higher polarity DCM, **Figure 5.1g**, with a slightly smaller redshift of the main emission peak and a smaller contribution from the new low energy band.

From Time-resolved emission measurements, **Figure 5.1h**, a short prompt and long-lived delayed fluorescence emission is observed. The amplitude of the DF component is four orders of magnitude lower compared to the prompt component indicating the small contribution of the DF to the overall emission of v-DABNA. The contribution of the DF was completely quenched in the presence of oxygen, providing an $I_{\text{vac}}/I_{\text{ox}}$ of 1.25, **Figure 5.1i**.

Molecular rigidity and planarity usually enhance intermolecular interactions such as π -stacking and dimerization. While the peripheral phenyl rings of v-DABNA are sterically orthogonal to the molecular core, which should hinder such interactions, recent reports have shown that phenyl substituents on large aromatic structures can still suffer significant flattening outside of solution or gas phase.²³ The increased intensity on the red side of the emission band, which is seen in all solvents as well as in films, *vide infra*, and with the position of the underlying feature found to be dependent on the environment, is therefore characteristic of an intermolecular state. The ratio between the main $S_0 \leftarrow S_1$ transition and the underlying band was found to increase non-linearly with concentration in solution, **Figure 5.1d**. No evidence of a weak absorption band below the excitonic absorption band was found, that might otherwise be associated with a ground state dimer. Thus, this red emission comes from an excimer state.

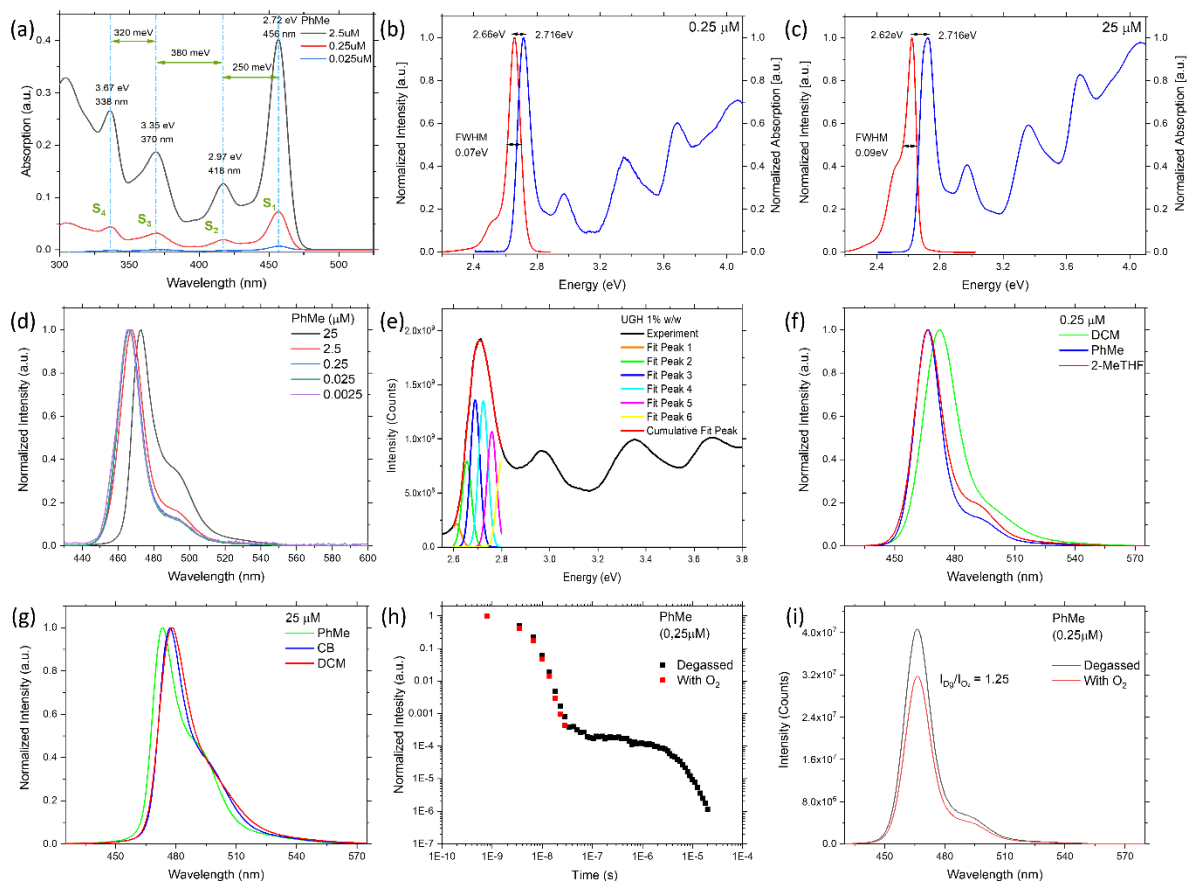


Figure 5.1. v-DABNA solution photophysics. (a) Absorption at different concentrations, absorption (blue) and fluorescence (red) spectra at (b) 0.25 μM and (c) 25 μM concentration, and (d) concentration dependence fluorescence spectra in toluene solution. (e) Excitation profile of v-DABNA in DPEPO (collection at 500 nm). Multiple Gaussian peak fitting of the leading component (FWHM tied). Solvatochromism at (f) 0.25 μM and (g) 25 μM concentration. Effect of oxygen on time-resolved PL decay (h) (inset v-DABNA structure) and steady state PL.

Time-resolved transient PL measurements of v-DABNA in a range of solvents, with different dielectric coefficients (from 2.21 to 37.5) and viscosities (0.37 to 0.8 cp) are shown in **Figure 5.2**. The environmental polarity affected the intermolecular excimer interactions, with the red component emission becoming more intense in some solvents, most notably 2-MeTHF. For two concentrations of v-DABNA in toluene; 0.25 μM (prompt lifetimes: 4 ns and 30.7 ns; delayed lifetime: 3.5 μs) and 25 μM (prompt lifetimes: 11 ns; delayed lifetime: 5 μs), it is apparent that increasing concentration extends the lifetimes of the prompt and delayed emission (**Figure 5.2a, d**). The longer prompt lifetime is therefore assigned to the excimer state

contribution and is Time-resolved PL emission is well resolved in the prompt regime (delay time > 10 ns), in 2Me-THF and MeCN solvents (**Figure 5.2k, l**).

The decay kinetics of the emission of *v*-DABNA were measured in the same range of solvents. The decays were analysed following the kinetic fitting model previously reported by Haase et al.²⁴ From this, the *krISC* is, within error, independent of the solvent polarity, ranging only between 3×10^5 to $5.5 \times 10^5 \text{ s}^{-1}$, and viscosity. This indicates that the mechanism of DF in *v*-DABNA is not analogous to the intramolecular charge transfer D-A type molecules.^{25,26} The fitted ISC rate is an order of magnitude less than the radiative decay rate, consistent with measured PLQY's of 0.7-0.9.¹⁸ This indicates that internal conversion in *v*-DABNA must be very low, as expected for a highly rigid molecule.

As the excimer state was most readily observed in the time-resolved spectra of 2Me-TFH solutions, this glass-forming solvent was also investigated at cryogenic temperatures. At low concentration (0.25 M) and room temperature, **Figure 5.3a**, the initially excited exciton state decays with a lifetime of 4.5 ns. A second lower energy emission band grew in over 50 ns. This band decays within 100 ns to leave a long-lived delayed emission band which persists into the 10s of μs . The DF clearly arises only from the monomolecular (exciton) emission, with no DF arising from the transient red species. Lower temperatures (80 K) completely suppress the *rISC* mechanism and no DF was observed, **Figure 5.3c**. Comparing RT to 80 K, at early times (2 ns) the emission is dominated by the intense exciton band. At 80 K the linewidth of the excimer band increases dramatically, with its on-set increasing to 3.10 eV from 2.77 eV, thus extending to energies higher than the exciton emission, **Figure 5.3b**. Such a broad emission spectrum indicates a large distribution of inhomogeneous excimer states/geometries with emission energy highly dependent on the distance and orientation between the interacting molecules.

In addition to the excimer emission, at low temperatures, a weak but very long-lived emission is observed, with an identical spectrum to the exciton $S_0 \leftarrow S_1$ transition, **Figure 5.3d**. This is indicative of local triplet state phosphorescence that is degenerated with the singlet exciton and so ΔE_{ST} is close to zero. Such degeneracy implies that SOC between these two states is forbidden²⁷ and that some other thermally activated mechanism must give rise to the strong TADF at RT - but which is completely suppressed at 80 K. Again, no DF or phosphorescence arises from the excimer state.

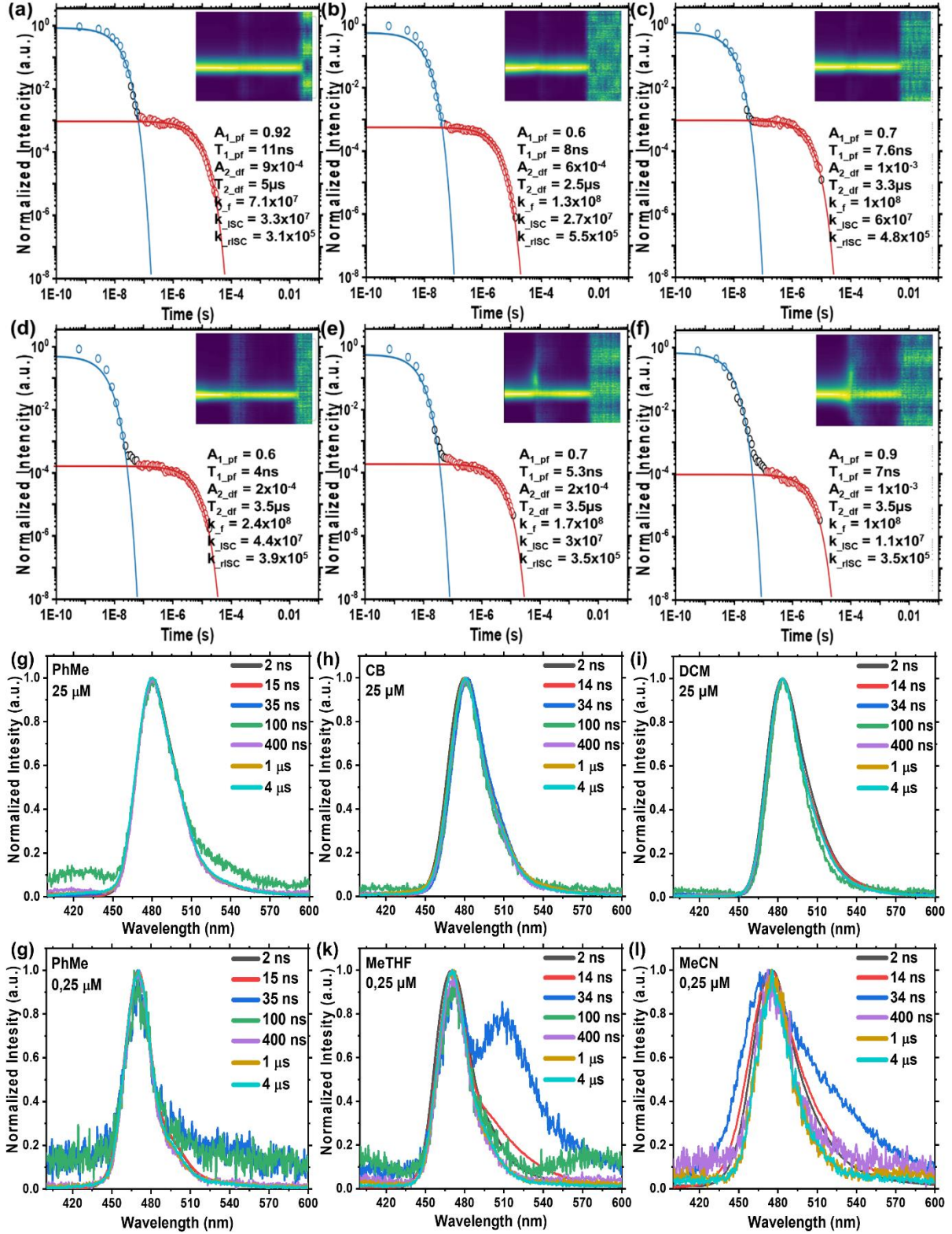


Figure 5.2. Time-Resolved PL decay and spectra of v-DABNA in (a) and (g) PhMe solution 25 M, (b) and (h) CB solution 25 M, (c) and (i) DCM solution 25 M, (d) and (g) PhMe solution 0.25 M, (e) and (k) 2-MeTHF solution 0.25 M and (f) and (l) MeCN solution 0.25 M

concentration, respectively, at 298 K. Excitation at 355 nm. Inset of (a)-(f) contour plots of time-resolved PL and kinetic fitting results.

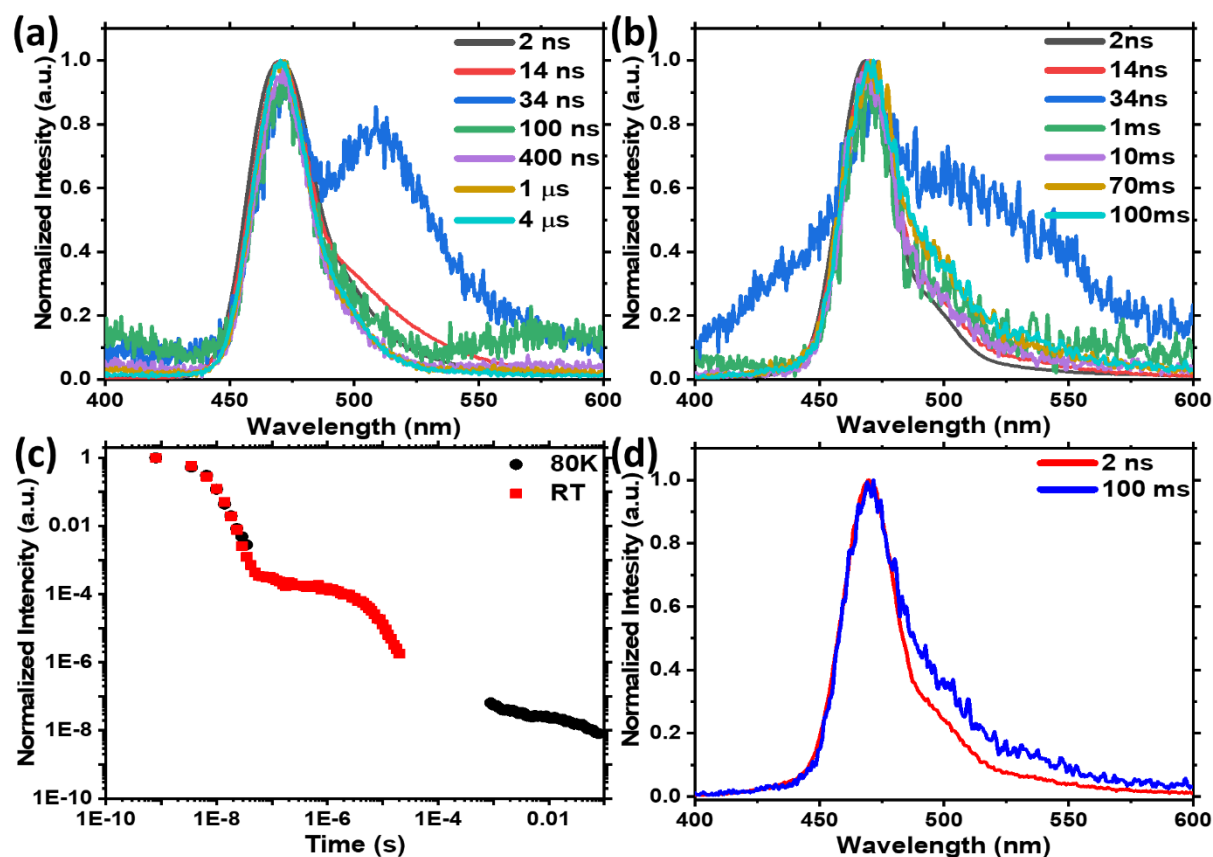


Figure 5.3. Prompt and delayed Time-Resolved PL spectra of v-DABNA in 2Me-THF solvent, 0.25 M concentration, at (a) room temperature (RT) and (b) 80 K. (c) Time-Resolved PL decay at both temperatures and (d) the prompt and phosphorescence emission at 80K. Excitation at 355 nm. Breaks in the decay curve indicate a signal below the noise floor of our detection system, indicating extremely low or no sample signal is present.

Solid-state measurements greatly add to this complex picture. Similar to chapter 4, a set of different host materials were investigated; zeonex, a non-polar soft polymer matrix; UGH, a low dielectric rigid matrix; and DPEPO, a high dielectric and rigid matrix. Neat films of v-DABNA were also investigated, in which excimer formation was anticipated to be maximised. Steady state emission spectra at different v-DABNA loadings are given in **Figure 5.4**.

Zeonex gives a certain degree of freedom to the motion of the molecule, but less than a solution. Thus it acts as an intermediate between solution and solid-state materials used as OLED hosts, facilitating comparison and in-depth investigation of the excimer contribution and concentration dependence in each. A clear onset of excimer emission contribution was

observed, above 0.01 wt% loading in zeonex (**Figure 5.4a**). This indicates that the increasing excimer emission is intermolecular in nature, as no change in ground state absorption was seen. In both UGH and DPEPO, the low energy excimer state emission was seen to increase as concentration increases (**Figure 5.4b, c**). The excimer emission started at very low loading levels, well below those used in device applications, indicating a very strong association constant for the v-DABNA excimer. As expected in neat film the excimer emission band totally dominates (**Figure 5.4d**). The neat film spectra showed some exciton emission (as a knee on the blue edge of the emission) as well as an indication of the highly disordered solid, with a distribution of excimer geometries and energies resulting in the long excimer band tail stretching past 575 nm. In UGH and DPEPO matrix (5 wt% films) the peak of the excimer band corresponds very well with the peak of the neat film emission, supporting our interpretation of shared excimer formation in each.

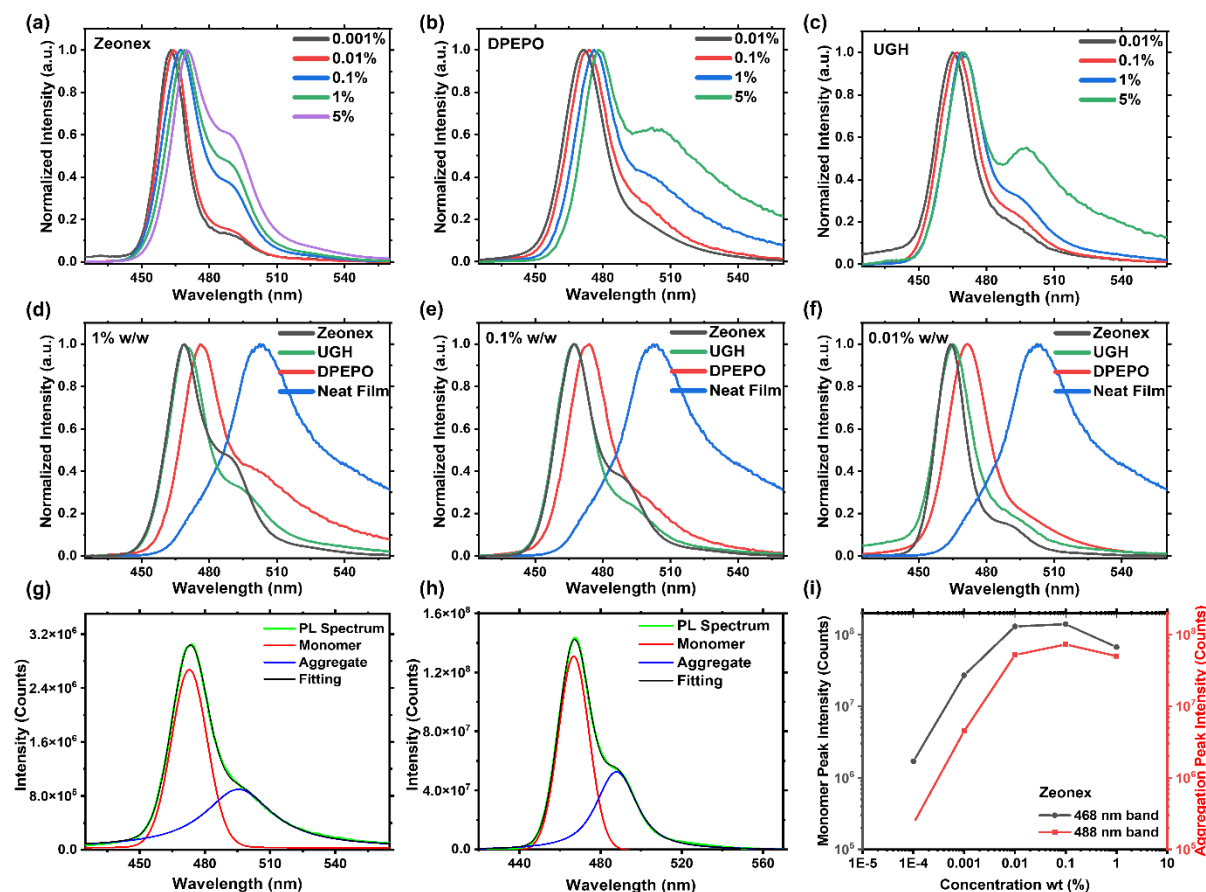


Figure 5.4. Solid state, steady state v-DABNA photophysics. Normalized PL spectra of v-DABNA in (a) zeonex, (b) DPEPO and (c) UGH matrix, at various concentrations, at RT. Comparison of different hosts and neat film at (d) 1, (e) 0.1, and (f) 0.01 wt% of emitter to host ratio. Deconvoluted emission spectrum of v-DABNA in (g) DEPEPO and (h) zeonex 1 wt%,

using Voigt profile for S_1 - S_0 monomer (red) and aggregation related (blue) transition. (i) Peak intensity of S_1 - S_0 monomer (black) and aggregation related (red) at different concentrations in zeonex matrix. Excitation at 370 nm.

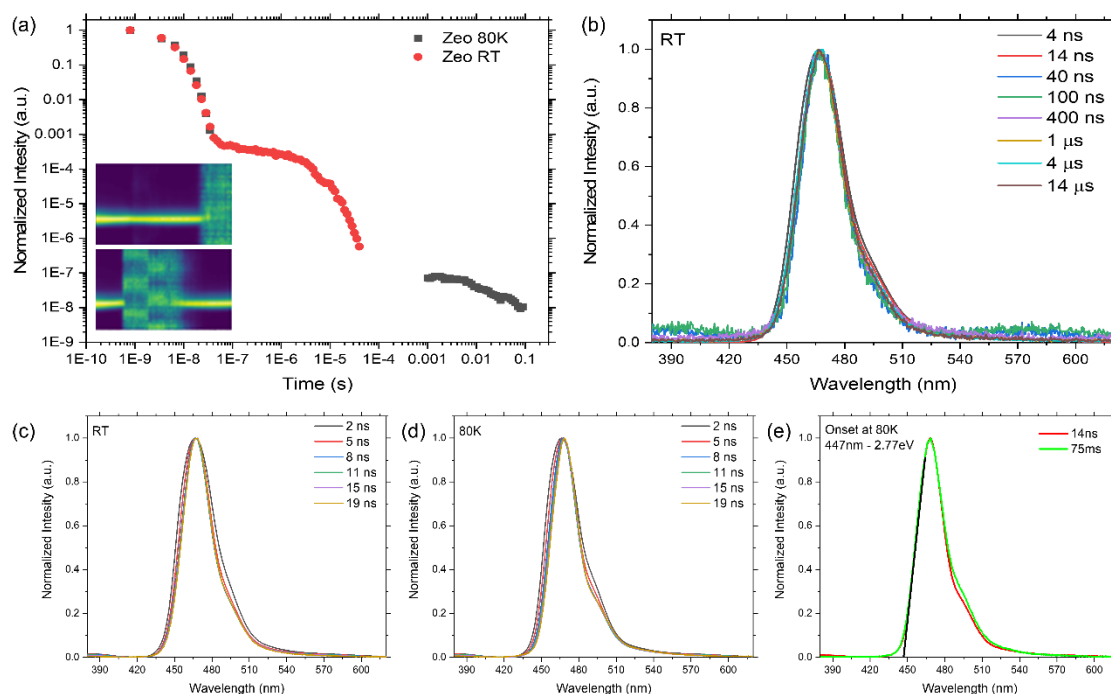


Figure 5.5. (a) Time-Resolved PL decay of 0.01 wt% v-DABNA in zeonex, at RT and 80 K. Inset graph: contour plots of emission spectrum over time at RT (top) and 80 K (bottom). (b) RT time-resolved emission spectra, analytical early time emission spectra at (c) RT, (d) 80 K and (e) fluorescence and phosphorescence spectra at 80 K. Excitation at 355 nm.

The concentration dependence PL measurements of 1 wt% v-DABNA in zeonex and DEPEO were fitted using a Voigt band shapes (**Figure 5.4g, h**). The relative change in intensity of the two transitions in zeonex are plotted in **Figure 5.4i**. The excimer band intensity was increasing faster compared to the exciton band intensity as concentration increased and may indicate exciton migration and/or energy transfer to excimer forming sites in film. This also shows that excimers are stabilised in the solid-state, compared to solution where they can more freely diffuse and dissociate. Further, the exciton and excimer transitions redshifted comparably with increased concentration in zeonex, **Figure 5.4a**. In UGH and DPEPO matrix, the excimer band red shifts further compared to the exciton emission, **Figure 5.4**, indicating that the (energy) distribution of excimer states changes with concentration in rigid environments.

The Time-resolved PL of 0.01 wt% v-DABNA in zeonex, to minimize intermolecular interactions, is shown in **Figure 5.5**. The room temperature decay profile is similar to solution (**Figure 2**) indicating once again that v-DABNA triplet harvesting rate is environment independent. At 80 K, the DF was quenched, and phosphorescence can be observed in the ms regime. At both temperatures, the spectral evolution appeared constant over time. Interestingly, in zeonex matrix at 80 K the ΔE_{ST} appears to be zero (**Figure 5.5e**).

The temporal evolution of the excited states was again followed in the early nanosecond time regime, **Figure 5.6**. At 1 wt% v-DABNA in zeonex, no clear excimer contribution was observed, at RT, but only a very small excimer signature at 80 K (**Figure 5.6d, g**), in contrast with the 0.01 wt% loading where only excitonic emission was observed, **Figure 5.5**. In UGH (1 wt%), initially excitonic emission was dominant with the grow-in of the excimer band occurring over 20 ns, which appeared even stronger at low temperatures (**Figure 5.6e, h**).

In DPEPO the temporal evolution of the excimer emission was much faster. At RT the exciton band was quenched over the first 20 ns and a well-defined excimer band is observed (**Figure 5.6f**). Similar to UGH, by 20 ns the total emission intensity is already very weak. However, at 80 K in DPEPO the behaviour is distinct from UGH or 2Me-THF. A well resolved, broad excimer band was dominant with a near complete quenching of the exciton emission (**Figure 5.6i**). Given that the 1 wt% DPEPO film excimer emission onset and peak position are very similar to those observed in 10 wt% UGH film (**Figure 5.8a**), it shows that the excimer state is not strongly affected by the host's ground state dipole moment, but instead is more dependent on (different) host packing forces.²⁹

From the time-resolved decay fitting, **Figure 5.6a-c.**, the characteristic prompt emission from the exciton was observed and decayed within 5 ns in all hosts. The very broad excimer band was dominant in the intermediate unfitted region and has a lifetime of 50 and 42 ns in UGH and DPEPO respectively. This long prompt lifetime arises from the rigidity of v-DABNA molecule and extremely weak vibrational coupling, meaning non-radiative decay does not interfere despite slow rISC. DF was observed only from the excitonic band with a lifetime of 4.26 and 3.8 μ s in UGH and DPEPO respectively, **Figure 5.6b, c**. In all hosts the DF was highly suppressed at 80 K in line with solution measurements. The fitted lifetimes in the three different hosts provided the kinetic traces of v-DABNA. Similar to solution measurements the k_f , k_{ISC} , and k_{rISC} were again environment independent with values around 1×10^8 , 7×10^7 , and 6×10^5 s⁻¹, respectively.

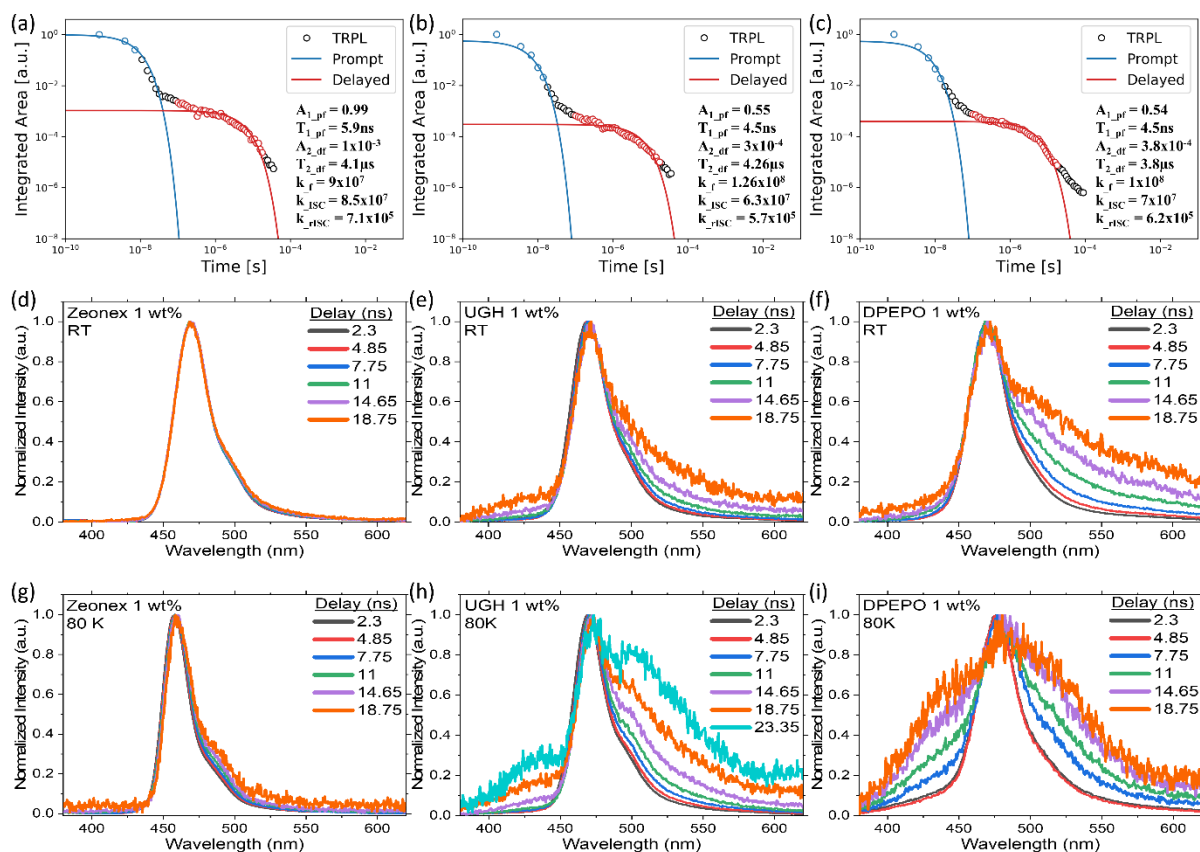


Figure 5.6. Time-Resolved PL decays and kinetic modelling results of 1 wt% v-DABNA in (a) zeonex, (b) DPEPO, and (c) UGH, at 298K. Time-Resolved prompt emission of 1wt% v-DABNA in zeonex at (a) RT and (d) 80 K, UGH at (b) RT and (e) 80 K, and DPEPO at (c) RT and (f) 80 K. Excitation at 355 nm.

Focusing on the low TDM UGH host, the 1 wt% v-DABNA film temperature dependence behaviour is shown in **Figure 5.7**. With decreasing temperature, an evolution of the emission decay curves was observed with DF being quenched while its lifetime was increasing (**Figure 5.7a**). At 80 K, the DF was very weak, and the decay was no longer exponential (**Figure 5.7b**). Long exposure measurements reveal that the PL spectrum from 10 μs to 75 ms did not change and was still perfectly representative of the exciton emission seen in the ns, **Figure 5.7c**. This could indicate that once the monomolecular triplet spin upconversion mechanism is frozen out, weak TTA can still occur, consistent with a triplet population no longer being depleted by the upconversion process. Laser excitation intensity measurements showed that the DF of v-DABNA in UGH was linear with excitation power, excluding bi-excitonic processes at room temperature, **Figure 5.7e, f**. This rules out the TTA mechanism for DF generation at RT in v-

DABNA.²⁸ The estimated ΔE_{ST} in UGH was measured to be different compared to the one in zeonex host, with a value of 20 meV (**Figure 5.7d**).

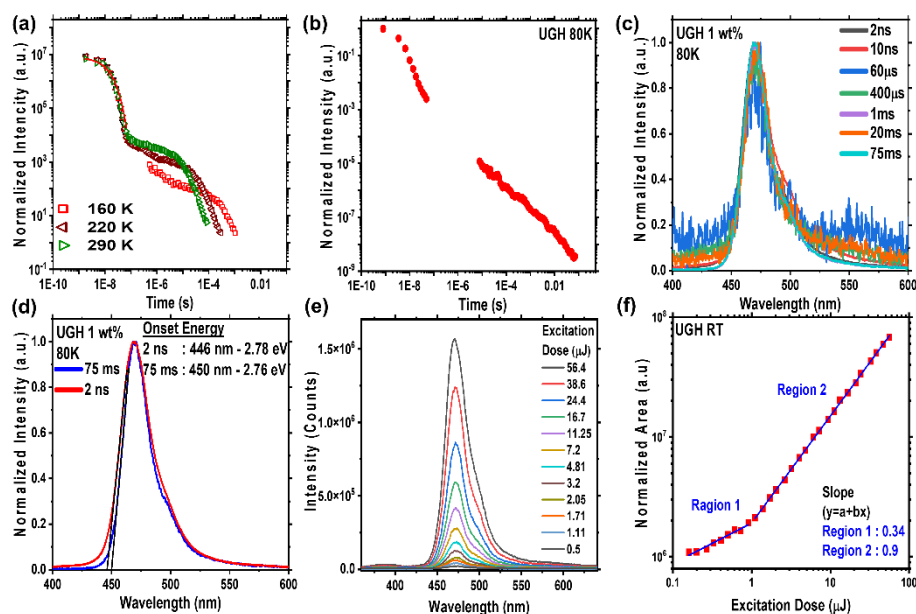


Figure 5.7. 1 wt% v-DABNA in UGH time-resolved; (a) temperature dependent DF decay kinetics, (b) decay and (c) spectra, at 80K, and (d) singlet-triplet energy gap; (f) Fluence dependence (e) spectra of the delayed emission, at RT. Excitation at 405 nm.

The time-resolved emission of v-DABNA neat film unveil the excimer effect observed in the small molecule hosts. Similar to the 80 K time-resolved PL spectra of the 10 wt% UGH and DPEPO films (**Figure 5.81, b**), in neat film 80 K measurement a new species was dominant and any sharp 460 nm exciton emission was weak or masked (**Figure 5.8d**). Instead, a fast-decaying emission around 440 nm with a gaussian line shape and lifetime 5.5 ± 1.5 ns was observed, **Figure 5.8f**. A second band at lower energy (PL_{max} at 510 nm) was dominating with a distorted Gaussian like band shape, and lifetime of 4.2 ± 2.6 ns (**Figure 5.8b**). These spectra, together with those of 10 wt% v-DABNA in UGH and DPEPO, show that these are two distinct spectral bands corresponding to different emitting species, which are highly dependent on temperature and concentration. Total emission in the neat films is however very weak, likely suffering strong aggregation quenching. At RT the high energy band was not observed in v-DABNA neat film, although the exciton band at 460 nm was observed and being quenched within 5 ns (**Figure 5.8c**). This is very similar to the feature observed in 10 wt% v-DABNA in DEPEPO and dominates the neat film steady state emission, **Figure 5.4**. At room temperatures, the red species redshifted in time, indicating possible exciton migration to lower energy sites,

leading to rapid excited state quenching within the film. At 80 K this was not observed. Because of this, there was no delayed emission in neat film, concluding that exciton migration significantly impacts the properties of the neat film.

