Synthesis and properties of novel phthalocvanines and related N-containing macrocycles.

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Submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, Durham University.

Submission date TBC.

Declaration

The work described in this thesis was carried out in the Chemistry Department of Durham University between October 2002 and November 2005. This thesis is the work of the author except where acknowledged by reference, and has not been submitted for any other degree.

Abstract

Phthalocyanines and other closely related compounds are an important class of macrocycles with many commercial applications. They display interesting optoelectronic and coordination properties, which has resulted in their utilisation in a wide range of fields including optical data storage, electrochromic and optical limiting devices, photosensitizers and medicinal therapeutic agents, and multistage-redox-dependent fluorophores.

The synthesis, optoelectronic and surface-assembly properties of several new axially disubstituted silicon phthalocyanines are detailed in this work. Axial ligands include phenyl, terphenyl, thienyl and pyrenyl derivatives. Their absorption and emission spectra are reported and fluorescence lifetimes and quantum yields are correlated with the ligand structures. The optoelectronic properties of a novel free-base phthalocyanine bearing peripherally attached fluorene substituents are also described.

Several of these silicon-phthalocyanines were used to assemble thin films on electrode surfaces, and techniques such as scanning Kelvin nanoprobe microscopy and atomic force microscopy, as well as chronoamperometric measurements were used to probe these surfaces.

A number of free-base porphyrins bearing a variety of aryl substituents at the *meso*-positions are also described. The conversion of some of these free-base porphyrins to metalloporphyrins is detailed, and a thorough examination of the fluorescence properties of all synthesised porphyrins is also presented.

Pyrazinoporphyrazines are a closely-related analogue of phthalocyanines, and several new examples of these systems have been synthesised. As with both the phthalocyanines and porphyrins, their fluorescence properties have been investigated in detail.

Acknowledgements

First and foremost, my thanks go to Martin Bryce, who has been of great help throughout my PhD. By always being there to bounce ideas off when needed, and by allowing me to just get on with the work in my own particular fashion throughout my time in the group, he has been the ideal supervisor.

My thanks go also to those members of the department I have worked with over the three years of my PhD. Several members of the Bryce group, namely Changsheng Wang, Xianshun Zeng, Igor Perepichka and Sylvia Bettington, in particular have proved invaluable on numerous occasions, supplying knowledge on a variety of subjects and for this they have my eternal gratitude.

For his work on the various crystal structures obtained, often from extremely poor quality material, I thank Andrei Batsanov.

With regards to the fluorescence studies of the compounds I would like to thank Laurent Porres, Karen Findlay and in particular Andrew Beeby for the use of his lab on many occasions and for his special brand of sarcasm.

With regards to the surface chemistry, I thank Aidan Rhodes and Alan Massey for their work with the phthalocyanine compounds. This work includes the preparation of all phthalocyanine films and electrodes used and the running of all AFM, SKN and CV experiments. I thank Ritu Kataky for allowing me to collaborate on the interpretation of this work in the first place, and for her help and advice with the associated section of this thesis.

Though far too numerous to name here, the various members of staff within the department have been absolute stars over the last three years. In particular I would like to thank Elizabeth Wood and Tony Baxter in the Stores, Dave Parker for running endless MALDI-ToF spectra for me, and Catherine Heffernan and Ian McKeag for persevering with NMRs on weakly soluble macrocycles, and not complaining at all.

Finally, I would like to thank my family for supporting me during my time at university (I wouldn't be here without them), and most importantly of all an enormous thank you to my other half and partner in crime, Helen Vaughan. She has put up with me in my "grot-bags" phase over the last two year with tremendous patience, and I only hope that I am able to do the same for her in a year's time.

Table of Contents

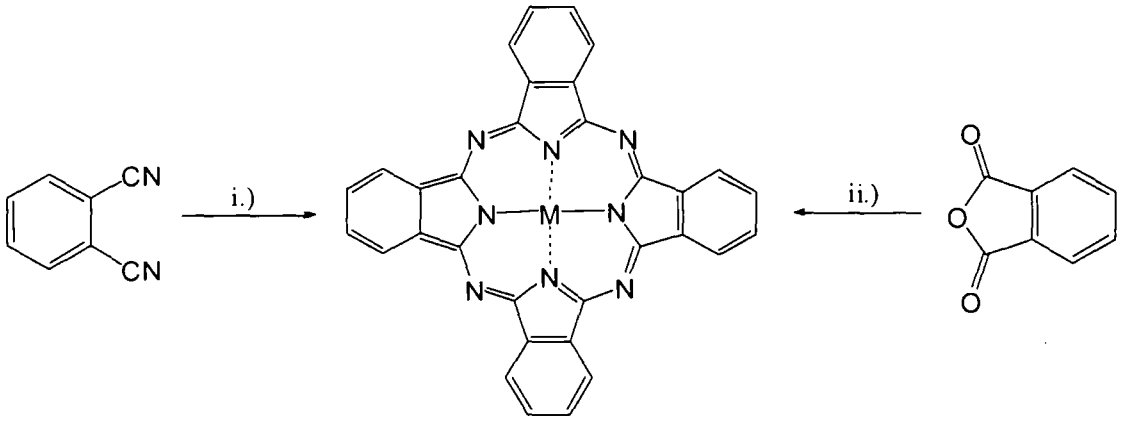
List of Figures and Tables

Chapter 1. Literature Review

1.1 Phthalocyanines

1.1.1 Background

The first occurrence of phthalocyanines (Pcs) in the literature was in 1907, when the macrocycle was unexpectedly produced by heating *o*-cyanobenzamide in refluxing ethanol which gave a blue compound in low yield.[1] However, it was not until 1934 that analysis and X-ray diffraction showed the ring structure to be similar to that of the naturally occurring porphyrins.[2-9] Linstead's group increased yields to ~40% via the inclusion of metal or metal salts in the reaction (the template effect), producing a metallophthalocyanine which could then be demetallated with cold concentrated H_2SO_4.[2] After it was found that treatment of phthalonitrile with a number of reagents including sodium, ammonia gas, lithium n-pentoxide and other alcohols,[3,10-12] gave a Pc in relatively high yields, the potential for facile synthesis of substituted phthalocyanines was realised. Phthalocyanine may also be synthesised from the analogous cyclic tetramerisation of phthalic anhydride, although these reactions generally tend to be less clean then those using phthalonitrile (Fig 1). However the anhydride is preferred in industry due to the cheaper precursor, even though a nitrogen donor such as urea is required as a co-reactant.



i.) metal or metal salt, heat; ii.) metal salt + nitrogen donor, heat

Fig 1: Basic synthesis of a phthalocyanine

Complexes of the Pc ring with cations derived from over 70 different elements are known. In addition, certain transition metal ions prove extremely difficult to remove from

the central cavity once complexed (*e.g.* Cu^{2+} and Ni^{2+}), and instead result in the destruction of the macrocycle.[13]

The core macrocycle comprises an 18-π electronic system and in addition to this, the π-systems of the peripheral six-membered rings give extra conjugation to an already electron-rich molecule. This large electron density coupled with the effects of the 8 nitrogen atoms contained within the macrocycle results in a bathochromic (or red) shift in the UV-Vis spectrum, compared with that of the porphyrin chromophore, and an increase in the intensity of the absorbance at this higher wavelength. Hence phthalocyanines have long been employed as components of various intense blue and green dyes.

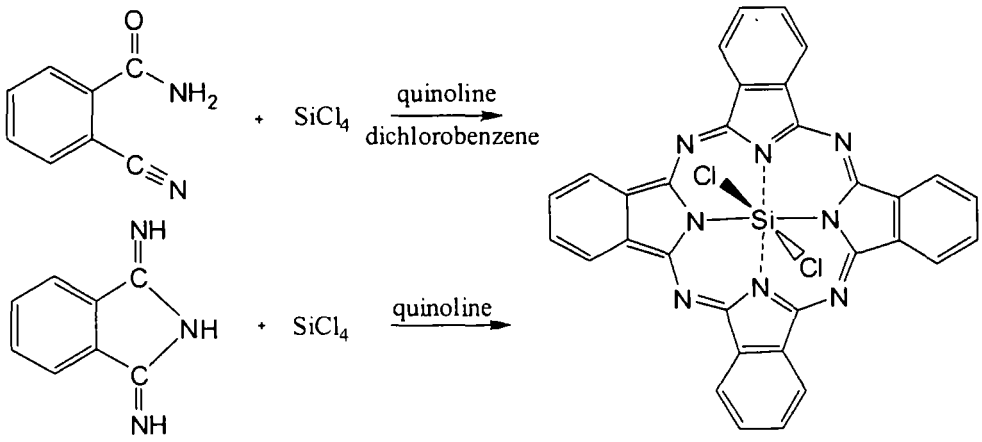
Within the last seventy years, a great deal of attention has been given to Pc derivatives[13-16] Currently two major commercial uses are as photoconductors[17] and as a component of recordable CDs.[18] Other fields include medicinal therapeutic agents,[19,20] multi-stage redox-dependent fluorophores,[21] catalysts,[22] photosensitisers,[23] non-linear optics[24] and chromatography.[25]

Pcs may be substituted either peripherally on the outer ring or axially via ligand addition to the metal centre. The former type of substitution is perhaps the easier to achieve and is achieved by functionalisation of the phthalic precursors,[26-29] or less commonly via coupling reactions at the periphery of the pre-formed Pc.[30-32] Peripheral substituents include tetrathiafulvalene (TTF) groups,[26,28] dendrimers,[33,34] solketals,[35,36] ferrocenes,[37] crown ethers[38,39] and direct sulphonation of the benzo-moieties.[40] More recently, functional groups such as TiO_2 surfaces,[41] porphyrins,[42] and fullerenes have also been utilised.[43] Axially-substituted Pcs can be difficult to purify as reaction mixtures generally contain two or more Pc species. Nonetheless, a great number of axial derivatives have been previously synthesised from Pcs containing a wide range of central metal atoms such as gallium,[44-46] titanium,[47,48] nickel,[49] manganese, iron,[50-52] osmium,[53] cobalt,[54,55] and silicon.[56-58] The potential for the synthesis of axially-polymerised phthalocyanine stacks has also been thoroughly explored.[59-61]

1.1.2 Silicon Phthalocyanines

1.1.2.1 Background

A silicon-centred Pc was first reported in 1960 when Kenney and co-workers synthesised dichloro(phthalocyanino)silicon via reaction of *o*-phthalonitrile with either silicon tetrachloride or hexachlorodisiloxane.[62,63] This has remained a key starting material in SiPc chemistry. More convenient approaches to $Si(Pc)Cl_2$ (**1**) were rapidly developed, utilising both *o*-cyanobenzamide and 1,3-diiminoisoindoline in place of the phthalonitrile (see Fig 2).[64]



$PcSiCl_2$ (1)

Fig 2: Syntheses of $Si(Pc)Cl_2$[64]

Recently the crystal structure of **1** was elucidated by Silver *et al.*, showing that the Si(IV) ion lies in a distorted octahedral environment (see Fig 3). The crystal structures of two axially-substituted silicon phthalocyanines bearing carboxylate ligands were also obtained.[65]

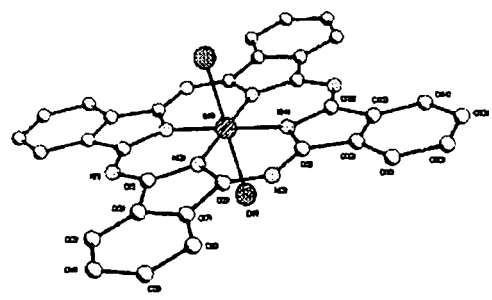


Fig 3: Crystal structure of **1**, hydrogens omitted for clarity.[65]

The labile Si-Cl bond in $Si(Pc)Cl_2$ allows easy ligand substitution at the central metal atom. For example, hydrolysis was achieved via refluxing $Si(Pc)Cl_2$ with $NaOCH_3$ in a mixture of water and ethanol to give $Si(Pc)(OH)_2$ (**2**).[64] Kenney *et al.* synthesised a wide range of axially-substituted Si-Pcs containing ligands such as alkoxides, siloxy derivatives, halides and aryl derivatives.[62,66-71]

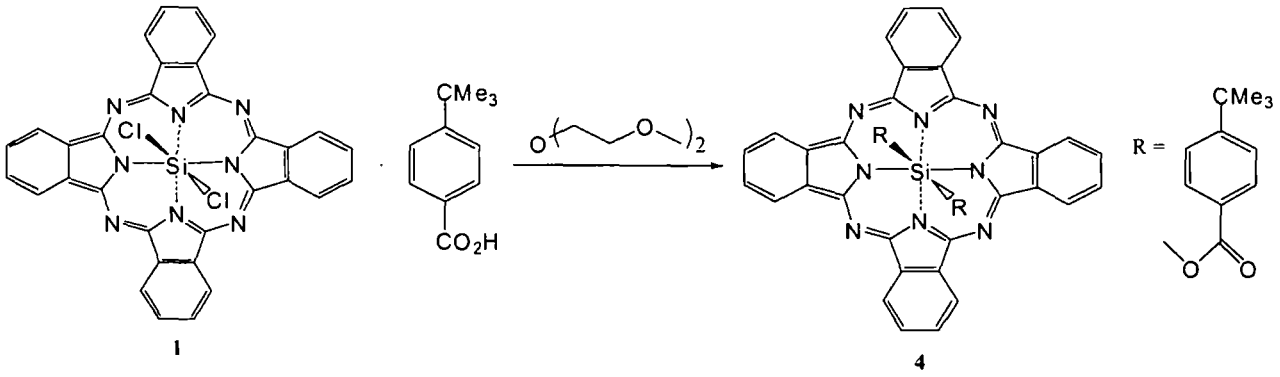
The more simple alkoxides can be easily synthesised from $Si(Pc)Cl_2$ by reaction with the corresponding alcohol in the presence of $NaBH_4$,[72] or by refluxing $Si(Pc)Cl_2$ in the alcohol itself (which can lead to polymeric material).[73] For more complex or bulky alkoxides, synthesis is more easily facilitated via reaction of the alcohol with compound **2**.[72] Predictably, the solubility of these compounds increases with the length of the ligand, and is accompanied by a decrease in thermal stability. In compounds where the ligands have a much greater electron affinity [i.e. $PcSi(OCH_2CCl_3)_2$ (**3**)], a slight blue shift can be observed in the UV-Vis spectrum. This can be attributed to the fact that electron-withdrawal from the macrocycle hinders the $\pi - \pi^*$ transition. The reaction of $Si(Pc)(OH)_2$ with R-OH may be influenced by the low solubility of $Si(Pc)(OH)_2$ in a variety of organic solvents, the acidity of the R-OH reagent and the strength of the Si-OR bond which is formed. A variety of mechanisms have been proposed for these reactions, the most plausible of which is protonation of a hydroxyl ligand, followed by loss of water and addition of the RO^- anion (see Fig 4).[72]

$$HO(Pc)SiOH \xrightarrow{R\text{-}OH} HO(Pc)SiOH_2^+ \xrightarrow{-H_2O} HO(Pc)Si^+ \xrightarrow{RO^-} HO(Pc)SiOR$$

Fig 4: Suggested mechanism for formation of PcSi alkoxides.[72]

1.1.2.2 PcSi Esters

More recent work with the formation of Si-O bonds has centred not on the formation of bis-ethers but on a series of *trans*-axially substituted bis-esters.[58,74] e.g. silicon phthalocyanine bis(4-*tert*-butyl)benzoate (**4**), studied in our laboratory (see Fig 5).[74]



1 4

Fig 5: Synthesis of silicon phthalocyanine bis-(4-tert-butyl)benzoate (**4**) reference compound.[74]

Its high solubility and minimal electronic and steric interaction between the ligand and macrocyclic core make it an ideal reference for this group of compounds which included thiophene and dimethoxyphenyl derivatives via a general synthesis involving reaction of $Si(Pc)Cl_2$ with acid derivatives in 2-methoxyethylether as solvent. X-Ray studies elucidated how these axially substituted Pcs pack in the crystal, and showed that flexibility of the ligand is important. All of the compounds synthesised exhibited monomeric behaviour in the absorption spectra, indicating the effectiveness of the axial ligands in preventing intermolecular interaction between the chromophoric macrocycles. Quantum yields and fluorescence lifetimes were high for all compounds.