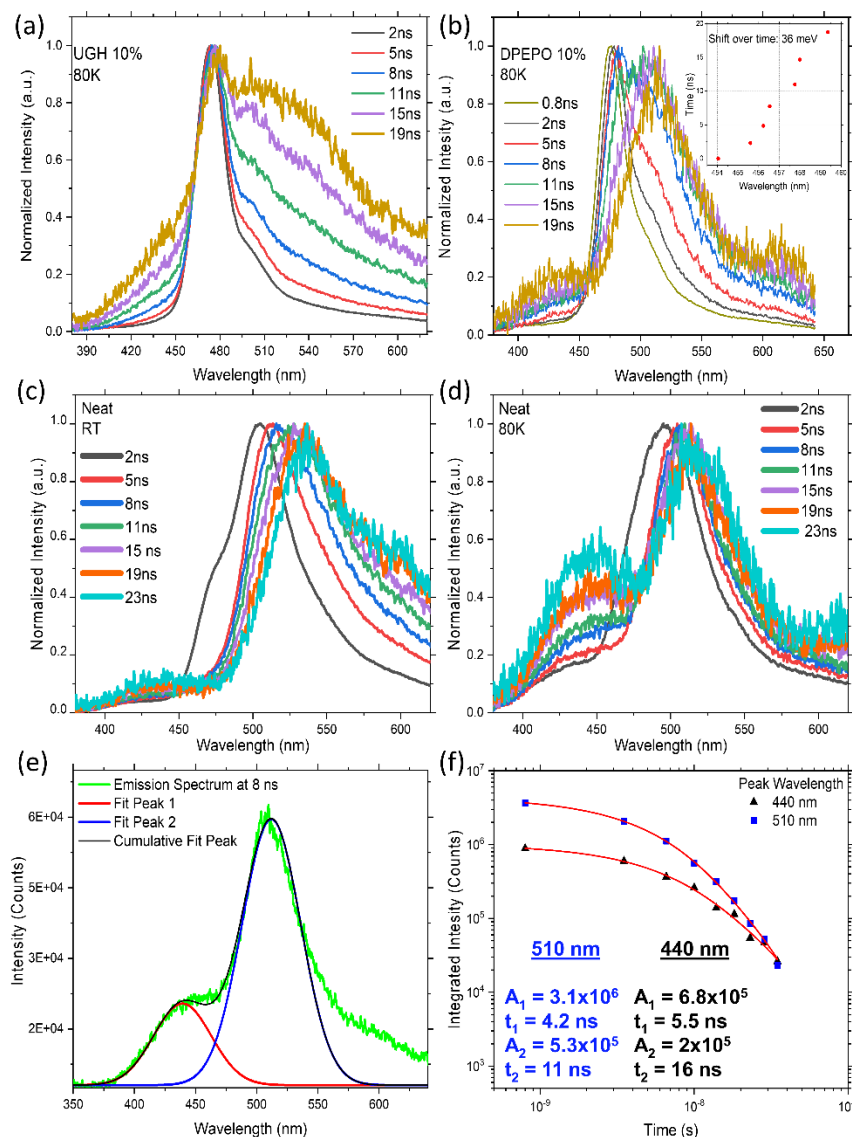


Figure 5.8. Time-resolved PL spectra of; 10 wt% v-DABNA in (a) UGH and (b) DPEPO, at 80 K; v-DABNA neat film at (c) room temperature and (d) 80 K; (e) Example of a deconvoluted time-resolved PL spectrum of v-DABNA neat film, at 80 K. All time-resolved spectra were deconvoluted and fits made for the respective spectral features (f) to identify the lifetime of each species. A consistent second component with the same lifetime was identified in both decays assigned to an underlying contribution from the exciton decay at 475 nm.

Further, considering the neat film high energy band absence at room temperature, compared to 80 K, clearly suggests that the two bands are distinct excimer states, pointing to two different

orientations of *v*-DABNA molecules giving two different excimer configurations. The high energy state must be thermally unstable, i.e. weakly bound, so it is not observed at RT nor in zeonex at 80 K where the *v*-DABNA molecules have more free volume to reorient. This spectral feature was dominant in neat film and observed at high concentration guest-host films and frozen 2Me-THF glasses, consistent with excimer states. However, the lower energy emission band was dominating in many environments at RT. In 2Me-THF it grew in within 30 ns and decayed completely by 100 ns, as compared to films where it was observed from the first time frames. Further, in frozen 2-MeTHF and UGH at 80 K (**Figure 5.3b** and **Figure 5.6 h, i**), everything became extremely broad and ill defined, indicative of large scale disorder. All these observations taken together indicate excimer states that are weakly coupled and highly disordered in films, especially at low temperatures, with additional excimer geometries becoming prevalent at higher concentrations.

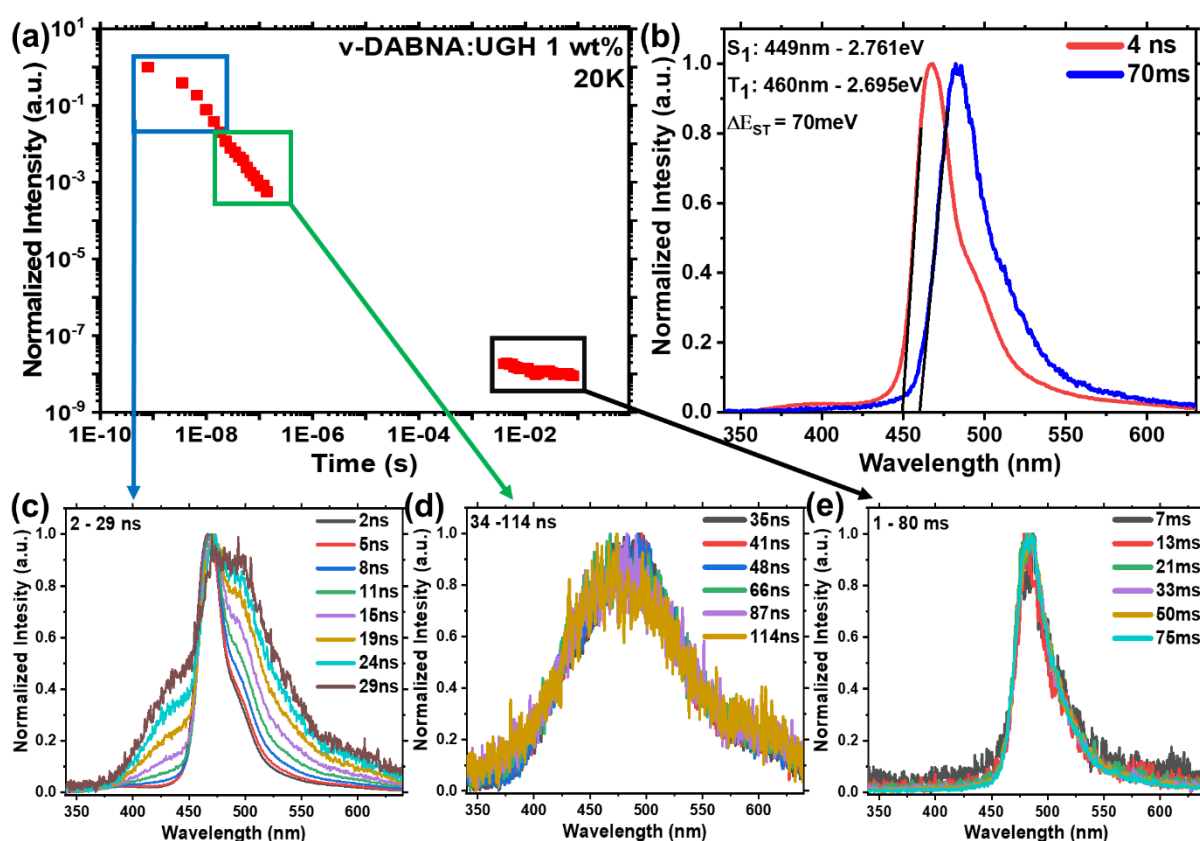


Figure 5.9. Time-Resolved (a) PL decay curve, (b) Singlet triplet energy gap and PL spectra at a time range of (c) 0-30 ns, (d) 35-120 ns and (e) phosphorescence at 10-75 ms, of *v*-DABNA 1 wt% in UGH matrix at 20 K. Excitation at 355 nm.

From the 80 K ν -DABNA in 2Me-THF and zeonex host the ΔE_{ST} was estimated to be very small (< 5 meV), while in UGH was measured at 20 meV. Further, ν -DABNA ΔE_{ST} , using thermal estimations (Arrhenius plot) was previously reported to be 70 meV.¹⁸ Unfortunately, no low temperature phosphorescence spectra have ever verified that. Considering this, and the effect of lower temperature on suppressing vibrational motion and minimizing rISC, 20 K measurements were carried out (**Figure 5.9**). Even at 20 K the phosphorescence spectrum (75 ms time delay) is nearly identical to the singlet exciton emission band shape showing that it has an identical orbital character to the singlet, **Figure 5.9b**. This measurement indicates a triplet energy of 2.58 ± 0.05 eV (peak), 2.69 ± 0.05 eV (on-set), which was stabilized after 3ms and remained constant until some hundred ms, **Figure 5.7e**. This yields a ΔE_{ST} of 70 meV (from the band on-sets) which is in excellent agreement with the singlet triplet gap estimated from Arrhenius analysis previously.¹⁸ Thus, clearly this is the energy of the lowest triplet state of ν -DABNA but the triplet energy appears temperature dependent, so at 80 K was increased by some 50 meV. This could be through a small decrease in the conjugation of the lowest triplet state at high temperatures. TD DFT calculations previously showed small torsional changes of the peripheral phenyl rings in the excited state, especially those in the tertiary amine groups, could account for this.¹⁸

One very intriguing observation for ν -DABNA in UGH (1 wt%) is that the FWHM of the exciton emission band (5 ns) increases with increasing temperature, from 109 meV at 20 K, to 137 meV at 80 K and at 157 meV RT. Further, the shape of the early time RT exciton band is poorly defined, unlike at lower temperatures, and a 65 meV red shift of the energy of the exciton band was seen between RT and 20K, which arises through a loss of the blue edge emission at low temperatures. Very similar behaviour was also seen for DPEPO 1 wt% films. This indicates a large population of vibrational excited states at RT contributing to radiative decay, not present at lower temperatures. Given the shown coupling of the 35 meV (285 cm^{-1} , **Figure 5.1e**) vibrational mode to this exciton transition, at RT the populations of the first two excited vibronic sub levels of S_1 will have very high Boltzmann factors of 0.5 and 0.25, respectively. This then gives rise to hot transitions from these populated states ($S_{1,1}$ and $S_{1,2}$) to $S_{0,0}$ pushing the band on-set further into the blue compared to at cryogenic temperatures.

From the ν -DABNA time-resolved spectra measured at 80 K at 0.01 wt% in zeonex (**Figure 5.5d**) and 10 wt% in DPEPO (**Figure 5.8b**), a red shift of the (whole) prompt exciton emission band is observed over the first 20 ns, whereas at RT there is a small shift. The maximum shift

is ca. 36 meV (290 cm^{-1}) over 8 ns. This corresponds very well with the energy difference calculated between the $S_1@S_0$ and $S_1@S_1$ geometries and from the decomposition of the absorbance spectrum,¹⁸ which could indicate a small planarization of the v-DABNA molecule over this time, at low temperatures. However, no shift was observed at RT, 80 K or 20 K in UGH host, **Figure 5.7** and **Figure 5.9**. This may indicate that UGH packs more tightly than both zeonex and DPEPO constraining v-DABNA molecules in the ground state configuration, while these vibrations are continually requilibrated through the decay leading to no apparent wavelength shift.²⁹ Thus effects of both molecular vibrational motions of the core and peripheral units of the v-DABNA on the FWHM and emission band position can be observed, which give rise to appreciable increases to the FWHM, at RT.

5.4.2 Devices

To evaluate the effect of the excimer state on the electroluminescence (EL) performance, devices using v-DABNA as a terminal emitter in hyperfluorescence (HF) OLEDs were fabricated and analysed. This approach has recently emerged as a strategy to achieve excellent device colour from the v-DABNA, with improved rISC and roll-off characteristics provided by the TADF co-host.^{15,30–33}

The devices had the following structure:

Indium tin oxide (ITO); N,N-bis(naphthalene-1-yl)-N,-bis(phenyl)benzidine (NPB, 40nm); 4,4'-(Diphenylsilanediyl)bis(N,N-diphenylaniline) (TSBPA, 10nm); 65-x wt% DPEPO, 35 wt% TADF emitter, and x wt% v-DABNA emitter (30nm); 2,2,2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, 40nm); lithium fluoride (LiF, 0.8 nm); aluminium (Al, 100nm) (**Figure 5.10a**).

Previously the optimum v-DABNA emitter concentration was estimated to be 1 wt%.¹⁸ To explore the excimer effect in this work 1 wt% to 0.5 wt% doping was compared, approaching the lower limit of doping achievable by triple co-evaporation. The OLEDs performance is shown in **Figure 5.10**. A cyan D-A-D TADF emitter (DTMA-TTXO₂) employed as a co-host is designed based on a simple modification of a previously reported series of TADF molecules, **Figure 5.10e**.³⁴ By introducing v-DABNA into the device, the external quantum efficiency (EQE) increased by 13.3% ($\text{EQE}_{\text{max}} = 25.5\%$) for 1 wt% and 22.2% ($\text{EQE}_{\text{max}} = 27.5\%$) for 0.5 wt% concentration (at approximately 4.5 V, 1 mAcm^{-2} and 850 cdm^{-2} in both cases), compared to the control TADF only device ($\text{EQE}_{\text{max}} = 22.5\%$), **Figure 5.10c**. Further, the EL spectrum

was significantly improved in the v-DABNA devices, **Figure 5.10d**, due to its narrow emission compared to the broad CT emission of the D-A-D sensitizer, **Figure 5.10e**.

As anticipated, the use of v-DABNA with previously reported maximum EQE of 34.4% using DOBNA-Oar host,¹⁸ led to a major increase in device efficiency. However, given that some of this performance has since been demonstrated to arise from spontaneous molecular alignment of the v-DABNA and non-lambertian angular emission profile leading to enhanced device outcoupling,³⁰ the performance of the HF devices is still not as high as expected. In the best-case scenario, an estimated 1.3-fold outcoupling enhancement due to aligned emission combined with the very high intrinsic EQE and rISC of the TADF co-host in the control device, would lead to EQEs >30% in our hyperfluorescent devices. This comparison leads to the conclusion that a variety of mechanisms must suppress the performance below what may otherwise be achievable. According to the photophysical studies, the excimer state quenches emission even at concentrations close to 0.1 wt%. Thus, v-DABNA excimer quenching is identified as at least one of the causes of below-expectation EQE in these devices. Excimer quenching also explains the reduced performance as the v-DABNA doping concentration increases from 0.5% to 1%.

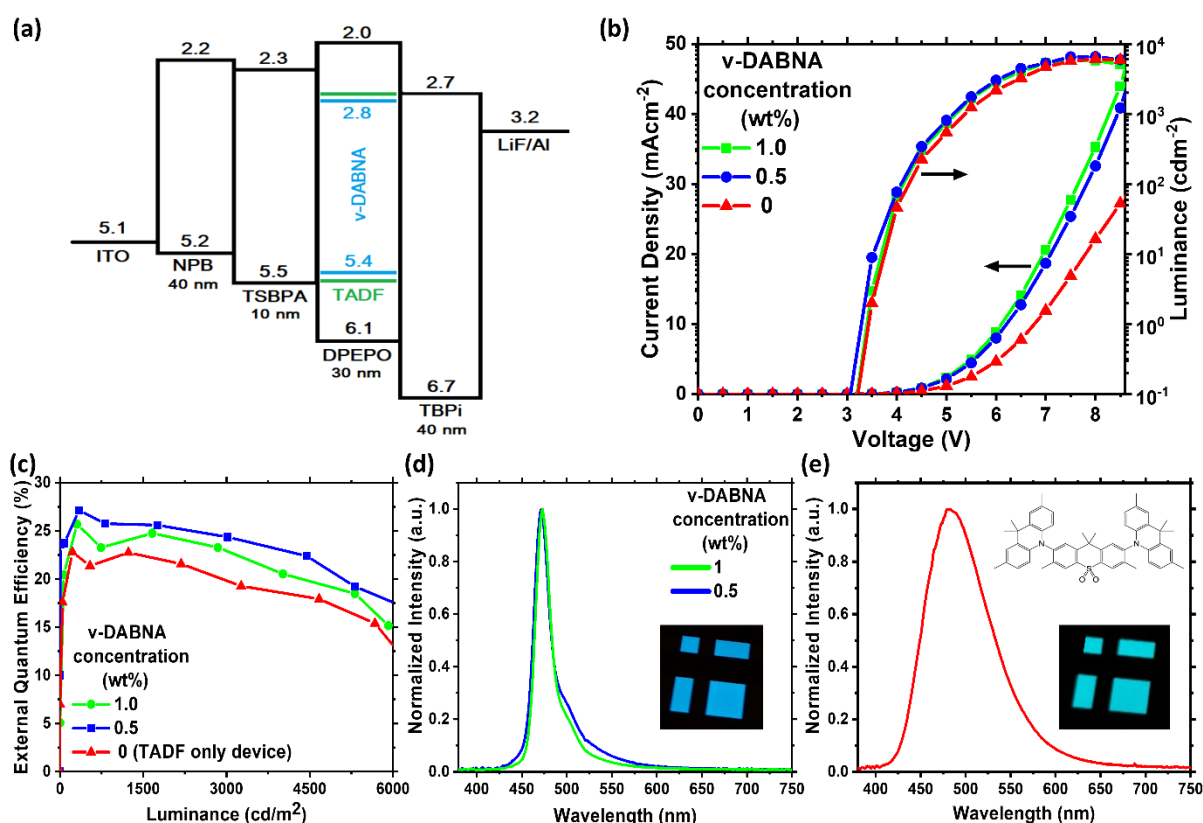


Figure 5.10. TADF only (red) and HF OLED performance with 0.5 wt% (blue) and 1 wt% (green) v-DABNA concentration. (a) Device structure with ionization potentials and electron affinities (in eV) for each layer. (b) Current density and luminance versus driving voltage. (c) EQE versus luminance. Normalized EL spectra of (d) HF and (e) TADF OLEDs. Inset: Operating devices and TADF sensitizer chemical structure.

The operation of hyperfluorescence OLEDs relies on FRET from the S_1 energy the TADF donor to the slightly lower but much narrower FWHM S_1 state of the terminal emitter. To investigate this further FRET analysis was done. The spectral overlap using the area normalized PL spectrum of the donor (TADF emitter) and the absorption (extinction coefficient) spectrum of the acceptor (v-DABNA) are shown in **Figure 5.11**. The calculated J value was $1.944 \times 10^{15} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$, resulting in an R_0 of 4.81 nm (for more information see chapter 3). This is a relatively large Förster radius, but in keeping with the nearly complete overlap of emission and absorption spectra in this case.

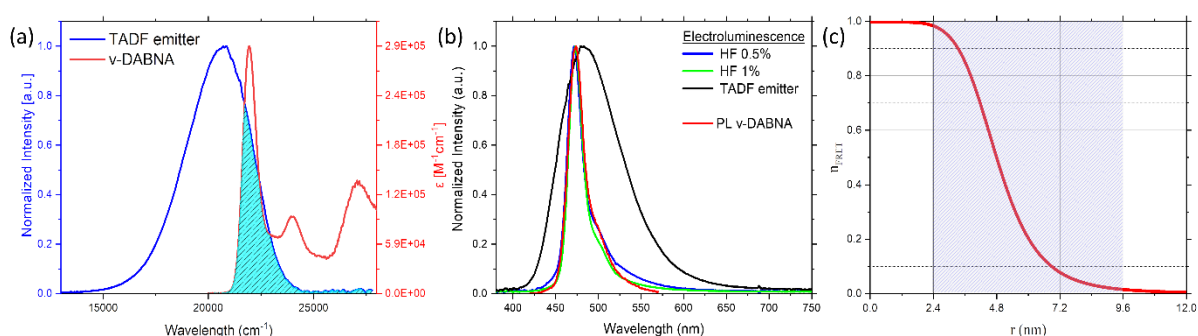


Figure 5.11. Förster radius analysis. (a) Spectral overlap between donor emission spectra and acceptor extinction coefficient. (b) Comparison of TADF only and HF OLEDs EL spectra, PL spectra of v-DABNA for comparison. (c) FRET efficiency (n_{FRET}) as a function of D-A distance (r).⁴⁰

The EL spectra of control and HF devices, with 1 and 0.5 wt% doping, along with the v-DABNA PL spectrum are shown in **Figure 5.11b**. Comparing the photo-excited emission of v-DABNA (red) with the two different concentration HF devices, one can observe the ideal overlap at 1 wt%, translating to near-complete Förster energy transfer and a D-A average distance (r) smaller than $0.5 R_0$ ($r < 2.4 \text{ nm}$), **Figure 11c**. On the other hand, 0.5 wt% HF device shows an increased emission width, especially at 0.1 maximum height, which contributes to the overall emission both at higher and lower energies. This emission comes from the TADF emitter itself, indicating incomplete FRET. As a result, FRET efficiency is

lower, although evidently still above 50% due to the small contribution of the TADF emitter to the overall device emission. In this case, according to **Figure 11c**, the estimated D-A distance is in the range of $2.4 < r < 4.8$ nm, which is larger due to the smaller concentration of *v*-DABNA.

5.4.3 Discussion

From these measurements, it is clear that there are both intrinsic and extrinsic factors which control both the emission linewidth and rISC mechanism in *v*-DABNA. Across the range of environments a very similar feature with an ill-defined Gaussian-like band shape was observed, peaking around 495 nm to 510 nm, ascribed to an excimer band. At low temperatures this excimer band broadens significantly, indicating molecular disorder consistent with a weakly coupled intermolecular excimer state. The steric hindrance of the peripheral phenyl rings on *v*-DABNA make close intermolecular interaction difficult, adding to the disorder and weak coupling such that the energy shift between the exciton band and the excimer is small. Nonetheless, the x-ray crystal structure of *v*-DABNA (obtained from Prof. Takuji Hatakeyama's group), **Figure 5.12**, demonstrates the close approach of molecules below the Van der Waals radii, indicating that weak excimer interactions are indeed possible. In zeonex and solvents such as toluene, much less of the excimer state was observed, in part because such weakly interacting states also dissociate in fluid environments. However, the extremely planar, π rich *v*-DABNA molecules can readily form intermolecular interactions even at exceptionally low concentrations.

The excitonic state displays minimal solvatochromism and little change in rISC rate with solvent polarity, clearly indicating that there is little or no change in the ground and excited state dipole moment upon excitation and that the excited state has a small dipole moment.³⁵ This behaviour contrasts strongly to D-A(-D) TADF molecules which have large changes in between ground and excited state dipole moments.³⁶ From previously reported electron density distributions in the HOMO and LUMO orbitals of *v*-DABNA¹⁸ there is only a small shift in electron density on excitation, similar to BODIPY fluorophores. As in BODIPY molecules, this gives a net change in dipole moment along the short axis of the molecule, whereas the transition dipole moment (TDM) would be expected to lie along the long axis of the molecule (having the largest π electron conjugation). A TDM orthogonal to the (solvent induced) change in dipole moment therefore results in negligible solvatochromism.^{37,38} The TDM aligned with

the long axis of the ν -DABNA molecule would also account for the highly anisotropic emission in films and enhanced out-coupling in OLED devices observed.³⁰

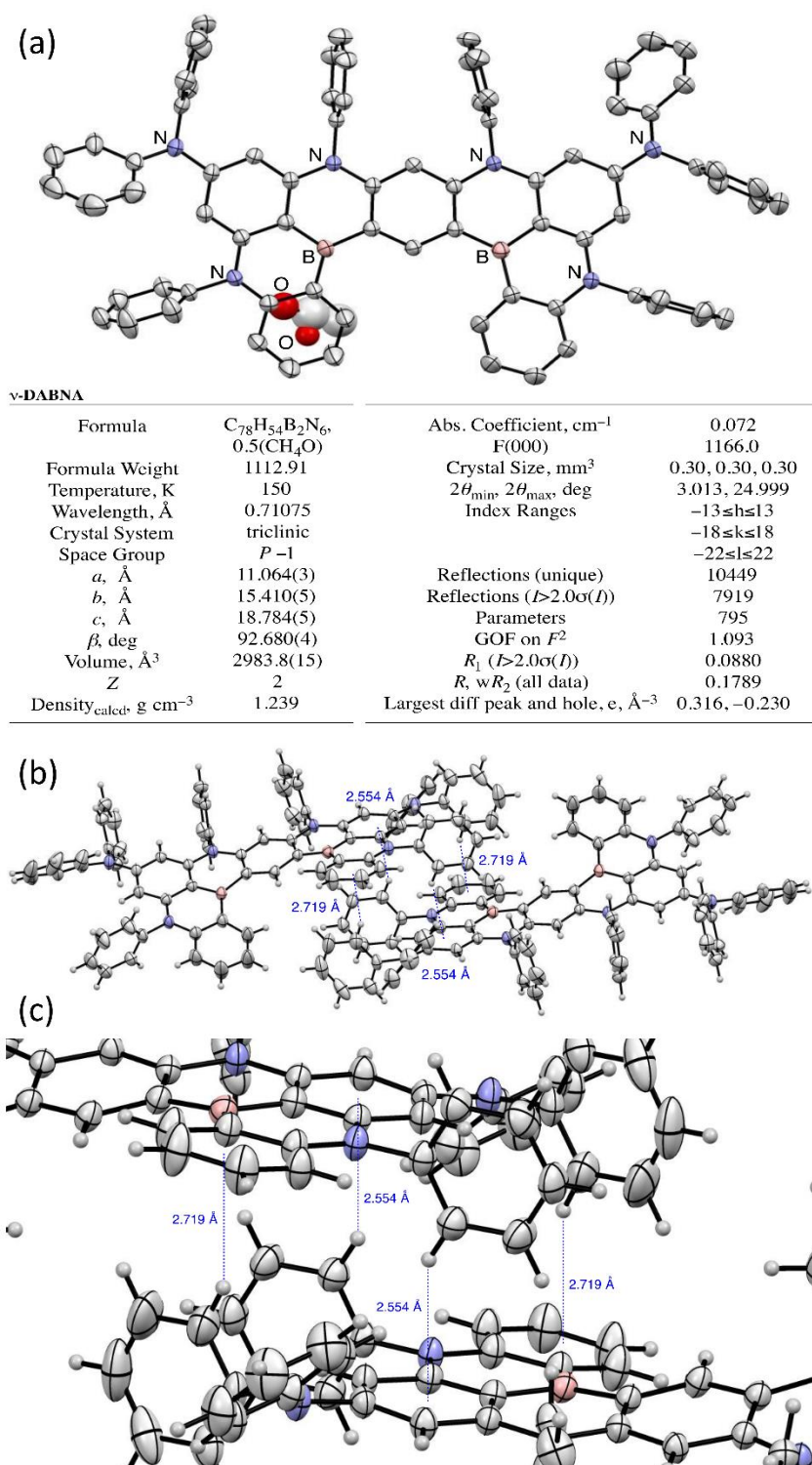


Figure 5.12. (a) X-ray structure of ν -DABNA molecule (including one MeOH solvent molecule) obtained from Prof. Takuji Hatakeyama's group. (b) Molecular crystal packing

indicating short range intermolecular distances (below Van der Waals radii) in cyan. MeOH solvent molecule is omitted for clarity. (c) Expanded view of (b).

From the fitted decay kinetics, relatively high ISC rates indicate that unenhanced SOC cannot be responsible for coupling the near-degenerate S_1 and T_1 states (with near-identical spectra). Instead, this points to an efficient upper state crossing between S_1 and energetically adjacent T_2 or higher triplet states, within 70-100 meV. As shown, at room temperature there is a large occupancy of upper vibrational levels of S_0 . Similar hot exciton populations in S_1 could facilitate the ISC to an upper triplet level e.g. T_2 or T_3 . In this case, cooling the material will greatly reduce ISC as well as any concomitant rISC, as both are effectively thermally activated. This could be why such a strong overall temperature dependence in the DF is observed - all of which strongly support both ISC and rISC transition occurring via upper triplet states. This also explains why in films where the apparent ΔE_{ST} is zero the same moderate rISC rate is measured, with 0 to 70 meV S_1 - T_1 energy gaps and also the same as found in solution.

As rISC in ν -DABNA is strongly thermally activated yet insensitive to the environment, one potential mechanism is for T_1 states to undergo thermally activated reverse internal conversion (rIC) to an upper triplet state (T_2 or T_3 for example)²⁸ which also allows rISC back to S_1 (or S_N as they are close lying, **Figure 5.1a**). This mechanism was recently reported in another highly rigid TADF molecule, triquinolonobenzene, where intramolecular proton transfer provides a small ΔE_{ST} but rISC follows after a thermally activated rIC step.³⁹ Supporting this mechanism, calculations by Northey and Penfold⁵ show that in a related DABNA material non-adiabatic coupling of S_1 to higher lying singlet states mediates enhanced SOC via vibronic coupling, mainly between S_1 and T_2 . As there is only one large amplitude vibration (120 meV) coupling to the electronic excited state in ν -DABNA (wagging motion of the peripheral N-biphenyl groups), both models would yield highly temperature dependent rISC as shown here. This molecular motion is potentially mediating the spin conversion. Therefore, triplet upconversion in ν -DABNA (and other similar multi-resonant systems) is possible to occur through a rIC upper-triplet state crossing mechanism that gives rise to ΔE_{ST} (optically determined) insensitive to environment, with an invariant rISC rate that remains strongly thermally activated.

5.5 Conclusions

The photophysics of ν -DABNA is surprisingly complex for a rigid molecule with high photoluminescence quantum yield and few coupling vibronic modes. In this chapter, the two

main vibrations are shown to couple to the electronic states; the low amplitude modes of the peripheral phenyl units and more importantly a large amplitude mode of 120 meV associated with the N-biphenyl end groups. This mode likely drives vibronic coupling in the molecule to mediate reverse internal conversion from the lowest triplet states, and thus enable rISC. Measurements in both solution and solid state show very strong temperature dependence to the observed DF. Phosphorescence measurements reveal that even at 80 K the phosphorescence emission is still red shifting after 40 ms, revealing a temperature sensitive ΔE_{ST} that approaches the previously reported Arrhenius-derived value of 70 meV only at 20 K. From all of these observations the rISC mechanism in v-DABNA, is suggested to mediate by strongly thermally activated rIC of T_1 states to T_2 (or higher) followed by rapid rISC from T_2 (or higher) to S_1 , in line with the theoretical prediction of Northey and Penfold.⁵ Both ISC transitions between S_1 and these upper triplet states are likely further enhanced at RT through large populations of the first and second excited vibronic sub-levels of S_1 , which enable more efficient crossing to these higher level triplet states.

Importantly for OLED applications, a strong prevalence for v-DABNA to form excimers is shown. Although weakly coupled with large disorder, these form even at 0.1 wt% v-DABNA loading in a host - well below the concentrations used in devices. Hyperfluorescence OLEDs consequently show increased EQE of 13.3% ($EQE_{max} = 25.5\%$) and 22.2% ($EQE_{max} = 27.5\%$) for 1 wt% and 0.5 wt% doping respectively, compared to the single TADF emitter device; the performance diminishing as the v-DABNA concentration is increased. These excimer states have very low emission and are unveiled as a major route for exciton quenching in all v-DABNA devices, also contributing to lower-than-expected performance in the hyperfluorescent devices explored here. Förster analysis shows that the concentration needs to be close to 1 wt% v-DABNA to achieve full energy transfer from the TADF co-host, which will require future molecular design to prevent excimer formation at such concentrations. While small modifications to the v-DABNA peripheral groups could prevent excimer formation and increase PLQY at increased doping levels, these must be carefully designed to avoid introducing new vibrational modes which increase the FWHM of the exciton emission band and may interfere with vibronic coupling mediating rIC and so effectively killing rISC.

5.6 References

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6 MR-TADF Tuning for Hyperfluorescence Applications

Developing high-efficiency purely organic blue LEDs is a major current research challenge. Hyperfluorescent device approaches achieve in large measure the desired high performance by combining the advantages of a high-efficiency TADF assistant dopant with a narrowband deep-blue MR-TADF terminal emitter. However, this approach theoretically requires suitable spectral overlap to support FRET between the two. In this chapter, the colour tuning of a recently reported MR-TADF B,N-heptacene core through control of the boron substituents is demonstrated. While there is little impact on the intrinsic TADF properties - as both singlet and triplet energies decrease in tandem - this approach improves the emission colour coordinate as well as the spectral overlap for blue HF OLEDs. Crucially, the red-shifted and more intense absorbance of α -3BNMes allowed the pairing of this new MR-TADF emitter with a high-performance TADF assistant dopant, achieving an EQE_{max} of 15% at colour coordinates of (0.15, 0.10). The efficiency OLED values recorded here, at a practical luminance of 100 cd m⁻² are among the highest reported for HF TADF OLEDs with CIE_y ≤ 0.1.

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6.1 Introduction

OLED display technology is advancing rapidly, and high-resolution displays must adhere to strict colour emission standards (BT.2020-2),¹ which are defined according to the Commission International de l'Éclairage (CIE) 1931 coordinates: (0.13, 0.05) for blue, (0.17, 0.80) for green, and (0.71, 0.29) for red.² Currently, achieving these colour standards involves using absorptive filters or microcavities to produce saturated blue, green, and red emissions.^{3,4} However, this method inherently reduces the devices' efficiency by filtering out unwanted emission wavelengths. A promising alternative is to develop materials with inherently narrowband emissions to ensure colour purity without sacrificing efficiency.

Commercial OLED material types for display applications, reported in chapter 1 and explained in chapter 2, either lack of efficiency or narrowband emission, especially in the blue. MR-TADF compounds^{5,6} on the other hand, because of their rigid structure show narrowband emission, typically with full width of half maxima (FWHM) of around 20-30 nm. Thus, MR-TADF emitters show the potential to generate the required deep blue emission demanded by industry and support the development of stable, efficient, pure blue narrowband emitting organic materials that are expected to revolutionize OLED displays.⁷ Despite their many advantages, the k_{ISC} rates of MR-TADF materials typically lag ~ 100 times slower than those of leading D-A or D-A-D TADF materials.^{6,8-10} This limitation frequently leads to inefficient triplet harvesting and low performance of the OLEDs at practical luminance. To circumvent this limitation, MR-TADFs have found a parallel application as terminal emitters in HF OLEDs.¹¹ Indeed, ground-breaking device performances have been achieved by efficient energy transfer from a high k_{ISC} D-A assistant dopant to a narrowband MR-TADF terminal emitter via FRET.¹²⁻¹⁶ FRET mechanism depends on FRET radius, which is proportional to the overlap between the emission spectrum of the TADF sensitiser and the absorption spectrum of the MR-TADF terminal emitter. This requires development of deep-blue D-A TADF assistant dopants, but such emitters (and suitable hosts) remain persistently elusive. Thus, synthetic control over both the emission and absorption spectra^{8,17-19} of MR-TADF materials is crucial to enable and optimise their use in HF OLEDs.

A linear B,N-doped ladder type heptacene that emits at 390 nm (near UV) with a FWHM of 31 nm (240 meV) in THF solution was previously reported.²⁰ The material displayed weak TADF due in part to the large ΔE_{ST} of 0.31 eV, along with significant TTA contribution

reflected in the extended ms-timescale of the emission decay. Due to the near UV emission and subsequent paucity of suitable OLED hosts, the investigated device performance was poor and there were no D-A TADF materials identified as compatible assistant dopants for HF OLEDs.²¹ In this chapter the replacement of the hydroxyl groups for mesityl substituents in α -3BNMes is presented (**Figure 6.1**), which leads to a desired red-shifting of the emission towards an ideal-blue emission colour coordinate, as well as a red-shifting of the absorption that supports HF compatibility with available D-A TADF assistant dopants. Together, these changes in optical properties compared to α -3BNOH allow α -3BNMes to be used in deep-blue HF OLEDs with EQE_{max} of 15% and colour coordinates of (0.15, 0.10). These results represent highly competitive device performance metrics at this colour coordinate that are enabled by the finely-tuned emission and absorption spectra of α -3BNMes (**Table 1**).

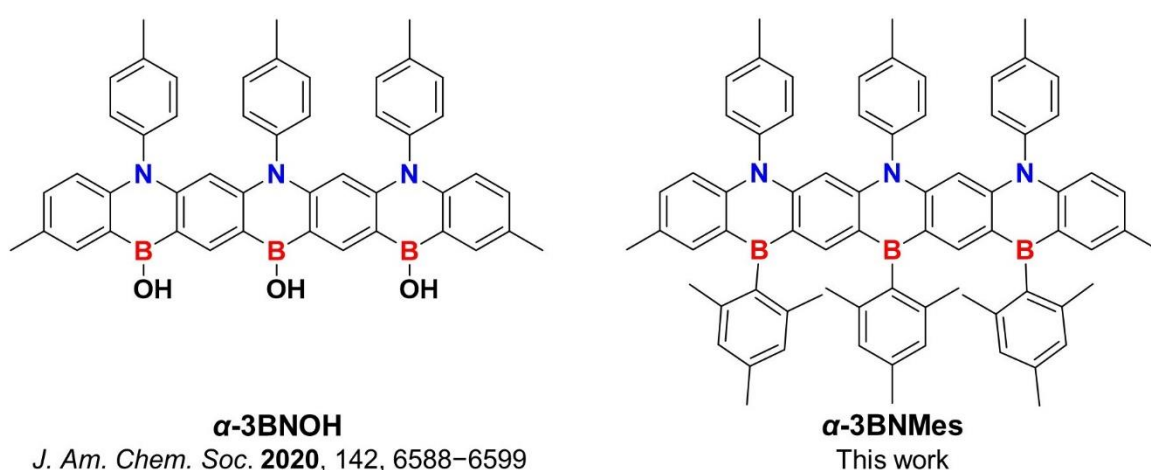


Figure 6.1. Structures of α -3BNOH and α -3BNMes.

6.2 Collaborator Contribution

All solution and film samples were made by myself. The steady state and time-resolved PL measurements were done by myself. The OLEDs were fabricated by myself. DtBuAc-DBT was synthesised by Dr. Nadzeya A. Kukhta. α -3BNOH and α -3BNMes were synthesised and analysed by Dr. Subeesh Madayanad Suresh. The crystallographic data were collected by Prof. Alexandra M. Z. Slawin. The calculations were made by Dr. David Beljonne and Prof. Yoann Olivier. Brief details of this work are given for completeness.

6.3 Experimental Methods

6.3.1 Sample Preparation

Photophysical characterization of solutions was performed in tetrahydrofuran (THF) solvent, at 20 μM concentration. Solid-state samples were fabricated by drop-casting onto quartz and transparent sapphire substrates. All host–guest drop-cast films were produced PMMA and zeonex at 1 wt% emitter concentration and DPEPO, mCP, PPBi, and CDBP at 10 wt% emitter concentration.