The work was expanded to include several bis-axial substituted phthalocyanines containing a range of TTF substituents (see Fig 6).[58]

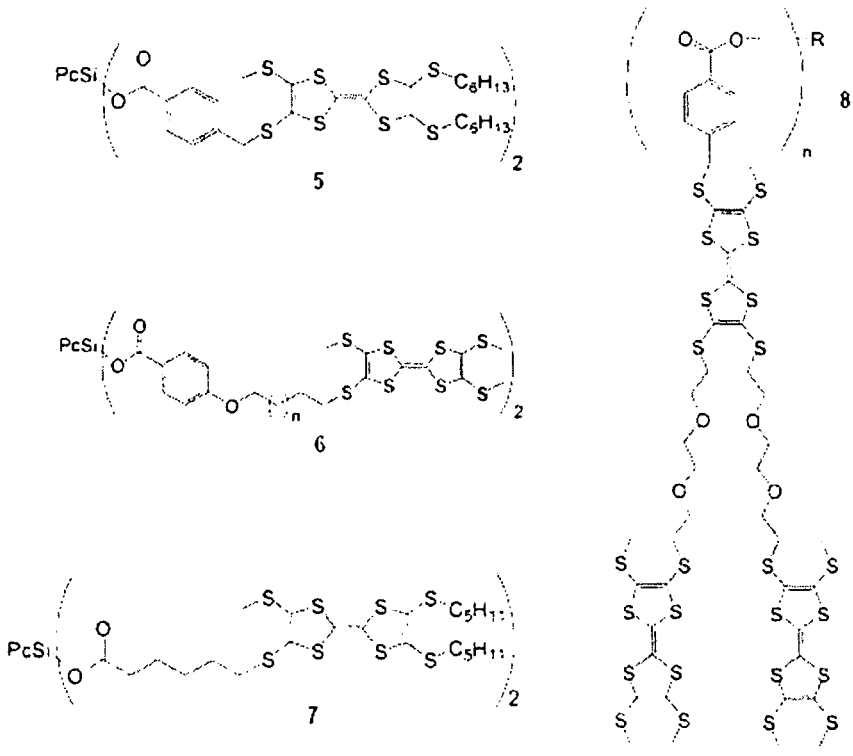


Fig 6: Synthesis of Pc-TTF hybrid structures[58]

Variations in the length of the linking group, substitution position on the pendant benzene ring, temperature effects and the presence of the TTF groups allowed a full exploration of the electrochemical and spectral properties of these compounds. These highly electron-rich compounds reduced the phthalocyanine fluorescence to less than half of that of the benzoate reference compound. An increase in the separation distance between the Pc and TTF units resulted in a decrease in fluorescence quenching as the two π-systems are moved further apart. The fact that the ligand itself becomes more flexible does not aid in quenching as might be expected if there were an interaction directly between the π-systems rather than along the ligand chain. In contrast, altering the substitution on the benzene ring from the *para* position to the *ortho* and *meta* positions greatly increases quenching as the two π-systems are forced into close proximity. Absence of the benzene spacer group in the ligand chain increased fluorescence quenching by increasing ligand flexibility but the compound (**7**) was found to be unstable in solution. This problem was overcome by synthesis of a dendritic species (**8**) consisting of several TTF groups which was stable in solution and still maintained the high degree of quenching exhibited by **7**.[58]

Fluorescence emission increased as temperature decreased due to the solvent solidifying around the ligands, causing them to freeze into their thermodynamically favourable positions away from the macrocycle.

In solution electrochemical studies the Pc-TTF hybrids display two reversible one-electron TTF oxidations. One-electron waves were also observed for the phthalocyanine. As the first oxidation potential of TTF is lower than that of the phthalocyanine, it was possible to selectively oxidise the TTF substituents. As the radical cation and dication exhibit acceptor, and not donor, properties, it was hoped that this oxidation would prevent quenching of the phthalocyanine, leading to an electrochemical switch. However, the emission of the phthalocyanine remained unchanged despite selective oxidation of all compounds. A possible explanation is a reverse quenching pathway between the excited state of the phthalocyanine and the TTF radical cation (see Fig 7).[58]

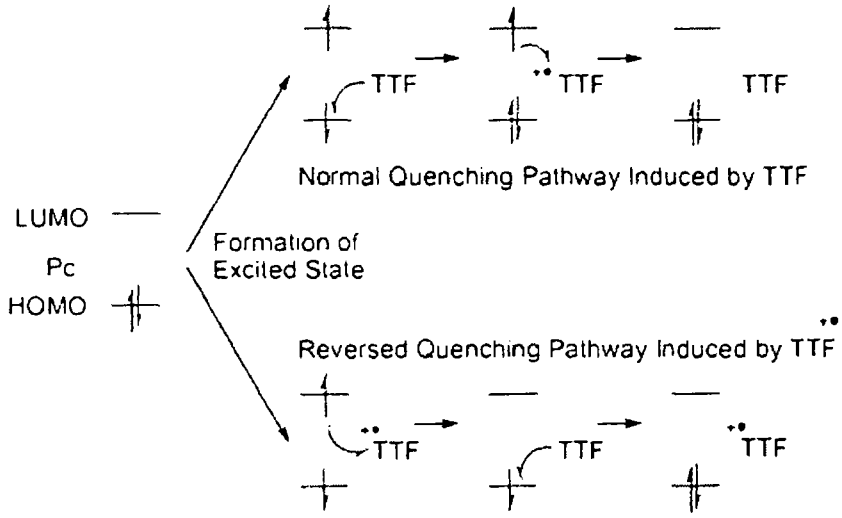


Fig 7: Molecular orbital picture of proposed Pc emission quenching pathways.[58]

Recently, Rodriguez-Redondo *et al.* have synthesised a photoswitchable Si-Pc derivative with two azobenzene units at the axial sites (**9**) (see Fig 8).[57] The photoemissive properties of the molecule can be modulated by isomerisation of the azoarenes, creating a reversible fluorescence switch. The advantages of this system over previously published electrochemical switches involving macrocycles is that the recovery of the initial state does not depend only on the rate of the thermal reaction as it can be selectively controlled and the difference in the "turn on" and "turn off" wavelengths is significant.

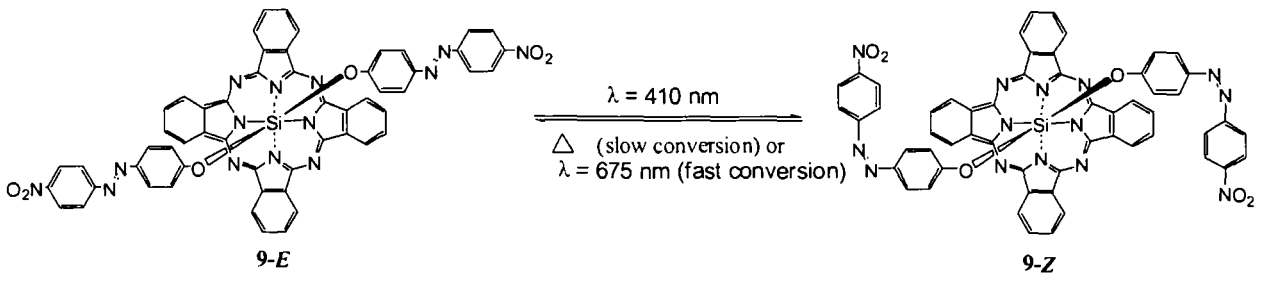


Fig 8: Structure of photoswitchable azobenzene-Pc-azobenzene triad (**9**).[57]

Another library of Si-Pc bis-esters has recently been synthesised by Sosa-Sánchez *et al.* via the reaction of $Si(Pc)Cl_2$ with the potassium salts of fatty acids.[75] Crystal structures were obtained for several of the compounds and as for $Si(Pc)Cl_2$, the Si atom in these molecules lies in a distorted octahedron, with the axial ligands orientated *trans* to each other with respect to the plane of the macrocycle (see Fig 9).

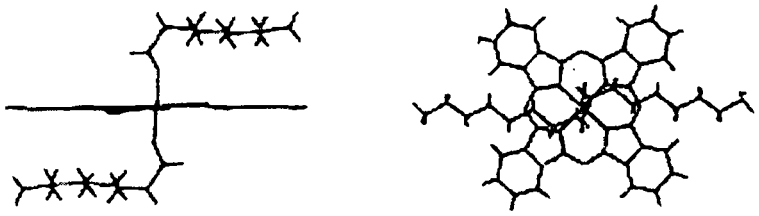


Fig 9: Lateral and Pc plane views of a fatty-acid substituted PcSi (**10**).[75]

The synthesis of the novel ferrocene-containing SiPc species, bis(ferrocenecarboxylato)(phthalocyaninato)silicon (**11**), was achieved by Silver *et al.* via reaction of $Si(Pc)Cl_2$ with ferrocenecarboxylic acid.[76] The crystal structure of the molecule (see Fig 10), was compared with other axially substituted SiPcs, and it was shown that the size of the silicon atom's atomic radius varies with the nature of the attached ligand.

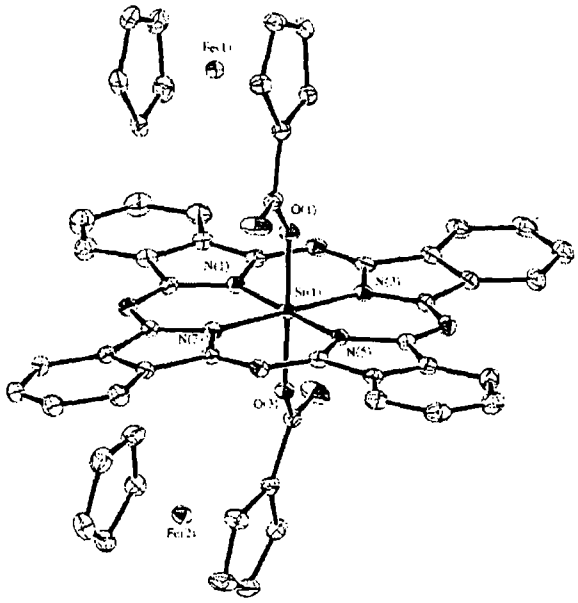


Fig 10: Obtained crystal structure of bis(ferrocenecarboxylato)(phthalocyaninato)silicon (**11**), hydrogens omitted for clarity.[76]

1.1.2.3 Photosensitizers

Phthalocyanines have, in recent times, found much use as components of potential photosensitizer molecules for use in photodynamic therapy (PDT).[77-79] Their maximum light absorption in the red band is attractive as long wavelengths penetrate into tissues, and also because melanins located in pigmented tissues and tumours lower the yields of earlier photosensitizers such as porphyrins due to the absorption of their activating wavelengths in the 500-600 nm Q band.[80] The use of axially substituted Pcs (notably Si and Al derivatives) is of particular advantage as it allows an increase of photocytotoxicity in addition to the attachment of hydrophobic groups on the macrocycle's periphery.[81-84]

Brasseur *et al.* showed that a bis-siloxy substituted silicon naphthalocyanine (**12**) gave high PDT efficiency accompanied by minimal damage to adjacent tissues, and thus has potential as a far-red absorbing photosensitizer (see Fig 11).[83]

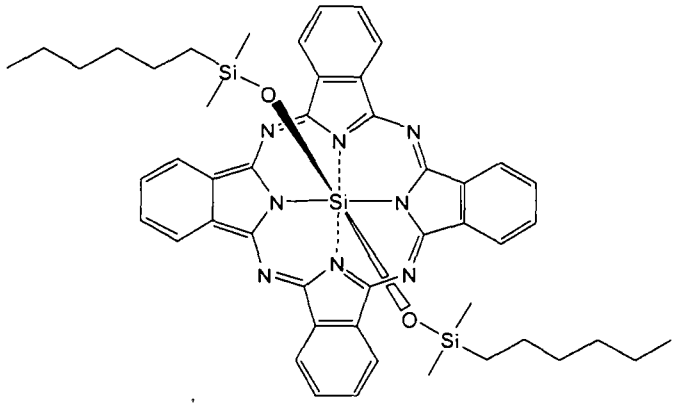


Fig 11: Structure of potential PDT agent, bis(dimethylhexylsiloxy)silicon 2,3-naphthalocyanine (**12**).[83]

Subsequently, He *et al.* studied the SiPcs (see Fig 12)[82] and concluded that a small axial ligand, such as the hydroxy group, is not necessary for efficient photosensitization as there was little difference in the efficiency of the mono- and bis-substituted derivatives. The elongated aminosiloxy ligands reduced the compounds efficiency. It was concluded that the axial attachment of substituents leading to a better interaction between the photosensitizer and its cellular targets would be of more use then substituents which would enhance the already acceptable photochemical and photophysical properties.

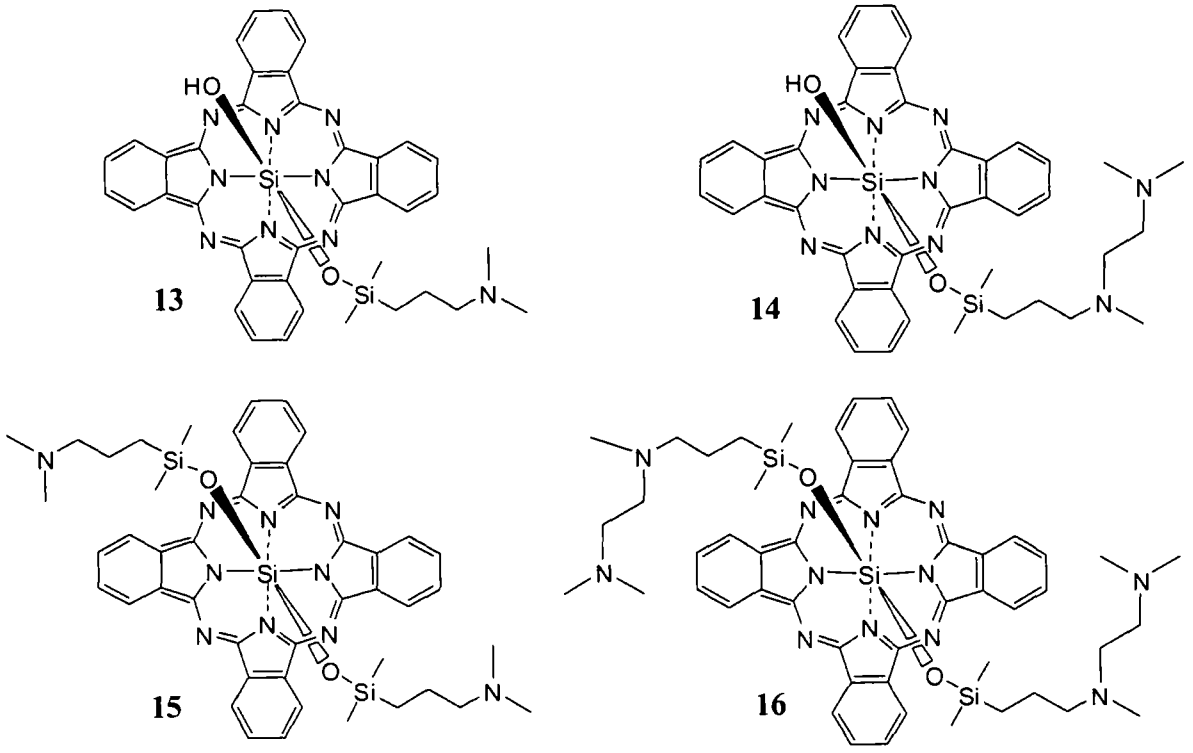


Fig 12: Structures of a series of aminosiloxy based SiPc photosensitizers.[82]

This hypothesis was subsequently addressed by Decréau *et al.* between 1998-2004 on the attachment of axial substituents which would either add lipophilic character or increase molecular recognition.[81,85-87] The attachment of tri-n-hexylsiloxy, octyloxy, cholesteroloxy, cholesteroloxy-diphenylsiloxy and epiglobulyloxy substituents gave a series of new SiPc derivatives (see Fig 13) which were compared to the known photosensitizer, chloro-aluminium Pc.[81]

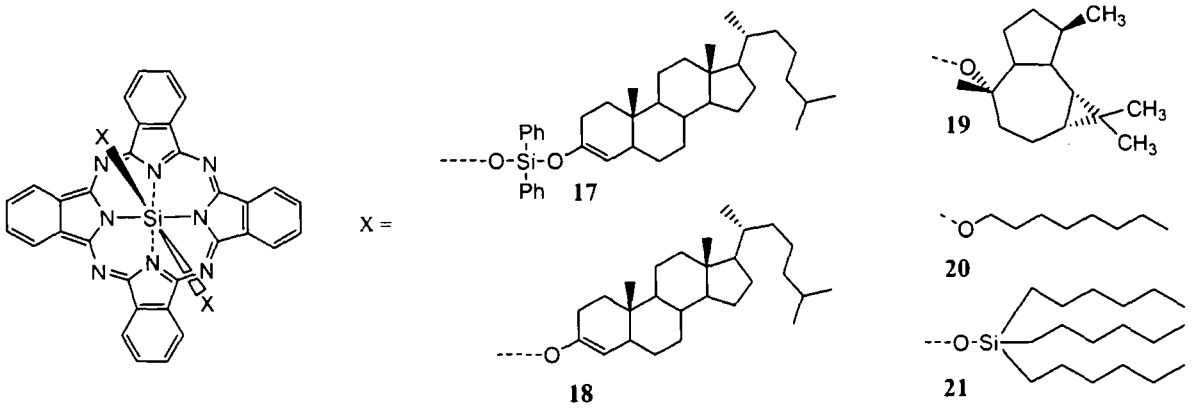
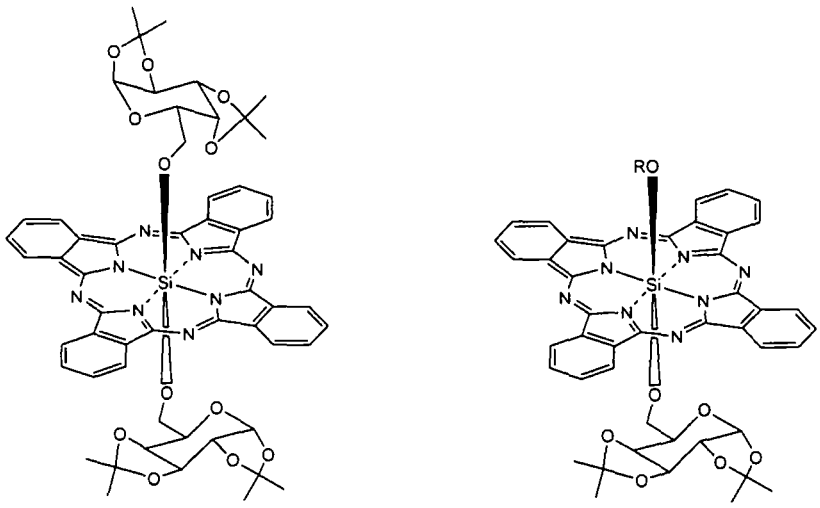


Fig 13: Structures of a series of SiPcs bearing bulky axial groups for use in PDT.[81]

The cholesteroloxy (**18**) and octyloxy (**20**) derivatives had the best photokilling efficacy on pigmented melanocytic cells and were more efficient then the known ClAlPc photosensitizer. However, the larger substituents were less effective, suggesting that as well as steric hindrance and photochemical considerations, the nature of the ligand is also an important factor.

More recent work has included the continuation of work begun by He *et al.*[82] with the synthesis of SiPcs with more complex aminooxy and aminosiloxy axial ligands,[56,88] and the complexation of dicationic pyridinium based SiPcs with bovine serum albumin as a transport vehicle for targeted delivery.[89,90]

The synthesis of SiPcs axially substituted with either one or two acetal-protected galactose substituents produces compounds which also exhibit high photodynamic activity against cancer cells (see Fig 14). All the compounds synthesised were shown to be excellent singlet-oxygen generators and therefore have a high potential as photosensitisers.[91]



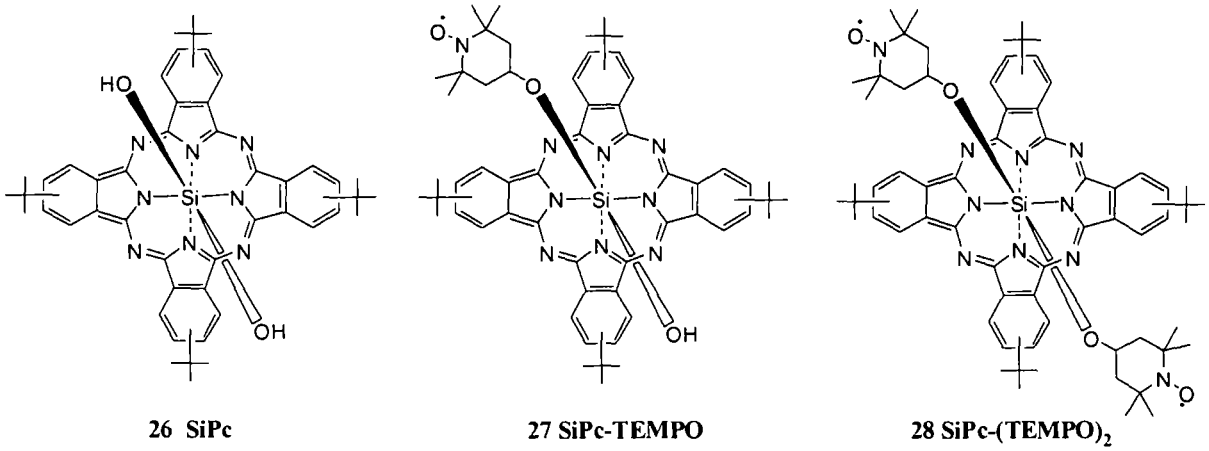
22

23 R = C_2H_5
24 R = n-C_5H_{11}
25 R = n-C_8H_{17}

Fig 14: Structure of SiPcs bearing galactose-based axial substituents.[91]

1.1.2.4 Radicals

The influence of nitroxide radicals on the photophysical properties of metalloPcs has been studied by Ishii, Kobyashi *et al.* via the use of time-resolved electron paramagnetic resonance (TREPR) studies.[92-95] With reference to SiPcs in particular, the attachment of one or more nitroxide-derived radicals to the central silicon atom presents a new way of controlling the Pc's magnetic properties via photoexcitation (see Fig 15).



26 SiPc **27 SiPc-TEMPO** **28 SiPc-$(TEMPO)_2$**

Fig 15: Structures of nitroxide-substituted SiPcs.[93]

As the absorption and fluorescence spectra of these radical species were shown to be similar to those of SiPc, it was concluded that the interaction between the nitroxide

radicals and the phthalocyanine is weak. However, there was a marked quenching effect upon the fluorescence quantum yield of SiPc with the consecutive addition of nitroxide radicals. This is due to a change in the rate of inter-system crossing between the singlet excited state and triplet excited state of the SiPc moiety, which becomes a spin-allowed transition.[94,95]

In addition to this, the singlet oxygen quantum yield obtained for compounds **26-28** is significantly increased by the attachment of the nitroxide radicals. The increase in the quantum yield of the triplet state and the enhanced excited-state lifetimes allow the photochemical reaction with molecular oxygen to occur. In general, the incorporation of paramagnetic species produces a very short lifetime of the triplet state and so effectively renders the Pc inactive, and therefore this observation is unusual and provides an alternative method to the use of harmful heavy elements for controlling the singlet oxygen quantum yield, which may be useful in photodynamic therapy.[93]

1.1.2.5 Other ligands

Phthalocyanine-fullerene dyads as donor-acceptor ensembles, where the intensely absorbing phthalocyanine functions as an "antenna" which funnels the absorbed energy to the electron accepting fullerene moiety, are currently of interest, with the majority of examples consisting of a fullerene derivative covalently connected to the Pc periphery.[43,96] In contrast to this, Kim *et al.* have synthesised a SiPc bearing two axial fullerenes,[97] via reaction of a bis-adduct of fullerene bearing an alcohol functionality and $Si(Pc)Cl_2$ in the presence of sodium hydride. An analogous compound without the C_{60} component was studied as a model (see Fig 16).

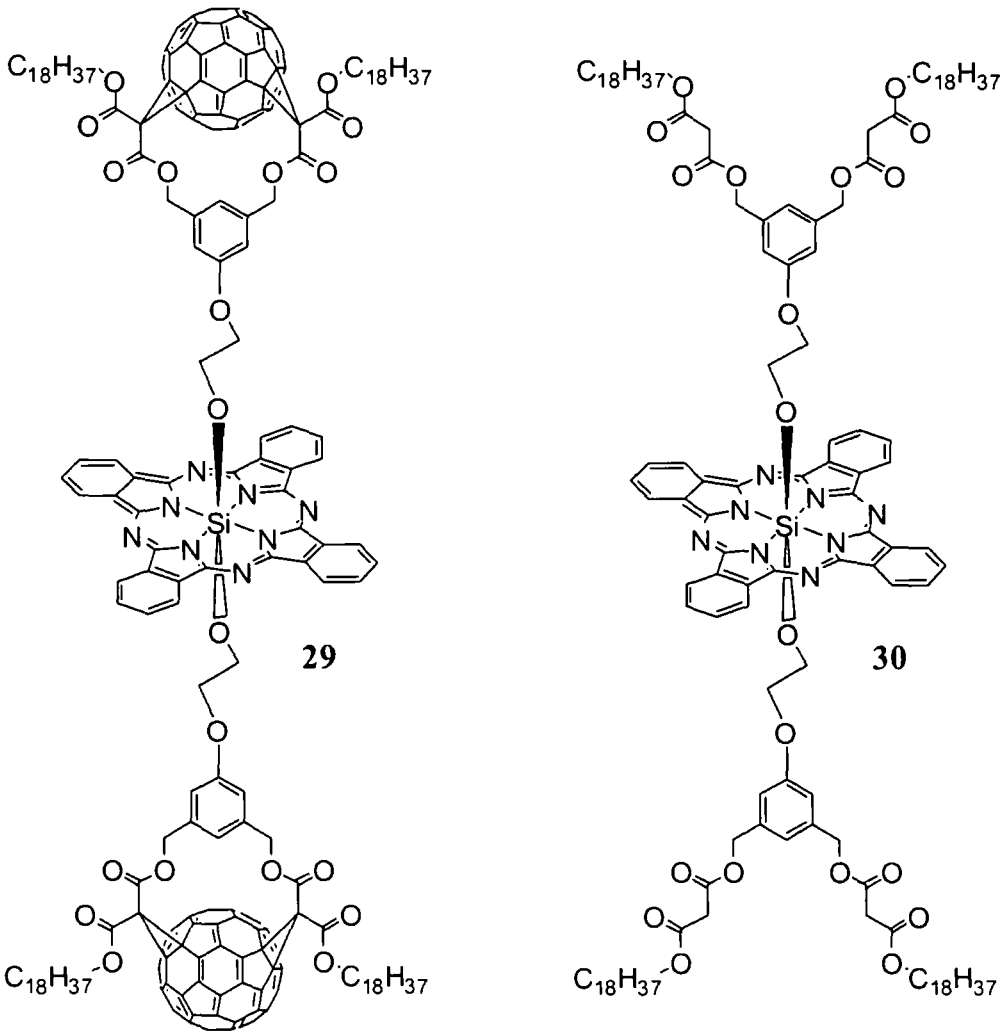


Fig 16: Structures of fullerene-substituted SiPc (**29**) and analogue without C_{60} (**30**).[97]

By comparison of the SiPc-C_{60} species with the non-fullerene analogue and other model C_{60} derivatives, thirteen separate redox reactions were observed in the cyclic voltammogram of **29**. Three of these were assigned to the phthalocyanine species and the remaining reactions are due to the fullerene moiety. The UV-Vis absorption spectrum of **29** showed characteristic absorption bands at around 675 nm, due to the SiPc (see Fig 17).