6.3.2 Crystal structure

Crystals for α -3BNMes were obtained by slow evaporation of a saturated tetrahydrofuran solution at room temperature over several days. The data were collected on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K α radiation. Of the 32743 reflections that were collected, 11756 were unique ($R_{\text{int}} = 0.3129$). Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).²² The linear absorption coefficient, μ , for Cu-K α radiation is 4.424 cm^{-1} . An empirical absorption correction was applied which resulted in transmission factors ranging from 0.604 to 0.996. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods²³ and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement²⁴ on F^2 was based on 11756 observed reflections and 718 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.3418$ and $wR_2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2} = 0.7348$. All calculations were performed using the CrystalStructure²⁵ crystallographic software package except for refinement, which was performed using SHELXL Version 2018/3.²⁶

6.3.3 Quantum Chemical Calculations

The calculations were performed with the Gaussian 09 revision D.018²⁷ suite for the density functional theory (DFT) and with the Turbomole/7.4 package²⁸ for SCSCC2 calculations. Ground-state optimized structures were calculated using the PBE0²⁹ functional and the 6-31G(d,p) basis set.³⁰ Molecular orbitals were visualized using GaussView 6.0 software.³¹ Spincomponent scaling coupled-cluster singles-and-doubles model (SCS-CC2)^{32,33} was also

used in conjunction with cc-pVDZ basis set for excited state calculations (T1 – T2³⁴ and S1 – S5³⁵) based on the PBE0/6-31G(d,p) optimized geometry.³⁶ Different density plots were used to visualize change in electronic density between the ground and excited state and were visualized using the VESTA package.³⁷

6.4 Results and Discussion

6.4.1 Chemical Characterization & Quantum calculation

α -3BNMes was synthesized in three steps, where the key borylation step proceeds in 57% yield. The structure of α -3BNMes was established from single crystal X-ray diffraction analysis (**Figure 2**), by growing single crystals via slow evaporation of the compound in THF. The data obtained are adequate to demonstrate connectivity and gross structure but do not merit discussion of bond lengths (**Figure 6.2**). Like the parent α -3BNOH, in α -3BNMes the heptacene core remains planar, and the aryl substituents attached to boron and nitrogen align nearly orthogonal to the main acene core.

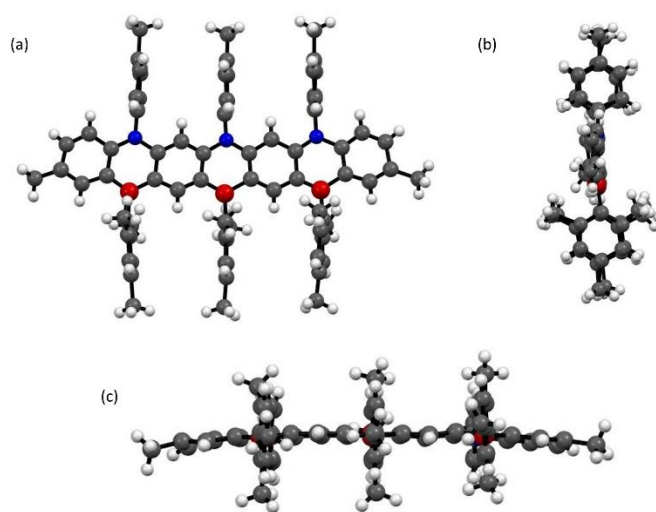


Figure 6.2. (a) Ball and (b), (c) stick representation of α -3BNMes obtained by single crystal X-ray Computational modelling provides a clear description of this MR-TADF compound. DFT calculations at the PBE0/6-31G(d,p) level of theory in the gas phase predict a large HOMO-LUMO gap of 4.03 eV.

The electron density distribution patterns of these orbitals are typical for MR-TADF compounds (**Figure 6.3**).⁶ The HOMO density is mainly localized on the nitrogen and carbon atoms positioned *ortho* to them, while in the LUMO, electron density is mainly localized on

the boron atoms and the carbons *ortho* to them. The applied spin component scaling second order approximate coupled-cluster (SCS-CC2) accurately predicted the nature and energies of the excited states and the ΔE_{ST} (**Figure 6.3b**).^{6,38} α -3BNMes showed a gratifyingly smaller ΔE_{ST} of 0.20 eV compared to that of α -3BNOH (ΔE_{ST} of 0.29 eV), but at the expense of a slightly smaller oscillator strength (f) for the transition to S_1 of 0.08 compared to α -3BNOH (f of 0.09).²⁰ The predicted S_1 energy was also stabilized to 3.40 eV compared to 3.69 eV in α -3BNOH. The difference density plot of the S_1 state shows the characteristic alternating pattern of increasing and decreasing electron density on adjacent atoms that is characteristic of MR-TADF compounds.³⁸ The patterns revealed in the difference density plots for T_1 and T_2 differ slightly from that of S_1 . This difference in the nature of the excited singlet and triplet states will result in enhanced spin-orbit coupling and assist in rISC following El Sayed's rules.³⁹

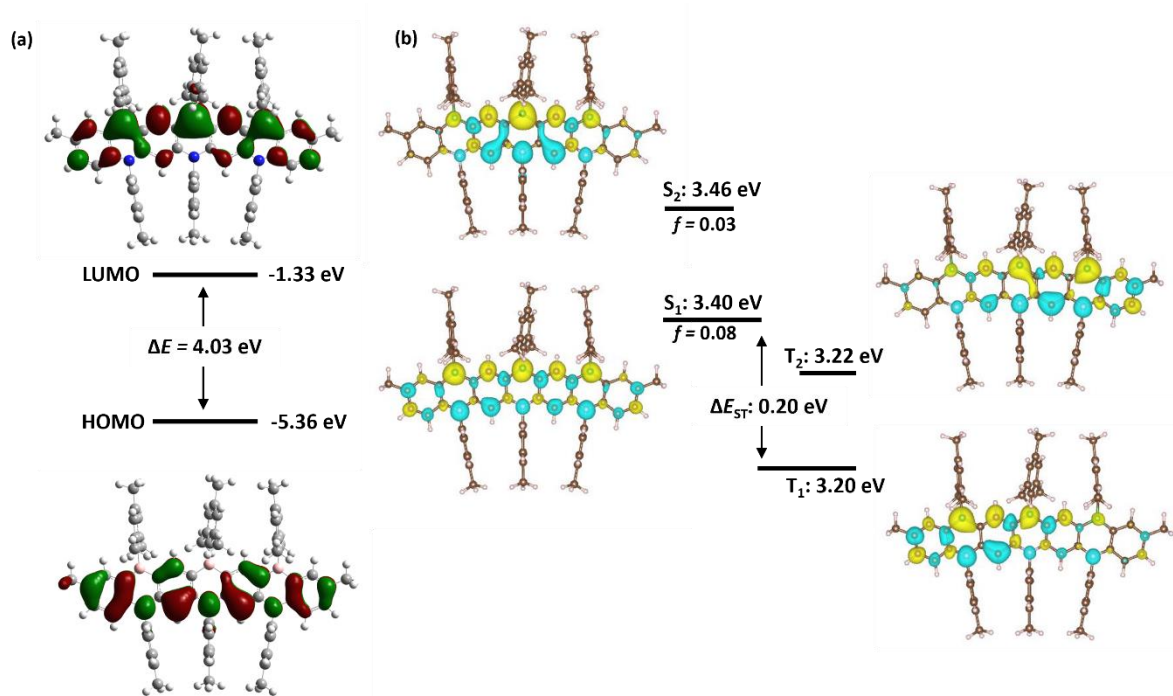


Figure 6.3. a) HOMO (bottom) and LUMO (top) energy distribution in α -3BNMes calculated using PBE0/6-31G (d,p), isovalue = 0.02; (b) Difference density plots for the lowest-lying two singlets and triplets excited states for α -3BNMes calculated in the gas phase by using SCS-CC2/cc-pVDZ. Blue colour represents an area of decreased electron density and yellow represents an increased electron density between the ground and excited states, isovalue = 0.001.

6.4.2 Optical Properties

Steady-state photophysical properties of both α -3BNMes and the previous α -3BNOH in dilute THF are shown in **Figure 6.4**. In the case of α -3BNMes, a bathochromic shift of 330 meV compared to α -3BNOH is observed in both the main π - π^* absorption band at 3.50 eV (354 nm) and the S_1 short-range charge transfer (SRCT) excited state, for more details see chapter 2, at 2.94 eV (421 nm). By replacing the strongly mesomerically electron-donating hydroxyl groups with inductively electron-withdrawing mesityl substituents, both the HOMO and LUMO levels are stabilized although the LUMO to a greater extent. This results in a net stabilization of the excited states in α -3BNMes, and red-shifts both its absorption and emission spectra. The molar extinction coefficient for the dominant high-energy band (S_4) is also increased by a factor of two, although this still appears at very short wavelengths, and thus is unsuitable for FRET and HF OLED applications using available D-A TADF assistant dopants. Nonetheless, this demonstrates that significant control over the absorption spectrum is indeed possible. Promisingly, the HF device-relevant SRCT absorption bands at longer wavelengths are increased by a factor of 1.4 along with a useful red-shift to wavelengths beyond 400 nm in α -3BNMes.

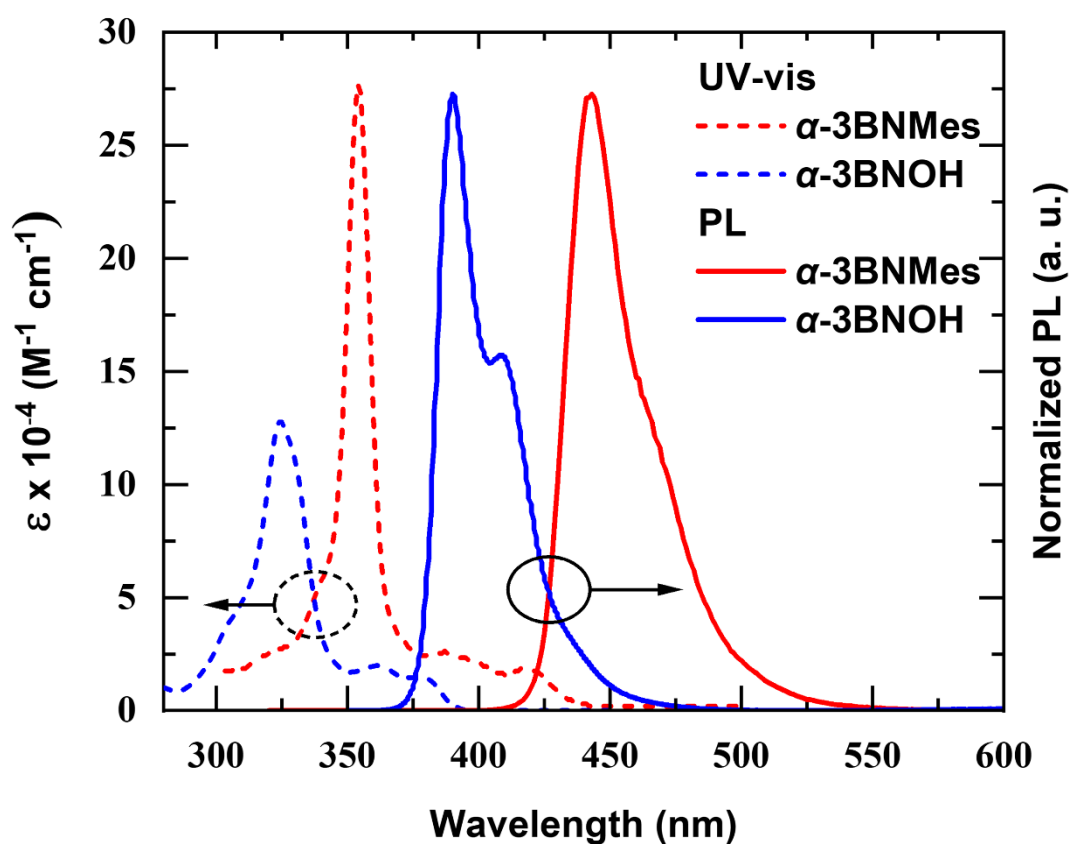


Figure 6.4. Absorption (dotted line) and emission spectra (solid line) of α -3BNMes and α -3BNOH in dilute THF solution. $\lambda_{\text{exc}} = 310$ nm for emission spectra.

Although these device-relevant SRCT bands remain smaller and at higher energies than in ν -DABNA (**Figure 6.5**), limiting HF compatibility with available D-A TADF co-hosts), they still represent a significant improvement compared to α -3BNOH. It remains unclear how the structure of ν -DABNA leads to its lowest-energy absorbance band becoming dominant, compared to the S_4 band in the heptacene systems. Computational and experimental work to further map out the largely unknown chemical space of MR-TADF emitters continues at pace both in research groups around the world.^{25,48,49}

The solution photoluminescence spectrum of α -3BNMes shows a narrow emission centred at $\lambda_{\text{PL}} = 2.80$ eV (442 nm), with FWHM of 190 meV (30 nm) and a small Stokes shift of 140 meV (20 nm). Gratifyingly, the replacement of the hydroxyl groups with the mesityl substituents leads to a yet narrower, deep-blue emission, shifting the CIE coordinates of the PL spectrum from (0.17, 0.01) to (0.15, 0.04). These CIE 1931 values are considered ideal for blue OLEDs as defined by BT.2020-2.¹ Together, these THF solution results establish the absorption- and emission-tuning abilities of the boron substituents towards synthetic control of the singlet states of the B,N-heptacene core.

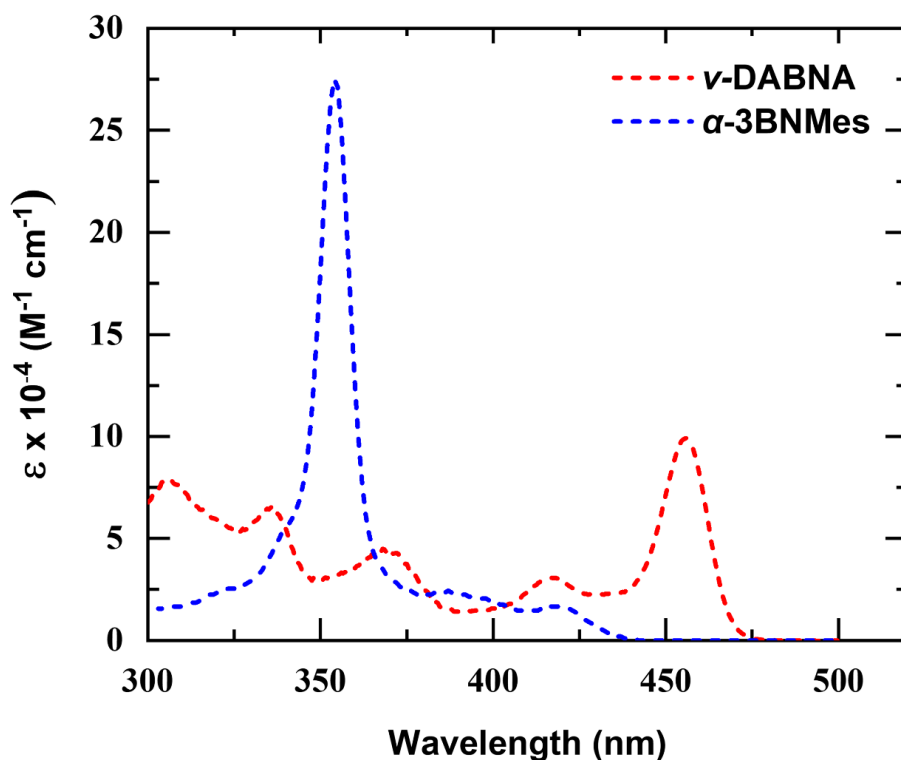


Figure 6.5. Absorption spectra of α -3BNMes and ν -DABNA.

The solid-state prompt fluorescence and phosphorescence spectra are shown in **Figure 6.6a**. The already established red-shifting behaviour of the singlet states in identical THF environments allows us to consider the trends of the triplet states energies (from film phosphorescence) more broadly. The ΔE_{ST} 's are very similar in both materials, indicating that the mesityl substitution of the boron atoms results in similar changes to both the singlet and triplet state energies of α -3BNMes compared to α -3BNOH.

Time-resolved photoluminescence decays of α -3BNMes doped at 1 wt% in PMMA matrix are shown in **Figure 6.6b**. Similar to previous reports of the photophysics of α -3BNOH²⁰ and many other reported MR-TADF materials, the delayed fluorescence from α -3BNMes is weak and long-lived compared to D-A TADF materials,^{40–43} indicating only a moderate rate of rISC. At lower temperatures, the delayed emission component (after 100 ns) was suppressed, evidencing the TADF mechanism. At longer delay times (beyond 0.1 ms) and at temperatures below 150 K the emission decay rate changes significantly, which has with a strong spectral red-shift (**Figure 6.6c**), indicative of the phosphorescence regime from which the phosphorescence spectrum (**Figures 6.6a**) was extracted.

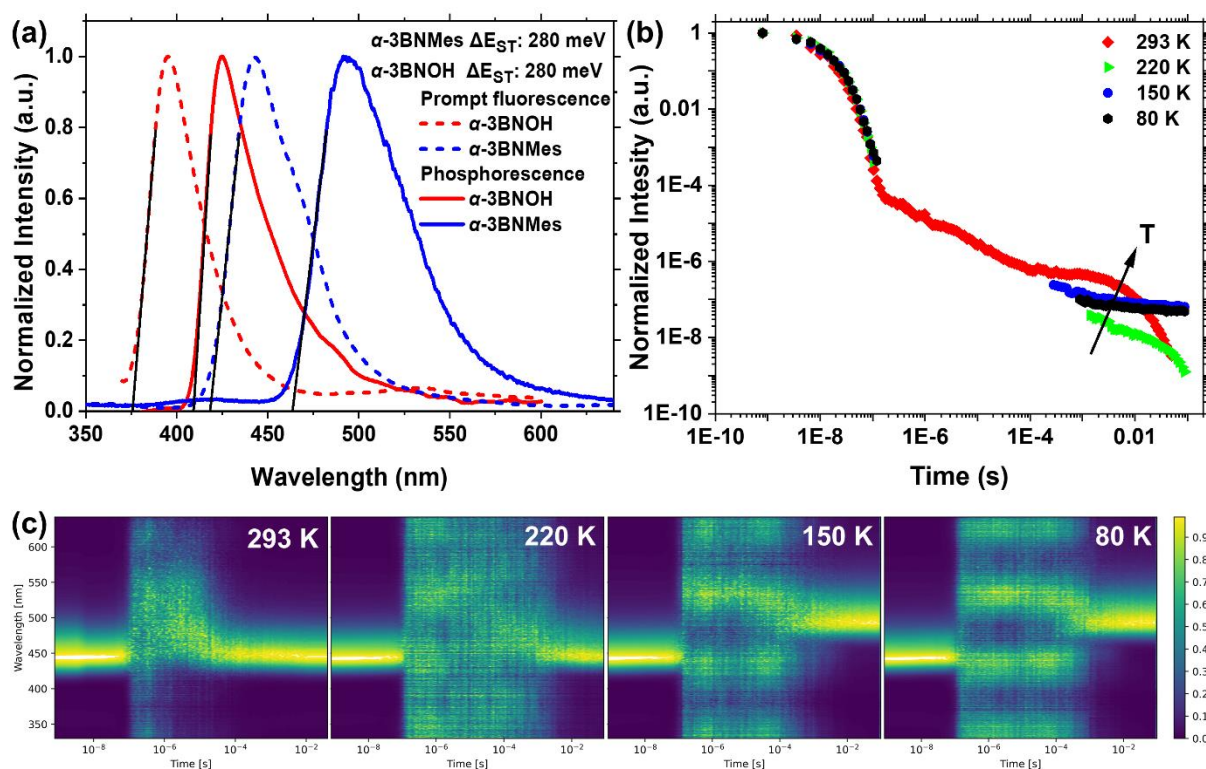


Figure 6.6. (a) Time-resolved prompt fluorescence (prompt, delay time 10 ns and gate width 5 ns) and phosphorescence (delayed, delay time 70 ms and gate width 15 ms) spectra of α -3BNOH²⁸ and α -3BNMes 1 wt% in PMMA, at 80 K. (b) Temperature-dependent time-resolved

emission decay of α -3BNMes 1 wt% in PMMA. (c) Contour plots of time-resolved emission spectra at various temperatures (regions between 100 ns and 100 μ s at lower temperatures). Exponential fitting of the room temperature decay shows three different components: the prompt fluorescence with a lifetime of 10 ns, and two main components of the delayed emission with lifetimes of 9.08 μ s and 7.06 ms (**Figure 6.7a**). The shorter of the delayed lifetimes, corresponding to a regime of dual emission, is attributed to simultaneous emission from a monomer and a red-shifted aggregate species (**Figures 6.6c, 6.7c**), most probably associated with excimer emission as described in chapter 5,¹¹ something common in planar MR-TADF emitters. Notably, the contribution to the emission decay from these species is minimal and energetically is at the same positions as for α -3BNOH.²⁰ The longest delayed component is attributed to pure monomer emission with mono-excitonic origin as demonstrated in the power dependence measurement, in **Figure 6.8**. In contrast, α -3BNOH was found to have bi-excitonic TTA contribution, but no quadratic-to-linear (slope 2 to slope 1) regime change in the DF intensity was observed, as excitation pulse energy was increased, for α -3BNMes.²⁰

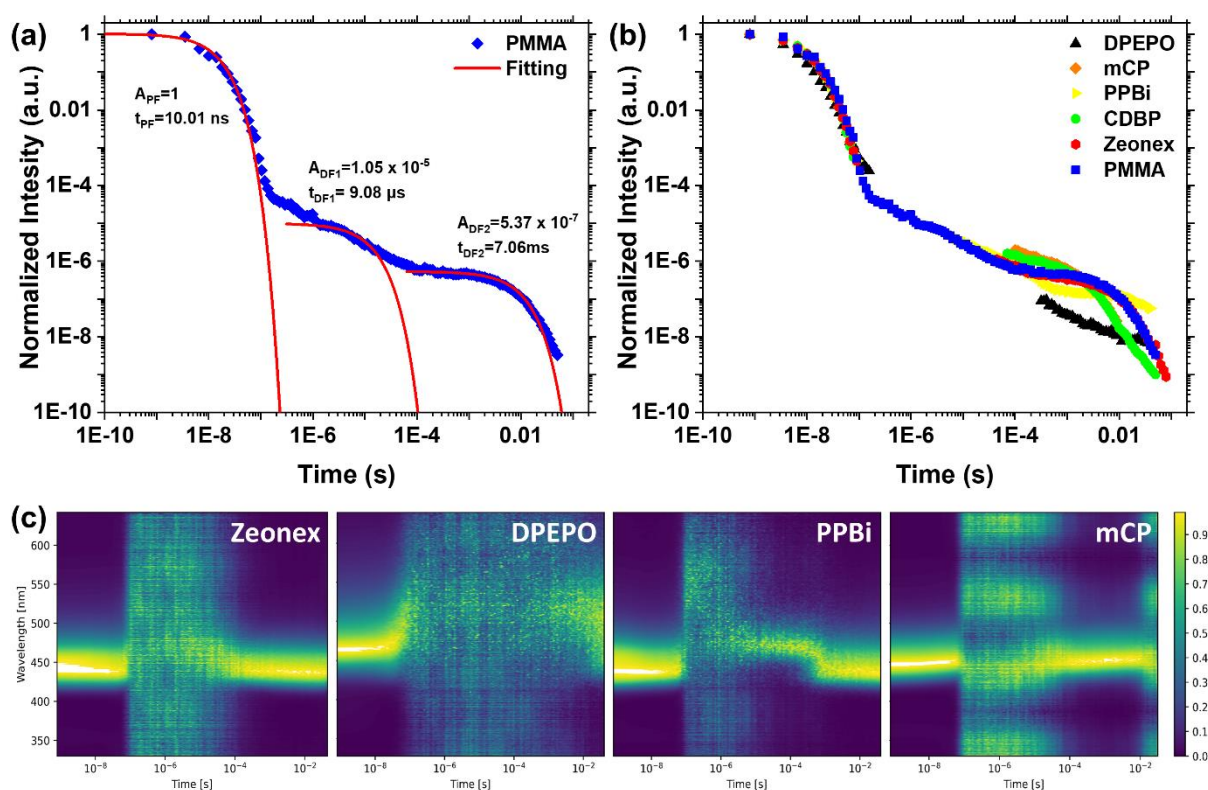


Figure 6.7. Time-resolved PL decays of α -3BNMes in: (a) PMMA 1 wt%, multi-exponential fitting included, and (b) in PMMA (blue), Zeonex (red) at 1 wt% concentration and DPEPO

(black), mCP (orange) and PPBi (yellow), CDBP (green) at 10 wt% concentration. (c) Contour plots of emission over time, in different hosts. $\lambda_{\text{exc}} = 355$ nm.

Similar to chapter 5 and other recent studies of MR-TADF materials,^{10,11} and in strong contrast to the CT states of D-A TADF molecules, changing the host matrix was found to have only a modest influence on the SRCT states and their TADF properties (**Figure 6.7b**). The photoluminescence quantum yield (PLQY) of α -3BNMes in 1% mCP doped film was determined to be 63%, thus nearly double that of α -3BNOH (35% in 1 wt% mCP), and sufficiently high to support OLED applications. Finally, using the determined PLQY, along with the time-resolved PL decay lifetimes the k_f , k_{ISC} and k_{rISC} constants in mCP were estimated, according to Wada *et al.*⁴⁴ These were found to be $5.25 \times 10^7 \text{ s}^{-1}$ for k_f , $1.98 \times 10^7 \text{ s}^{-1}$ for k_{ISC} and $5.9 \times 10^2 \text{ s}^{-1}$ for k_{rISC} . These values represent a fast k_f (as expected for a rigid polycyclic aromatic hydrocarbon), a reasonably fast rate of ISC (enabled by the SRCT states of the B,N network), and a slow rISC rate, which is still common amongst MR-TADF emitters due to their upper-state T_n - S_1 rISC mechanism.⁴⁵

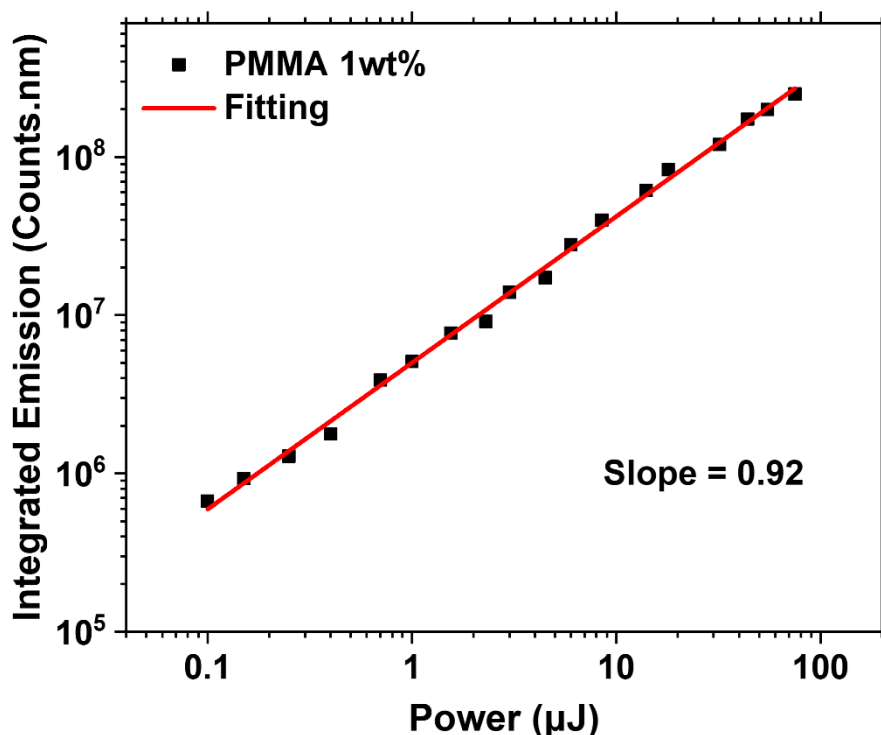


Figure 6.8. Power dependence of α -3BNMes 1 wt% in PMMA, at room temperature. Time delay 2 ms, integration time 60 ms. $\lambda_{\text{exc}} = 355$ nm.

6.4.3 Devices

Having confirmed the weak TADF activity of α -3BNMes, its use as an emitter in OLEDs was nonetheless preliminarily assessed. Devices using a stack of ITO (anode) | NPB (HIL/HTL, 40 nm) | mCBP (EBL, 10 nm) | α -3BNMes:host x wt% (EML, 30 nm) | T2T (HBL, 10 nm) | T2T:LiQ 45% (EIL/ETL, 35 nm) | Al (cathode, 100 nm) were fabricated, with representative performance shown in **Figure 6.9**.

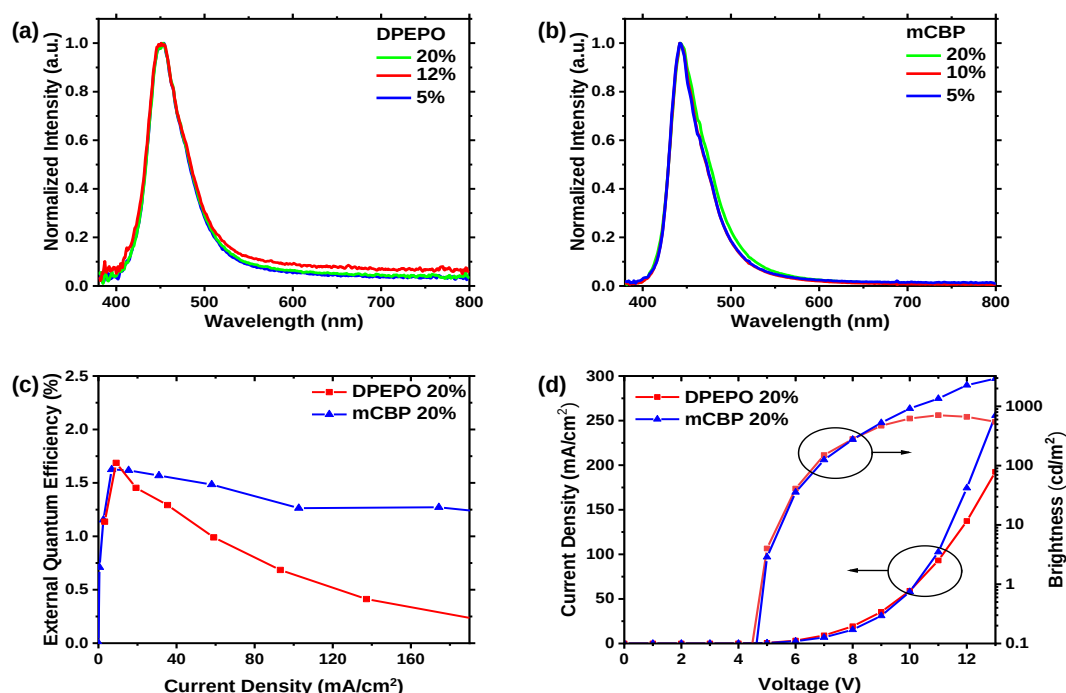


Figure 6.9. OLED performance of α -3BNMes. EL spectra at different concentration in (a) DPEPO and (b) mCBP. (c) EQE vs Current density and (d) JVL characteristics in both hosts.

Two different hosts were used, DPEPO (electron transporting, $E_T=3.05$ eV) and mCBP (hole transporting and otherwise similar to mCP, and with $E_T=2.85$ eV now confirmed high enough to be compatible with the emitter $E_T=2.7$ eV), with varying concentrations of α -3BNMes ranging from 5 up to 20 wt%. With increasing doping concentration, no significant differences were observed in the current density-voltage-luminance (JVL) curves, spectra, or EQE in both host environments. Consequently, no qualitatively different behaviour was anticipated in the MR-TADF only devices with lower doping concentration, which were not investigated. More interestingly, no broadening of the electroluminescence (EL) spectrum was observed upon increasing concentration, indicating suppression of excimer formation even at high concentrations. Maximum EQEs of 1.7 % at ~ 100 cd m⁻² were achieved in devices with each

of the two hosts. The poor performance is due to the weak TADF (poor triplet harvesting) of the material, leading to low efficiency combined with additional efficiency roll-off in the DPEPO OLEDs,^{46,47} especially at high current densities (**Figure 6.9c**). Nonetheless, the CIE coordinates are very attractive at (0.15, 0.08), which are the same as in the photoexcited film and similar to that determined in THF solution.

To compensate for the poor intrinsic exciton harvesting performance of α -3BNMes while still taking advantage of its ideal emission spectrum it was then applied as a terminal emitter in HF OLEDs in combination with a D-A(-D) TADF sensitizer. In order to ensure adequate spectral overlap necessary for the energy transfer, DtBuAc-DBT was employed as a TADF sensitizer (**Figure 6.10c**), previously reported to give ~11% EQE_{max} with CIE coordinates of (0.16, 0.17), and suitably high-energy blue emission to overlap with the absorption spectrum of α -3BNMes (**Figure 6.11**).⁴⁰ This D-A-D TADF assistant dopant was co-evaporated at 25 wt% in the EML, alongside 1 wt% α -3BNMes and 74 wt% DPEPO. The device architecture was chosen to be the same as the one previously reported,⁴⁰ with the addition of α -3MesBN as the terminal emitter, using ITO (anode) | NPB (HTL, 40 nm) | TSBPA (EBL, 10 nm) | α -3BNMes:DtBuAc-DBT:DPEPO 1:25:74 wt% (EML, 30 nm) | DPEPO (HBL, 10 nm) | TBPi (ETL, 40 nm) | LiF (EIL, 1 nm) | Al (cathode, 100 nm). Both control “D-A-D only” TADF and combined HF OLEDs were produced in the same deposition run to provide a suitable comparison.

The resulting HF OLEDs possess good efficiency, with an EQE_{max} of 15% and an EQE₁₀₀ (at 100 cd/m²) of 10.2%, with a FWHM of 290 meV (49 nm) and CIE of (0.15, 0.10), which is enabled by triplet harvesting by the D-A-D sensitizer, together with narrow deep blue emission from the α -3BNMes (**Figure 6.10**). Although the EQE_{max} is improved at 15% in the HF OLED (compared to 11% for the DtBuAc-DBT device) the larger roll-off at higher current densities results to an EQE₃₀₀ of 6.2% and 8.8% for the HF and TADF OLEDs, respectively. The severe roll-off in the HF OLEDs is mainly assigned to the long triplet exciton lifetime (slow k_{rISC}) of α -3BNMes, leading to enhanced triplet quenching phenomena. The α -3BNMes high triplet population at higher current densities occurs either via ISC from α -3BNMes singlet state or via Dexter energy transfer from the TADF sensitizer's triplet state. Further, the differences in EQE at different driving regimes are a result of compromise between detrimental factors (e.g., the moderate PLQY of α -3BNMes as the terminal emitter, competing unproductive Dexter energy transfer, *in-situ* charge trapping, etc.) and beneficial effects (e.g., α -3BNMes alignment/anisotropic emission, and good FRET overlap outcompeting DtBuAc-DBT non-

radiative decay), although some of these factors are deceptively difficult to quantify by established experimental methods.⁴⁸ The overall HF OLED performance is nonetheless competitive with other recent leading reports at similar colour coordinates (**Figure 6.12** and **Table 1**).

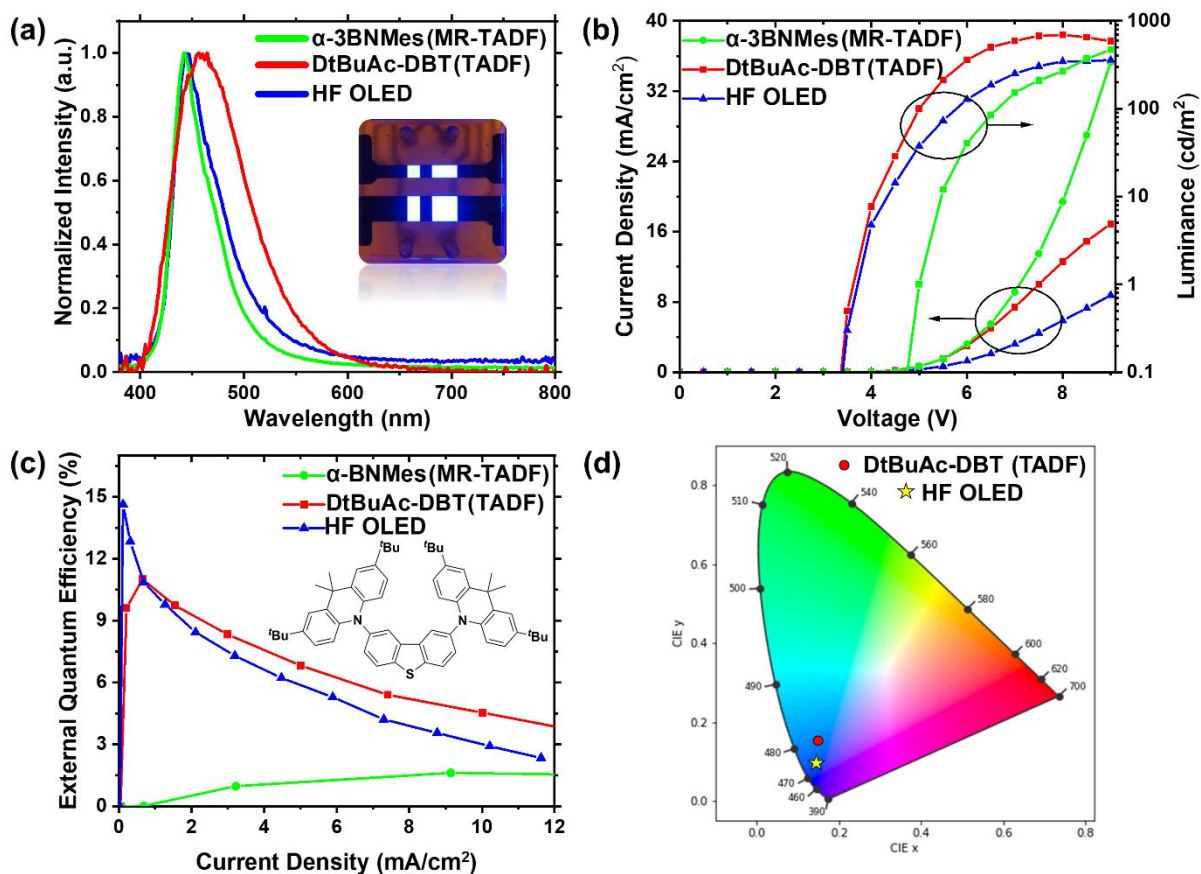


Figure 6.10. Performance of MR-TADF (green), D-A-D (red), and HF (blue) OLEDs. (a) EL spectra. Inset: Operating HF OLED. (b) JVL characteristics. (c) EQE vs Current density. Inset: DtBuAc-DBT structure. (d) CIE coordinates.