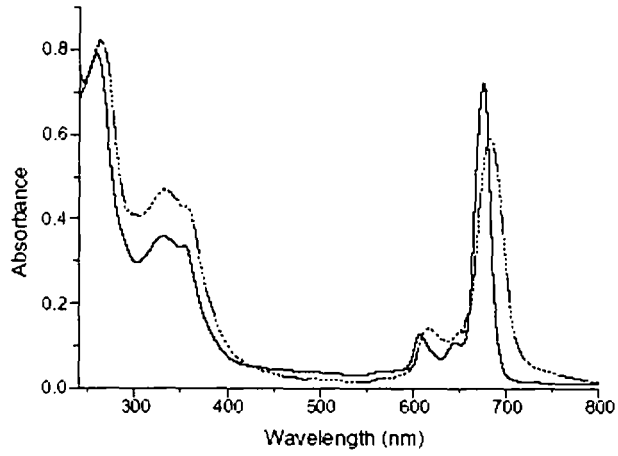


Fig 17: UV/Vis absorption spectra of **29** in $CHCl_3$.[97]

The attachment of polyfluorinated axial ligands showed that the polyfluoroalkyloxy groups (**33**) gave a higher degree of solubility than the corresponding polyfluoroalkanoyloxy (**32**) and alkoxy (**31**) derivatives (see Fig 18). Ether was found to be the best solvent for these compounds.[98]

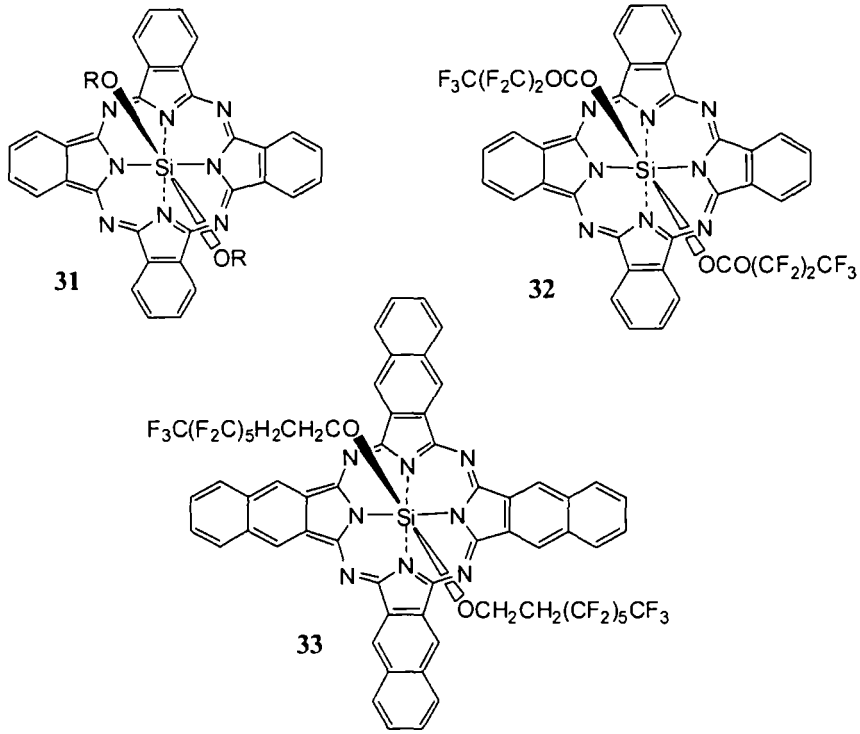


Fig 18: Structure of SiPcs bearing polyfluorinated ligands.[98]

The attachment of simple alkyl and aryl axial groups was achieved by Tamao *et al.* via the use of Grignard reagents.[99] The bis-phenyl and bis-octyl derivatives were synthesised. Secondary alkyl groups could not be attached to the axial positions, possibly due to steric hindrance. These dialkyl and diaryl Pcs were then reacted with a variety of

reagents, e.g. N-bromosuccinimide, halogens and copper(II) halides, which readily cleaved the alkyl-silicon bond. An electrophilic aromatic substitution mechanism was postulated for the NBS and halogen cleavages (see Fig 19).

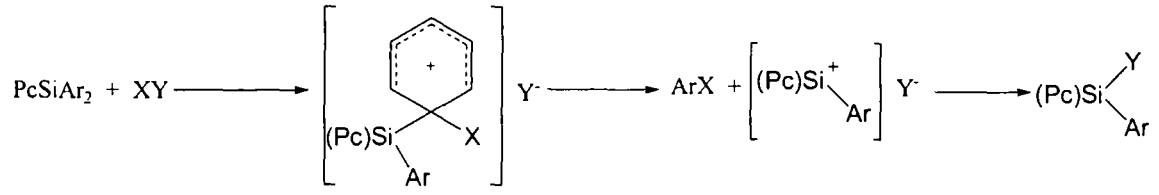


Fig 19: Electrophilic cleavage of $PcSiAr_2$ by NBS or Hal_2.[99]

The monoxide derivative of a SiPc (**35**) has been synthesised from the dihydroxy precursor (**34**) via intramolecular dehydration using sodium methoxide (see Fig 20).[100]

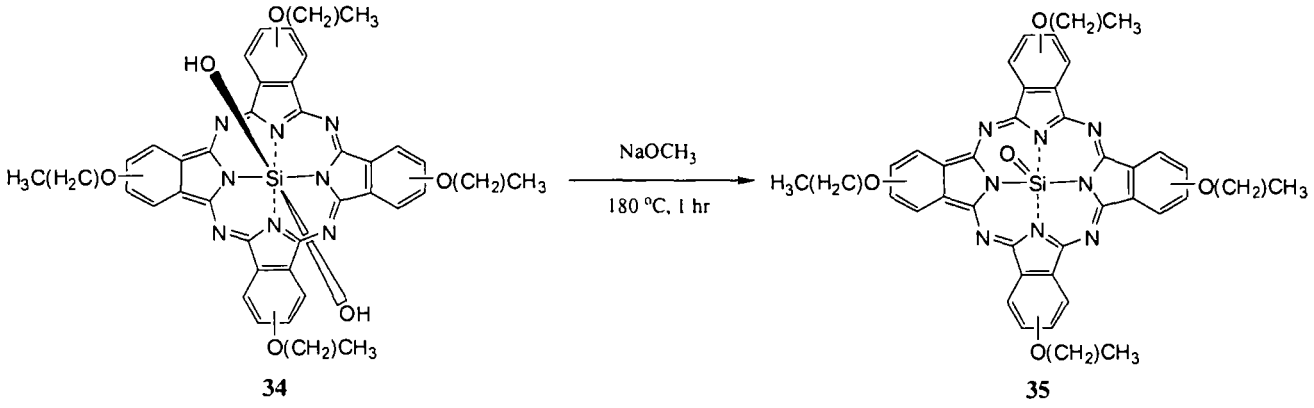


Fig 20: Intramolecular dehydration of a $Si(Pc)(OH)_2$ derivative (**34**) to the monoxide (**35**).[100]

1.1.2.6 Dendrimers

Very few examples of Pc-centred dendrimers are known in the literature, the first example being a ZnPc with poly-ether amide dendrimer chains attached to the periphery.[101] The first example of a dendrimer containing a SiPc moiety (**40**) was published by Kraus *et al.* in 1998, and involved the attachment of a number of Pcs to a central triazine-based core (**38**) via the axial sites, and the subsequent addition of the resulting adduct to 1,3,5-tribenzoic acid (see Fig 21).[102]

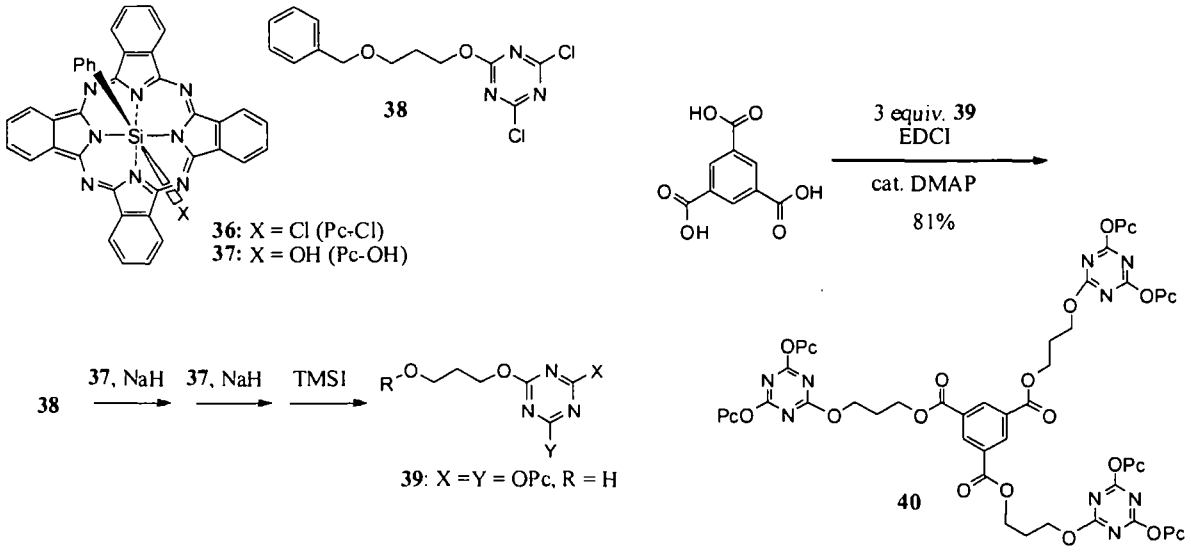


Fig 21: Synthesis of the first SiPc-containing dendrimer (**40**).[102]

More recently, McKeown *et al.* have formed SiPc-centred dendrimers (**41-43**) by attaching aryl-ether oligomers to either the peripheral or axial sites.[33,103,104] Axial substitution was achieved by reaction of $Si(Pc)Cl_2$ with the relevant benzyl alcohol derivative (see Fig 22). The ^{1}H-NMR spectra of these compounds are informative as similar regions within the axial dendrons may be distinguished from each other due to their differing distances from the strong ring current of the macrocyclic core. A crystal structure of one of the compounds was obtained and the packing diagram clearly shows a Pc stacking arrangement where the outer benzyl rings of each ligand form an interlocking intermolecular arrangement (see Fig 23).[103]

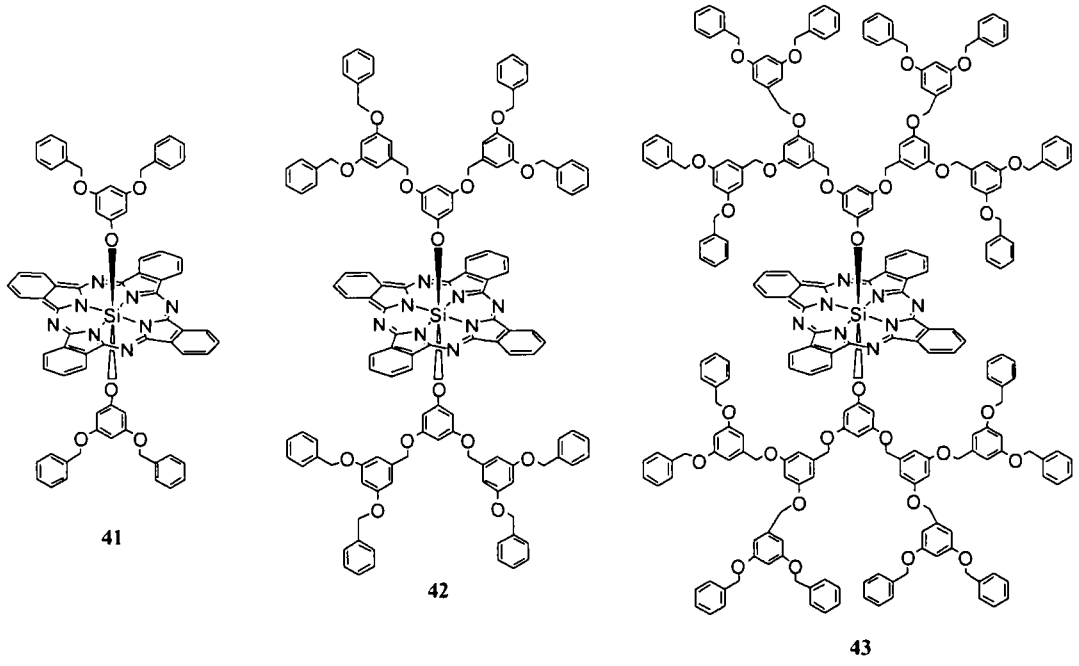


Fig 22: SiPcs bearing axial aryl ether dendritic substituents (**41-43**).[103]

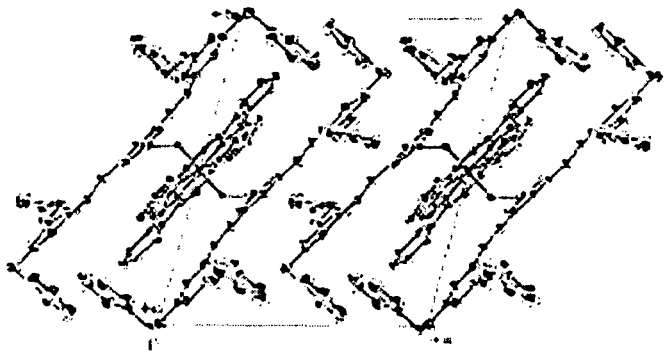


Fig 23: Packing diagram of compound **42** viewed along the c axis.[103]

The synthesis of peripherally substituted Pc dendrimers was achieved via the use of lithium pentanolate to mediate cyclotetramerisation of the pre-synthesised phthalonitrile precursors.[33] Unlike the axially-substituted dendrimers, these compounds displayed aggregation in solution even at low concentrations. Both ^{1}H-NMR spectra and UV-Vis absorption spectra exhibited line broadening and the attachment of oligo(ethyleneoxy) groups at the periphery of the dendritic ligands did not appear to reduce the degree of aggregation.[104]

By synthesising an analogous compound starting from tetra-*tert*-butyl-PcSi, Uchiyama and co-workers prepared axially substituted dendrimers (**44**) which were capable of forming spherical micelles (see Fig 24).[105] When one axial ligand was substituted with a thin hydrophobic alkyl chain, and the other with a hydrophilic poly(aryl ether) dendrimer with terminal carboxyl groups, the resulting mushroom-shaped molecule is able to self-assemble to form the micelles. The micelle was shown to be pH sensitive and could be shuttled between aqueous and organic phases (see Fig 25). The potential for delivery of hydrophobic small molecules was therefore realised.

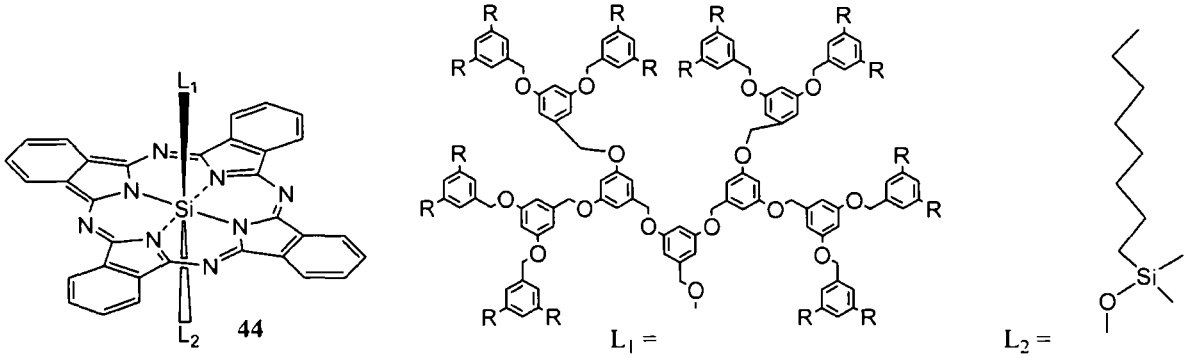


Fig 24: Structure of an umbrella-like SiPc dendrimer (**44**).[105]

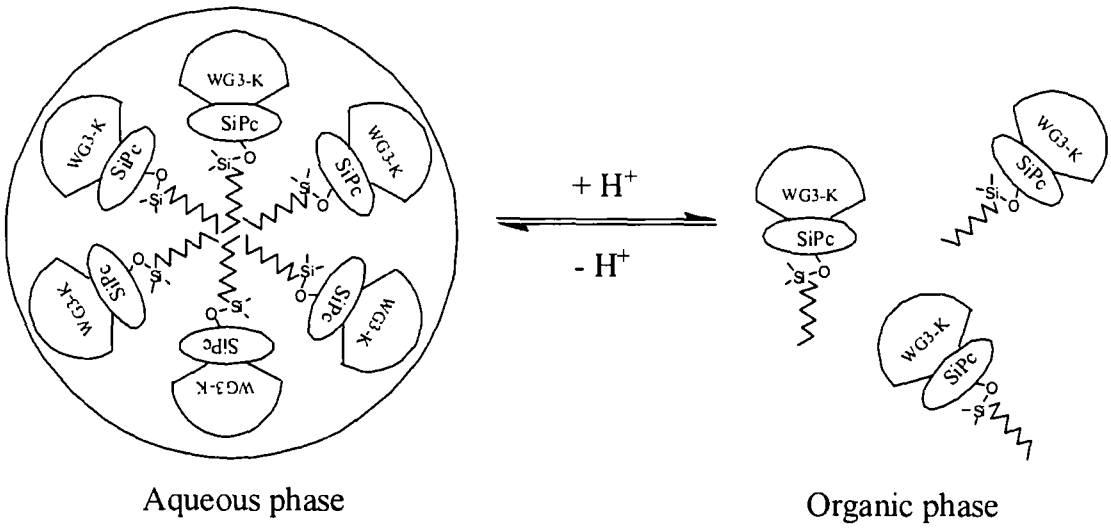


Fig 25: Proposed micelle conformations of **44** in aqueous and organic phases.[105]

1.1.2.7 Polymers

The discussion here will be restricted to cofacially stacked Pc polymers and Pcs pendant to organic polymer chains.[15]

SiPcs are well suited to the formation of cofacially-linked chelates due to the octahedral configuration of the central Si atom. Such polymers are of interest as they generally exhibit high electronic conductivity.

The formation of a simplistic oxo-bridged cofacial SiPc polymer was first published by Kenney *et al.* from $Si(Pc)(OH)_2$ (see Fig 26),[106] and since then, many additional papers have adapted this procedure and described alternative routes to these compounds.[61,73,107,108] The attachment of a variety of groups to the Pc periphery in these compounds has also been extensively explored.[109-113]

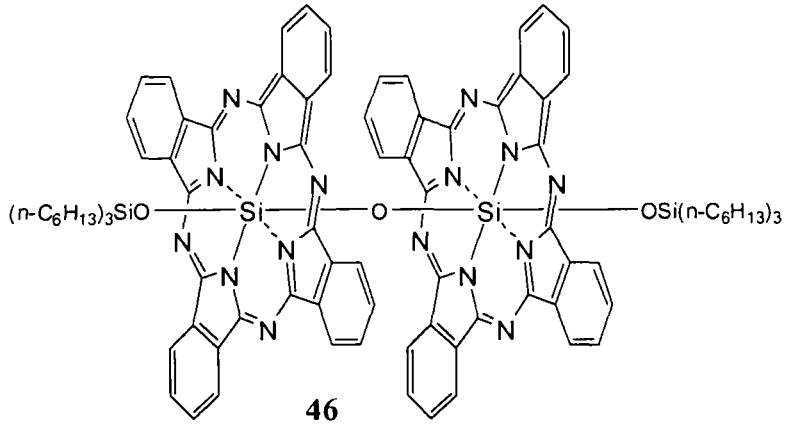
$$\underset{\textbf{2}}{nSi(Pc)(OH)_2} \xrightarrow[\text{or catalyst}\\ \text{or dehydrating agents}]{\triangle} \underset{\textbf{45}}{HO[Si(Pc)\text{-}O]_n\text{-}H} + (n-1)H_2O$$

Fig 26: Polymerization of $Si(Pc)(OH)_2$ (**2**).[106]

Dirk *et al.* improved on Kenney's original thermal synthesis of the polymer.[107] Estimation of the molecular weights of the polymers was performed via end group analysis by identifying the M-O stretching modes in the vibrational spectra and gave typical degrees of polymerisation of *ca.* 120. Oxygen labelling demonstrated that this value could be varied substantially with changing the conditions of the polymerization. Halogen-doping of these materials was investigated as a method for producing electrically conductive partially-oxidised polymers.[114]

The production of siloxy oligomers has also been well-studied. In some cases, such as early work by Kenney *et al.*[68] and the attachment of oxy-cholesterol moieties to $Si(Pc)(OH)_2$ by Decréau *et al.*,[86] the unwanted formation of oxygen-bridged dimers as minor products has been observed.

Wheeler *et al.* achieved the intentional synthesis of a siloxy-substituted SiPc dimer (**46**) (see Fig 27), trimer and tetramer by first forming a mixture of SiPc oligomers via mixing $SiPc(OH)_2$ and $SiPcCl_2$ in a heated solution consisting of tri-*n*-butylamine and quinoline, and then reacting this mixture with tri-*n*-hexylchlorosilane in pyridine. Purification of the resultant mixture by column chromatography yielded the oligomers.[115,116]

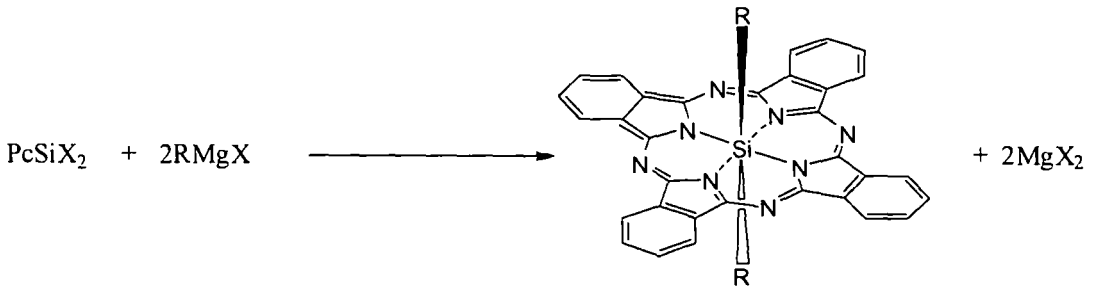


46

Fig 27: Structure of siloxy-substituted SiPc oxy-dimer (**46**).[115]

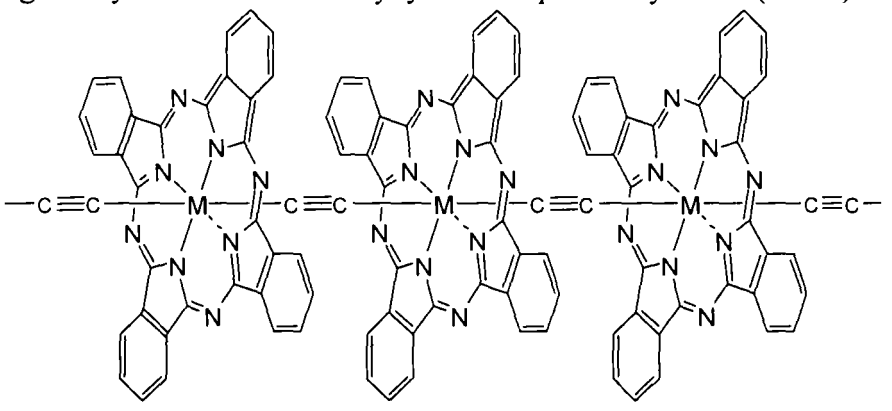
Further work in this area includes the synthesis of a soluble dimer of tetra-(methoxy)-tetra-(octyloxy)-substituted SiPc by Ferencz *et al.*,[117] and the production of siloxy end-capped SiPc-oxy oligomers by both Gunaratne *et al.*[118] and Cammidge *et al.*[60] Cammidge's oligomers differ from those of Gunaratne *et al.* by having solubilising alkyl chains at the Pc periphery. In addition, the synthesis of siloxy oligomers with crown-ether substituents attached to the periphery allows for cationic ion-channel formation whilst increasing the solubility of the oligomers.[119]

SiPc polymers comprising Pc rings separated by more complex groups or chains are also known. Hanack *et al.* first postulated cofacial metalloPc polymers with alkyne-based axial spacer groups (**53**) in their work with Si, Ge and Sn centred Pcs.[120] The linear bidentate alkyne spacer should produce a polymer with a stacked arrangement of macrocycles, with an energy band structure giving rise to charge transport within the stack.[121] Hanack *et al.* synthesised several *trans*-bis-1-alkynyl PcSi compounds (**47-52**), via treatment of $Si(Pc)Cl_2$ with 1-alkynyl Grignard reagents in THF (see Fig 28), as model compounds for the analogous polymeric materials (see Fig 29).



47 R = CH_3
48 R = C_6H_5
49 R = C≡CH
50 R = C≡C−CH_3
51 R = C≡C−$C(CH_3)_3$
52 R = C≡C−C_6H_5

Fig 28: Synthesis of bis-1-alkynyl-metallophthalocyanines (**47-52**).[120]



53

Fig 29: Structure of the cofacial alkyne-based polymer (**53**).[120]

Although the synthesis of polymeric Pcs of this type was subsequently achieved with both Sn and Ge centred-macrocycles, these materials readily decomposed, no analogous Si compound was reported.[122] A polymer of a similar structure (**54**) was prepared by Shim *et al.* by using a bis-Grignard derivative of *p*-diethynylbenzene (see Fig 30).[123]

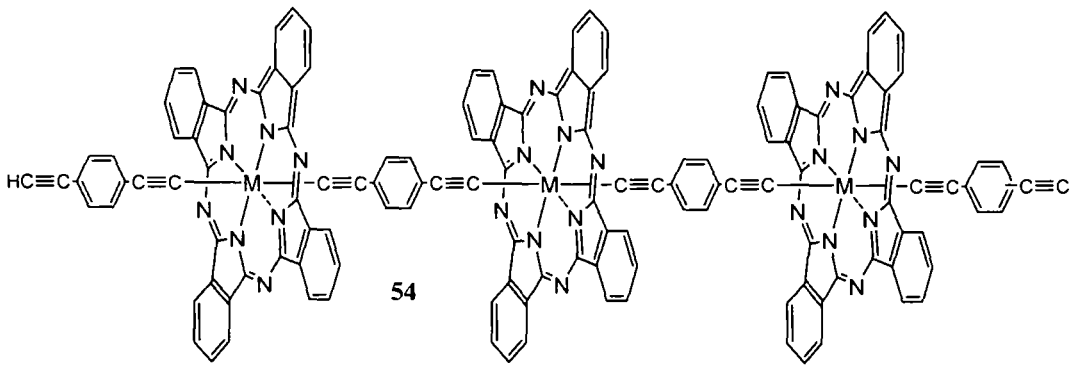


Fig 30: Structure of synthesised -[PcSi-C≡C-Ph-C≡C]$_n$- polymer (**54**).[123]

Lauter *et al.* utilised both 4,4'-dioxybiphenyl and 2,6-dioxynaphthalene spacers in the synthesis of similar rigid rod-like polymers via catalysis with thallium trifluoromethanesulfonate.[124] More recently, Chen *et al.* have detailed the synthesis of a number of cofacial PcSi polymers with a variety of amide spacer groups connecting the silicon-centres.[59,125,126] Spacer groups such as bis(silyloxy)alkanes[127] and terephthalates[128] have also been employed.