The EL spectrum of the HF OLEDs is nearly identical, but slightly broader to the α -3BNMes spectrum, indicating efficient FRET (this issue of HF OLEDs is addressed in chapter 8) with only a small contribution of the D-A-D TADF sensitizer at ~525 nm. This efficient FRET is in good agreement with the calculated FRET radius of 2.27 nm, using the spectral overlap in **Figure 6.11** and classical energy transfer models (see chapter 3, equation 3.20).¹¹ This result in particular highlights the importance and challenge of both emission and absorption spectral tuning for developing high-efficiency blue HF OLED material combinations. While it is incredibly challenging to further deepen the emission colour of available D-A-D TADF

assistant dopants, the need to do so can be avoided in HF OLEDs by instead red-shifting the absorption spectrum of the MR-TADF terminal emitters, as demonstrated in this chapter. Similarly, while stable high-triplet hosts with good charge transport properties remain elusive, the need for these could be circumvented in future if FRET compatibility for MR-TADFs can be extended to cyan or green D-A TADFs, for which such hosts are much more attainable.

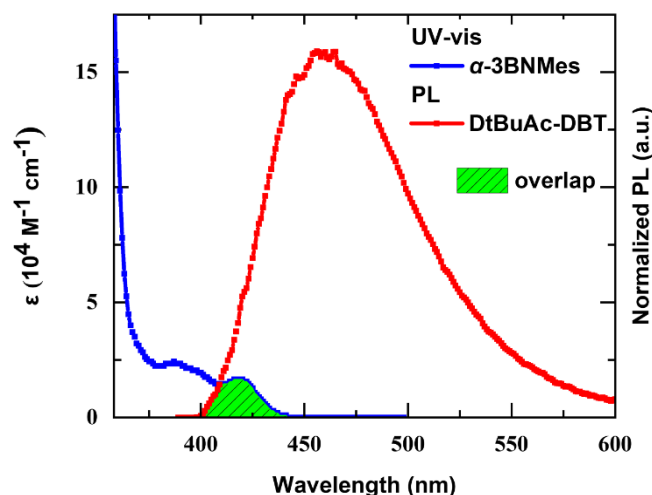


Figure 6.11. Overlap between the normalized emission spectrum of the DtBuAc-DBT donor and the absorption spectrum of the α -3BNMes acceptor for FRET radius analysis.

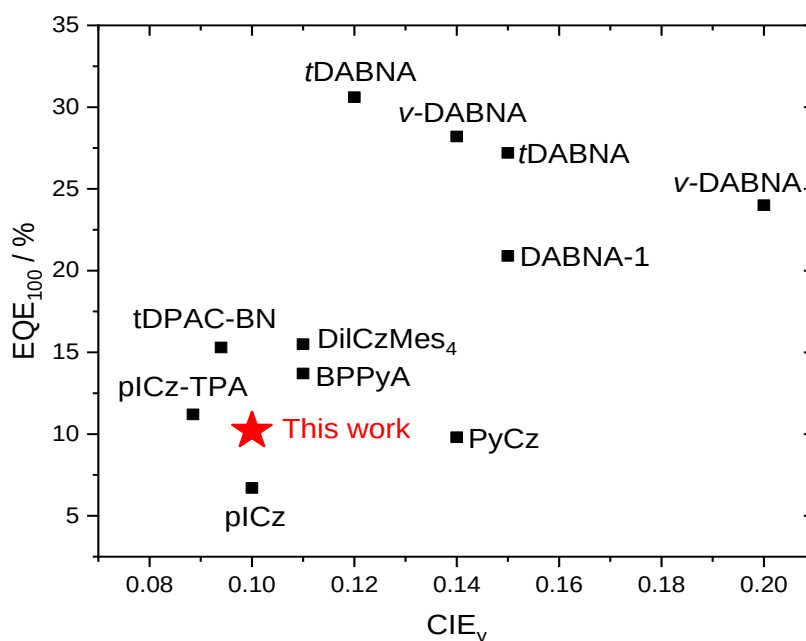


Figure 6.12. Graphical representation of EQE₁₀₀ vs CIE_y of previously reported blue HF OLEDs. Values obtained from **Table 1**.

Table 1. Summary of previously reported deep blue HF OLEDs.

Assistant Dopant	Terminal Emitter	Von / V	EQE _{max} / %	EQE ₁₀₀ / %	EQE ₁₀₀₀ / %	CIE (x,y)	EL _{max} / nm	Ref
DtBuAc-DBT	α -3BNMes	3.4	14.6	10.2	/	0.15, 0.10	443	This work
DMAC2- TMXanSO ₂	DiICzMes ₄	3.4	16.5	15.5	12.9	0.15, 0.11	446	[17]
DPAC-tCzBN	pICz	3.5	32	6.7	/	0.15,0.10	445	[55]
DPAC-tCzBN	Picz-TPA	3.6	34.7%	11.2	/	0.15, 0.085	447	[55]
DMAC-DPS	t-DABNA	N/A	31.4	27.2	19.8	0.13, 0.15	N/A	[56]
DMAC-DPS	DABNA-1	N/A	23.4	20.9	15.3	0.14, 0.15	N/A	[56]
DMAC-DPS	tDPAC-BN	3.5	21.6	15.3	5.4	0.135, 0.094	460	[57]
P4TCPhBN	t-DABNA	N/A	32.5	30.6	23.2	0.13, 0.12	459	[21]
PCzTRZ	v-DABNA	N/A	33.5	/	24.3	0.12, 0.18	473	[20]
HDT-1	v-DABNA	N/A	27	24	20	0.15, 0.20	470	[22]
DMAC2- TMXanSO ₂	v-DABNA	N/A	27.5	/	25.7	0.12, 0.17	474	[19]
PtON7-dtb	v-DABNA	N/A	32.2	28.2*	25.4	0.11, 0.14	473	[58]
DMAC-DMT	BPPyA	N/A	15.5	13.7**	11.4	0.15, 0.11	N/A	[59]
CzAcSF	TPBe	N/A	17.2	N/A	12.4	0.14, 0.19	N/A	[60]
3CzBN-Cz	Py-Cz	4.1	10.2	9.8*	N/A	0.15, 0.14	468	[61]

* Values extracted from graph.

** At 500 cdm⁻².

In parallel to the study presented in this chapter, I was involved in a project with Pof. Eli Zysman-Colman's group on the first MR-TADF emitter without the need for acceptor units, such as boron atoms. DiICzMes₄, an indolocarbazole based emitter, was proven to have TADF based on SRCT states.⁹ Similar to α -3BNMes, DiICzMes₄ suffered from slow triplet harvesting rate resulting in inefficient OLEDs (**Figure 6.13**). Using the HF approach, and high k_{HSC} TADF sensitiser HF OLEDs with EQE_{max} of 16.5% at deep-blue colour coordinates (0.15, 0.11) with

improved relative (compared to the TADF OLEDs) efficiency roll-off. This work verifies the importance of HF OLEDs for narrow emission device fabrication and was published in Materials Horizon.

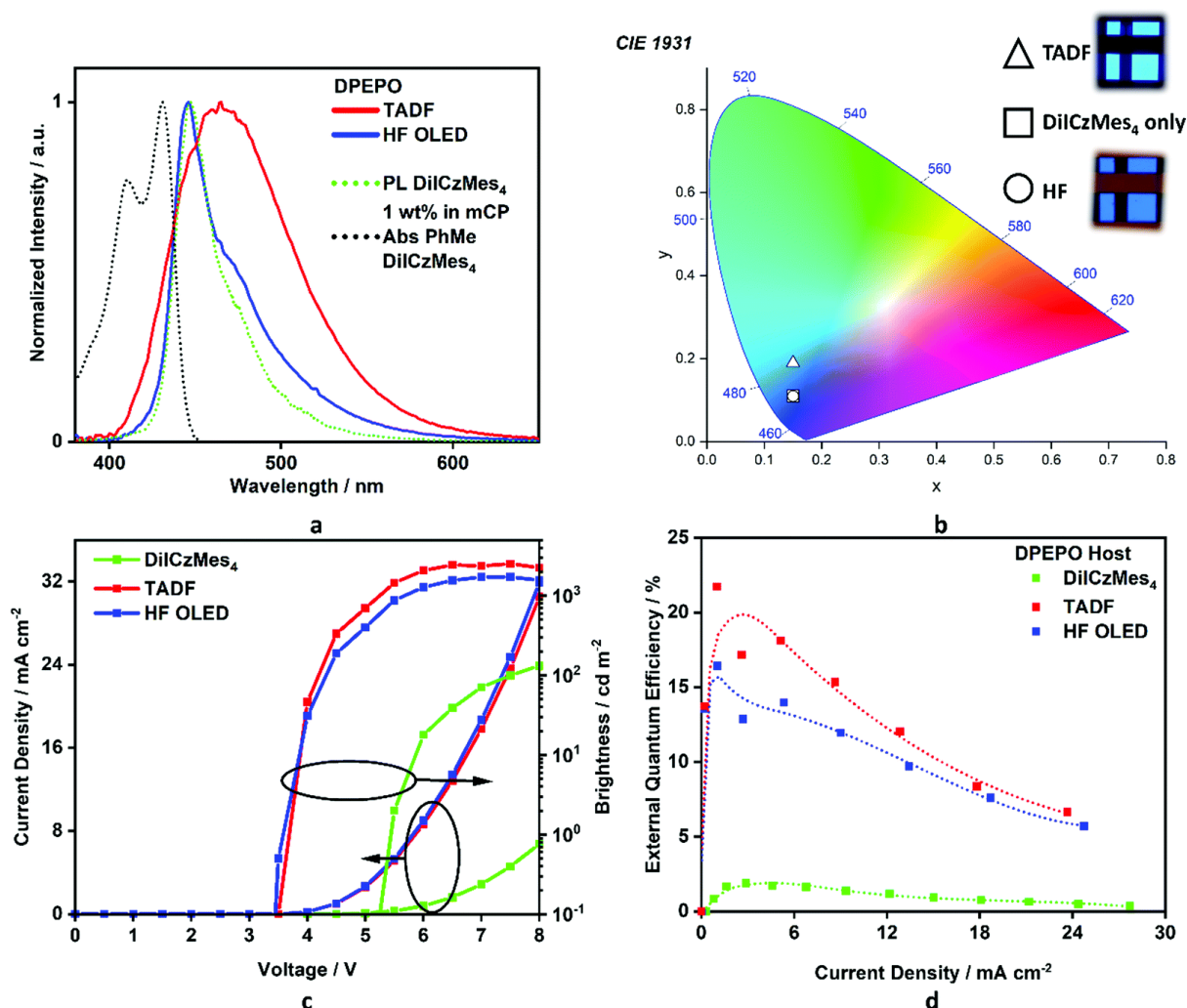


Figure 6.13. OLED performance for different EMLs. (a) EL spectra of TADF D–A–D 35% (red), HF OLEDs 1:35 wt% (blue) in DPEPO host, absorption (black dotted) and PL (green) spectra of DiICzMes₄ 1 wt% in mCP for comparison. (b) CIE coordinates, where square (DiICzMes₄ only) and circle (HF) overlap, (c) JVL curves, and (d) EQE vs. current density, where fitting has been applied (dotted line) to guide the reader.

6.5 Conclusions

In this chapter, emission and absorption colour tuning in a deep blue non-triangulene type MR-TADF compound was achieved by altering the boron substituents in a B, N-doped heptacene. Compared to the parent UV emitter α -3BNOH, these changes imbue α -3BNMes with near ideal

CIE coordinates for blue OLEDs (**Figure 6.14**), and suitable absorption spectrum for FRET compatibility with existing D-A TADF co-hosts. The resulting HF OLEDs achieved an EQE_{max} of 15% and deep-blue colour coordinates of (0.15, 0.10), compared to < 2% efficiencies for the unassisted α -3BNMes OLEDs.

Further, the non-triangulated structure of α -3BNOH exhibits a much smaller oscillator strength of the S_0 to S_1 transition compared to the triangulated MR-TADF structures (such as v-DABNA, **Figure 6.5**). Although the reason remains unclear, this highlights the complexity of the MR-TADF emitters. Nonetheless, computational and experimental work to further map out the largely unknown chemical space of MR-TADF emitters continues at pace in research groups around the world.^{17,57,58}

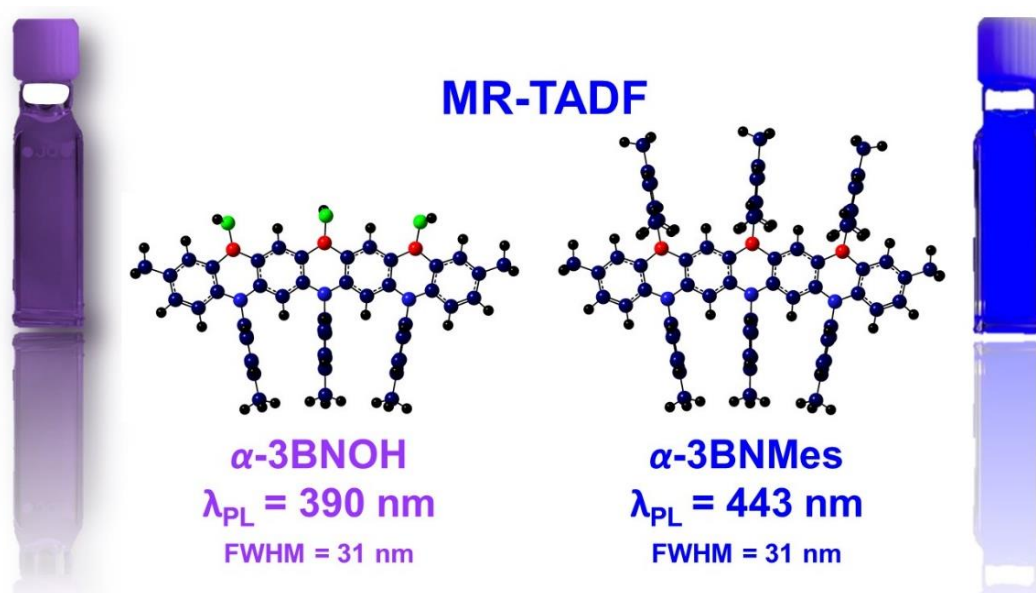


Figure 6.14. Structure of α -3BNOH (left) and α -3BNMes (right) emitter. Through delicate molecular modification and emission colour is tuned from UV to the ideal blue, according to BT.2020-2 colour standards.

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7 The Peculiar Case of DMAC-TRZ as a Hyperfluorescence Sensitizer

The hyperfluorescence approach has proved to work well in the previous HF systems. In all cases, a good spectra overlap was required to achieve efficient FRET. In this chapter, the very well-known TADF emitter, DMAC-TRZ (used as a probe molecule to explore the guest-host interactions in chapter 4) was used as a sensitizer, with minimal spectra overlap with the *v*-DABNA terminal emitter to explore the FRET limitations. Although DMAC-TRZ is a heavily studied molecule, here, because of the unexpectedly improved FRET to *v*-DABNA compared to similar or bluer sensitizers, DMAC-TRZ well-hidden intrinsic/structural properties were unveiled. Based on experimental and computational studies two DMAC-TRZ conformers were found (previously known to have only one stable conformation), a quasi-axial (QA) and a quasi-equatorial (QE). The energy transfer efficiency from the QA to the QE conformer is observed to be high, even at low concentrations, and depending on the host environment. While the contribution of the QA conformer in devices partially explains the good performance of the material in non-doped OLEDs, in HF OLEDs direct energy transfer from the QA conformer to *v*-DABNA explains the relatively improved FRET compared to similar HF systems. Highly efficient OLEDs are demonstrated, with greenish light emitting diodes (TADF-only devices) converted to blue (HF devices) with EQE_{max} remaining close to 30%.

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7.1 Introduction

The high physical complexity of organic emitting molecules was highlighted in chapter 2. While already complicated enough, chapter 4 demonstrates the guest-host interactions effect in TADF systems, increasing the complexity factor. In the same category, intermolecular interactions such as: homo-molecular interactions (between the same type of molecules, dimer/excimer), hetero-molecular interactions (between different types of molecules, complex/excimer), and conformational effects enhance the complexity. Focusing on the latter, two types of conformation effects have been mainly explored so far: the distribution of dihedral angles between the D-A moieties¹⁻³ and the possible ground and/or excited state conformers (*i.e.* planar, axial, equatorial etc).⁴⁻⁶ In the context of the second type of conformational effect, several D-A and D-A-D molecules have been reported whose donor unit is non-planar, leading to two configurations where the D-A are near orthogonal, *i.e.* axial and equatorial orientations.⁵

In 2014, Tanaka *et al.* reported PTZ-TRZ, a structural analogue of PXZ-TRZ that has a sulphur atom instead of oxygen in the donor unit.⁴ This distorted the donor allowing axial and equatorial conformations to co-exist, and dual emission was observed originating from two ICT transitions derived from conformational heterogeneity (quasi-axial (QA) and quasi-equatorial (QE)). A similar effect was shown by Su *et al.*, but instead of using a hetero atom, adamantane was attached to the acridine donor, showing the same dual conformational emission.⁷ Other cases of D-A systems also presented dual conformer emission.⁸ Such conformers in D-A-D systems have also been reported, and their photophysical behaviour has been described in detail.^{5,9}

In this chapter, the TADF emitter DMAC-TRZ¹⁰ was investigated, a molecule that theoretically does not fulfil the requirements presented before to have dual conformer emission. Surprisingly, under specific conditions, a QA conformer can be observed, although the QE conformer appears to be dominant. In solution state, the molecular interconversion from the QA to the QE is labile and the emission from the first only contributes to a very small extent. In solid-state, however, because of environmental restrictions (hindering molecular relaxation), the QA emission appears stronger. At low temperatures, this effect is even stronger, while a structured QE CT emission can also be observed. The energy transfer process between the two conformer species appears to be very efficient, even at concentrations below 0.1 wt%, and the TADF efficiency appears to increase by increasing concentration. Above 1 wt% concentration,

aggregation occurs which appears to dominate above 5 wt% loading, however, still enhances the TADF efficiency. Under specific conditions, at low temperature, the origin of the phosphorescence spectrum appears to come from the QA conformer, mainly because the lowest lying triplet state of the QE conformer has a pure CT character and if it can decay radiatively any phosphorescence would be vanishingly weak. In OLEDs the QA conformer appears to efficiently transfer its energy to the QE conformer and only in specific hosts a QA contribution can be seen. Using DMAC-TRZ as a sensitizer in hyperfluorescence (HF) OLEDs^{11–13} the QA conformer can directly pump the terminal emitter (because of the terminal emitter higher oscillator strength and better spectral overlap compared to DMAC-TRZ QE conformer). Thus, Förster resonance energy transfer (FRET) from the QA conformer to the terminal emitter outcompetes the FRET from the QA to the QE conformer. This significantly improves the FRET efficiency of the system, compared to similar sensitizer-terminal emitter systems. HF-OLEDs with maximum external quantum efficiency (EQE_{max}) close to 30% were fabricated but most importantly, a green TADF sensitizer was converted to blue HF-OLED.

7.2 Collaborator Contribution

All solution and film samples were made by myself. The steady state and time-resolved PL measurements were done by myself. Larissa G. Franca performed and analysed the TCSPC measurements. The OLEDs were fabricated, measured and analysed by myself. Tobias Böhmer and Luka M. Duben did the quantum chemical calculations, briefly described in the next subsection. Brief details of this work are given for completeness.

7.3 Experimental Methods

7.3.1 Sample Preparation and Measurements

Steady-state absorption and emission spectra were measured using a double beam Shimadzu UV-3600 UV/VIS/NIR spectrophotometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, respectively. Solution-state samples were dissolved at 20 μM concentration. Solid-state samples were prepared from toluene solutions of host and guest molecules at specific mass ratios and dried in vacuum following drop-casting upon sapphire or quartz substrates. Fresh samples were used for all steady state measurements to minimize the possibility of emitter degradation. Time-resolved measurements were performed using a

spectrograph (Horiba Triax) and a Stanford Computer Optics 4Picos ICCD camera, where samples were excited with a Nd:YAG laser (EKSPLA, 10 Hz, 355 nm) under vacuum.

7.3.2 Computational Details

The molecular equilibrium geometries were optimised with Gaussian16¹⁴ employing the LC- ω *-HPBE¹⁵ density functional. The range separation parameter was set to $\omega=0.195\text{ a}_0^{-1}$ for the QE conformer, as determined by Dhali et al.¹⁶ in an optimal tuning procedure. For the QA conformer a slightly smaller value of $\omega=0.175\text{ a}_0^{-1}$ was found to be optimal. For all atoms, the split-valence def2-SV(P) basis set was utilised.¹⁷ A methyl cyclohexane environment was mimicked with a polarisable continuum model [PCM] as implemented in Gaussian16. Electronic spectra were computed with the combined density functional theory and multireference configuration interaction DFT/MRCI method¹⁸ in the short parameterisation form suggested by Lyskov et al.¹⁹ To this end, the PCM point charges were exported and transferred to the Turbomole program package²⁰ which was used to generate molecular orbitals and three-index two-electron integrals required by the DFT/MRCI program. Energies and wavefunctions of 20 excited singlet and 20 triplet states were solved for in the DFT/MRCI step. Franck–Condon and Herzberg–Teller spectra were computed with a modified version of the VIBES program.²¹

7.4 Results and Discussion

7.4.1 Photophysics

The solvatochromic behaviour of DMAC-TRZ in both excitation and emission measurements is shown in **Figure 7.1**. In MCH the excitation spectrum shows two distinct bands with peaks at 376 nm (Ab1) and 413 nm (Ab2) (**Figure 7.1a**). Upon increased solvent polarity, the Ab2 band decreases in intensity and a tail appears at 450 nm, an expected behaviour for a CT excited state, but loses in oscillator strength with increasing polarity. The Ab1 band appears unaffected and slightly blue-shifted in acetonitrile (CH₃CN).

Deconvolution of the excitation spectra in the four different solvents, using two Gaussians, showed an Ab1 band maximum of about 376 nm in all cases (with a minor 5 nm hypsochromic shift in CH₃CN), and a full width half maximum (FWHM) of $55 \pm 4\text{ nm}$ (**Figure 7.2**). This behaviour is expected from a strongly localised excited state. The Ab2 band maximum is observed at 413 nm in all solvents but reduces in intensity and increases in FWHM (from 35

nm in MCH to 63 nm in CH₃CN) with increasing solvent polarity. The latter follows the FWHM behaviour of the emission spectrum (**Figure 7.1b**) and is undoubtedly from the CT state between the donor and acceptor moiety. The Ab2 band appears to have a mixed, local (LE) and CT character in MCH, giving a structured excitation and photoluminescence (PL) spectrum.

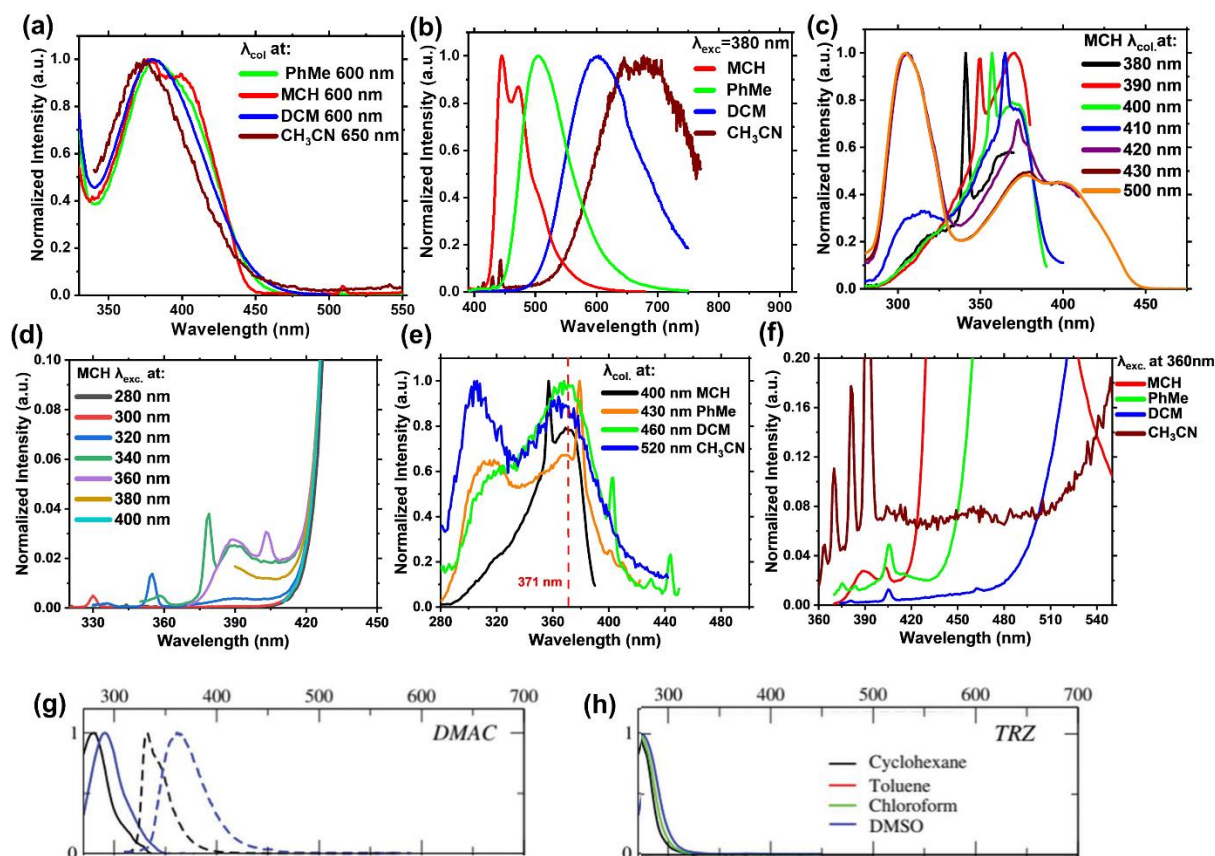


Figure 7.1. Steady-state photophysics of 20 μ M DMAC-TRZ solutions, at room temperature. (a) Excitation and (b) PL spectra in different solvents. (c) Excitation and (d) PL spectra (of Em1) in MCH, using different collection and excitation wavelengths respectively. (e) Ab1 excitation and (f) Em1 PL spectra in different solvents, using different collection and excitation wavelengths, respectively. Sharp peaks in the spectra are Raman peaks of the solvent. Absorption and PL spectra of (g) DMAC donor and (h) TRZ acceptor units in different solvents. TRZ is not emissive at room temperature. Copied with permission from reference 16.

In MCH and upon excitation at wavelengths between 320 and 380 nm, a shorter wavelength emission band appeared (Em1) with an emission maximum at 390 nm (**Figure 7.1d**). The relative intensity of the Em1 band maximum was the highest when excited at 360 nm, where the intensity of the Ab1 band is close to its maximum, and the Ab2 band is close to its minimum

value (**Figure 7.2a**). Interestingly, when exciting at shorter wavelengths ($\lambda_{\text{exc}} < 310$ nm) the Em1 band is not observed. The excitation profile of the Em1 band is well resolved, solvent independent (**Figure 7.1e**) and appeared very similar to the deconvoluted Ab1 spectra (**Figure 7.2a**). With increasing solvent polarity, the relative PL intensity of Em1 band decreases and its peak position has a minor redshift, compared to the main PL (Em2) band (**Figure 7.1f**). The absorption and emission spectra of the individual D and A units (**Figure 7.1g, h**) were studied before and are energetically in higher positions than the Ab1 and Em1, respectively.¹⁶ Hence these two distinct emission bands can only be assigned to two different conformers of the DMAC-TRZ molecule.⁵

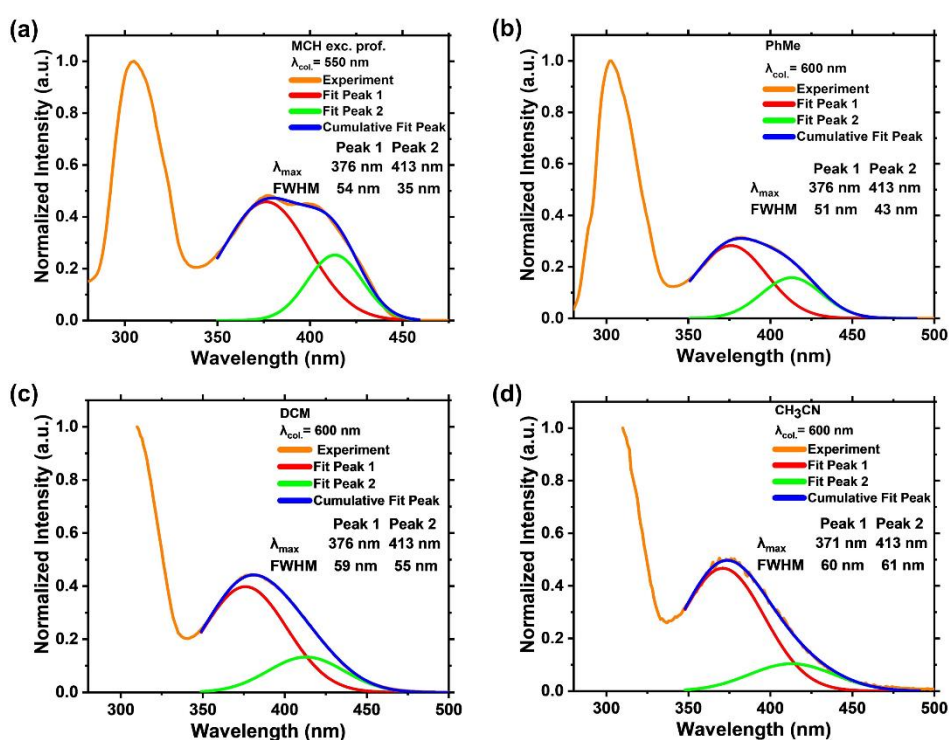


Figure 7.2. Deconvoluted excitation spectra of 20 μM DMAC-TRZ solutions, at room temperature, in (a) MCH, (b) PhMe, (c) DCM and (d) CH₃CN solvent. Red Ab1 band and green Ab2 band.

Similar behaviour is observed using a zeonex polymer matrix as a host (**Figure 7.3**). Due to the steric hindrance from the solid-state matrix, conformational relaxation (or interconversion) is prevented to a much higher degree, in contrast to the solvent environments. Consequently, the Em1 band is more intense (**Figure 7.3b, c**), compared to solution-state, and provides better-resolved excitation spectra upon collections between 390–420 nm (**Figure 7.3a**). From the excitation spectra, two isosbestic points are observed, one at 325 nm and another at 390 nm,

which suggest the presence of two distinct species. It is important to reiterate that the contribution of the local D and A units (below 325 nm) to the excitation spectra is minimal when collecting at a wavelength where only the Em1 exists.

Low-temperature steady-state measurements of the same film show that the increased hindrance introduced by freezing the environment enhances the relative contribution of the Em1 band (**Figure 7.3f**). From excitation spectra, a decrease in relative intensity of the Ab2 band and a better resolved Ab1 band can be observed (**Figure 7.3h**), while the Stokes shift between Ab1 and Em1 is very small (**Figure 7.3g**). The Em2 band is more structured when compared to room temperature and appears better resolved upon direct excitation of the Ab2 band only (**Figure 7.3i**, green curve). The broader, with higher onset energy, PL spectrum of the Em2 band at 80 K presumably occurs due to the suppression of the dielectric effect of the host, even for zeonex which has a low dielectric constant, which makes the excited state have a stronger local character compared to room temperature. Here it is important to mention that the phosphorescence contribution to the total DMAC-TRZ emission, even at low temperatures, is minimal as shown in chapter 4.²

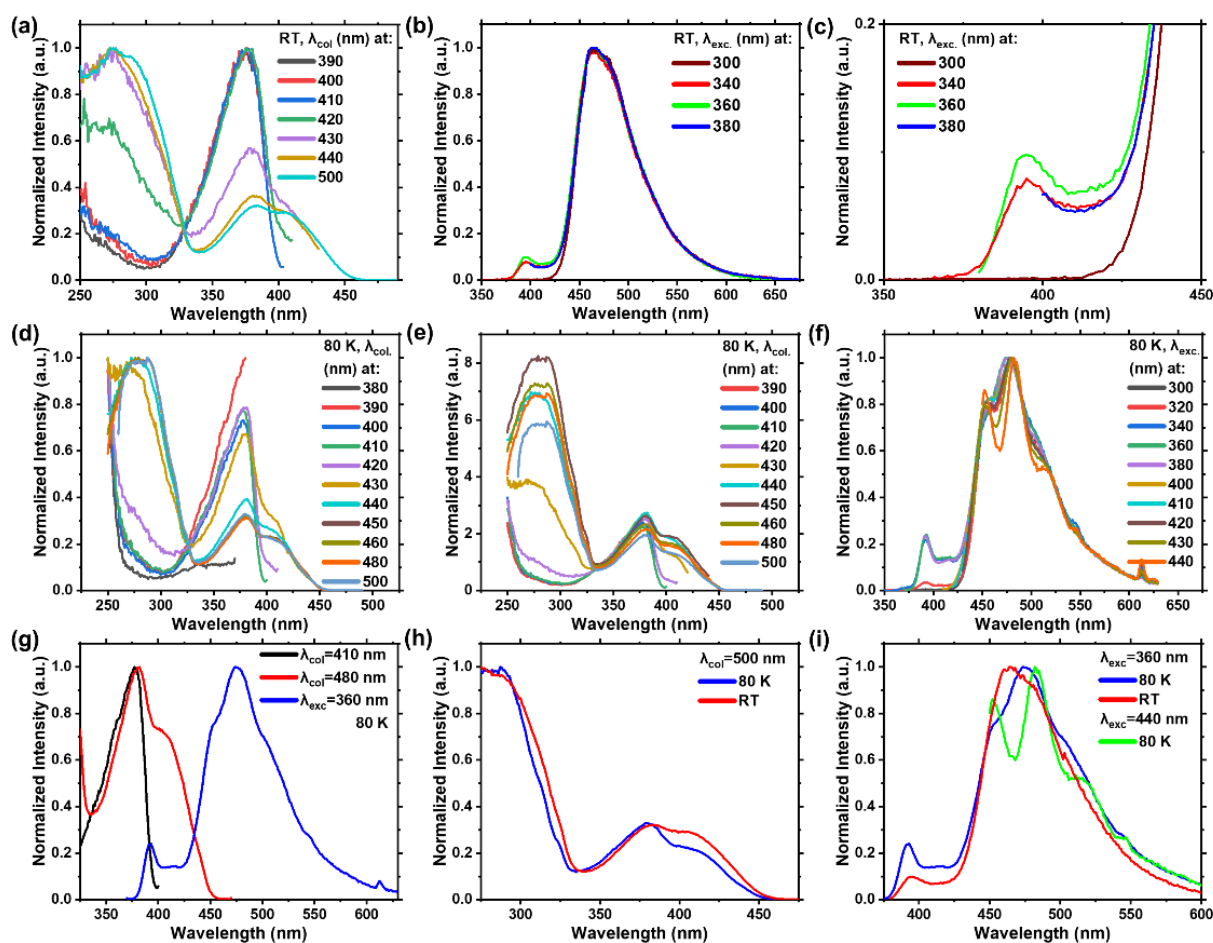


Figure 7.3. Steady-state photophysics of 1 wt% DMAC-TRZ in zeonex host. (a) Excitation and (b), (c) PL spectra at different collection and excitation wavelengths, respectively, at room temperature. (d) Normalized, (e) area normalized excitation, and (f) PL spectra at different collection and excitation wavelengths, respectively, at 80 K. (g) Excitation and PL spectra of the two conformers at 80 K. (h) Excitation and (d) PL spectra at room temperature (red) and 80 K (blue). The green PL spectrum was obtained by exciting the Ab2, at 80 K.

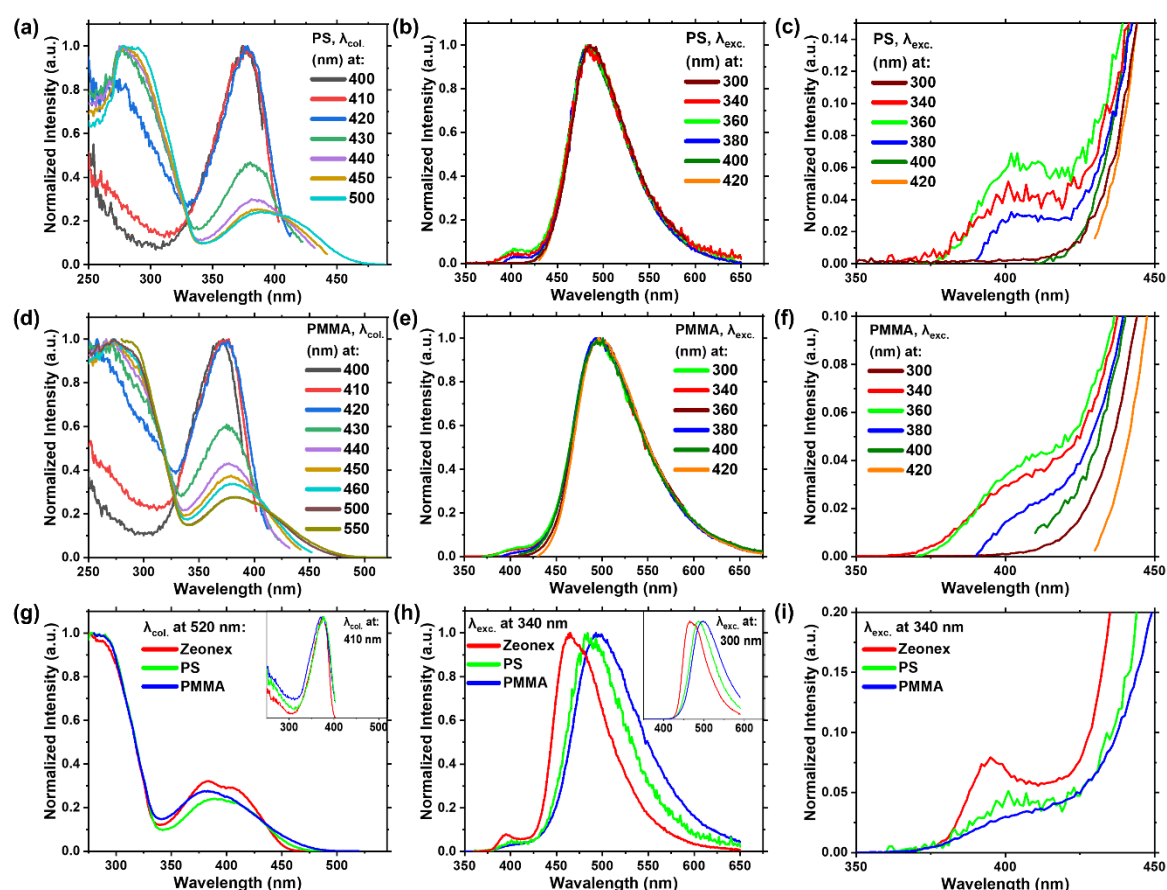


Figure 7.4. Steady-state photophysics of 1 wt% DMAC-TRZ in different polymer hosts, at room temperature. (a) Excitation and (b), (c) PL spectra in PS host using different collection and excitation wavelengths, respectively. (d) Excitation and (e), (f) PL spectra in PMMA host using different collection and excitation wavelengths, respectively. (g) Excitation and (h), (i) PL spectra comparison in different hosts. Inset of (g) collecting at the Em1 band (λ_{col} . At 410 nm), and (h) exciting the local donor and observing only the Em2 band.

Using two polymer hosts with stronger ground state dipole moment (*i.e.* enhanced relative polarity) a bathochromic shift was observed in the Ab2 and Em2 band, in excitation and emission spectra respectively (**Figure 7.4**). In both PS and PMMA hosts, the Ab1 band was

well resolved, collecting at wavelengths below 430 nm (**Figure 7.4a, d**), and similar to the one in zeonex. The Em1 band appeared less structured and reduced in relative intensity (to the EM2 band), in both hosts (**Figure 7.4c, f**). In PS, the Em1 band intensity appeared reduced by a factor of two while in PMMA by a factor of almost three (**Figure 7.4i**) compared to in zeonex. The onset of the Em1 band was the same in all cases while the peak wavelength had a small bathochromic shift. This indicates that the Em1 excited state of the first conformer has a mixed (LE & CT), but stronger LE, character compared to the Em2 excited state of the second conformer which has a pure CT character. Again, upon excitation at wavelengths below 310 nm the Em1 was not observed (**Figure 7.4h**). By collecting at the Em1 emission band, the excitation spectra are identical in all hosts (**Figure 7.4g**). The latter is in good agreement with the solution results, see above.

Small molecule hosts were also studied, and the two bands were again observed in various hosts (**Figure 7.5**). Unfortunately, the most common carbazole-based hosts, often used in OLEDs could not be used as most of them emit in the same region as the higher energy conformer (Em1), such as the case of BCPO (**Figure 7.5c**). The 1 wt% DMAC-TRZ in UGH-3 spectrum is similar to the one in zeonex, with a small increase in the relative intensity due to possible extra steric hindrance from this small molecule host (**Figure 7.5b**). In DPEPO, a much smaller contribution from the Em1 band was observed. Finally, the neat DMAC-TRZ film hasn't shown any contribution from the Em1 band, most probably because the intermolecular distance between the two conformers is minimal, leading to more efficient FRET.

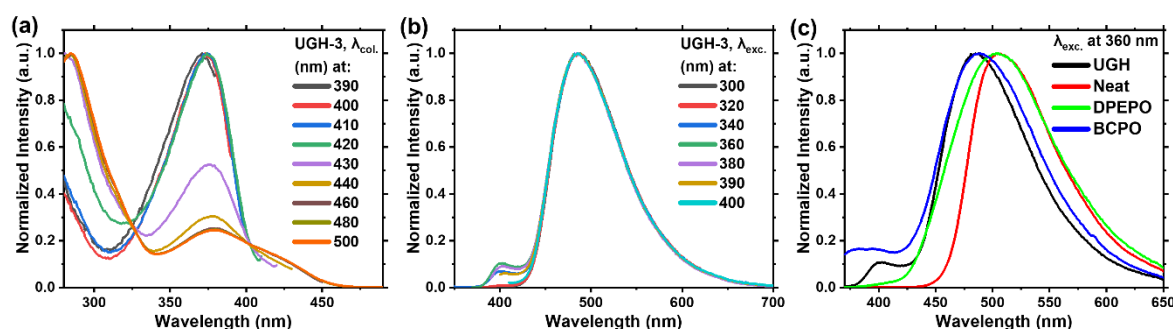


Figure 7.5. Steady-state photophysics of 1 wt% DMAC-TRZ in different small molecule hosts, at room temperature. (a) Excitation and (b) PL spectra in UGH-3 host using different collection and excitation wavelengths, respectively. (c) Comparison of DMAC-TRZ PL spectrum in different hosts and neat film.

7.4.2 Calculations

Quantum chemical calculations were used to understand the nature of the conformers. Two stable conformers of DMAC-TRZ, a QE conformer with planar DMAC donor and TRZ acceptor moieties arranged perpendicular to one another (**Figure 7.6c**) and a QA conformer in which DMAC adopts a kinked structure tilted by about 40° with respect to the TRZ plane (**Figure 7.6d**). In MCH solution, the QE conformer is favoured over the QA conformer by 0.19 eV including zero-point vibrational energy (ZPVE) corrections and hence represents the majority component. Combined density functional theory and multi-reference configuration interaction (DFT/MRCI) calculations yield vertical excitation energies of 3.06 eV (405 nm, Ab2) and 3.35 eV (371 nm, Ab1) for the S_1 states of the QE and QA conformers, respectively which compare favourably with the experimentally observed band maxima in this solvent (**Figure 7.1b**). However, while the $S_1 \leftarrow S_0$ transition of the QA minority conformer is characterised by a mixed CT/LE excitation with high oscillator strength, the $S_1 \leftarrow S_0$ CT transition of the C_{2v} -symmetric QE conformer is electric dipole forbidden in Franck–Condon (FC) approximation. Coupling between the electronic degrees of freedom and torsional vibrations about the molecular axis lends intensity to this CT transition which therefore becomes weakly allowed in Herzberg–Teller (HT) approximation and for ensemble averages. That both peaks were observed with nearly equal intensity in the excitation spectrum is thus a consequence of the small concentration of the optically very bright QA conformer in MCH solution on the one hand and the necessity to vibronically enhance the electric dipole-forbidden transition of the QE majority conformer on the other hand. Examination of the experimentally measured QE absorption band (Ab2) in MCH reveals a weak vibrational structure arising from the vibronic coupling to the electronic transition (**Figure 7.6a**). The estimated vibronic energy spacing of this HT transition is 1170 cm^{-1} indicative of a coupled C-N band stretch,²² most likely the C-N bridging bond between D and A. Even small changes in this bond length and torsion will radically change the radiative coupling, highlighting the sensitivity and important role of the C-N donor acceptor bridging bond plays in these TADF materials.

With regard to the photophysics of the QE conformer, the presence of a $T_{LE(TRZ)}$ state in energetic proximity of the lowest-lying S_{CT} and T_{CT} states is noteworthy as it can mediate their ISC and rISC processes and lead to efficient TADF (**Figure 7.6a**).^{23,24} For the QA conformer, two triplet states were found to lie below the S_1 state and a third one lies slightly above the S_1 state in the FC region (**Figure 7.6b**). The substantial energy gap between the S_1 and T_1 states,

caused by the local $\pi\pi^*$ contributions to their wavefunctions, rules out TADF for this conformer. A detailed computational study investigating the role of the higher-lying triplet states in the photophysical deactivation pathways of both conformers is currently under way by Prof. Christel Marian's group.

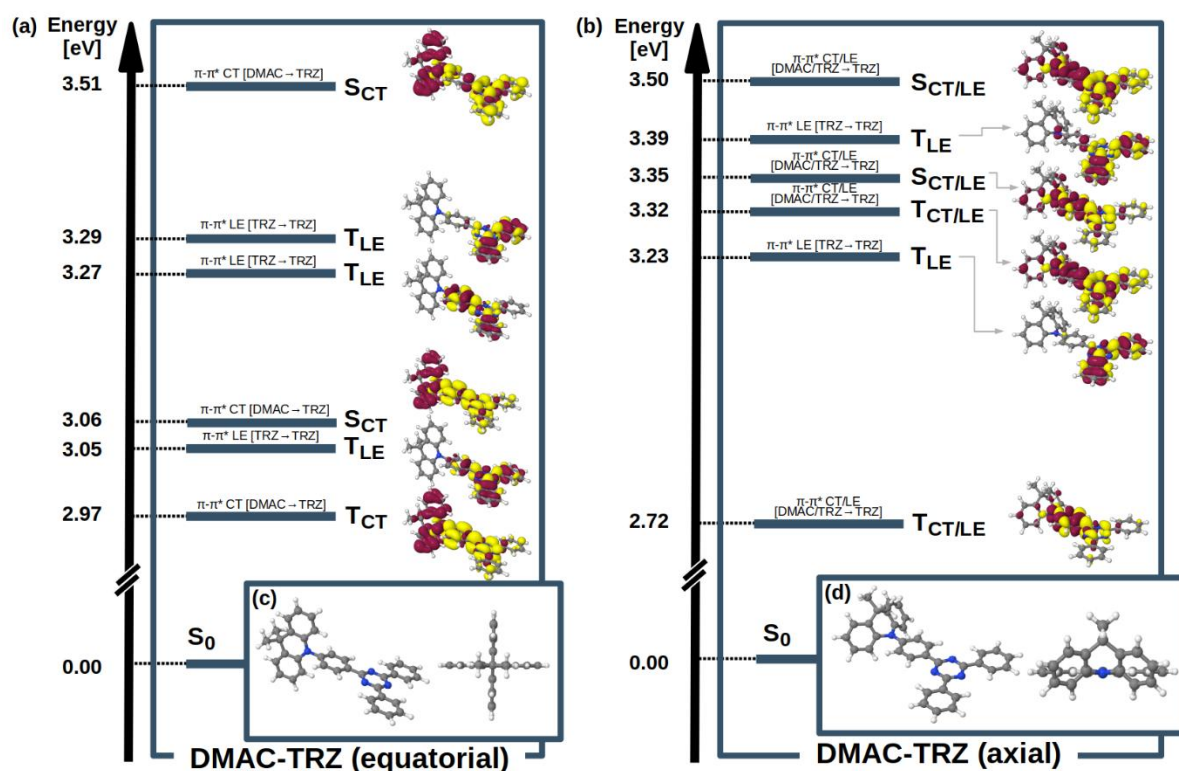


Figure 7.6. Calculated vertical DFT/MRCI excitation energies and state characteristics of the (a) QE and (b) QA conformers of DMAC-TRZ at the respective ground-state geometry in methylcyclohexane solution. The QE conformer is favoured over the QA conformer by 0.19 eV including ZPVE corrections. A loss of electron density w.r.t. the electronic ground state is indicated in red, a gain in yellow. Geometric structures of the (c) quasi-equatorial and (d) quasi-axial conformers of DMAC-TRZ in the electronic ground state.

The oscillator strength (f) of the two conformers in MCH was calculated to be 0.00006 for the QE conformer and 1.09379 for the QA conformer. The big difference can be explained by the strong local character of the QA conformer, compared to the CT character of the QE conformer. The population of both conformers in MCH can be approximately estimated from the ratio of the absorbance to the oscillator strength for the two individual conformers. This results to an approximate ratio of 1000:1 population of QE to QA conformers, in MCH solution. This estimated population is completely dependent on the theoretically estimated transition

oscillator strengths. Rama *et al*,¹⁶ previously reported the phosphorescence and excitation spectrum of DMAC-TRZ in a frozen solution. From the excitation spectrum results, which are now understood to include both QA and QE contributions, the QA population appears to be much larger in frozen solution, compared to our estimate from room temperature solution. This makes sense, as the interconversion of the QA to QE conformer requires cooperative motion of the molecule, which must be hindered because of the frozen conditions, slowing down the interconversion and potentially giving a higher QA population. In solid-state, and more specifically in evaporated films, where the solvent is not present, and the conformation entropy of the system will be different, the population of the QA conformer is expected to be much higher. Further, the QA conformer contribution in the PL spectrum is expected to be much higher due to matrix hindering possible interconversion between the two conformers, something that is possible in solution environments, especially with the presence of excess energy in the system. The latter is verified by the absence of the QA emission, in MCH solution, when exciting at wavelengths below 300 nm (**Figure 4h**, inset).

7.4.3 Conformer Photophysics

At very low emitter concentrations (0.01 wt%) in zeonex the maximum PL intensity of the QA conformer band (Em1) is comparable with that of the QE band (Em2) (**Figure 7.7**). This observation can clearly be reconciled with low FRET due to the higher spatial separation between the individual molecules. With increasing concentration, the QA PL band decreases considerably in relative intensity monotonically (**Figure 7.7c-e**). Also, the high ground state dipole moment of DMAC-TRZ molecules, compared to the host, potentially change the ground state of the environment at higher concentrations (intermolecular interactions) and the QE absorption/emission stabilises to a lower energy. Further, at higher concentrations there will be a higher probability for excitons to reach lower energy states on average because exciton hopping is more efficient, leading to higher QE PL peak shift.

From **Figure 7.7a** spectra, the mixed CT/LE character of both bands is clear, especially in zeonex host, because of their structured PL emission. With increasing host dipole moment, both bands lose their structured shape and shift towards longer wavelengths. The QA band showed a small bathochromic shift of 115 meV, going from 395 nm in zeonex to 410 nm in PMMA, which could occur due to increasing overlap with the QE absorption band. The QE band shifted by 247 meV, going from 448 nm in zeonex to 490 nm in PMMA (**Figure 7.7b**). This indicates that the QA and QE conformers have stronger LE and CT character, respectively.

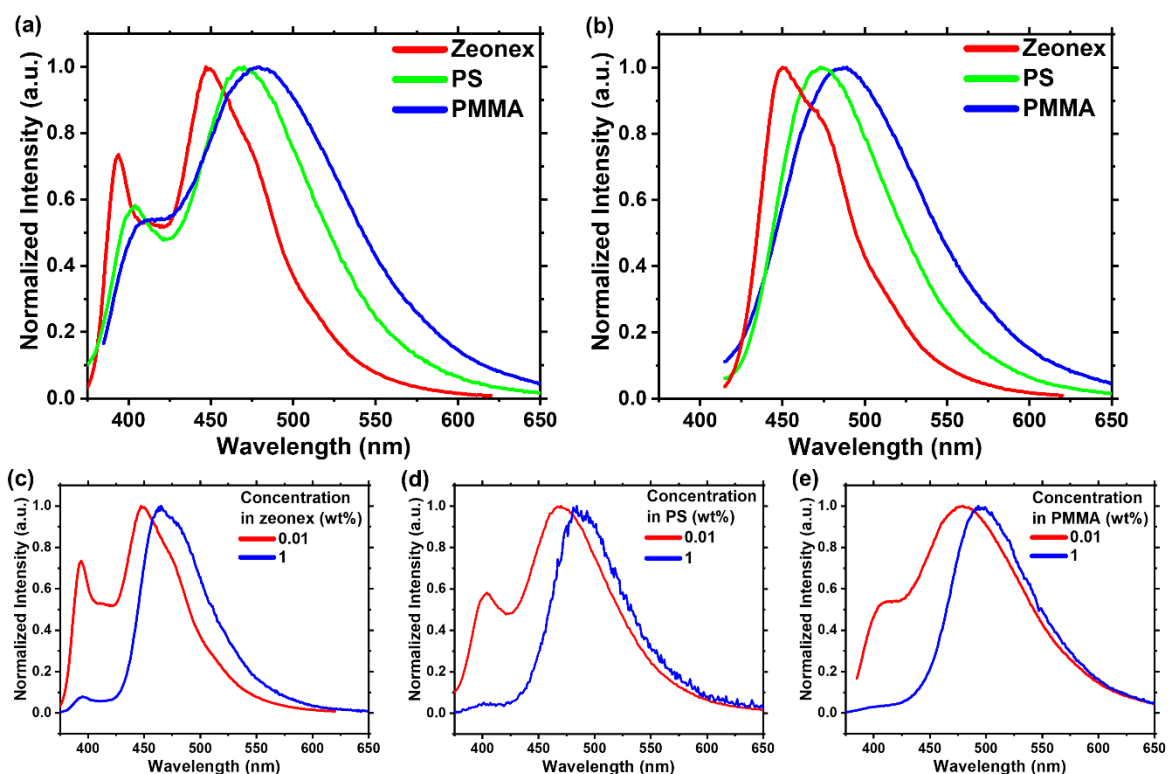


Figure 7.7. Steady-state PL of DMAC-TRZ in different polymer hosts, at room temperature. (a), (b) at 0.01 wt% concentration and (c)-(e) comparison between 1 and 0.01 wt% concentration, in each polymer host.

Temperature dependent steady state spectra of 0.01 wt% DMAC-TRZ in zeonex are shown in **Figure 7.8**. Upon exciting both conformers (at 360 nm), structured emission was observed from both, at room temperature. This indicates that aggregation formation at higher concentrations potentially enhances the dielectric of the system leading to a broader emission compared to the well dispersed DMAC-TRZ molecules at 0.01 wt% concentration, which exhibit a stronger local character. Lowering the temperature, the QA emission (395 nm) increases in relative intensity indicating that a possible conformational interconversion of the QA to the QE conformation was hindered because of the frozen matrix and low temperature (**Figure 7.8a**). The QE emission was also affected by the temperature, becoming more structured and the spectral band maxima changing from the 0-0 transition to the 0-1 transition. This effect was also observed with direct excitation ($\lambda_{\text{exc}} > 400$ nm) of the QE CT (**Figure 7.8b**) and is attributed to hindering the torsional motions because of the frozen environment, leading to better resolved spectra, with stronger local character at low concentrations. Further, in all PL spectra, a weak emission band around 500 nm was observed which increases in relative intensity with decreasing temperature. To understand the origin of this band, excitation

spectra at different collection wavelengths are shown in **Figure 7.8e-h**. When collecting below 500 nm the excitation behaviour was similar to the 1 wt% DMAC-TRZ in zeonex (**Figure 7.3a**). Collecting above 500 nm, a further weak excitation band was observed between 450-500 nm (**Figure 7.8g, h**). This new band didn't appear in solution or at higher concentrations in solid state measurements and had the same structure at all temperatures. Thus, it can only be assumed that originates from a dimer species that can be formed in solid-state, even at very low concentrations, and is only observed in low ground state dipole moment environments. It cannot be observed at higher concentrations or higher dielectric media because it overlaps with the redshifted CT emission. Nevertheless, the contribution of this species at room temperature can be considered minimal.

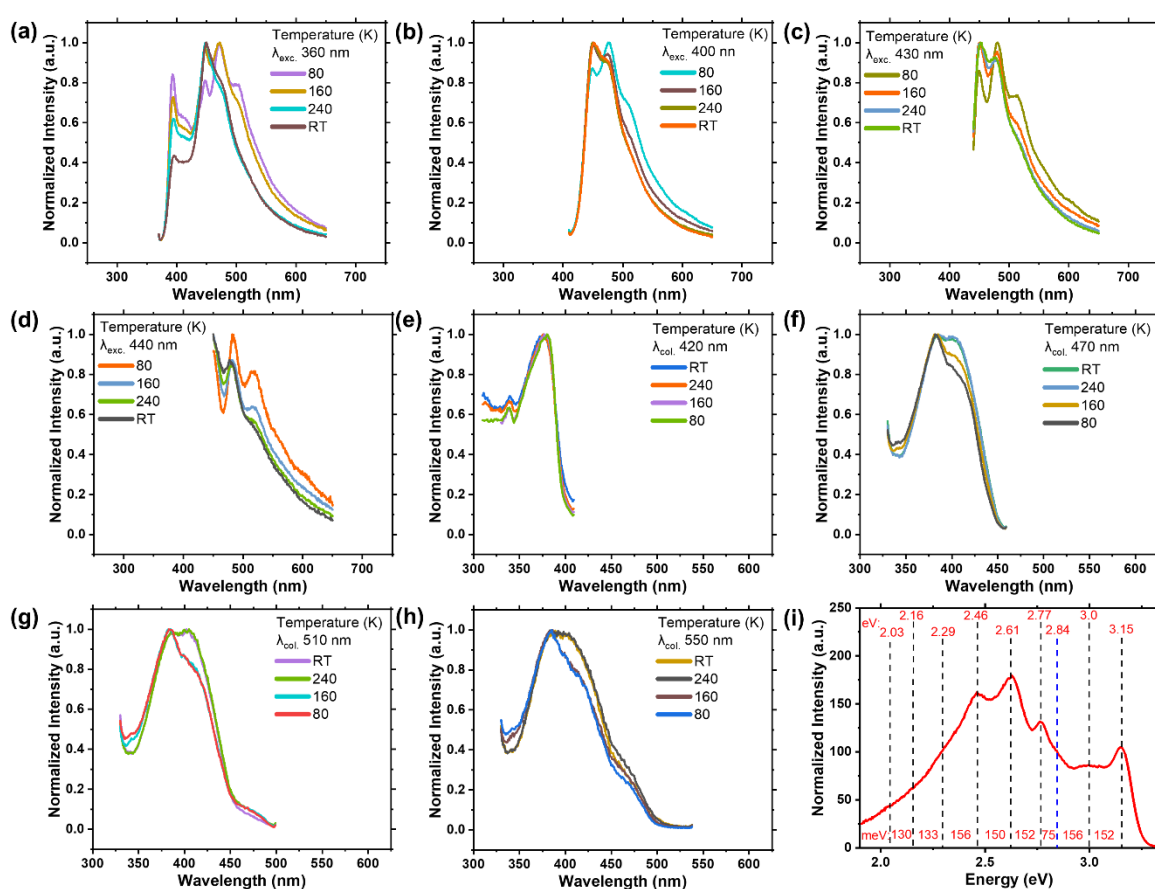


Figure 7.8. Steady-state photophysics of 0.01 wt% DMAC-TRZ in zeonex hosts. PL spectra at different temperatures with λ_{exc} at (a) 360, (b) 400, (c) 430, and (d) 400 nm. Excitation spectra at different temperatures with λ_{col} at (a) 420, (b) 470, (c) 510, and (d) 550 nm. (i) Jacobian conversion of PL spectrum at 80 K, λ_{exc} at 360 nm.

Using the Jacobian transform converted PL spectrum (wavelength to eV, see subsection 3.7.5), of the 0.01 wt% DMAC-TRZ in zeonex at 80 K, three distinct emission bands were identified (**Figure 7.8i**). Three regions with constant vibronic intervals were found; at high energy the QA conformer appears to have at least three observable vibronic contributions of 152 meV between 3.15 and 2.84 eV. After a short gap of 75 meV, the QE conformer PL was observed between 2.77 and 2.29 eV, again with 152 meV vibronic spacing. The third region below 2.29 eV has a narrower spacing of 130 meV, assigned to aggregated emission.

The steady state behaviour of 0.01 wt% DMAC-TRZ in different polymer hosts is shown in **Figure 7.9**. An energy relaxation effect was observed upon excitation at 360 nm, which became less pronounced at lower temperatures for both the QA and QE conformers (**Figure 7.9a-c**). The vibronic structure of the QE emission appears to be less defined in polystyrene and even less in PMMA. Exciting at 430 nm (mainly the QE conformer), the energy relaxation effect is clearer at room temperature, compared to 360 nm excitation, and reduces at lower temperatures (**Figure 7.9d-f**). The latter could indicate that at low temperatures the possible side group motions of the polymer chain are reduced, reducing the slow reorganizational effects that can lead to the relaxation of the CT energy.¹ At 0.01 wt% loading, this cannot be an effect of energy migration to low energy sites in the density-of-states (DOS). From the excitation spectra, the very weak red dimer band ($\lambda = 475$ nm) observed in zeonex cannot be observed (**Figure 7.9g-i**), for reasons explained in the previous paragraph.

Time-resolved spectra from 0.01wt% DMAC-TRZ in zeonex, at various temperatures are shown in **Figure 7.10a**. At early time (0.5 ns time delay) and all temperatures, the emission maximum (395 nm) comes mainly from the QA conformer, because of the faster radiative rate of this excited state which has strong local character. The contribution of the QE CT band was observed at 450 nm and appears to decrease in intensity with decreasing temperature, relative to the QA band. This verifies that the frozen matrix hinders the molecular relaxation of the QA to the QE conformation, resulting in a higher QA population, and thus stronger emission from the QA conformer at early times (<10 ns) (**Figure 7.10a**). At later prompt fluorescence (PF) times, the emission comes from the QE conformer and becomes more structured with decreasing temperature, indicating that under specific conditions a CT state can have vibronic character (note that the band does not blue shift at all with temperature).²⁵ At μ s times, only the room temperature measurement showed emission which comes from the QE CT band. In ms time delays, the emission mainly comes from the phosphorescence with an energy onset of

2.75 eV (450 nm). At RT a small contribution of DF was observed which decreases in contribution with decreasing temperature (small band below 450 nm, **Figure 7.10a**). The PF emission area normalised spectra (**Figure 7.11a**) clearly show the presence of two species (QA and QE conformer), with an iso-emissive point at 430 nm. A second iso-emissive point at 530 nm is only obvious at lower temperatures (**Figure 7.11b**). This is assigned to the aggregated species, as stated above.

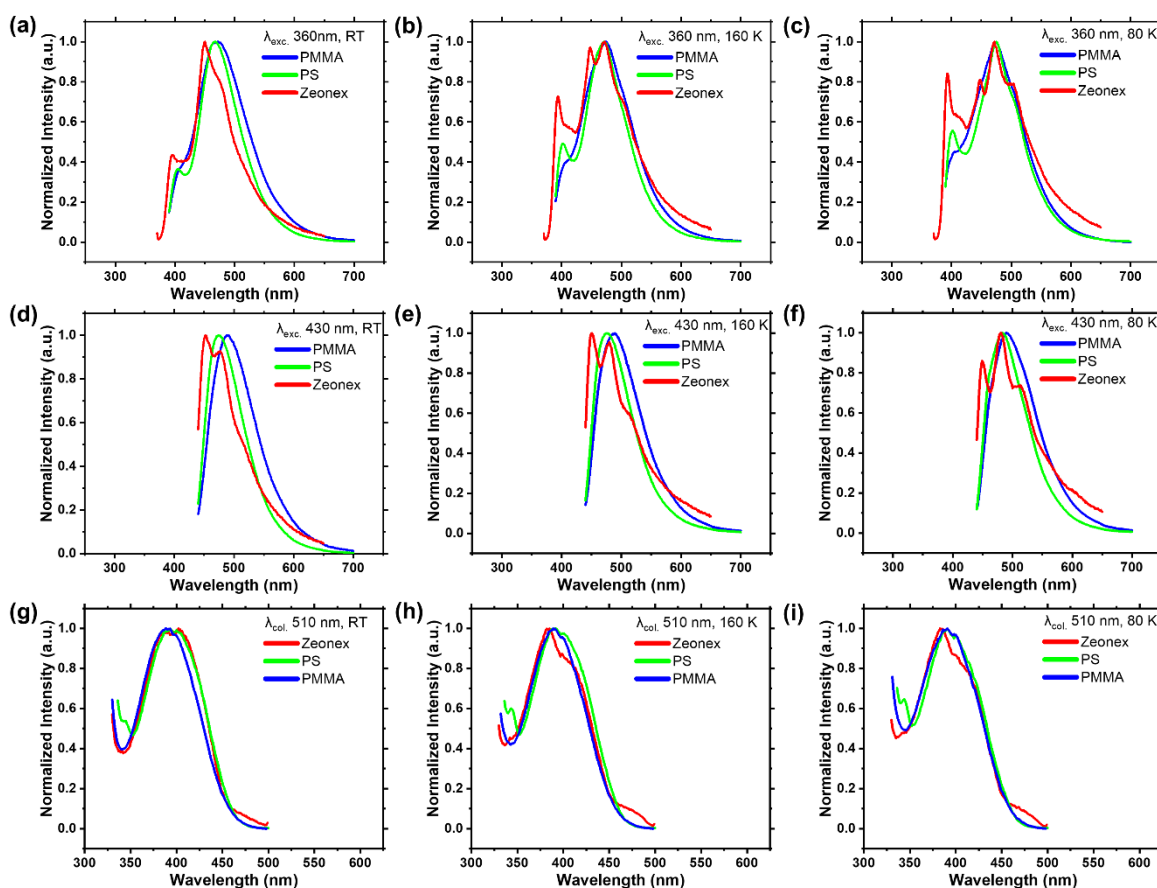


Figure 7.9. Steady-state photophysics of 0.01 wt% DMAC-TRZ in different polymer hosts. PL spectra at λ_{exc} . 360 nm, at (a) RT, (b) 160 K, and (c) 80 K. PL spectra at λ_{exc} . 430 nm, at (d) RT, (e) 160 K, and (f) 80 K. Excitation spectra at λ_{col} . 510 nm at (g) RT, (h) 160 K, and (i) 80 K.

The effect of temperature on the time-resolved spectra of 0.01 wt% DMAC-TRZ in polystyrene and PMMA hosts are shown in **Figure 7.10b, c**. In both cases a strong contribution from the QA conformer is observed in early times. Here, it is worth mentioning that polystyrene and PMMA themselves emit around 380nm, when excited at 355 nm (**Figure 7.11g, h**), but the PL contribution from the first host is minor compared to the second. As a result, the PMMA spectra

had a strong PL contribution from the host itself (along with the QA emission) compared to the other two hosts. At the later PF regime ($t > 10\text{ ns}$) both films showed dual emission, the main band coming from the QE conformer and the high energy band ($\sim 400\text{ nm}$) from the host (Figure 7.11c-f). In all three hosts, a high energy iso-emissive point is observed in the area normalised spectra, between QA and QE emission.

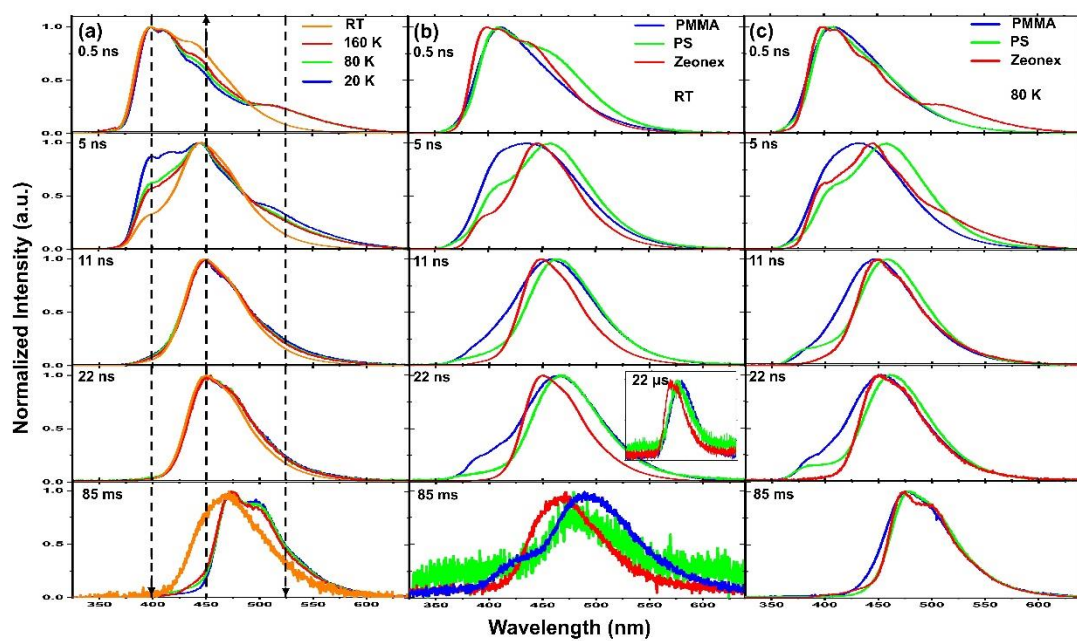


Figure 7.10. Time-resolved spectra of 0.01 wt% DMAC-TRZ in different polymer hosts. (a) In zeonex host at different temperatures and time delays. In three polymer hosts at different time delays at (b) room temperature (Inset: DF spectra) and (c) 80 K. Excitation wavelength 355 nm.

Comparing all three hosts, at RT, one can see the large contribution from the QA conformer at early times, pumping the QE conformer which dominates after 10 ns and continues into the DF regime (Figure 7.10b). The QE TADF emission is clear at 22 μs as shown in the inset of Figure 7.10b. At 85 ms delay time, DF was still observed in all hosts with PMMA having a high energy band which appears similar to the PMMA emission. The phosphorescence spectra are similar in all cases, with an energy onset of 2.75 eV, being in good agreement with the results in chapter 4.² PMMA film exhibited slightly higher phosphorescence energy onset which is practically TADF contribution, even at 80 K, because of the smaller ΔE_{ST} compared to the other polymer hosts (Figure 7.10c).

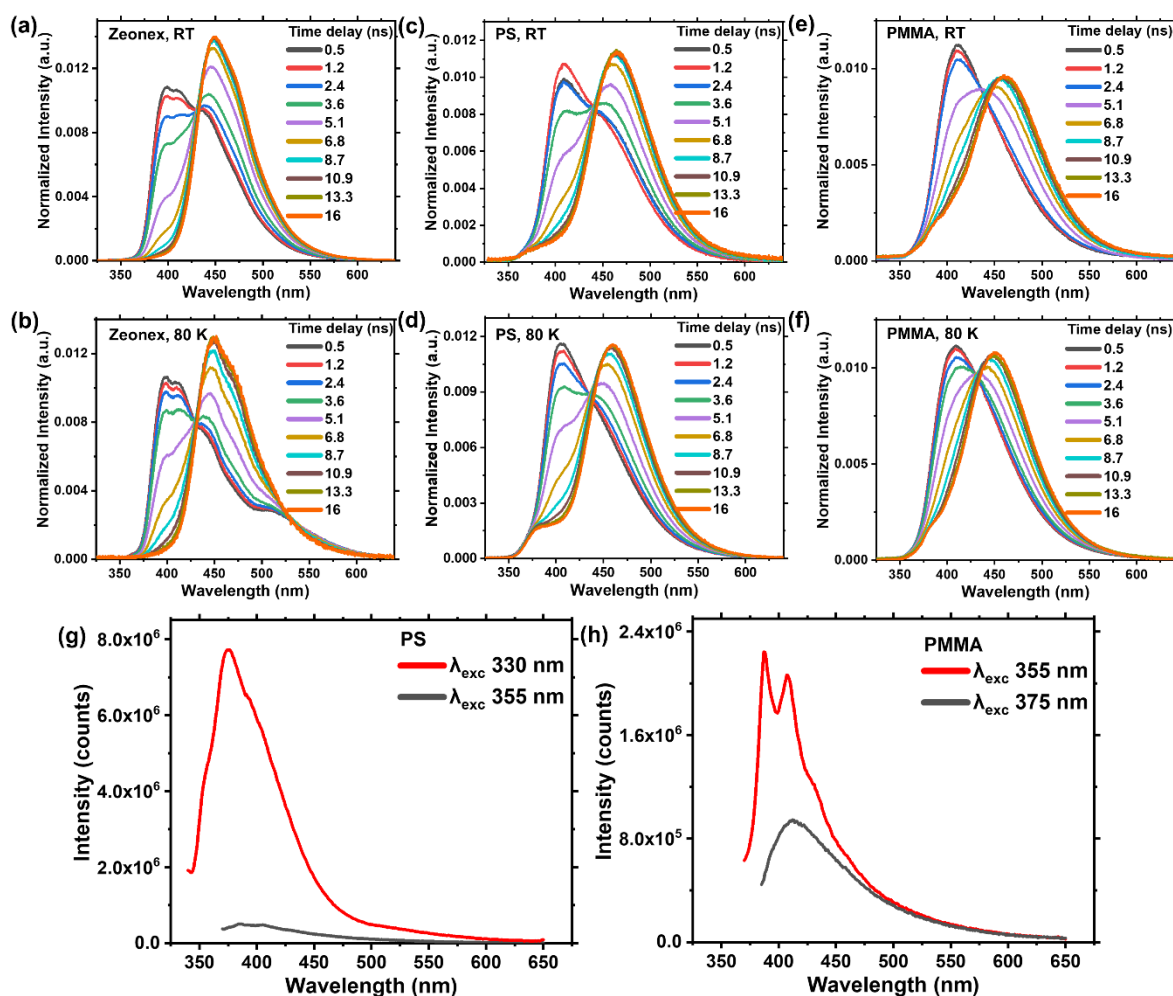


Figure 7.11. Prompt fluorescence time-resolved spectra of 0.01 wt% DMAC-TRZ in different polymer hosts. In zeonex host at (a) RT and (b) 80 K. In PS host at (c) RT and (d) 80 K. In PMMA host at (e) RT and (f) 80 K. Excitation wavelength 355 nm. PL spectrum of (g) PS and (h) PMMA neat films at different excitation wavelengths.