Materials with Pc units connected to an organic polymer backbone are of interest in photoreceptor devices, e.g. Cu- and Ru-Pcs.[129,130] However, to date, only one example of a polymer of this type incorporating a SiPc is known. Sounik *et al.* synthesised a monomethacrylate SiPc/ methyl methacrylate copolymer starting from $Si(Pc)Cl_2$ (see Fig 31).[131]

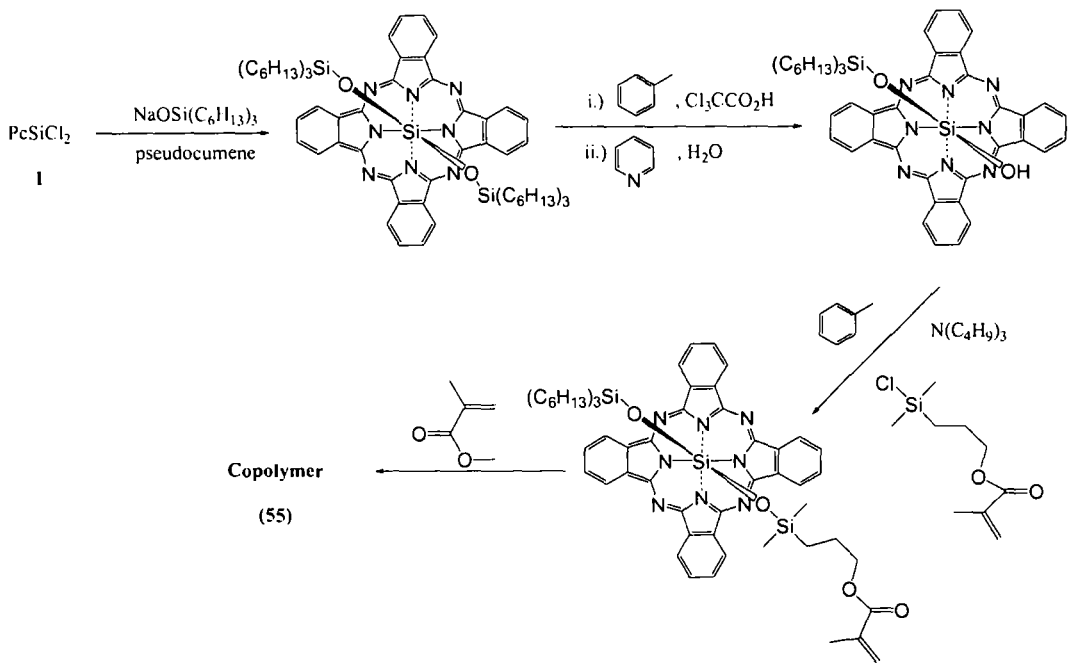


Fig 31: Synthesis of PcSi / methyl methacrylate copolymer.[131]

The attachment of polymeric linear chains to the axial sites of SiPc has recently been achieved. Work by Ng *et al.* has centred on the reaction of peripherally halogenated-$Si(Pc)Cl_2$ with poly(ethylene glycol) methyl ether in the presence of NaH to form SiPc-centred linear polymers (**56**) , and also the reaction of $Si(Pc)(OH)_2$ with both poly(caprolactone) and poly(sebacic anhydride) (**57** & **58**) (see Fig 32).[132-135] These materials show reduced aggregation due to the polymeric axial ligands and reduced fluorescence emission due to the heavier peripheral halogen atoms.

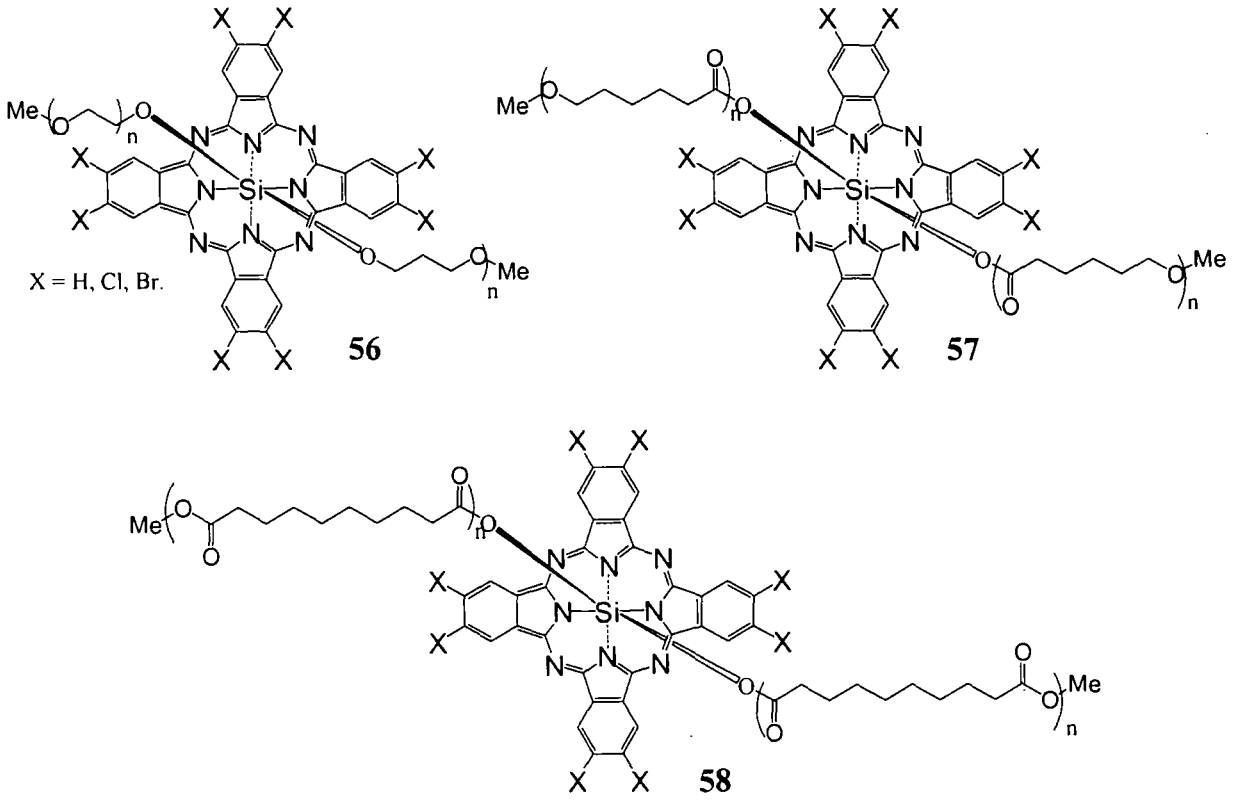


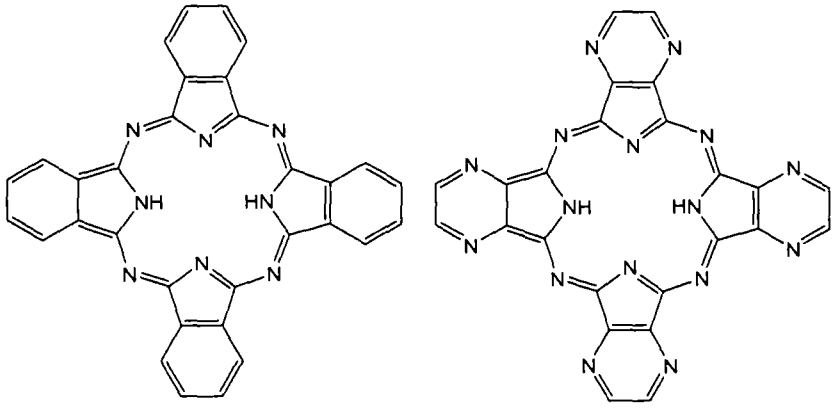
Fig 32: Structures of various Pc-centred linear polymers (**56-58**).[132-135]

1.1.3 Other metallophthalocyanines and free-base phthalocyanines

There is a wealth of literature involving Pcs containing other metals including gallium,[44-46] titanium,[47,48] nickel,[29,49,136-138] manganese,[59] cobalt,[21,42,139,140] zinc,[28,32,35,36,96,141-147] palladium,[43] copper,[148-153] iron,[41,154] vanadium,[155] indium,[155,156] lead,[157] magnesium,[158] samarium,[159] lutetium,[160] and holmium.[161] In addition to this, the study of free-base phthalocyanines is well-documented in recent literature.[27,162-164] However, as this thesis mostly concerns SiPcs and only one new free-base phthalocyanine, a review of the literature on both metallo- and free-base Pcs will not be included.

1.2 Pyrazinoporphyrazines

Tetrapyrazinoporphyrazines (Tppz) are a closely-related analogue of Pcs, both compounds being members of the porphyrazine family of macrocycles (see Fig 33). The starting materials for the synthesis of Tppzs are usually derivatives of 2,3-dicyanopyrazine.



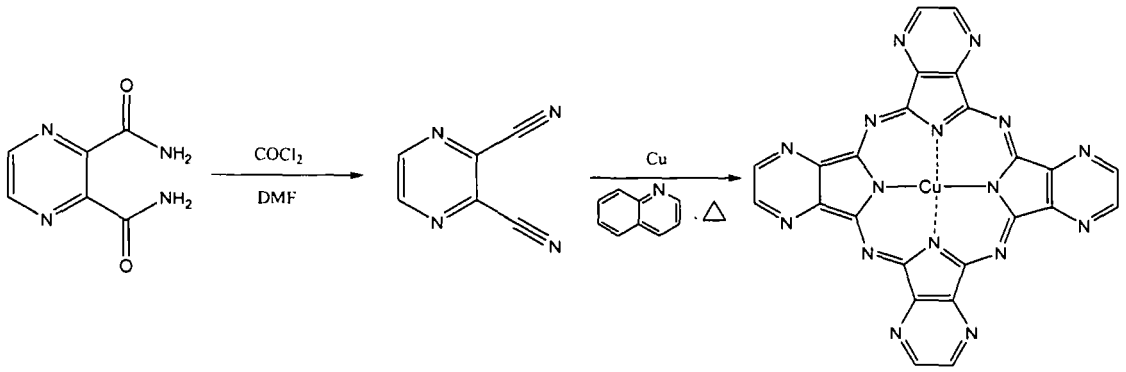
Phthalocyanine (Pc) Tetrapyrazinoporphyrazine (Tppz)

Fig 33: Comparison of Pc and Tppz structures.

The first synthesis of a Tppz was by Linstead *et al.* in 1937, who heated 2,3-dicyanopyrazine with either copper(II) chloride or etched magnesium to form the corresponding blue metallo-Tppzs. An attempt to produce the free-base derivative from the magnesium compound, by treatment with strong acid, was unsuccessful.[165]

The pyrazine starting materials can be made by reaction of diaminomaleonitrile with α-diketones,[165,166] dehydration of derivatives of 2,3-pyrazine-dicarboxylic acid diamide using phosgene,[167] reaction of bis-chloroimino-succinonitrile with alkenes,[168] and the reaction of 2,3-dichloropyrazines with tetraethylammonium cyanide.[169]

Danzig *et al.* produced the copper derivative of both tetrapyridino- and tetrapyrazinoporphyrazine (**59**) via the Linstead method, refluxing in quinoline (see Fig 34).[167]

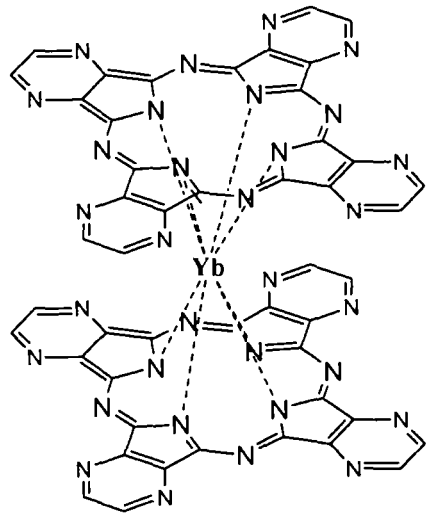


59

Fig 34: Synthesis of copper(II) tetrapyrazinoporphyrazine.[167]

Preparation of the pure free-base Tppz was first achieved via reaction of 5,7-diimino-6H-pyrrolo[3,4-b]pyrazine, using a method analogous to that for the preparation of Pcs from isoindoline derivatives.[11]

Other metals which have subsequently been complexed to the macrocyclic core include vanadium,[170,171] cobalt,[170-172] zinc,[170,171,173] iron,[172,174] aluminium,[171] gallium,[171] silicon,[175] nickel,[176,177] lithium,[178] manganese,[179] palladium and platinum,[180] and indium.[181] In addition to this several examples of sandwich-compounds, involving a lanthanide metal ion linked to the centre of two macrocycles (**60**) , are also known (see Fig 35).[182]



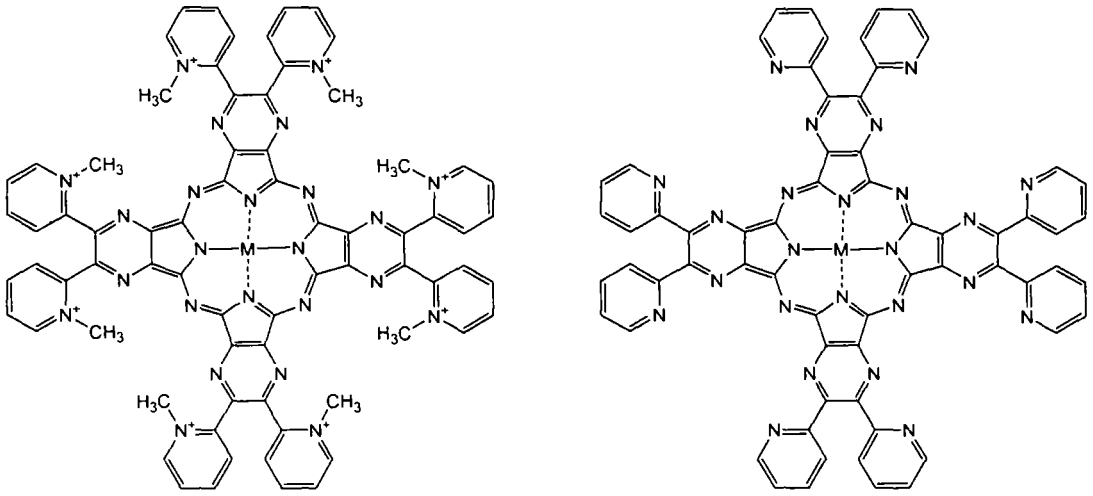
60

Fig 35: Example of a lanthanide bis(Tppz) sandwich complex.[182]