Further analysis of the effect of the two conformers on the overall photophysics was made using time-resolved emission decays, shown in **Figure 7.12**. Zeonex host was chosen as a neutral environment. Upon excitation of mainly the QA conformer, at 375 nm, and collecting at 395 nm, where the QA conformer emits (**Figure 7.12a**), a dominant very fast component with lifetime less than 1.15 ns was found, contribution from 86% (at 0.01 wt%) to 99% (at 1 wt%) (**Figure 7.12b, d-f**). This lifetime is assigned to the singlet lifetime of the QA conformer quenched by energy transfer to molecules in the QE conformation. This lifetime decreases with increasing concentration, as expected from a FRET related process. The unquenched PF lifetime of (isolated) QA conformers is 7.1 ± 0.2 ns with a population that decreases with increasing concentration. A third component appeared at 0.1 wt% DMAC-TRZ loading, having

the same lifetime as the QE PF component (**Figure 7.12d-i**). The latter indicates that even though the emission of the QE state at 395 nm should be minimal, as the FRET efficiency increases less unquenched QA emission occurs and QE emission can be observed.

Collecting at 550 nm, mainly the QE conformer emission is monitored (**Figure 7.12c**). The lifetime behaviour appears to be similar with increasing concentration, with only a minor increase from 13 ns (0.01 wt%) to 16.9 ns (1 wt%) as the concentration increases due to possible stronger contribution from intermolecular (dimer) states (**Figure 7.12d-f**). Upon excitation at 405 nm, where the QE conformer mainly absorbs, the decay lifetime results were similar with the 375 nm excitation decays.

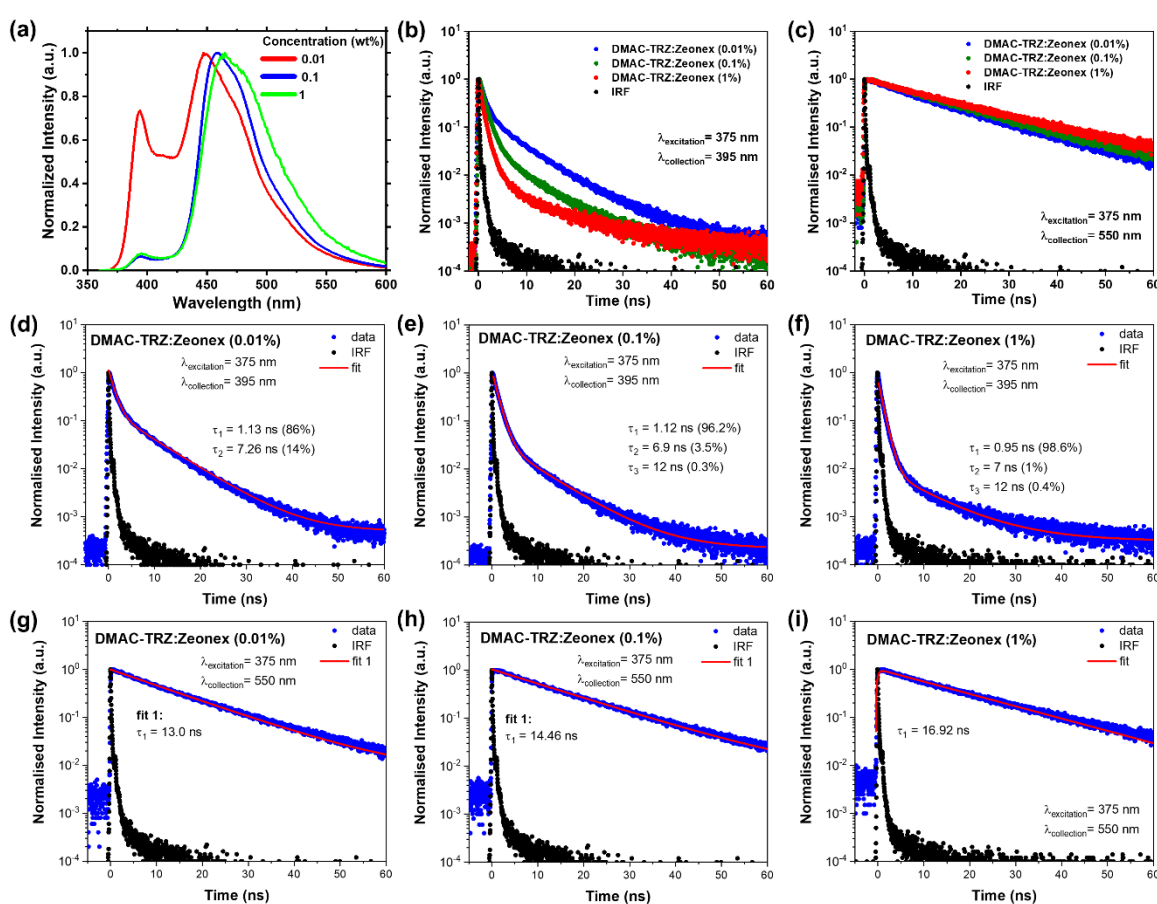


Figure 7.12. Photophysics of DMAC-TRZ in zeonex host, at different concentrations and room temperature. (a) Steady state PL. Time-resolved PL decays of the (b) ns and (c) μs regime. ns time-resolved PL decays of (d) 0.01, (e) 0.1, and (f) 1 wt% DMAC-TRZ concentration. μs time-resolved PL decays of (g) 0.01, (h) 0.1, and (i) 1 wt% DMAC-TRZ concentration. Fitted decay lifetimes shown in each plot.

A larger concentration series in zeonex, from 0.01 wt% up to 25 wt% DMAC-TRZ loading, was studied using time-resolved PL spectra, to highlight the effect of the QA conformer contribution (**Figure 7.13**). At 0.01 and 1 wt% DMAC-TRZ concentration the QA PL contribution is dominant at early times. With increasing concentration, the intermolecular separation decreases and the FRET efficiency increases resulting in a better energy transfer from the QA to the QE conformer. Because of the latter, at 25 wt% loading no QA contribution was observed. Increasing the emitter concentration also had an impact on the QE emission spectrum which appeared to redshift (**Figure 7.13**). The emission spectrum of this band though appears to be identical in 5, 10, and 25 wt%. The latter indicates that the ΔE_{ST} decreases with increasing concentration, up to a specific value (5 wt%), due to the change of the environment's dielectric, and then remains stable.² The small decrease in ΔE_{ST} appeared to have a disproportionate effect on the increase in DF contribution, especially for concentrations above 1 wt% (**Figure 7.13f**). This implies that other phenomena might have an impact on the DF contribution.

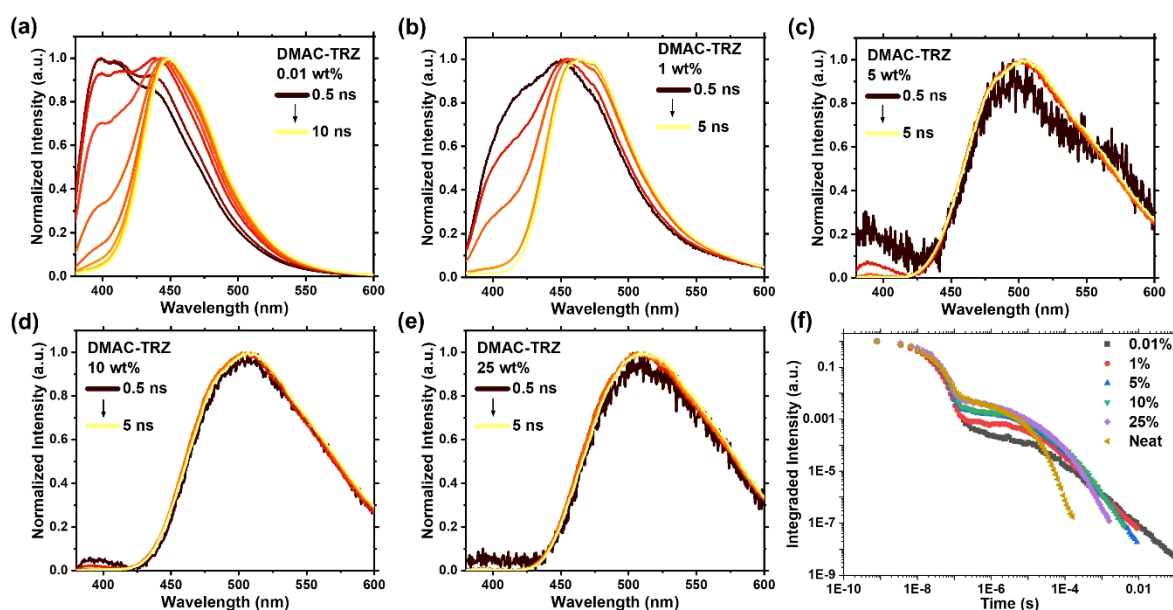


Figure 7.13. Time-resolved measurements of DMAC-TRZ in zeonex host, at different concentrations and room temperature. Prompt fluorescence time-resolved spectra at (a) 0.01, (b) 1, (c) 5, (d) 10, and (e) 25 wt% concentration. (f) Time-resolved decays. Excitation wavelength 355 nm.

Any potential DF contribution from the QA conformer was not observed because the DF time-resolved PL spectra, at all concentrations, have the QE conformer profile. This is because FRET is orders of magnitude faster than ISC causing most excited states to be transferred to

the QE ^1CT state, even at very low concentrations. Instead, DMAC-TRZ aggregate emission has already been observed in chapter 4, especially for concentrations above 10 wt%. From the neat film PLQY, it is clear that the aggregated state efficiency is high with a value of 75%, compared to nearly 100% at 10 wt% doped film in mCBPCN host (see chapter 4).² Also, the through space analogue of DMAC-TRZ, TpAT-tFFO,²⁶ that has among the best TADF performance, is basically an exciplex of controlled D-A distance. Thus, the enhanced DF contribution potentially comes from a faster intermolecular krISC and not a change of the environment's dielectric (because of the increasing concentration of the dopant), at least not at concentrations above 5 wt%. Nevertheless, despite the improved krISC, the aggregated emission state has lower PLQY than DMAC-TRZ monomer due to enhanced non-radiative pathways.

In chapter 4, the DMAC-TRZ triplet energy value was reported to be at 2.75 eV (450 nm).² The triplet value of the individual donor and acceptor units have also been reported to have much higher values ($T_{D,A} > 3$ eV).¹⁶ In addition, TpAT-tFFO which is incapable of having a QA conformer, has been reported to have a ^3CT character lowest triplet state,²⁷ and its value depends on the distance between the D-A units. This experimentally has been difficult to prove and the lowest lying triplet energy was calculated to be above 3 eV.²⁶ All the above imply that the 'low' triplet value observed in DMAC-TRZ could either be due to the state being of ^3CT or of mixed $^3(\text{CT}/\text{LE})$ character. As a mixed $^3(\text{CT}/\text{LE})$ state is easier to observe because the oscillator strength increases dramatically, this is what was potentially observed in DMAC-TRZ and this then explains the structured phosphorescence emission observed in DMAC-TRZ, in specific environments (**Figure 7.14**).

Further, in chapter 4 the triplet energy of DMAC-TRZ was showed to be temperature dependent. At 20 K, the phosphorescence spectrum was blue shifted compared to that at 80 K, observed in all hosts and neat film, except zeonex where the phosphorescence spectrum was identical at both temperatures (**Figure 7.14a**). At 80 K, in mCPCN and mCBPCN hosts, where the triplet value of the host is only slightly higher than the triplet value of the DMAC-TRZ, a Gaussian shape emission spectrum appeared with a wavelength onset of 460 ± 1 nm in both cases, which is redshifted compared to the DMAC-TRZ:zeonex film at the same temperature (**Figure 7.14b, c**). Energetically, the phosphorescence spectrum is at the same position as the low temperature DF spectrum (coming from the QE CT state), which appears to contribute in the delayed regime, even at low temperatures (as low as 80 K), because of the efficient krISC.²

At 20 K, in both hosts, where the DAMC-TRZ TADF contribution is minimal based on the time-resolved spectra,² the phosphorescence spectrum was blue shifted and appeared identical to the phosphorescence spectrum measured in films of neat hosts (**Figure 7.14b, c**). This indicates that the host phosphorescence was dominant at 20 K, because both the host and the guest were directly excited ($\lambda_{\text{exc.}}$ at 355 nm), so at very low temperatures some host triplet states do not migrate to the guest sites at 1 wt% concentration, and can be observed because of their stronger oscillator strength compared to the DAMC-TRZ lowest lying triplet, which must have a strong ³CT character. Although the host triplet appears to be the lowest observable triplet state of the system, this cannot be the case in these guest-host systems (in mCBPCN and mCPCN) because DF emission from the QE ¹CT was observed at room temperature,² which means that the up-conversion involved QE ³CT does not get quenched by the triplet of the host. Therefore, the lowest energy triplet of DAMC-TRZ QE conformer must be below the ones of these two hosts (mCBPCN and mCPCN).

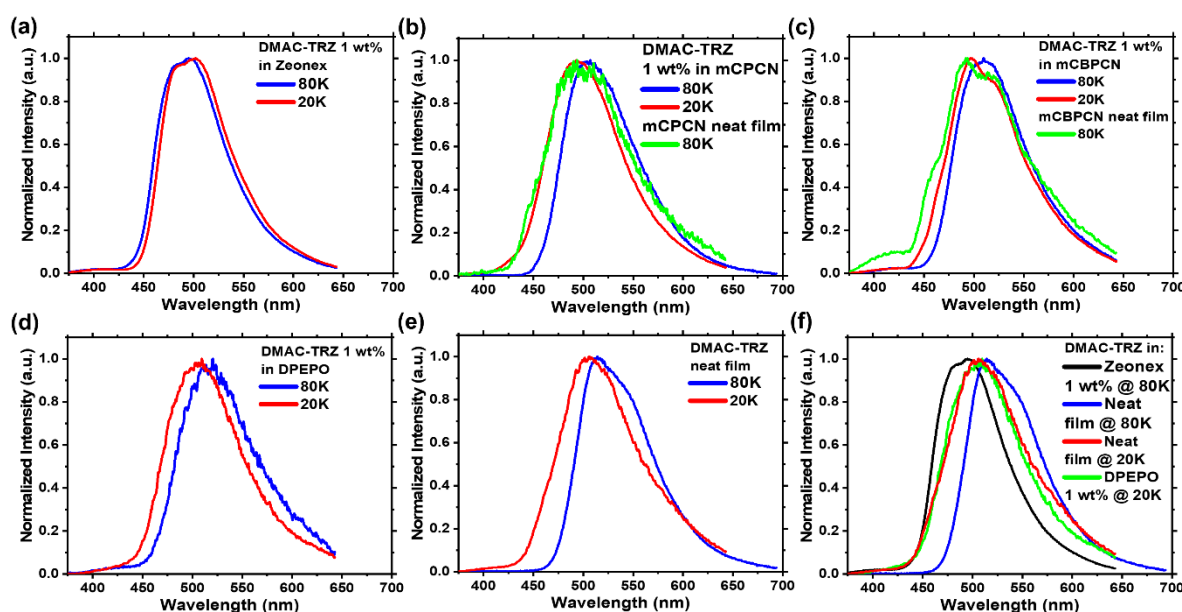


Figure 7.14. Phosphorescence spectra of 1 wt% DMAC-TRZ films in (a) zeonex, (b) mCPCN, (c) mCBPCN, (d) DPEPO host, and (e) neat film at 80 and 20 K. Comparison of DMAC-TRZ phosphorescence in different hosts and temperatures. Excitation wavelength 355 nm. Delay time 85 ms.

When the hosts lowest lying triplet energy is much higher compared to the guest, this effect does not occur. In DPEPO host ($T_1 \sim 3$ eV),²⁸ the 80K phosphorescence spectrum of 1 wt% DMAC-TRZ film appears similar to that observed in mCBPCN and mCPCN hosts (**Figure**

7.14d), another indication that DF is still observable at this temperature. At 20 K, a blue shift of the onset was observed towards 445 nm (from 460 nm), similar to the DMAC-TRZ:zeonex film, and far from the triplet value of DPEPO. In the absence of a host (*i.e.* neat film) a structured emission appeared at 80 K with an onset of 475 nm assigned to aggregated emission (**Figure 7.14e**). Lowering to 20 K, a second band appeared with the onset of the high energy band at 2.82 eV (440 nm), similar to what was observed in the high triplet energy hosts and in frozen solution¹⁶ (**Figure 7.14e**). This indicates that the two conformers have distinct lowest triplet states. The QE conformer has a strong CT character triplet state, which must be energetically slightly below the ¹CT but is difficult to observe in all environments because of its low oscillator strength. This explains why in mCPCN and mCBPCN the host phosphorescence was observed but no guest phosphorescence. Thus, the triplet value observed at 20 K, in DPEPO and zeonex films is attributed to the QA triplet value (not the QE triplet), which has a mixed CT/LE character and so is emissive enough to be observed. This is in good agreement with the calculations (**Figure 7.6**).

Conformational heterogeneity² is a parameter that could affect the determination, regarding the origin, of the triplet state discussed above. One is sensible to speculate that a molecule with a lower dihedral twist angle between the donor and acceptor units could be the source of this triplet energy. Chapter 4 and the following studies I was involved in,¹⁻³ showed that conformational heterogeneity is environment dependent. Thus, the population of the low twisted angle D-A molecules should decrease with increasing dielectric, and in high dielectric DPEPO host this population will be negligible, thus its phosphorescence would be difficult, if not impossible, to observe. Further, a QE ³CT with some local character should be easier to change with the environment dielectric, compared to a ³LE with some CT character (the case of the QA conformer). Thus, it is concluded that the lowest triplet observed in different environments, which is dielectric independent, could only be the triplet of the QA conformer.

Finally, a set of different acridine donor materials, with a modified tri-phenyl-triazine unit, synthesized by Prof. Eli Zysman-Colman's group, were explored to verify the findings of this chapter (**Figure 7.15a, b**). DMAC-py-TRZ has been reported to have a dual conformation,²⁹ while DMAC-tTRZ has a comparable molecular structure to DMAC-TRZ with a reduced conjugation length due to the phenyl substitution with tert-butyl groups. Because of the latter, DMAC-tTRZ has very similar absorption and PL spectra with DMAC-TRZ in zeonex host with a small hypsochromic shift (**Figure 7.15c, d**). The QA band is also blue shifted compared to

DMAC-TRZ QA conformer band, showing also a relatively higher contribution to the PL spectrum, potentially indicating a slightly higher QA population. DMAC-py-TRZ on the other hand, showed a much higher QA conformer population, as indicated by its dominant absorption (375 nm band) and PL (410 nm band) intensity. This population is so high that even at 1 wt% loading the QA band was not quenched by the QE conformer, also indicative from the small quenching of the QA prompt lifetime with increasing concentration (**Figure 7.15d**) compared to DMAC-TRZ and DMAC-tTRZ (**Figure 7.15e**). TpAT-tFFO, the through-space analogue of DMAC-TRZ, was also explored for comparison, showing only optical signs of one stable conformer (missing the high energy absorption and emission band, **Figure 7.15c, d**).

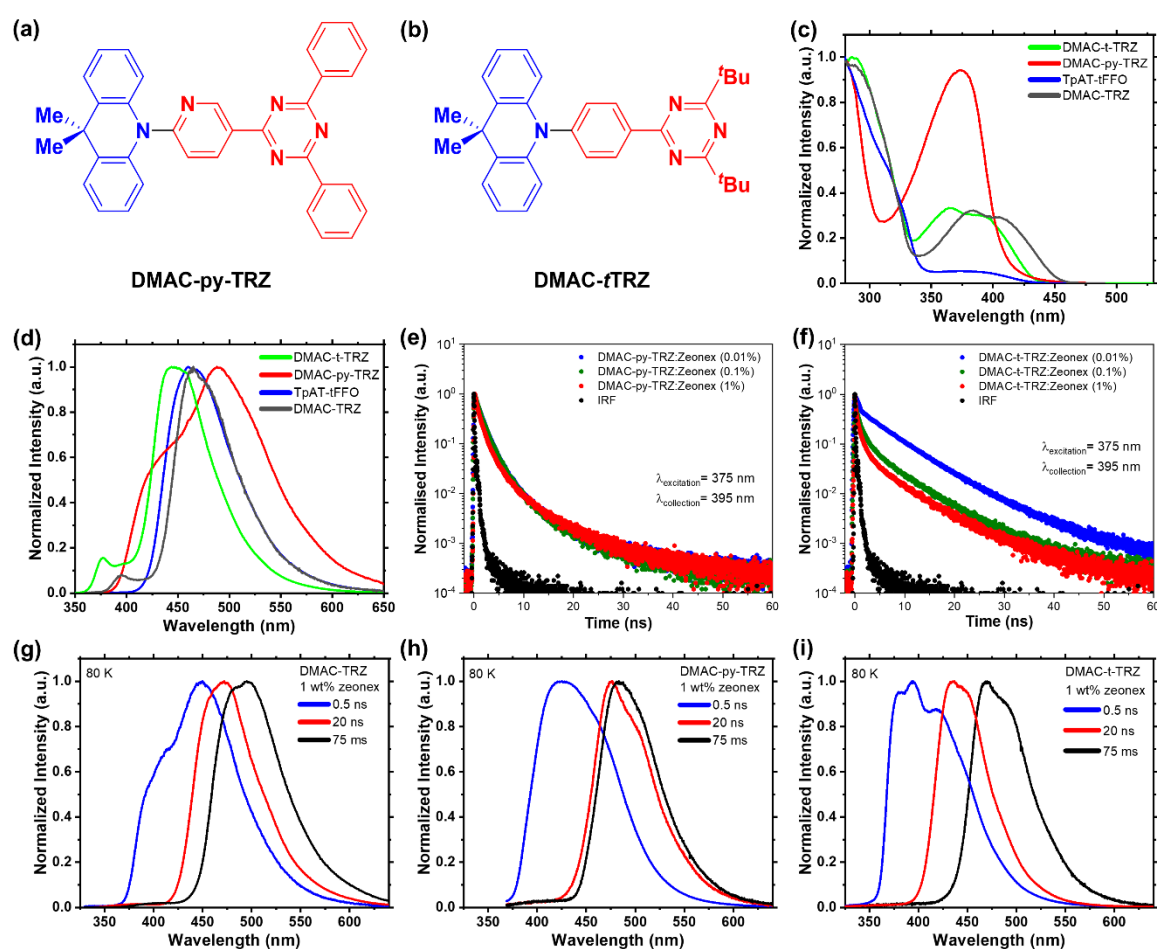


Figure 7.15. (a) DMAC-py-TRZ and (b) DMAC-t-TRZ molecular structures. (c) Excitation and (d) PL spectra of DMAC-py-TRZ (red), DMAC-t-TRZ (green), TpAT-tFFO (blue),²⁷ and DMAC-TRZ grey at 1 wt%, in zeonex, at room temperature. TpAT-tFFO is the through-space analogue of DMAC-TRZ, which cannot have a QA conformer. Prompt fluorescence time-resolved decays of (e) DMAC-py-TRZ and (f) DMAC-t-TRZ films, at different concentrations

and room temperature. Time-resolved spectra of (g) DMAC-TRZ, (h) DMAC-py-TRZ, and (i) DMAC-t-TRZ films at different delay times and 80 K.

From the time-resolved spectra at 80 K, the dual conformer behaviour was observed in all cases (**Figure 7.15g-i**). At early times (0.5 ns), the QA PL contribution was stronger in DMAC-py-TRZ, followed by DMAC-t-TRZ and DMAC-TRZ, verifying the initial steady state observations regarding the population of the two conformers in each system. At later prompt fluorescence times (20 ns), the QE spectrum could be observed in all cases, following the steady state PL energetic trend, with DMAC-t-TRZ being the bluer followed by DMAC-TRZ and DMAC-py-TRZ.

The dominant QA population of 1 wt% DMAC-py-TRZ in zeonex, with the small QE population leading to a small QA PL quenching (via FRET), and the much stronger oscillator strength of the QA conformer, leads to the conclusion that the phosphorescence emission in **Figure 7.15h** is the fingerprint of the QA triplet state. Further, as mentioned in the previous paragraph, the local D-A triplet energies are above 3 eV in all molecules and the QE ^3CT state is expected to have almost zero oscillator strength. Thus, considering that the QA steady state PL spectra energetic trend, and not the QE PL spectra, is similar to the phosphorescent spectra energetic trend, verifies the previous conclusion that the lowest optically observed triplet state in these systems originates from their QA conformers.

7.4.4 Devices

Devices were fabricated with a structure of ITO (anode) | NPB (HTL, 40 nm) | TSBPA (EBL, 10 nm) | DMAC-TRZ x wt% in different hosts (EML, 30 nm) | TPBi (HBL, 10 nm) | POT2T (ETL, 40 nm) | LiF (EIL, 1 nm) and Al (cathode, 100 nm). For the emissive layer (EML) a concentration series of 5, 15, and 25 wt% DMAC TRZ was used in a number of hosts with different ground state dipole moments (mCP, mCPCN, mCBPCN, BCPO, DPEPO and neat film). The OLED's resultant EL spectra in each host are shown in **Figure 7.16**, and the contribution of the QA conformer appeared in specific environments, similar to previous dual conformer emitter studies.⁴ The QA EL contribution was strongest in mCP and decreased in intensity with increasing host dielectric, because of better spectral overlap between the EL of the QA and the absorption of the QE conformer. In mCPCN, the QA contribution appeared to be minor and seemed to set the environment threshold for complete FRET between the two conformers, even at 5 wt% DMAC-TRZ concentration. In BCPO and DPEPO no contribution

from the QA conformer was observed. Possible host emission is excluded because of their different emission spectra, as shown in **Figure 7.16f**. Also, if the emission was coming from the hosts, it should have been observed in mCPCN and BCPO devices too. In all cases, where the QA emission was observed, its relative intensity appears to decrease with increasing DMAC-TRZ concentration, mainly because of increasing quenching by the QE conformers.

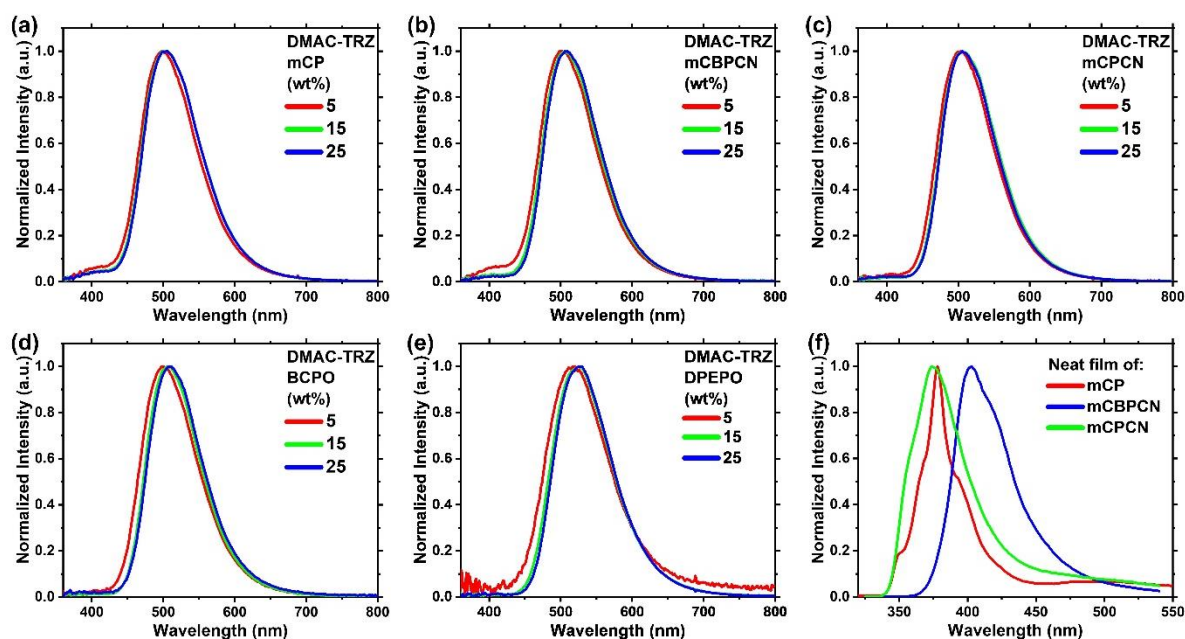


Figure 7.16. Electroluminescence spectra of DMAC-TRZ OLEDs at different concentrations. In (a) mCP, (b) mCBPCN, (c) mCPCN, (d) BCPO, and (e) DPEPO hosts. (f) PL spectra of neat host films.

To investigate further the QA effect on OLEDs, a new set of devices using DMAC-TRZ as a triplet harvesting/singlet sensitizer for v-DABNA as a terminal emitter was fabricated (device structure in **Figure 7.17**). Using this approach one can investigate the effect of energy transfer to the v-DABNA from the two conformers. **Figure 7.18a** shows the absorption and emission overlap between v-DABNA and DMAC-TRZ respectively, a critical parameter for efficient FRET.^{11,30} To my understanding, this system had the smallest spectral overlap reported, yet achieved high FRET efficiency, even at 1 wt% v-DABNA loading.

The electrical response of the DMAC-TRZ only and HF OLEDs appeared to be similar, while the maximum brightness of the HF devices was slightly lower (**Figure 7.17b**). The performance was comparable in the two cases and the EQE is divided into two regimes; below 1 mAcm⁻² where the EQE was slightly higher in the HF-OLEDs (~ 30%); and above 1 mAcm⁻²

² where the EQE was higher in the TADF only OLEDs (**Figure 7.17c**). Further, v-DABNA OLEDs in mCBPCN host were fabricated using the same device structure and although they cannot compete with the previously reported devices using DOBNA-oar as a host,³¹ they show the common MR-TADF EQE response, with two different regimes (**Figure 7.18e**); a high performance one below 1 mAcm⁻² and one above with low performance. The latter implies that at higher current densities the longer-lived DF lifetime of the v-DABNA terminal emitter results in excess triplet quenching mechanisms.

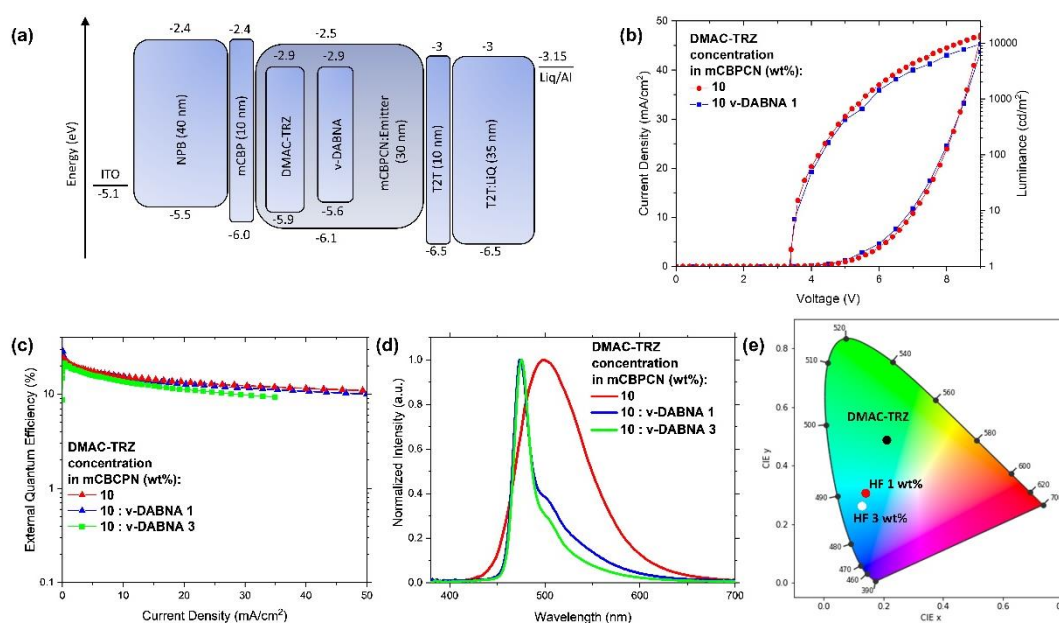


Figure 7.17. OLEDs performance. (a) Device architecture, (b) JVL curves and (c) EQE vs current density of TADF only and HF OLEDs. (d) EL spectra and (e) CIE coordinates collected at 8 V.

Focusing on the EL spectra one can observe that although there is a clear contribution of the sensitiser around 500 nm (**Figure 7.17d**), the EL results are comparable or even better (higher FRET efficiency) compared to previously published studies using deeper blue sensitisers with similar quantum yield.^{32,33} This did not seem possible considering the relatively lower spectral overlap of the specific set of DMAC-TRZ/v-DABNA system. Thus, it is concluded that the presence of the QA conformer acts as an extra (sensitiser emission) component that directly pumps the terminal emitter through efficient FRET, instead of just the QE conformer as seen in the TADF only devices. The QA conformer PL spectrum has much better overlap with the v-DABNA absorption spectrum, compared to the QE absorption spectrum (**Figure 7.18b, c**). Further, another important parameter for a high FRET radius is the extinction coefficient of the

acceptor, which is orders of magnitude higher in v-DABNA, compared to the QE conformer. The calculated FRET radius¹¹ from the QA conformer to the QE conformer or the terminal emitter (v-DABNA) was calculated to be 2.3 nm and 4.05 nm respectively (for more information see chapter 3). As a result, the energy of the initial QA population is expected to be mainly transferred to the v-DABNA molecules and not the QE configuration. FRET from the QE conformer to the terminal emitter was still occurring, but the efficiency was lower compared to the QA to terminal emitter energy transfer.

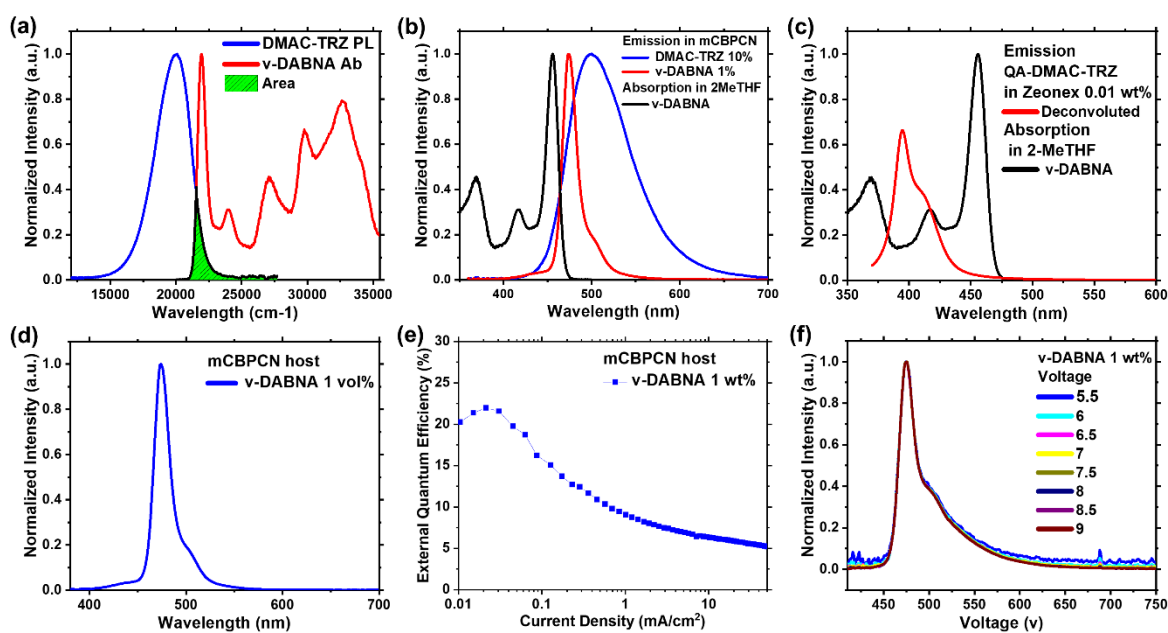


Figure 7.18. FRET analysis and OLED performance. (a) Absorption-PL overlap between v-DABNA and DMAC-TRZ respectively in wavenumbers. Absorption-PL overlap between v-DABNA and DMAC-TRZ (b) QE conformer and (c) QA conformer. (d) Electroluminescence spectrum at 8 V, and (e) EQE vs current density of 1 wt% v-DABNA in mCBPCN OLED. (f) Voltage stability of electroluminescence spectrum of the HF-OLED at 1 wt% v-DABNA.

To investigate further the energy transfer efficiency of the QE conformer to the terminal emitter, especially in the DF regime where triplet harvesting is critical for the OLED performance, time-resolved measurements in the three different systems are shown in **Figure 7.19a**. The HF-system (DMAC-TRZ:v-DABNA in mCBPCN) showed a small quenching of the late PF and early DF lifetime, compared to the DMAC-TRZ film but a much stronger quenching of longer DF lifetime, following the v-DABNA film lifetime. The latter indicates two different regimes, one with high and one with low FRET efficiency from the QE conformer to the terminal emitter. From the contour plot of the HF-system (**Figure 19b**), one can observe

a second spectral band increasing in the less efficient energy transfer regime ($15 < t < 1000$ ns). In the PF regime, the early time spectrum had an identical shape with the ν -DABNA film, confirming the high FRET efficiency of the QA conformer to the terminal emitter (**Figure 7.19c**). At later times, the second band appeared and contributed equally to the PL spectrum as the terminal emitter. This is the effect of the more orthogonal D-A QE conformers, which have longer wavelength emission and longer PF lifetime as shown in chapter 4.² In the DF regime, the opposite occurred. The longer wavelength QE conformer has shorter lifetime and was seen at early DF times, thus was observed in the HF system (**Figure 7.19d**). Over time, only the shorter wavelength QE conformers decay radiatively and have better spectral overlap with the terminal emitter, thus the PL emission mainly originated from ν -DABNA.. This implies that the FRET efficiency between the QE conformer and the terminal emitter is highly inhomogeneous and is entirely dependent on the dihedral angle distribution of the QE conformers. At late PF and early DF regimes the FRET efficiency will be relatively poor, while at early PF and late DF the efficiency will be higher, with a FRET radius of 3.45 nm. This less efficient energy transfer process resulted in a contribution of the QE emission in the overall EL spectrum, at 1 wt% concentration of ν -DABNA (**Figure 7.17d**).

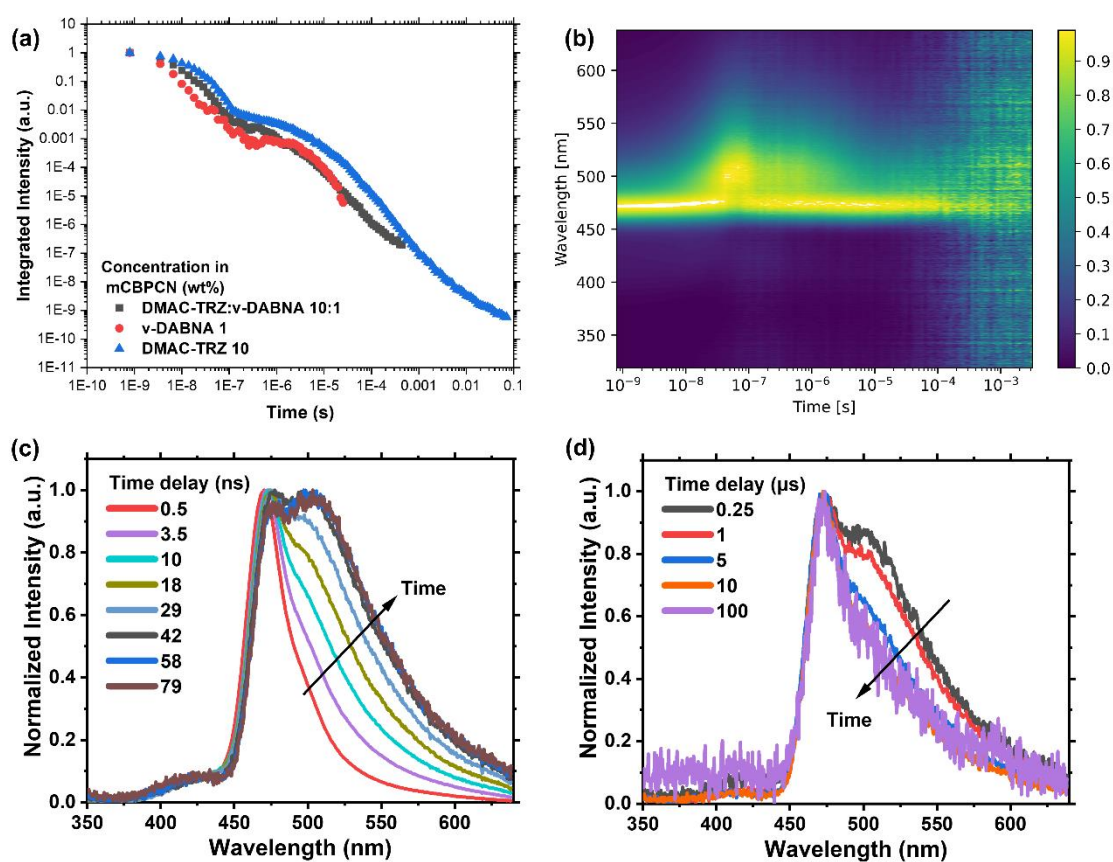


Figure 7.19. Time-resolved PL (a) decays of DMAC-TRZ, v-DABNA and DMAC-TRZ:v-DABNA in mCBPCN host, at room temperature. (b) Contour plot and time-resolved spectra of (c) prompt and (d) delayed fluorescence emission of DMAC:TRZ:v-DABNA in mCBPCN host, at room temperature. Excitation wavelength 355 nm.

With increasing terminal emitter concentration, an increase of FRET efficiency occurred resulting in a smaller contribution of the TADF sensitiser as observed in the EL spectrum (**Figure 7.17d**) which was much closer to the v-DABNA only OLED (**Figure 7.18d**). The EL spectra of the HF-OLEDs were stable with increasing voltage/current density (**Figure 7.18f**), excluding the presence of a current density dependent band and/or the contribution from an interfacial exciplex EL emission. The maximum EQE decreased with increased concentration, which I assume is, among other effects, due to stronger intermolecular interactions and excimer quenching,¹¹ but was still above 20%. The colour coordinates shifted from (0.21, 0.47) to (0.16, 0.31) and (0.14, 0.27) in DMAC-TRZ only, HF-OLED 1 wt % and 3 wt% respectively (**Figure 7.17e**).

7.5 Conclusions

DMAC-TRZ has been studied extensively before, but many aspects of its photophysics and device performance have not been revealed.^{1,2,10,16,34–36} The presence of a second conformer, the QA, has proven to be stronger than expected and its contribution to the photophysical performance in solid-state, especially at low concentrations, has proven to be dominant. At higher concentrations (above 1 wt%), the FRET efficiency to the QE conformer increases greatly and its contribution cannot be easily observed, this could be why it was not observed until now. A key parameter for its strong contribution is the presence of a rigid host, that hinders possible conformational relaxation to the QE conformation, with the presence of excess (excitation) energy. The sensitivity of the two conformers to the environment appears to be different, indicating a stronger local character for the QA and a stronger CT character for the QE conformer, verified by quantum chemical calculations. The DF appears to originate purely from the QE conformer mainly because of the high ΔE_{ST} of the QA preventing the formation of rISC channels from the T_1 to S_1 . Intermolecular interactions (dimer/excimer formation) improve the rISC rate and show that can be more efficient compared to the monomer performance. The triplet value mystery of DMAC-TRZ (the triplet is lower in energy than either the D or A units) has been resolved, with experimental proofs showing that the actual

triplet value observed in DMAC-TRZ systems originates from the QA conformer and not the QE. OLEDs of DMAC-TRZ show the contribution of the QA conformer to the EL spectrum of the device, only in specific environments and low concentrations. To explore the energy transfer process of the two conformers, HF devices using *v*-DABNA as the terminal emitter show high relative FRET efficiency compared to similar systems,^{32,33} indicating that the QA conformer transfers its energy directly to the terminal emitter instead of the QE conformer. The efficient energy transfer resulted in the fabrication of the first OLEDs that convert green EL emission into blue using the HF approach.

7.6 References

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8 Unveiling the requirements for efficient FRET in blue hyperfluorescence OLEDs

In chapter 7 the hyperfluorescence approach using a greenish sensitiser, with minimal spectra overlap with the ν -DABNA terminal emitter, provided valuable information about FRET sensitisation mechanism. Unfortunately, some intrinsic properties of DMAC-TRZ, including conformation inhomogeneity, prevented unveiling the full potential of the study. In this chapter, a rigid TADF sensitiser, ACRSA, with a similar PL spectrum to DMAC-TRZ and thus spectral overlap to ν -DABNA shows suppressed conformational inhomogeneity leading to nearly 100% FRET efficiency. Several photophysical properties of the sensitisers were explored highlighting their crucial role in HF-OLED performance, leading to the demonstration of the key requirements of a near-ideal sensitiser which diverge from an ideal TADF emitters. The sensitiser quantum yield need not be a limiting factor as rapid FRET can effectively outcompete non-radiative processes in HF systems. As a result, blue HF-OLEDs utilising a greenish sensitiser exhibited a remarkable tripling of external quantum efficiency (~30%) compared to the non-HF devices. This new understanding opens avenues for sensitiser design, indicating that green sensitisers can efficiently pump blue terminal emitters, thus reducing device exciton energies and improving blue OLED stability.

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8.1 Introduction

In the years since the introduction of the basic HF concept, many reports have featured HF-TADF OLEDs with external quantum efficiencies (EQEs) remaining surprisingly lower than their TADF counterparts.^{1,2} In other cases, the HF-OLED EQEs are higher,^{3,4} without any clear pattern or identifiable underlying cause for these differences. With the introduction of multiresonance (MR) TADF emitters⁵ and their ability to also harvest triplet excitons as terminal emitters, the performance of HF-OLEDs typically surpasses that of non-HF devices^{6–10} but the internal processes become yet more complicated compared to conventional fluorescent emitters. Similarly to EQE, in many cases the HF-OLED efficiency roll-off performance is better, but in some cases it is worse.^{10,11} It is noted that in almost all reports researchers use their ‘best’ TADF emitters in pre-optimised OLED stacks and then simply add a small concentration of the terminal emitter, which is *prima facie* a sensible strategy.^{2,12–14} This practice however also gives some clues as to why HF-OLED performance is not always better; the TADF emitter may already be performing at its maximum potential, and introduction of a terminal emitter opens up additional loss pathways such as through charge trapping or triplet migration onto the terminal emitter. While the terminal emitter can itself sometimes contribute to higher performance through higher photoluminescence quantum yields (PLQYs) or horizontally aligned emission dipoles (that improve light outcoupling), these evidently are not always able to outweigh these additional introduced loss pathways.^{15,16}

As an additional consideration, these ‘best’ TADF emitters chosen for use as HF-OLED sensitiser have their performance evaluated initially in TADF-only devices. For donor-acceptor TADF emitters though, it is now well-established that their performance relies on a delicately balanced HOMO-LUMO overlap.¹⁷ Too much overlap will increase oscillator strength and PLQY (itself the ratio of radiative and nonradiative decay rates), but is detrimental to reverse intersystem crossing (rISC) and triplet harvesting. Too little overlap can result in large rISC rates, but limits the PLQY.¹⁸ It therefore seems impossible for D-A TADF emitters with the fastest rISC rates (hence limited PLQYs) to produce high-performance OLEDs by themselves, and so these materials typically are not investigated in HF-OLEDs. Counterintuitively, in HF-OLEDs the PLQY of the sensitiser is not so crucial as long as the FRET rate (k_{FRET}) outcompetes the nonradiative decay, and instead the highest rISC rate is the key parameter that should be valued. However, candidate TADF emitters with such properties

will likely be overlooked for HF-OLED applications due to limited intrinsic performance. Indeed, this chapter suggests that many high-performance HF combinations go undiscovered due to this inappropriate self-selection effect.

Identifying this ‘blind-spot’ in current HF-OLED research, in this chapter extraordinary HF-OLED performance enhancement by TADF molecules used as sensitiser, which themselves only give moderate non-HF (sensitiser only) device performance, is demonstrated. Using the chapter 7 DMAC-TRZ results as a benchmark,^{19,20} it was found that despite the lower non-HF device performance of ACRSA, the latter enjoys a considerable performance boost in HF-OLEDs, with an almost tripling of the EQE_{max}.^{4,21} Similar results were also obtained using the recently reported deeper blue TADF emitter AZB-TRZ,²² which exhibits very fast rISC but is intrinsically limited by low PLQY. Surprisingly, despite the photoluminescence spectra of ACRSA and DMAC-TRZ being energetically similar (comparable J factor), ACRSA exhibited significantly higher overall FRET efficiency in HF systems, even when compared to the deeper blue AZB-TRZ sensitizer which has better FRET spectral overlap. This unexpectedly complete energy transfer arises as a result of ACRSAs rigid structure and very long-lived excited states, which are normally a detriment in OLEDs. These findings establish new and unexpected design rules for high-performance HF sensitiser, that would otherwise go unnoticed.

8.2 Collaborator Contribution

All solution and film samples, the steady state and time-resolved PL measurements were made and analysed by myself. Larissa G. Franca made and analysed part of the time-resolved PL measurements. The PLQY measurements were done by Dr. Andrew Danos. FRET calculation, OLEDs fabrication and analysis were made by myself.

8.3 Experimental Methods

8.3.1 Sample Preparation

Solid-state samples were evaporated on quartz substrates into a Kurt J. Lesker Super Spectros deposition chamber, at pressures below 10^{-7} mbar. Steady-state absorption and emission spectra were measured using a double beam Shimadzu UV-3600 UV/VIS/NIR spectrophotometer and a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, respectively. Time-resolved measurements were performed using a spectrograph (Horiba Triax) and a Stanford Computer

Optics 4Picos ICCD camera, where samples were excited with a Nd:YAG laser (EKSPLA, 10 Hz, 355 nm) under vacuum.

8.4 Results and Discussion

8.4.1 Photophysics

The steady-state photoluminescence (PL) spectra of ACRSA and DMAC-TRZ at 10 wt% in mCBPCN host are shown in **Figure 8.1**. DMAC-TRZ:mCBPCN films exhibit one strong emission band centred at 500 nm which was shown in chapter 4 and 7 to be attributed to ^1CT emission from its highly twisted quasi-equatorial conformer.²⁰ Importantly, the intrinsic broadness of the CT photoluminescence (PL) spectrum is due to a sum of PL contributions from different molecular configurations with different D-A dihedral angles in the film (G1 and G2), together with some aggregate emission (G3, **Figure 8.2b**).^{23,24} These contributions have different radiative lifetimes and rISC rates as well as spectra and were seen independently in the time-resolved spectra, in chapter 7, even when FRET to a terminal emitter was active (in this case v-DABNA)^{5,14} (**Figure 7.18**).

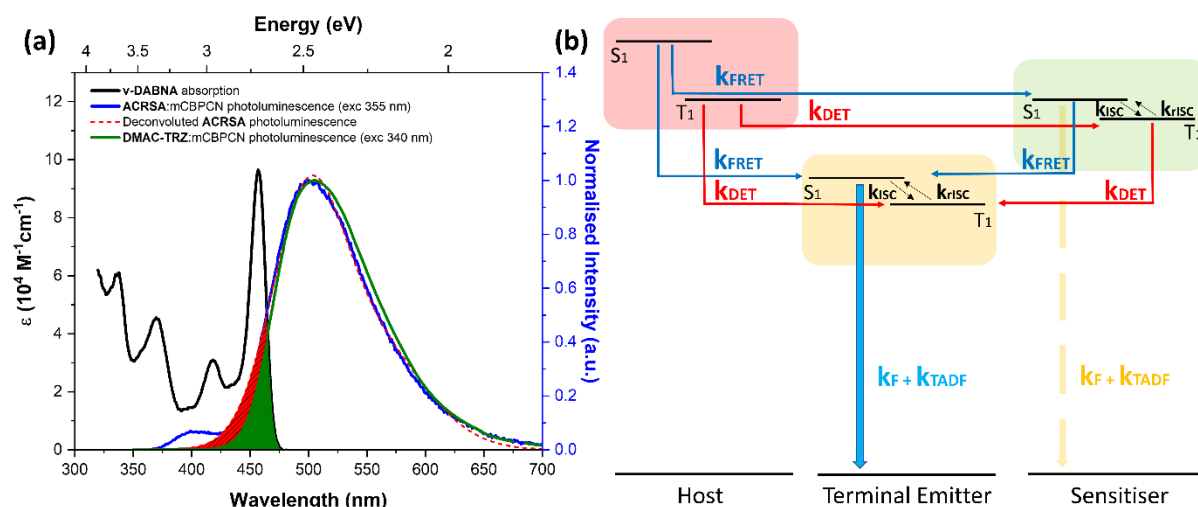


Figure 8.1. (a) Steady-state absorption of v-DABNA in toluene solution, alongside photoluminescence spectra of ACRSA:mCBPCN (10% wt) and DMAC-TRZ:mCBPCN (10% wt) films, excited at 355 and 340 nm respectively. The filled areas are the spectral overlaps between the curves used to analyse the FRET radius. (b) FRET mechanism in a guest:sensitiser:terminal emitter system. Emission from the sensitiser (Yellow arrow) occurs when FRET is significantly less than 100% efficient.

In ACRSA:mCBPCN film dual emission was observed in the PL spectrum. The higher energy band at ~400 nm came from the mCBPCN host (excitation 355 nm), as the ACRSA absorption in the region is very weak. The broader emission band at ~500 nm is characteristic of ACRSA ^1CT emission in solid-state hosts.²⁵ The ACRSA PL spectrum was deconvolved considering three Gaussian contributions (**Figure 8.2a**) corresponding to i) mCBPCN at 400 nm (G1); ii) ACRSA ^1CT at 497 nm (G2); and iii) ACRSA aggregate contributions at 545 nm (G3). Detailed characterisation of ACRSA has identified these species previously.²⁵ The absence of dihedral angle inhomogeneity in ACRSA resulted in a narrower monomer PL spectrum as seen in the deconvoluted spectra of ACRSA. This is verified by the absence of a dynamic time-resolved red-shift of ACRSA PL spectra, at low emitter concentration, compared to DMAC-TRZ, indicating a homogeneous rISC rate which was previously reported by Franca *et al.*^{24,25}

Excluding the mCBPCN contribution to the ACRSA PL spectrum and comparing the spectral overlap of the two TADF emitters with ν -DABNA absorption,¹⁴ ACRSA as sensitizer displayed slightly increased spectral overlap because of its higher energy PL onset, highlighted by the red-filled area in **Figure 8.1a**, with DMAC-TRZ overlap highlighted green. For both emitters only the very blue edge of the highest energy sensitizer emission overlaps with the narrow S_0 - S_1 absorption transition of ν -DABNA, but efficient FRET was surprisingly still ensued for both materials (although for different reasons, *vide infra*). The calculated FRET radii between the sensitizers and the terminal emitter were 2.8 nm and 3.2 nm for ACRSA and DMAC-TRZ respectively (for more details see estimation of FRET properties in Chapter 3). Despite the slightly better spectral overlap of ACRSA with ν -DABNA, the calculated FRET radius was lower compared to DMAC-TRZ because the ACRSA PLQY is 3 times smaller.

The FRET dynamics in the two HF systems were investigated using time-resolved emission spectroscopy. **Figure 8.2c** shows the time-resolved spectra of ACRSA:mCBPCN (10 wt%) film at room temperature. As mentioned above in the context of the deconvolution of the steady-state spectrum, three resolvable species contribute to the overall emission. These are the mCBPCN itself, ACRSA ^1CT , and ACRSA excimers, which have lifetimes of 2.95 ns, 322 ns, and 7.9 μs respectively (**Table 8.1**). The unusually long ^1CT decay lifetime arises from the highly decoupled nature of the spiro-linked ACRSA D-A units,²⁶ and becomes crucially important for its use as a sensitizer in HF systems as discussed below. With the additional presence of 1 wt% ν -DABNA, the prompt fluorescence (PF) lifetime has two components. Direct (355 nm) excitation of ν -DABNA leads to a component of emission with a lifetime of

3.5 ns, the same as v-DABNA in mCBPCN. The FRET-accelerated PF lifetime of ACRSA in the HF film reduces from 322 ns to 39.27 ns (**Table 8.1**). To put this significant ACRSA emission lifetime quenching into context, the PF lifetime of DMAC-TRZ in mCBPCN is 21.66 ns and reduces to 15.55 ns with the introduction of 1 wt% v-DABNA. This has an enormous impact on the FRET efficiency (η_{FRET}) and subsequent HF-OLED performance of this system (**Table 8.1**).

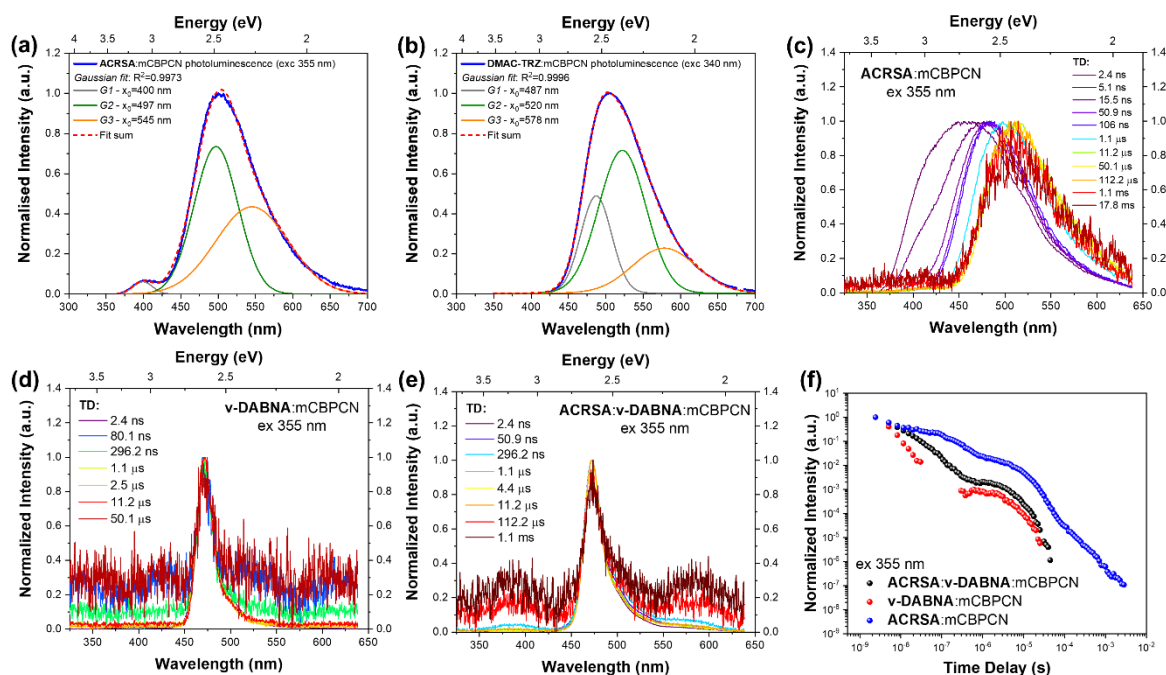


Figure 8.2. Deconvoluted steady-state PL spectrum of 10 wt% (a) ACRSA and (b) DMAC-TRZ in mCBPCN host, at room temperature. Time-resolved photoluminescence spectra of: (c) ACRSA:mCBPCN (10%), (d) v-DABNA:mCBPCN (1%) and (e) ACRSA:v-DABNA:mCBPCN (10:1:89 wt%). (f) Photoluminescence decay traces of the evaporated films at room temperature. $\lambda_{\text{exc}}=355$ nm.

The FRET rate (k_{FRET}) and efficiency (η_{FRET}) of the HF systems can be estimated from the changes in sensitizer PF lifetime in the presence and absence of the terminal emitter (see estimation of FRET properties in chapter 3).²⁷ In the ACRSA HF system, the η_{FRET} was calculated to be 87.8% (**Table 8.2**), which is very high given such a limited spectral overlap between the sensitizer and terminal emitter (**Figure 8.1a**). In the DMAC-TRZ HF system the η_{FRET} was instead calculated to be 28.2%. This value is obviously at odds with the photoluminescence and the electroluminescence (EL) spectra of the HF-OLEDs in chapter 7, because so far only considered the QE conformer emission from DMAC-TRZ was

considered.²⁰ Additional FRET from the QA conformer to the terminal emitter (that otherwise undergoes energy transfer to the lower energy quasi-equatorial conformer) means that the FRET radius, k_{FRET} and η_{FRET} are larger in the actual DMAC-TRZ:v-DABNA HF system.²⁰

Table 8.1. Key photophysical characteristics of ACRSA, DMAC-TRZ, and v-DABNA in mCBPCN, and HF films at room temperature. $\lambda_{\text{exc}} = 355 \text{ nm}$.

<i>Photophysical Characteristics</i>	ACRSA:v-DABNA:mCBPCN (HF)	ACRSA:mCBPCN	DMAC-TRZ:v-DABNA:mCBPCN (HF)	DMAC-TRZ:mCBPCN	v-DABNA:mCBPCN
Concentration (wt%)	10:1:89	10:90	10:1:89	10:90	1:99
^a λ_{max} (nm)	476	500	477	502	477
^a FWHM (nm)	17.7	96.1	18.5	101	17.5
^b Φ_{PL} (%)	66.1	30.7	66.1	98	60.9
^c τ_{LE} (ns)	3.5 (v-DABNA)	2.95 (Host)	3.5 (v-DABNA)	-	-
^c $\tau_{\text{PF},1}$ (ns)/(A _{PF})	15.99 (78%)	72.1 (60%)	15.55	6.3 (57.4%)	3.5
^c $\tau_{\text{PF},2}$ (ns)/(A _{PF})	60.93 (22%)	391 (40%)	-	26.57 (42.6%)	-
^d $\tau_{\text{PF},\text{av}}$ (ns)	39.27	322.03	15.55	21.66	3.5
^{c,d} $\tau_{\text{DF},\text{av}}$ (μs)	4.5	7.9	11.1	15.5	4.6

^a Values were obtained from the steady-state photoluminescence spectra. ^b Photoluminescence quantum yield (Φ_{PL}) under N₂, excited at 355 nm. ^c Lifetimes were obtained by fitting monoexponential and/or biexponential functions. ^d Average lifetime $\tau_{\text{PF},\text{av}} = (A_{\text{PF},1} * \tau_{\text{PF},1}^2 + A_{\text{PF},2} * \tau_{\text{PF},2}^2) / (A_{\text{PF},1} * \tau_{\text{PF},1} + A_{\text{PF},2} * \tau_{\text{PF},2})$.

While an unexpected conformer partially explains the surprisingly small calculated η_{FRET} for DMAC-TRZ, this cannot be the case for conformationally rigid ACRSA. Instead, ACRSA's very long ¹CT emission lifetime provides an ample window of opportunity for relatively slow FRET to achieve high η_{FRET} , despite ACRSA's smaller R_0 and r value (**Table 8.2**). Indeed, considering the rate constants derived from the emission decays,²⁸ the k_{FRET} for the ACRSA HF system was estimated at $2.24 \times 10^7 \text{ s}^{-1}$, with DMAC-TRZ HF system having a similar value ($1.81 \times 10^7 \text{ s}^{-1}$, **Table 8.2**). Further, in DMAC-TRZ k_{FRET} is in direct competition with intersystem crossing rate ($k_{\text{ISC}} = 3.37 \times 10^7 \text{ s}^{-1}$) and fluorescence rate ($k_{\text{f}} = 4.62 \times 10^7 \text{ s}^{-1}$, **Table 8.3**), and from the large PLQY of DMAC-TRZ the non-radiative rates are already known to be small.²⁹ In ACRSA k_{ISC} and k_{f} are both much slower, 1×10^6 and $3.1 \times 10^6 \text{ s}^{-1}$ respectively. Non-radiative rates must also be slow to support such long singlet exciton lifetimes in this emitter, thus allowing FRET to dominate far beyond what it can achieve with DMAC-TRZ (evidenced by the differences in η_{FRET} and relative PL contributions), despite the similar k_{FRET} values. To generalize, sensitizers with slow radiative and slow non-radiative rates provide

enough time for k_{FRET} to accumulate and dominate the exciton dynamics, even though these properties by themselves limit the potential performance of the sensitiser as a TADF emitter in its own right. The competing processes are summarised in **Table 8.3**.

Table 8.2: FRET properties of the hyperfluorescence systems. All parameters and equations

FRET properties	ACRSA: v-DABNA:mCBPCN	**DMAC-TRZ: v-DABNA:mCBPCN	AZB-TRZ: v-DABNA:mCP
Molecular weight (g/mol)	435.52	516.63	529.25
PLQY (%)	30.7	98	37.6
J ($\times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$)	2.515	1.791	4.197
FRET radius, R_0 (nm)	2.80	3.21	3.22
FRET efficiency, η_{FRET} (%)	87	28	37
FRET rate, $k_{\text{FRET, av}}$ ($\times 10^7 \text{ s}^{-1}$)	2.24	1.81	2.46
Average distance, r (nm)*	2.02	3.75	3.51

used are presented in subsection 3.7.4.

*All hyperfluorescence studies use wt% concentrations, thus the real number of sensitiser molecules in the film will depend on their molecular weight. Thus ACRSA, that has the smaller molecular weight, will have much higher number of molecules in the film compared to DMAC-TRZ and AZB-TRZ and smaller average distance.

** Considering the quasi-equatorial conformer only

While FRET properties can be estimated with great confidence,³⁰ this is not the case for Dexter rates.²⁷ Instead, in this chapter the average distance between the FRET energy donor (sensitiser) and energy acceptor (terminal emitter) molecules was estimated, based on the k_{FRET} and R_0 calculations (**Table 8.2**). In both cases, the average intermolecular distance is greater than a reasonable estimate of effective Dexter radius (~ 1 nm, requiring direct orbital overlap),²⁷ and thus is proposed that, on average, the Dexter transfer between the sensitiser and the terminal emitter will be negligible in these materials.

Is also noted that the calculated η_{FRET} represent the probability for singlet energy transfer across a single exciton lifetime. While this is appropriate for standard FRET between fluorescent materials, if the exciton is instead recycling (in some cases multiple times) between singlet and triplet states (as in a TADF sensitizer), the overall/cumulative chance of undergoing FRET

increases significantly with each cycle. Here, η_{FRET} was estimated using only the prompt lifetimes, thus TADF materials with fast k_{rISC} and high DF/PF ratio will have a much higher cumulative FRET efficiency. These high cumulative FRET efficiencies are then what is observed when considering emission intensities of sensitiser and terminal emitter in film PL or device EL spectra, which in some cases indicate far more complete FRET than the calculated η_{FRET} would otherwise imply (*vide infra*).

An additional factor contributing to the small calculated η_{FRET} in the DMAC-TRZ HF system is the significant emission contribution from lower energy conformers, discussed in chapter 4, evident in the late PF and early delayed fluorescence (DF) regime in the time-resolved spectra (Time delay 20 - 5000 ns, **Figure 7.18c, d**).²³ While not significantly detrimental in DMAC-TRZ OLEDs, these low-energy emitting conformers have vanishing spectra overlap with ν -DABNA resulting in a subset of DMAC-TRZ molecules trapped in molecular geometries with poor η_{FRET} . As a result, the surprisingly low calculated DMAC-TRZ η_{FRET} using the PF decay rates is very much an average representing a broad underlying distribution of conformers. The ACRSA HF system does not have a comparable broad distribution of conformers contributing to the time-resolved decay (**Figure 8.2e**), such that all excited states experience similar η_{FRET} with no ensemble averaging. This comparison highlights how homogenous emitter conformations in TADF materials yield key benefits in HF-OLEDs by supporting more complete FRET.

Table 8.3. Time-resolved decay kinetics.³¹

Quest-Host System	A_{DF}	Φ_{PF}	Φ_{DF}	τ_{PF}	τ_{DF}	k_{f}	k_{ISC} average	k_{rISC} average	k_{nr} singlet	k_{nr} triplet
ACRSA: mCBPCN	1.93E-02	2.51E-01	5.63E-02	3.22E-07	7.90E-06	3.11E+06	9.97E+05	9.65E+04*	1.76E+06	1.17E+05
DMAC-TRZ: mCBPCN	2.65E-03	5.03E-01	4.77E-01	2.17E-08	1.55E-05	4.62E+07	3.37E+07	1.25E+05	4.74E+05	2.60E+03
AZB-TRZ: mCP	4.30E-02	1.73E-01	1.94E-01	2.39E-08	1.30E-06	4.19E+07	2.37E+07	1.34E+06	1.25E+07	5.89E+05

* Although the rISC rate of ACRSA is not much lower compared to the average rISC rate of DMAC-TRZ, we note that the k_{rISC} of the fastest DMAC-TRZ conformers is an order of magnitude larger (**Figure 8.7**).

The DF regime is also important to consider for HF systems, as rISC controls triplet exciton harvesting and lifetimes that support high efficiency in devices. The ACRSA HF system has a DF lifetime of 4.5 μs , which appears to match that of ν -DABNA:mCBPCN (**Table 1**), while the ACRSA non-HF system has a DF lifetime of 7.9 μs , which is influenced by excimer states.

For comparison, ACRSA at 1wt% loading in zeonex or DPEPO films has DF lifetimes of 6.3 μ s and 7.3 μ s respectively with no excimer emission observed. At 10 wt% in DPEPO host, and similarly to mCBPCN host, the ACRSA DF lifetime is 8.7 μ s with clear excimer emission observed.²⁵ This implies that all of the ACRSA triplet population that was formed by ISC in the HF film, was successfully up-converted and transferred to the terminal emitter. ACRSA excimer emission, which appeared to be dominant in ACRSA:mCBPCN DF at 10 wt%, disappeared completely in the HF system despite the high ACRSA concentration. This comparison shows that the presence of the terminal emitter in the ACRSA HF system prevents excitons forming excimers, with FRET outcompeting the formation rate.

The DMAC-TRZ HF system DF is however divided into different time regimes (**Figure 7.18**). Initially, a fast component in the early DF regime ($\sim$ 500 ns) is observed with a high contribution to the time-resolved PL emission from the highly twisted DMAC-TRZ conformers (emission at 510 nm) that have limited overlap with the terminal emitter and thus low η_{FRET} (**Figure 7.18d**). The second DF regime is similar to the ν -DABNA:mCBPCN film DF, where efficient FRET occurs, and the last regime is an extension of the DF tail which comes from the slow up-conversion of unfavourable species in the inhomogeneous DMAC-TRZ system (less twisted conformers with slow k_{ISC}). The average DF lifetime is 11 μ s (**Table 8.1**), indicating that these slow species greatly increase the overall DF lifetime of the hyperfluorescent system, an undesirable phenomenon in OLEDs.

The above indicates that for a (conformationally) homogeneous hyperfluorescent sensitiser i.e. ACRSA, the FRET requirements to achieve high efficiency sensitisation are not as previously understood. As seen from the comparison of ACRSA emission to ν -DABNA absorption spectra, **Figure 8.1**, the spectral overlap for this hyperfluorescent system is extremely small, but this does not ultimately limit η_{FRET} . This realisation is very important for OLED applications, as it allows us to maintain efficient cumulative FRET while also minimising the excited state energies of the sensitiser as much as possible. This consideration is not something unique to ACRSA but arises from the fortuitous photophysical properties of the energy donor and acceptor, depicted in **Figure 8.3**. In ν -DABNA the S_0 - S_1 transition has a very high oscillator strength and very narrow bandwidth. For the energy donor (sensitiser) the vast majority of singlet excited state population resides in the S_1 0-0 vibrational state as the radiative lifetime is long compared to internal conversion. Thus, the overlap between the populated energy donor states and the spectrally narrow energy acceptor (terminal emitter) absorption

band remains suitably strong. Overlap of just the red edge of the acceptor absorption with the blue edge of the donor emission still ensures that all of the donor population can be transferred to the acceptor. This is all that is required to couple all the donor excited state population to the acceptor making the ACRSA:v-DABNA hyperfluorescent system an ideal situation for maximal η_{FRET} despite minimal spectral overlap. As a result, the lowest possible sensitiser singlet excited state energy, and therefore lowest triplet energy as well can still be used for blue OLED emission, increasing the range of usable host and emitter materials considerably. This realisation redefines the photophysical design requirements for sensitiser and terminal emitter to achieve optimal FRET with minimal sensitiser excited state energy for HF-OLEDs.

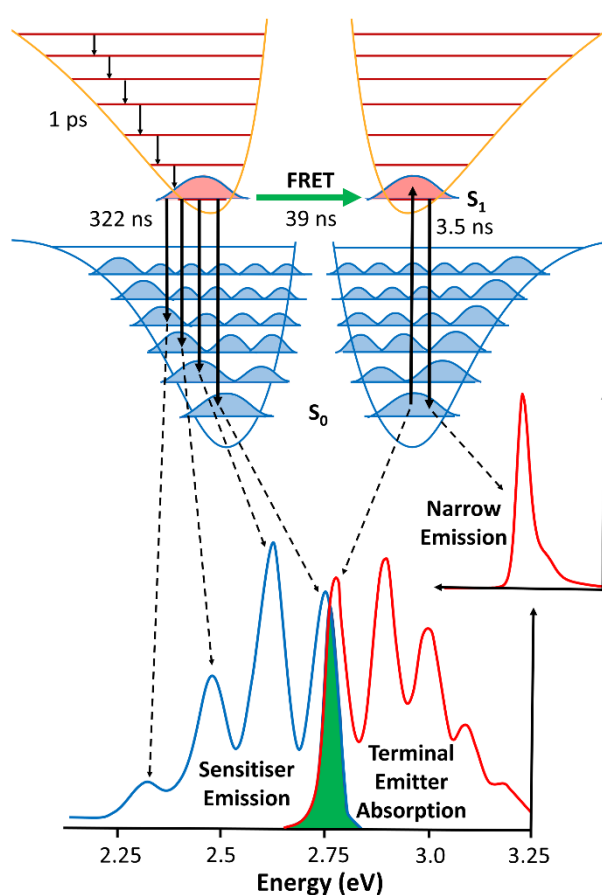


Figure 8.3. Schematic energy level diagram for FRET between a hypothetical TADF sensitiser and v-DABNA terminal emitter, showing how a very small spectral overlap can still give rise to fast and efficient energy transfer between them. FRET is relatively slow because the sensitiser (singlet CT state) transition dipole moment is very small. Thus, the dipole-dipole interaction is weak, such that we are in the weak coupling (FRET) regime. Note: The sensitiser's PL spectrum is vibronic for illustrative purposes, to allow easier correlation of the

vibronic levels with the energy diagram. Typically, and indeed in the examples examined in this chapter, the PL spectrum of a TADF sensitiser is broad and Gaussian shaped without clear separation of vibronic states.

8.4.2 Devices

OLED devices were fabricated using the same device architecture for all devices (**Figure 8.5a**). Although the device performance could change using different fully optimised device structures for each individual emitter combination, only by comparing the assistant dopant, terminal emitter, and HF combination in the same device structure can generate reliable insight into the FRET processes that occur within. Further, the similar HOMO/LUMO's of the sensitisers used in this study allows the same device structure to be used for all the sensitisers.