Unsymmetrical pyrazinoporphyrazines may be synthesised by using a number of different pyrazines in the same reaction.[183]

A variety of simple groups have been attached to the periphery of Tppzs in recent years, including propyl and dodecyl chains,[180,184] ethoxy carbonyl groups (resulting in a water-soluble macrocycle),[185] cyanides,[186] amines,[178] alkoxyphenyl groups,[187] camphor groups,[188] and sulfanyl groups.[178,189]

The use of peripheral heterocycles is also well known. The attachment of thiophene rings to both free-base and metal derivatives has been published by two separate groups,[177,190] and one of these groups has also synthesised the corresponding furan and pyridine derivatives.[177] Donzello *et al.* have detailed the preparation of 2-pyridyl substituted Tppzs as both free-base and metal-centred derivatives, as well as the preparation of the cationic analogues bearing N-methylpyridiniumyl groups (**61** and **62**) (see Fig 36).[179,191-193]



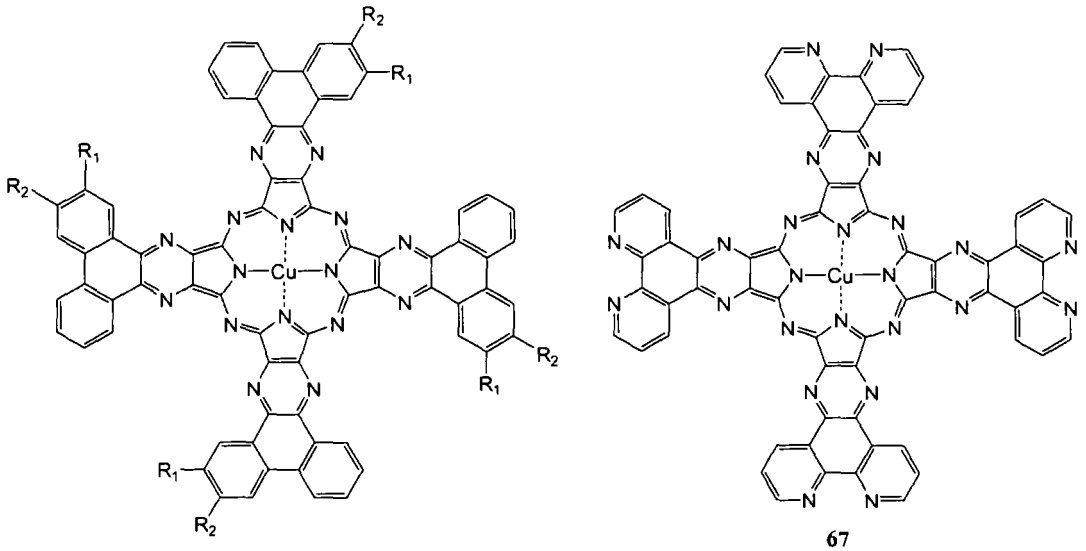
(M = H_2, $Mg^{II}(H_2O)$, Co^{II}, Cu^{II}, or Zn^{II}).

61 **62**

Fig 36: Structure of pyridyl- and N-methylpyridiniumyl-Tppzs.[191,192]

Great interest has been shown in the incorporation of directly-fused multicyclic substituents on the periphery of Tppzs. Compounds of this type should have a high degree of π-conjugation, resulting in a hypsochromic shift of the Q-band in their absorption spectra. Kudrevich *et al.* first synthesised metallo-Tppzs bearing peripheral phenanthrene and quinoxaline substituents by starting from the quinone derivatives of each moiety and first reacting them with diaminomaleonitrile to form the corresponding pyrazine, and then reacting them with a variety of metal salts to form the desired macrocycles.[171] Their work with the silicon derivative of these compounds was also extended to the formation of a number of axially-substituted bis-siloxy derivatives.[175] More recently, Wen *et al.* has included the synthesis of a very similar copper derivative, which only differs by having either a ketone or trimethyl group attached to each phenanthrene unit (**63-66**) (see Fig

37).[194-196] In contrast, compounds synthesised by Du *et al.* contained 1,10-phenanthroline units (**67**) (see Fig 37).[197]



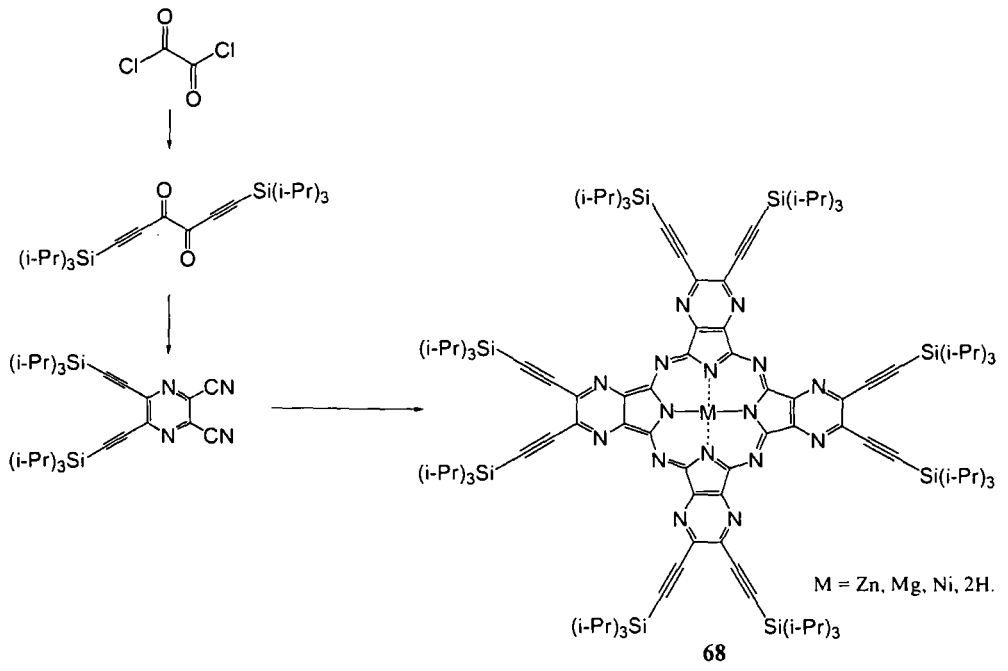
63: $R_1 = C_{12}H_{25}$, $R_2 = H$
64: $R_1 = H$, $R_2 = C_{12}H_{25}$
65: $R_1 = C_7H_{15}CO$-, $R_2 = H$
66: $R_1 = H$, $R_2 = C_7H_{15}CO$-

Fig 37: Structure of phenanthrene (**63-66**) and phenanthroline (**67**) substituted tetrapyrazinoporphyrazines.[194-196]

Another example of a multicyclic substituent incorporated directly into the PPz core is indolo-porphyrazines. Reaction of dichloro-5,6-dicyanopyrazine with carbonyl compounds or enamines produces either pyrrolopyrazines or their furan analogues, which can then be cyclised into the corresponding PPzs.[198,199]

Wang *et al.*, in our laboratory, synthesised a Tppz bearing eight peripheral tetrathiafulvalene (TTF) units on its periphery from the corresponding pyrazine precursors. The free-base, Zn and Cu derivatives were produced and showed no fluorescence upon excitation in the Q-band region, presumably due to quenching via intramolecular charge transfer with the TTF moieties.[173]

A three-step synthesis starting from 1,5-diyne-3,4-diones was used by Faust *et al.* to produce peripherally peralkynylated Tppzs (**68**) (see Fig 38). These compounds showed good solubility in organic solvents with reduced aggregation, and have high singlet oxygen yields making them suitable for photodynamic therapy.[176,200]



68

Fig 38: Synthesis of peralkynylated Tppzs (**68**).[200]

Kobayashi *et al.* reported the synthesis of fused pyrazinoporphyrazine-phthalocyanine dimers, produced by reacting a Pc bearing two cyanide units on one of its peripheral rings with a substituted diimino-pyrrolopyrazine compound.[201,202] The use of tetrapyrazinoporphyrazines in both dendrimers (**69-71**) (see Fig 39),[203] and polymers is also known in the literature.[204]

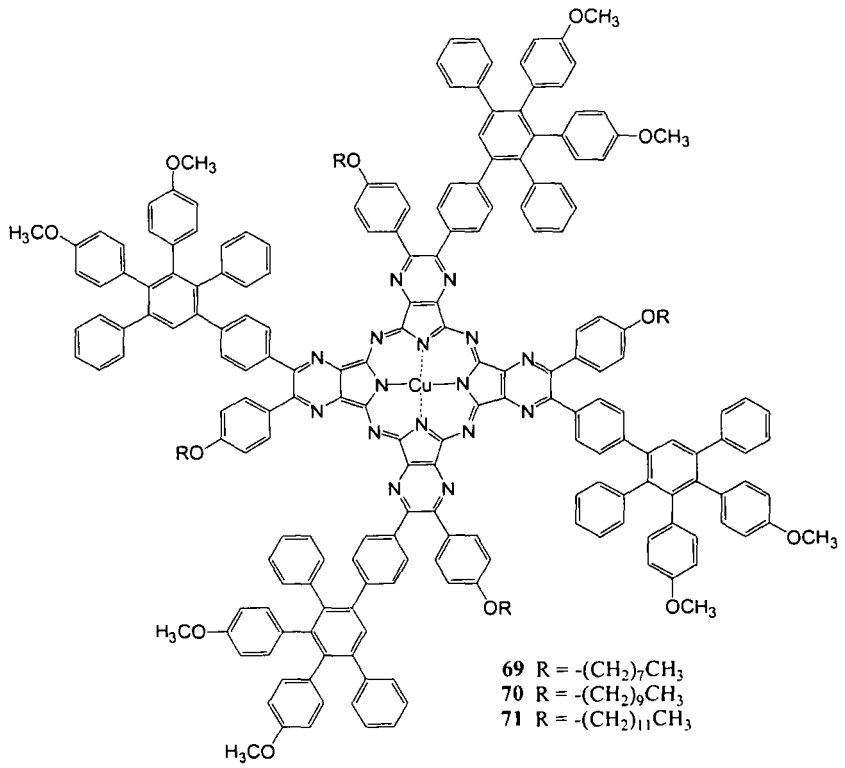


Fig 39: Structure of Tppz-centred dendrimers.[203]

1.3 Porphyrins

1.3.1 Background

Early work into the structure and chemistry of porphyrins was led by Fischer, who published the first synthesis of a porphyrin ring (**72**) in 1929 by a route based on the acid-catalysed cyclisation of the corresponding dipyrromethene. The yield of porphyrin was only 5% yield (see Fig 40).[205]

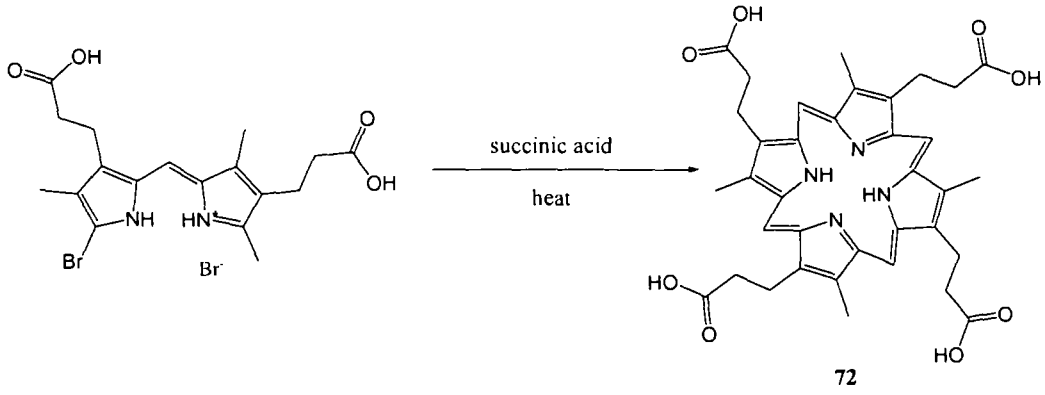


Fig 40: Fischer's synthesis of a porphyrin (**72**) from a dipyrromethene.[205]

A much simpler route to symmetrical tetra-substituted porphyrins was devised by Rothmund *et al.* in 1936, and involved the reaction of benzaldehyde and pyrrole in a sealed tube at 150 °C for 24 h (see Fig 41). Due to these harsh conditions, the yields were low and only a few starting materials survived the procedure.[206,207]

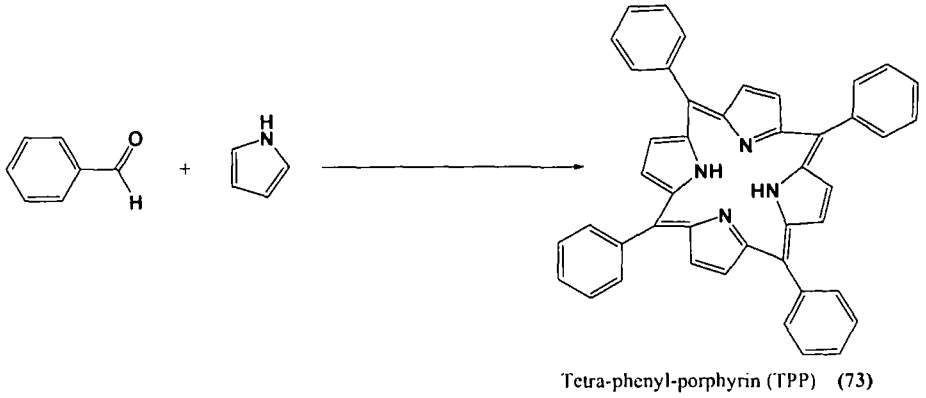
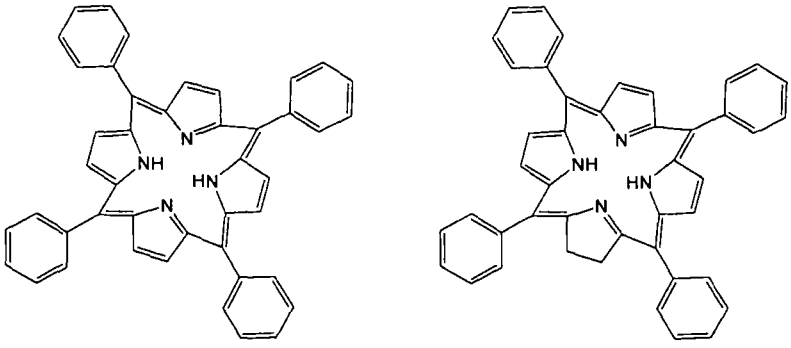


Fig 41: Formation of tetraphenylporphyrin (**73**).[206]

Adler *et al.* later improved this route by refluxing in propionic acid (141 °C) for 30 minutes leaving the reaction open to air.[208] These much milder conditions allow for a greater scope of starting reagents and higher yields (20-30%), and this route is still widely

used for larger-scale reactions. This protocol may also be used to obtain unsymmetrical porphyrins via the use of two different aldehydes, though in these cases purification can prove difficult.[209-213] Two inherent problems with this synthesis are the unwanted formation of the reduced porphyrin (chlorin) impurity (**74**) (see Fig 42), and the inability to use acid-sensitive aldehydes in the reaction.