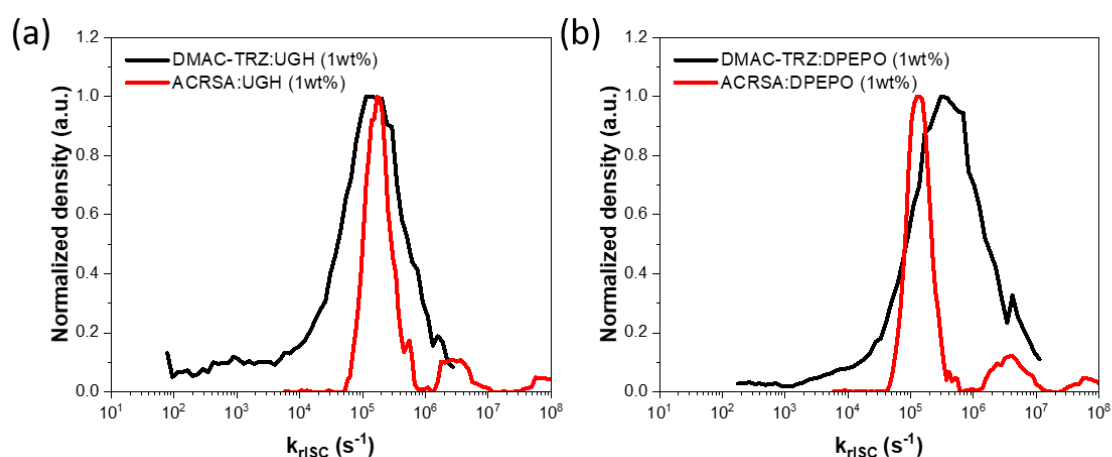


Figure 8.4. Distribution of k_{rISC} from time-resolved decays, calculated using an inverse Laplace transformation.²⁴

Turning to HF-OLEDs, the properties of every individual component of the emissive layer are crucial to understand the HF performance. Regarding the terminal emitter, it is well established that slow rISC in MR-TADF materials such as v-DABNA leads to unsatisfactory efficiency roll off at higher current densities in non-triplet harvesting host devices,^{6,7} as observed here (**Figure 8.5d-f**, blue curve). Although this is not the case in the original v-DABNA publication, it is still not clear why v-DABNA performs as it does in the DOBNA-Oar or similar hosts.³² As expected from previous reports,^{4,21} ACRSA does not perform as strongly in OLEDs as DMAC-TRZ. In the device stack used, the EQE_{max} was limited to ~11% for ACRSA compared to ~25% for DMAC-TRZ, both at 10 wt% concentration in mCBPCN host and largely a result of ACRSA's low PLQY and slow radiative decay rate (**Table 8.4**). The roll-off for ACRSA

was also worse than in DMAC-TRZ OLEDs, a result of its slower rISC and longer exciton lifetimes (**Table 8.3**). Although the rISC rate of ACRSA is not much lower compared to the average rISC rate of DMAC-TRZ, we also note that the k_{rISC} of the fastest DMAC-TRZ conformers is almost an order of magnitude larger (**Figure 8.4**).²⁴ For these reasons, it is understandable why ACRSA has not been widely investigated for high-performance HF-OLEDs.

Surprisingly though, upon introduction of 1 wt% v-DABNA the EQE_{max} of the ACRSA device almost triples to 28.5%. In striking contrast, the DMAC-TRZ HF-OLEDs retained nearly identical performance to DMAC-TRZ alone OLEDs (**Figure 8.5**). Furthermore, despite the similar EL spectra of ACRSA and DMAC-TRZ OLEDs, the FRET is significantly more complete in the ACRSA HF-OLEDs, as evidenced by its EL spectra being identical to that of v-DABNA, **Figure 8.5c**. Significant residual sensitizer emission was observed in the DMAC-TRZ HF-OLED.

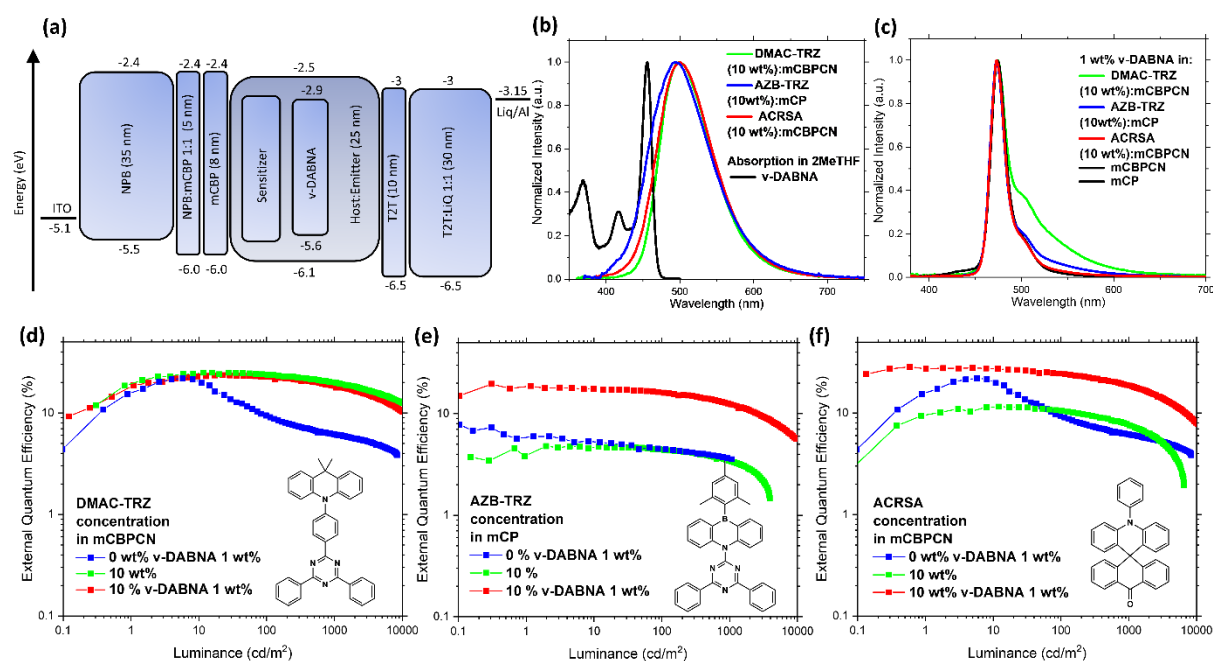


Figure 8.5. OLEDs performance. (a) Device architecture and electroluminescence spectra of (b) TADF devices, (c) HF-OLEDs. EQE versus luminance of (d) DMAC-TRZ, (e) AZB-TRZ and (f) ACRSA OLEDs with and without the terminal emitter (blue curve v-DABNA without the presence of the sensitizer for comparison).

Thus, it is proposed that this contrasting behaviour - with ACRSA enjoying significantly greater performance enhancement in the HF-OLEDs - actually arises from the same properties

that make ACRSA a less effective TADF emitter. In particular, the slow radiative and non-radiative/ISC rates of ACRSA are both extensively outcompeted by FRET to v-DABNA, largely obviating the disadvantages of its low PLQY. This long window of opportunity for energy transfer, as well as the absence of any unfavourable conformers having poor η_{FRET} (enforced by the rigid spiro-centre) means that FRET can be far more complete for ACRSA:v-DABNA than might otherwise be expected. In contrast, k_{ISC} and k_{F} are comparably fast in DMAC-TRZ, leading to less complete FRET despite similar spectral overlap (see J factors in **Table 8.2**). The high PLQY in DMAC-TRZ also means that radiative decay already outcompetes nonradiative decay, and so there is little headroom for additional FRET processes to improve the device performance further. There also exists a sub-population of DMAC-TRZ molecules in unfavourable configurations, with redshifted emission making these inaccessible for FRET.

Table 8.4. OLEDs performance.

OLEDs	V_{on}^{a} (V)	$\lambda_{\text{EL}}^{\text{b}}$ (nm)	FWHM ^c (nm)	$\text{EQE}_{\text{max}}^{\text{d}}$ (%)	EQE^{d} (%)	CE^{d} (cd A^{-1})	PE^{d} (lm W^{-1})	CIE^{e} (x, y)
ACRSA (10 wt%)	3	501	86	11.5	11.5/10.5/ 7.7	31/31/ 29/21	28/27/ 20/11	0.21, 0.44
ACRSA (10 wt%) v-DABNA (1 wt%)	2.9	473	19	28.5	27.3/24.6/ 18.6	37/37/ 33/25	36/31/ 22/12	0.13, 0.17
DMAC-TRZ (10 wt%)	2.9	501	81	25	24.6/23.9/ 19.9	71/70/ 68/56	62/60/ 46/29	0.21, 0.47
DMAC-TRZ (10 wt%) v-DABNA (1 wt%)	2.9	474	23	23.5	23.0/22.7/ 18.3	49/48/ 47/38	41/41/ 31/18	0.17, 0.32
AZB-TRZ (10 wt%)	3.4	494	94	4.8	4.7/4.4/ /3.4	12/11/ 10/8	9/8/ 6/4	0.21, 0.37
AZB-TRZ (10 wt%) v-DABNA (1 wt%)	3.3	473	19	19.6	17.5/16.3/ 12.5	30/28/ 26/20	27/22/ 16/9	0.14, 0.22

^a Turn-on voltage at the luminescence of 0.1 cd m^{-2} . ^b Maximum wavelength of EL spectrum. ^c Full width at half maximum. ^d External quantum efficiency (EQE), Current Efficiency (CE) and Power Efficiency (PE) at maximum (CE and PE only) and $10/100/1000 \text{ cd m}^{-2}$. The slightly higher current and power efficiency values of the DMAC-TRZ HF-OLEDs, compared to the other two HF systems, is attributed to the stronger contribution of the green DMAC-TRZ to the overall EL spectrum. ^e CIE (x, y) coordinates at 1000 cd m^{-2} .

In addition to the above, the similar EQE roll-off in the ACRSA TADF and HF devices indicate that triplet harvesting remains the exclusive role of the sensitiser and was not significantly impacted by the presence or absence of the v-DABNA terminal emitter (**Table 8.4**). The possibility of device degradation during the J-V-L measurements is excluded by identical

consecutive sweeps of the same pixel (**Figure 8.6a, b**). Nonetheless, the roll-off slope was improved at high luminance, indicating that the terminal emitter presence likely helped reduce the accumulation of ACRSA excitons by providing rapid FRET and emission pathways. It is again noted that the ability to achieve efficient FRET even with significantly low energy emitters (like ACRSA) opens up new possibilities for enhancing the lifetime of blue HF-OLEDs. Rather than relying on deep-blue emitters and associated high-triplet hosts,^{11,33,34} greenish emitting TADF sensitisers and their lower-triplet hosts can be significantly more stable in devices. This stability is due to both the wider choice of chemical groups usable at these energies (for both hosts and emitters), as well as the smaller exciton energies. Combined with the highly absorbing red edge of the terminal emitter (already effectively optimised for v-DABNA), this surprising effectiveness of HF systems with seemingly inadequate FRET overlap demonstrates a way to achieve highly efficient blue OLEDs, using attractive and well-developed green-emitting sensitisers.

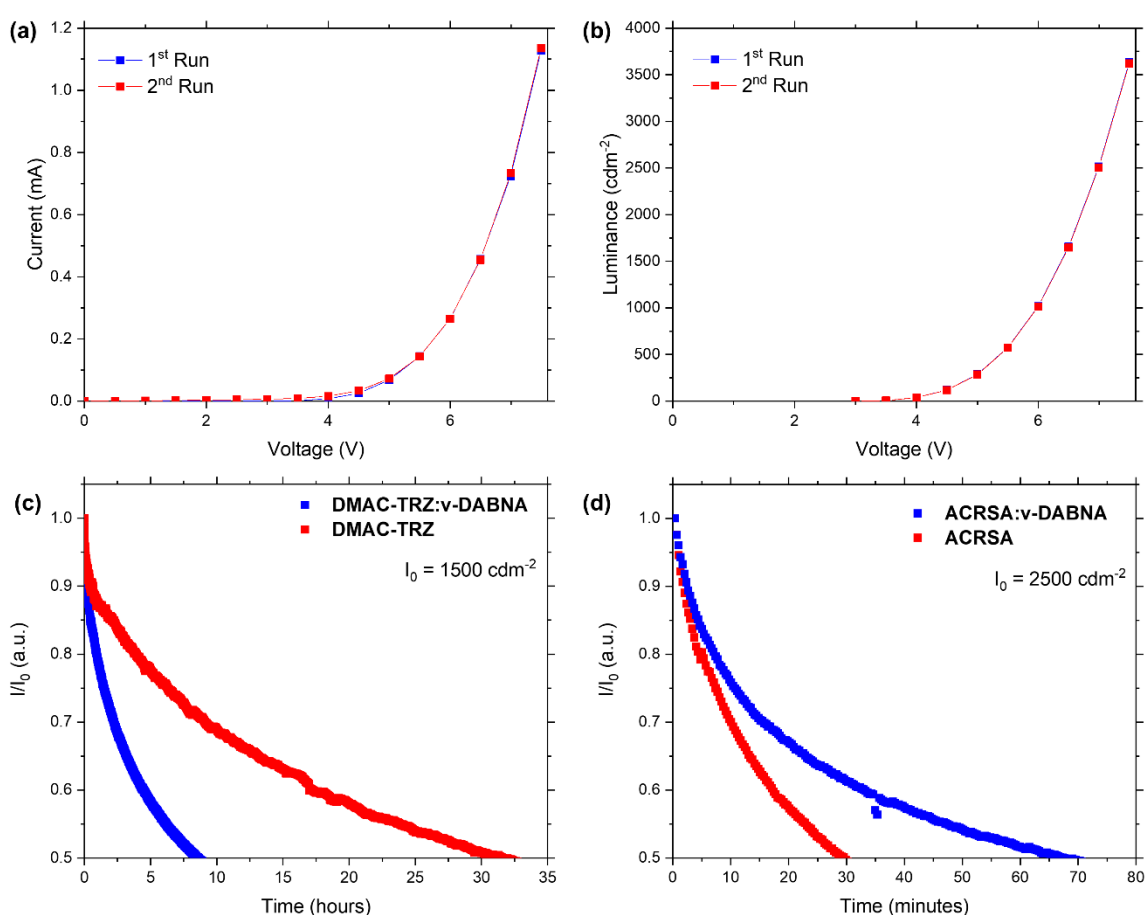


Figure 8.6. (a), (b) Consecutive JVL sweeps for the same ACRSA:v-DABNA:mCBPCN OLED pixel. Evidence that rapid degradation during the OLED measurements does not occur.

OLED lifetime measurements for (c) DMAC-TRZ series and (d) ACRSA series OLEDs, initial luminance at 1500 cd m^{-2} (at 2.5 mA cm^{-2}) and 2500 cd m^{-2} (at 10 mA cm^{-2}), respectively. The lifetime improvement in the HF-OLEDs for ACRSA follows the more efficient FRET and device performance improvement, compared to the DMAC-TRZ HF-OLEDs.

The stability of these devices is assessed in **Figure 8.6c, d**. The LT_{50} value for DMAC-TRZ OLEDs, at an initial 1500 cdm^{-2} , is surprisingly four times longer than the corresponding HF OLEDs (34 to 8.5 h). However, the opposite trend occurs in the ACRSA based devices, in which the lifetime improves by two and half times in the HF OLEDs (28 to 69 mins, at 2500 cdm^{-2}). The lifetime improvement in the HF-OLEDs for ACRSA follows the more efficient FRET and device performance improvement, compared to the DMAC-TRZ HF-OLEDs.

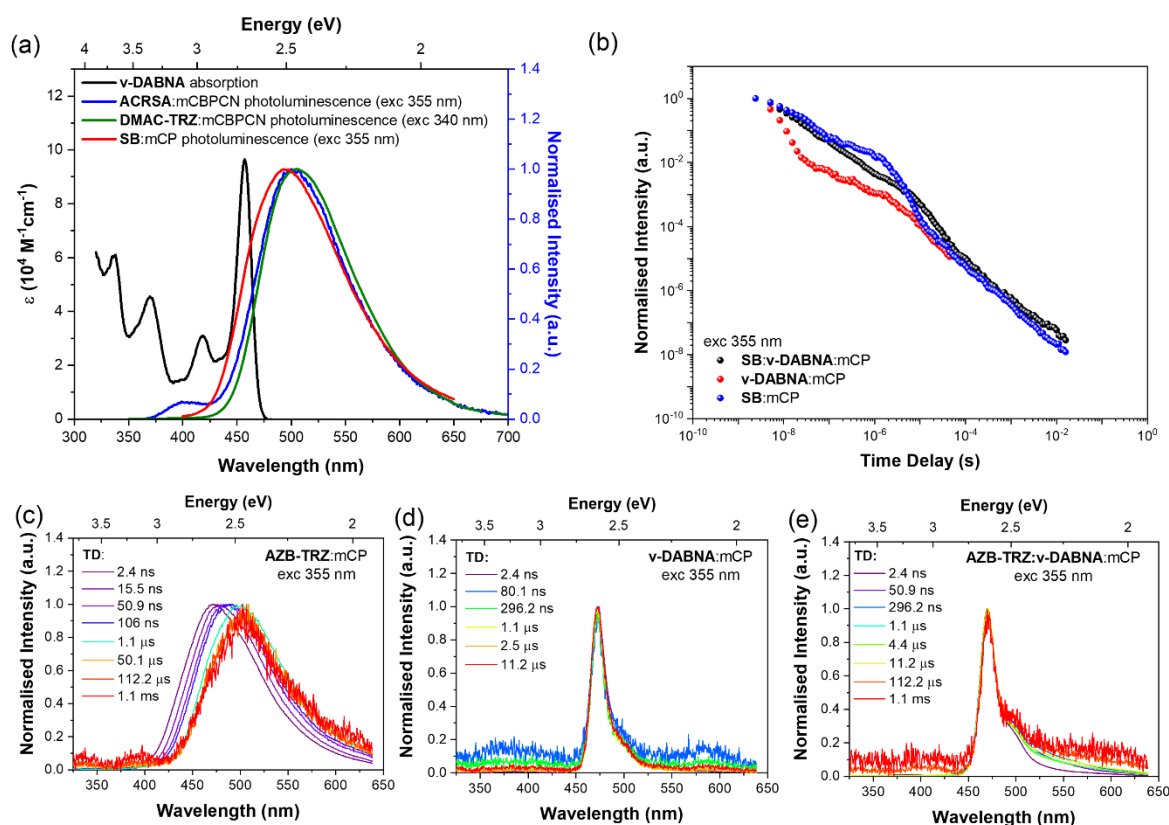


Figure 8.7. (a) Photoluminescence spectra of 10 wt % AZB-TRZ in mCP and 10 wt% DMAC-TRZ and ACRSA in mCBPCN compared to v-DABNA absorption spectrum. Time-resolved photoluminescence (b) decay traces of the evaporated films, and spectra of (c) AZB-TRZ:mCP (10%), (d) v-DABNA:mCP (1%), and (e) AZB-TRZ:v-DABNA:mCP (10:1 wt%). $\lambda_{\text{exc}} = 355 \text{ nm}$.

To explore this strategy further, an additional non-rigid TADF molecule was investigated, with blue-shifted emission compared to DMAC-TRZ (**Figure 8.7a**). AZB-TRZ (**Figure 8.5e**), part of a study conducted in collaboration with Prof. Eli Zysman-Colman's group, showed a considerably different balance of decay rates compared to ACRSA and DMAC-TRZ, with its intrinsic performance limited instead by a fast non-radiative decay rate and low PLQY (**Table 8.3**).²² Similar to DMAC-TRZ, a clear distribution of dihedral angles was observed through the time dependent PL spectra (**Figure 8.7c**) leading to limited spectral overlap of specific conformers (redshifted species) with the terminal emitter. The spectral overlap of the steady-state emission spectra with v-DABNA was nonetheless higher compared to ACRSA and DMAC-TRZ sensitiser (**Figure 8.7a**), leading to the highest J factor and FRET radius (**Table 8.2**) in this series of sensitiser.

Not surprisingly, the CT energy dispersion together with fast k_F and k_{ISC} (**Table 8.5**) of AZB-TRZ competes with the k_{FRET} leading to a seemingly low calculated η_{FRET} of 37% (**Table 8.2**), but also a more significant population of the triplet states. The latter indicates why η_{FRET} appears to be underestimated when considering the near-complete energy transfer apparent from the HF-OLED spectra, i.e. small contribution from the sensitiser to the EL spectrum (**Figure 8.5c**). As mentioned previously in this chapter, ISC/rISC cycling can depopulate and repopulate the singlet state (potentially multiple times) before emitting, and FRET will also occur during the DF/triplet regime. The calculated η_{FRET} from the PF decays represents the probability of FRET without considering these cycling events, rather than the larger cumulative η_{FRET} over the entire exciton lifetime.

The combination of FRET and fast rISC therefore helped to significantly enhance the AZB-TRZ HF device efficiency, although energy transfer was not as complete as in ACRSA and a small AZB-TRZ emission contribution was observed in the EL spectrum (~ 510 nm, **Figure 8.5c**). Indeed, the fast radiative and non-radiative singlet decay rates do not allow FRET to completely dominate the exciton dynamics for this TADF sensitiser, and the colour coordinate does not shift as much into the blue as for the ACRSA HF-OLEDs, surprisingly despite AZB-TRZ having higher energy emission and better spectral overlap (**Figure 8.8**). The device EQE_{max} nonetheless quadrupled, rising from 5 to 20%, and the excellent roll-off afforded by the rapid rISC of AZB-TRZ helped preserve and even enhance excellent roll-off performance in the HF devices compared to the TADF devices (**Figure 8.5e**). This case therefore represents

a near-ideal case study of the advantages of HF-OLEDs, with a highly effective sensitiser providing exceptionally fast triplet up-conversion to a near-ideal terminal emitter.

Table 8.5. Key photophysical characteristics of AZB-TRZ:v-DABNA:mCP, AZB-TRZ:mCP and v-DABNA:mCP films, at room temperature. $\lambda_{\text{exc}} = 355$ nm.

Photophysical characteristics	AZB-TRZ: v-DABNA:mCP	AZB-TRZ:mCP	v-DABNA:mCP
Concentration (wt%)	10:1:89	10:90	1:99
^a λ_{max} (nm)	476	495	476
^b Φ_{PL} (%)	45.88	37.6	29
^c $\tau_{\text{PF},1}$ (ns)	3.5 (v-DABNA)	4.91 (64%)	3.5
^c $\tau_{\text{PF},2}$ (ns)	15.05	29.5 (36%)	-
^d $\tau_{\text{PF},\text{av}}$ (ns)	15.05	23.88	-
^c $\tau_{\text{DF},\text{av}}$ (μs)	4.6	1.3	4.6

^a Values were obtained from the steady-state photoluminescence spectra. ^b Photoluminescence quantum yield (Φ_{PL}) under N_2 in drop-casted films, excited at 355 nm. ^c Lifetimes were obtained by fitting monoexponential and/or biexponential functions (**Figure 8.7**). ^d Average lifetime $\tau_{\text{PF},\text{av}} = (A_{\text{PF},1} \tau_{\text{PF},1}^2 + A_{\text{PF},2} \tau_{\text{PF},2}^2) / (A_{\text{PF},1} \tau_{\text{PF},1} + A_{\text{PF},2} \tau_{\text{PF},2})$.

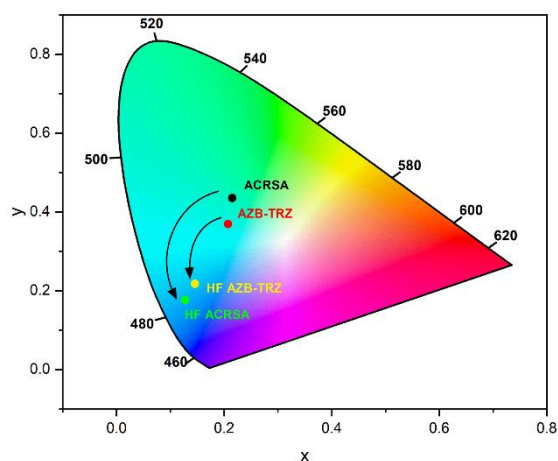


Figure 8.8. Comparison of CIE coordinates of ACRSA and AZB-TRZ OLEDs and HF-OLEDs, collected at 1000 cd m^{-2} .

The performance of ACRSA and AZB-TRZ HF-OLEDs both show a further important element of efficiency enhancement. In both cases, the power and current efficiencies of the respective HF-OLEDs were higher compared to the TADF and v-DABNA OLEDs (**Figure 8.9a-f**), only

partially explained by the improved quantum efficiency of the HF devices. In ACRSA, power and current efficiency raised from 31 cd A^{-1} and 28 lm W^{-1} in the greenish TADF OLEDs to 37 cd A^{-1} and 36 lm W^{-1} in the HF-OLEDs, despite their deep-blue colour coordinate. Similar results with much stronger improvement in efficiencies were observed for AZB-TRZ HF-OLEDs, rising from 12 cd A^{-1} and 9 lm W^{-1} in the TADF OLEDs to 30 cd A^{-1} and 27 lm W^{-1} in the HF-OLEDs. In contrast, DMAC-TRZ HF-OLEDs showed a decrease in power efficiency compared to the DMAC-TRZ devices because EQE remained unchanged and only the spectrum changes (**Figure 8.9g-i**). The slightly higher power efficiency values of the DMAC-TRZ HF-OLEDs, compared to the other two sensitisers, was attributed to the stronger contribution of DMAC-TRZ to the overall EL spectrum (**Table S6**). Indeed, due to physiological response curves a green emitter with similar radiance to a deeper blue emitter is always expected to have higher power efficiency – a trend that the overwhelming efficiency enhancements of our HF OLEDs disrupt.

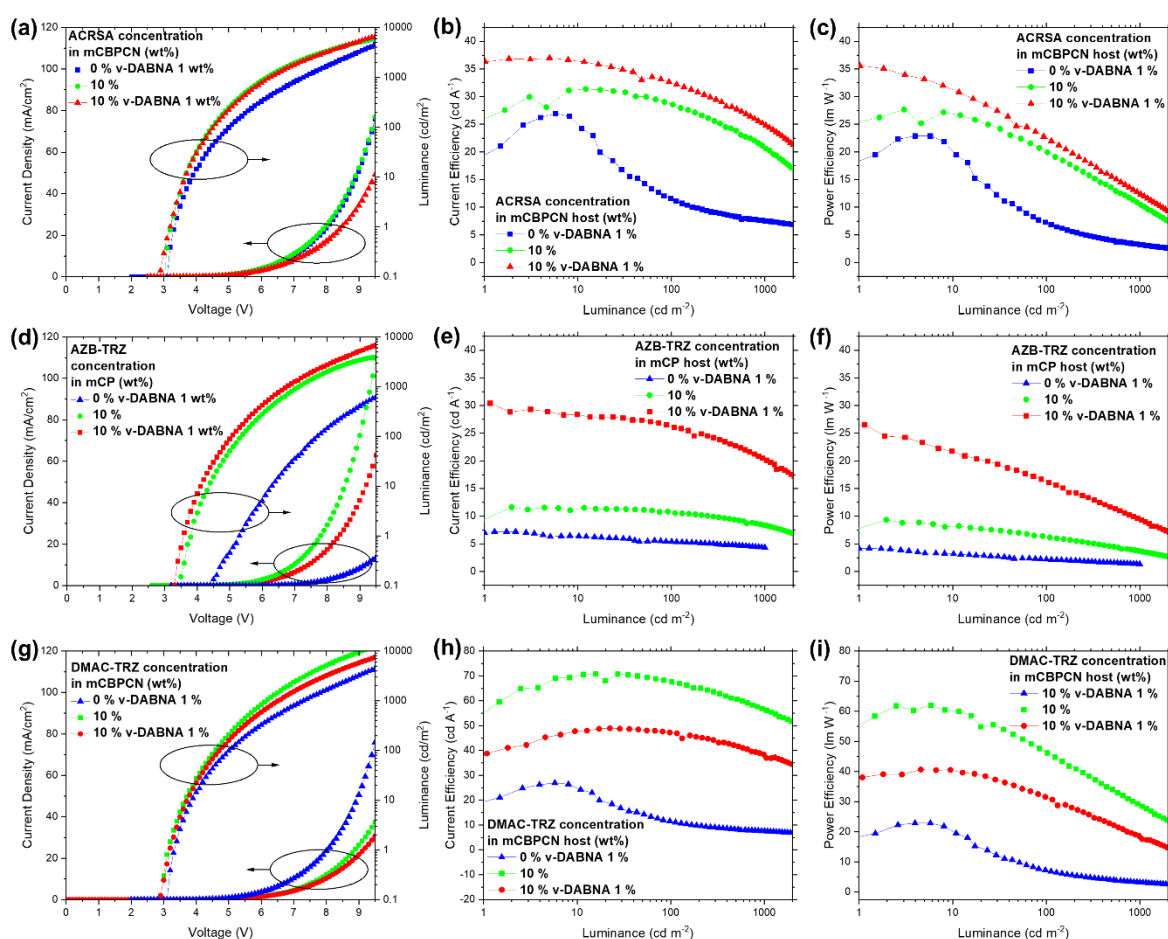


Figure 8.9. OLED performance. J-V-L curves, current efficiency over luminance, and power efficiency over luminance for (a)-(c) ACRSA, (d)-(f) AZB-TRZ, and (g)-(i) DMAC-TRZ series OLEDs, including the corresponding HF and v-DABNA only OLEDs for each series.

8.5 Conclusions

In this chapter the key photophysical parameters that support optimal triplet up-conversion sensitisation for use in HF-OLEDs were investigated. These parameters differ considerably from those required for a TADF molecule to exhibit strong performance as an OLED emitter. Importantly, rigid TADF molecules with homogeneity of the CT emission energy, exemplified by the spiro-linked TADF molecule ACRSA, allow all molecules in the film to undergo efficient FRET. Additionally, long radiative lifetimes and low ISC rates can be ideal for sensitisation, allowing small spectral overlaps to nonetheless support efficient cumulative FRET to the terminal emitter. Although high $rISC$ (and consequently high ISC) and radiative rates are desirable for achieving shorter triplet and singlet lifetimes and minimising triplet annihilation/quenching phenomena in TADF OLEDs, in HF-OLEDs a much slower k_{ISC} and k_r can still provide efficient sensitisation if they can strike a delicate balance between being fast enough to ensure device stability and slow enough to allow FRET to outcompete singlet photophysical and non-radiative processes. The efficient FRET can then circumvent the moderate PLQY of ACRSA and AZB-TRZ, also providing narrowband blue emission from v-DABNA. This strategy also enables the sensitizer excitation energies to be pushed as low as possible while retaining deep-blue emission, with significant benefits on choice of host material and device longevity.

These results therefore reveal an interesting ‘blind spot’ in TADF and hyperfluorescence research. By limiting the scope to only the ‘best’ performing TADF materials as sensitizers (such as DMAC-TRZ), it is likely that many excellent hyperfluorescent pairs using ‘less ideal’ TADF sensitizers have been overlooked and would likely never be considered or discovered. This ability to turn intrinsically ‘poor’ TADF emitters into blue HF-OLEDs with exceptional performance (**Figure 8.5**), could stimulate a re-evaluation of many previously reported and unreported TADF materials, as well as reassess the current perceptions of what defines novel photonic materials applicability.

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9 Conclusions

The thesis extensively addresses the complexity of organic molecules, particularly TADF emitters. The stability challenge in blue OLEDs is influenced by various factors, including the limited fundamental understanding of individual molecules and molecular systems holistically. This thesis aims to shed “light” on fundamental phenomena occurring in TADF molecules and systems through the utilization of photophysical and electrical experimental techniques. By integrating the discoveries from individual TADF and MR-TADF molecules, this investigation delves into their application in HF OLEDs, aiming to produce efficient blue HF OLEDs characterized by narrow emission spectra and enhanced stability.

9.1 D-A type TADF emitters

DMAC-TRZ, a prominent TADF emitter, was extensively studied both in solution and solid-state matrices to elucidate its intrinsic properties and hosting effects. While demonstrating efficient TADF performance and homogeneous emission in solution, solid-state behavior varied with concentration, revealing complexities influenced by intermolecular interactions. Lower film concentrations unveiled a strong dihedral angle inhomogeneity, resulting in a dispersion of charge transfer energies and exciton kinetics, stemming from the rigid host packing dynamics. Increasing concentrations reduced this effect, resulting in a narrower homogeneity distribution originating from strong intermolecular interactions (dimer/excimer formation). Although the inhomogeneity effect minimally impacts the OLED efficiency, the DMAC-TRZ molecules with smaller dihedral angle values exhibit slower k_{rISC} and thus longer triplet exciton lifetime. The latter enhances the probability of triplet-triplet and triplet-polaron annihilation, which potentially affects the stability of DMAC-TRZ OLEDs. Further, the CT energy dispersion significantly influenced FRET efficiency, when DMAC-TRZ was used as a sensitizer in HF OLEDs, as shown in chapter 7 and 8. The less twisted DMAC-TRZ molecules exhibit bluer emission and better spectral overlap with the terminal emitter (ν -DABNA) while the highly twisted molecules exhibit redder emission and limited spectral overlap with ν -DABNA leading to inefficient FRET.

At lower DMAC-TRZ concentrations (<1 wt%), a hidden conformational property was revealed, indicating the presence of a second conformer, the QA which has a strong local

character (QA oscillator strength 10 000 time higher compared to the QE conformer). The latter was verified from quantum chemical calculations. Despite its excited state instability in solution, the rigid host in the solid state facilitated dual emission from both QA and QE conformers. At higher concentrations (≥ 1 wt%), FRET efficiency from the QA to the QE conformer increased significantly, overshadowing the contribution of the QA to the PL spectrum. Utilizing DMAC-TRZ as a sensitizer in HF OLEDs alongside *v*-DABNA, a notably high FRET efficiency was observed compared to analogous systems,^{1,2} indicating direct energy transfer from the QA conformer to the terminal emitter, circumventing the QE conformer. This efficient energy transfer allowed for the fabrication of HF OLEDs converting greenish emission to blue.

9.2 MR-TADF emitters

Rigid MR-TADF molecules, particularly *v*-DABNA, present a scenario that is somewhat simpler in terms of conformational flexibility but more intricate regarding triplet harvesting. Chapter 5 reveals a notable temperature dependency in ΔE_{ST} and limited vibration modes available to enable rISC, suggesting the applicability of Northey and Penfold theoretical predictions regarding thermally activated rIC of T_1 to a T_n state followed by rapid rISC from T_n to S_1 .³ In solid state at relatively low concentrations (~ 1 wt%), *v*-DABNA was observed to form excimers, albeit weakly coupled and exhibiting significant disorder. Their influence was examined in HF OLEDs, with devices containing lower *v*-DABNA concentrations (0.5 wt%) showing higher EQE_{max} compared to the typically 1 wt% devices. However, FRET analysis showed that achieving full energy transfer from the TADF sensitizer necessitates *v*-DABNA concentrations close to 1 wt%, highlighting the need for future molecular design strategies to mitigate excimer formation at such concentrations.

In Chapter 6, new non-triangulene MR-TADF emitters, α -3BNOH and modified α -3BNMes, exhibited slow triplet harvesting but strong radiative rates. Compared to the α -3BNOH UV emitter, α -3BNMes showed near-ideal CIE coordinates for blue OLEDs and suitable absorption for FRET with an existing TADF sensitizer (DtBuAc-DBT). α -3BNMes HF OLEDs achieved comparable EQE_{max} to the TADF (sensitizer only) OLEDs, but suffered from severe EQE roll-off due to slow rISC of the terminal emitter. Nonetheless, deep-blue HF OLEDs with (0.15, 0.10) colour coordinates suggest that adjusting the absorption spectrum of terminal MR-TADF emitters can enhance FRET compatibility in HF devices.

9.3 Blue OLED optimization using the HF approach

In Chapter 8, combining all the work done in this thesis, the limitations of FRET efficiency in HF OLEDs were extensively investigated. Utilizing a series of greenish sensitizers with minimal spectral overlap with v-DABNA, the essential criteria for achieving efficient FRET were identified. These criteria diverge significantly from those necessary for a TADF molecule to function effectively as an OLED emitter. Molecular conformational homogeneity, extended radiative lifetimes, and slow ISC rates emerged as optimal properties for HF OLED sensitizers. These attributes facilitate minimal spectral overlaps with the terminal emitter, thus supporting efficient FRET. This effective FRET mechanism can compensate for moderate sensitizers' PLQY, as demonstrated by ACRSA and AZB-TRZ. This paradigm shift challenges the conventional understanding of ideal TADF sensitizers. By leveraging this approach, the sensitizer excited state energies can be minimized, a highly important parameter to reduce the device excited state energies, thus improve the probability of extended device lifetime, while the HF OLED maintains deep-blue emission from the terminal emitter. Notably, ACRSA HF OLEDs exhibited nearly tripled EQE_{max} and enhanced device lifetimes compared to TADF-only OLEDs.

9.4 Outlook and Concluding remarks

OLED technology has become integral to the global display market. Despite attempts to address the blue OLED operational lifetime issue through methods like larger pixel sizes or the tandem approach, which involves incorporating more than three evaporated single OLED structures into one device, the problem persists. The emergence of the latest OLED generation, hyperfluorescence, poised to enter the market, presents a promising solution with its narrow band emission and triplet harvesting of MR-TADF terminal emitters (compared to conventional fluorescence emitters). Though challenges remain in fully understanding and improving hyperfluorescence technology, early indicators are highly promising.

This thesis concentrates on TADF and MR-TADF OLED emitters, contributing to a deeper comprehension of their unique properties, particularly in guest-host systems. This promotes a deeper understanding of material design optimization. By combining TADF sensitizers with MR-TADF terminal emitters in HF OLEDs, this work establishes foundational principles for

an ultra-efficient sensitization process. This, in turn, enhances blue OLED performance and stability, pushing the boundaries of our current understanding of HF OLEDs.

9.5 References

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