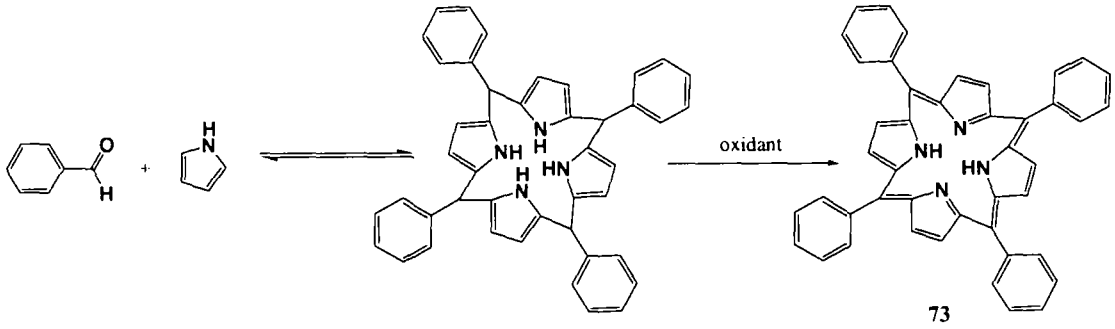
5,10,15,20-Tetra-phenyl-porphyrin (TPP) — **73**

5,10,15,20-Tetra-phenyl-chlorin (TPC) — **74**

Fig 42: Structures of TPP (**73**) and also TPC (**74**) impurity.[208]

Barnett *et al.* removed the chlorin impurity by treatment of the crude products with the oxidising agent 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) which is then removed via filtration of the reaction mixture through alumina.[214] This purification is applicable to both free-base and metal-centred porphyrins, giving pure products in high yields (~95% yield for purification step).

Developed in the late 1980s, the 'Lindsey method' addressed many of the drawbacks of the Adler methodology.[215] Dolphin had earlier proved the existence of the porphyrinogen intermediate in the Adler route to porphyrin (see Fig 43) and under acid catalysis, pyrrole and benzaldehyde form an equilibrium with this intermediate.



73

Fig 43: Formation of porphyrin from porphyrinogen.[215]

Lindsey *et al.* used dilute conditions to optimise this equilibrium before irreversibly oxidising the porphyrinogen to porphyrin. A variety of acid catalysts may be used,

including boron trifluoride and trifluoroacetic acid, and both 2,3,5,6-tetrachlorobenzoquinone (*para*-chloroanil) and DDQ are suitable oxidants (see Fig 44). The advantage of this route is that it allows the use of sensitive aldehydes not suitable for the Adler route,[216-219] giving higher yields (30-40%) and much easier purification. However, the necessity for dilute reaction conditions means that the reaction cannot be easily scaled up. In addition, the Lindsey method has been modified by other groups to include the use of clays,[220] and transition metal salts.[221] Porphyrins may also be prepared from pyrroles by the use of anionic micelles,[222] by catalysis with silica chloride,[223] via the replacement of the usual volatile organic solvents with a room temperature acidic ionic liquid,[224] or by utilising 2-substituted pyrroles as a single starting material.[225,226] In the latter case, the reaction may be catalysed by copper(II) acetate or hydrogen bromide.

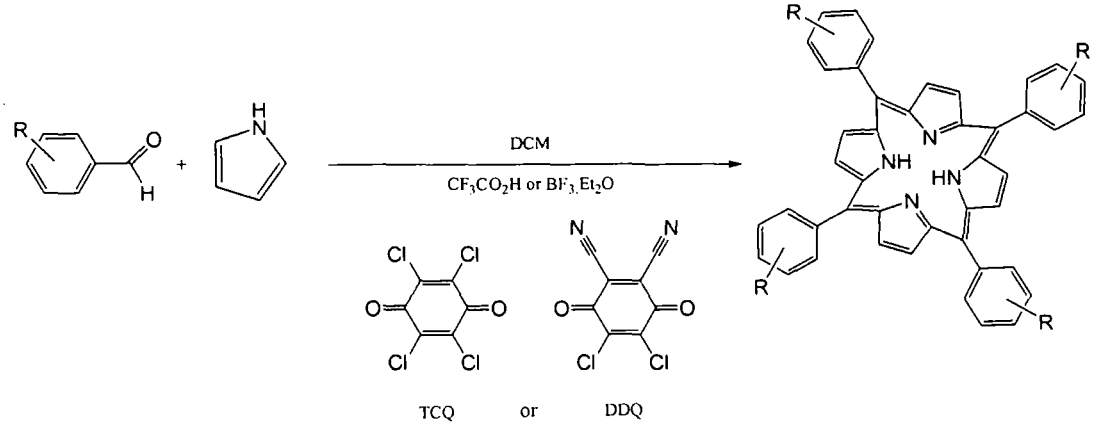


Fig 44: Lindsey route to porphyrins.[215]

In addition to the mono-pyrrole route to porphyrins, several other cyclisation methods are known, namely the 'Macdonald' [2+2] approach and also a [3+1] route.

The original [2+2] synthetic method employed the condensation of two different dipyrromethanes (see Fig 45).[227]

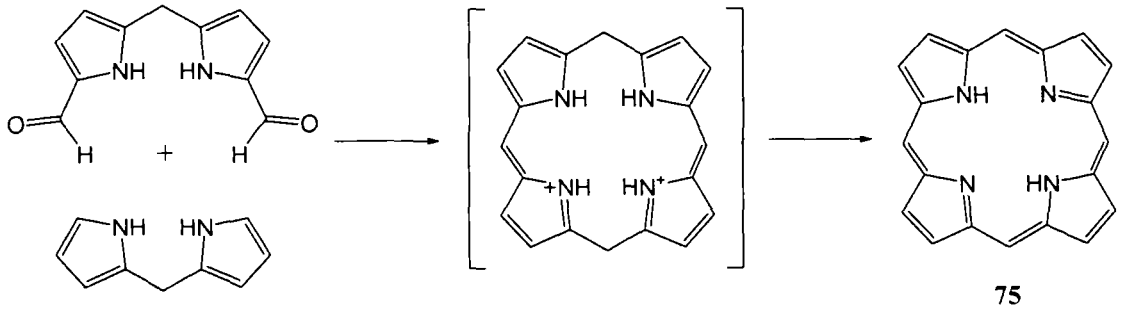


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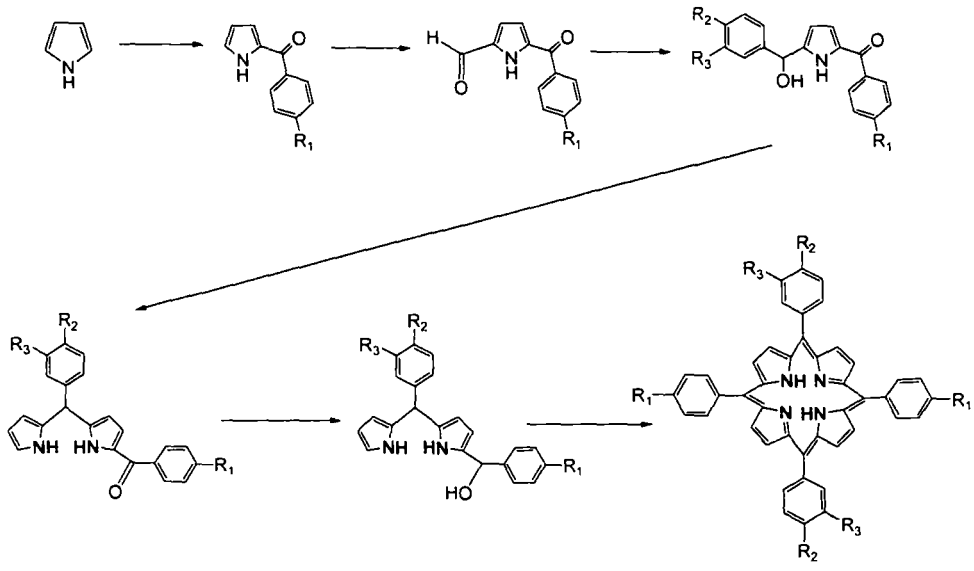
Fig 45: McDonald synthetic route to Porphyrins.[227]

Subsequent variations include the use of a single bridged-bisdipyrromethane compound,[228] the synthesis of porphyrin dimers,[229] synthesis of diphenylporphyrins,[230,231] and the use of unsymmetrically-substituted dipyrromethanes to produce porphyrins with either two-fold rotational symmetry (**76** and **77**) (see Fig 46), or four different peripheral substituents.[232,233]

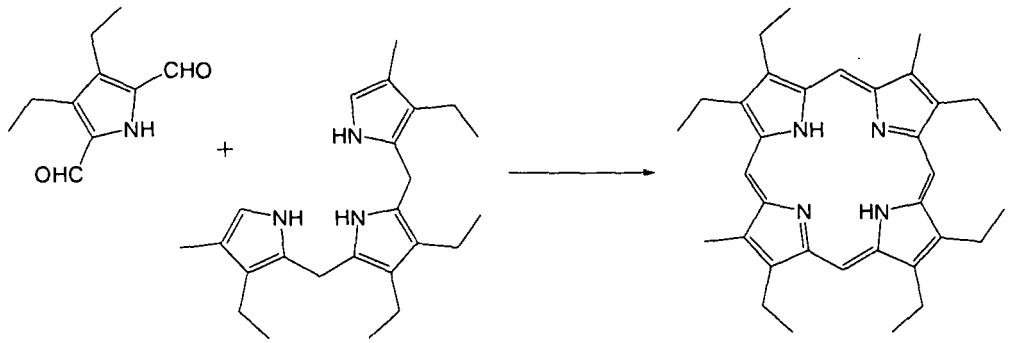


76: R_1 = H, R_2 = Me, R_3 = H

77: R_1 = OMe, R_2 = F, R_3 = Me

Fig 46: Synthesis of porphyrins with two-fold rotational symmetry.[232]

The [3+1] route involves a tripyrrane and a diformyl pyrrole unit. As with the [2+2] route, the reaction conditions are similar to those for the Lindsey method, usually involving acidic catalysis, followed by oxidation to obtain the pure porphyrin (**78**) (see Fig 47).[234-236]



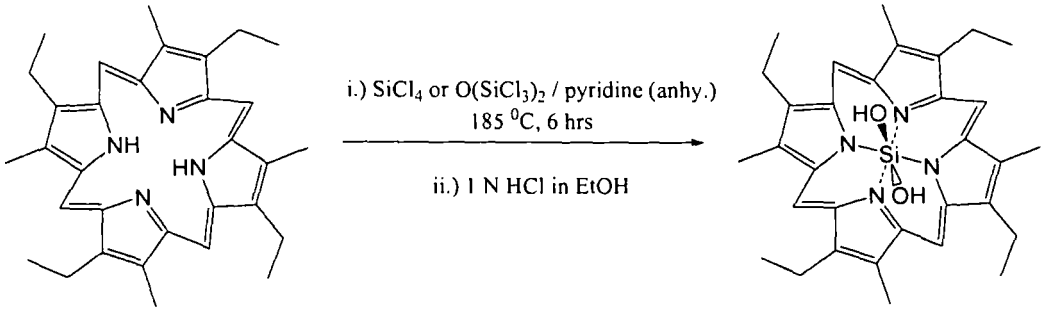
78

Fig 47: [3+1] cycloaddition route to porphyrins.[236]

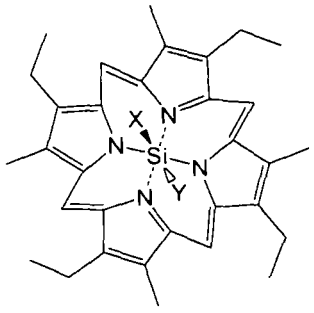
Linear tetrapyrroles (bilanes) undergo an oxidative cyclisation to form the macrocycle. This method is of use for synthesising porphyrins bearing four different substituents as the tetrapyrrole can be carefully synthesised via stepwise coupling reactions beforehand.[237-240]

1.3.2 Silicon Porphyrins

A silicon-centred porphyrin was published by Boylan *et al.* in 1967,[241] who inserted silicon into etioporphyrin (**79**) (2,7,12,17-tetraethyl-3,8,13,18-tetramethyl-porphyrin) via the method developed by Kenney *et al.* for the synthesis of silicon phthalocyanines.[242] The dihydroxysilicon complex (**80**) thus formed was a precursor to siloxy derivatives (**81-91**) via silylation with bis(trimethylsilyl)acetamide and separation of the subsequent product mixture (see Fig 48).



79 **80**

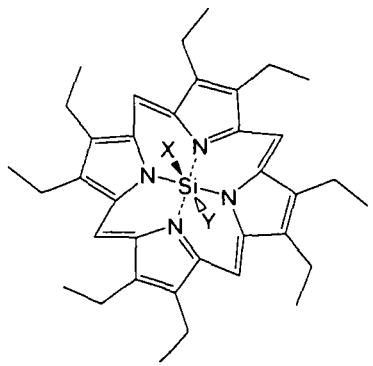


81: X = Y = OH
82: X = Y = OSi(CH3)3
83: X = Y = OCH2CH3
84: X = OSi(OCH2CH3)3, Y = OH
85: X = OSi(OCH2CH3)3, Y = OSi(CH3)3
86: X = Y = OSi(OCH2CH3)3
87: X = Y = OSiOC(CH3)3(OCH2CH3)2
88: X = Y = OSi(OC(CH3)3)2OCH2CH3
89: X = Y = OSi(OC(CH3)3)2OH
90: X = Y = OSi(OC(CH3)3OSi(CH3)3
91: X = Y = OSi(OC(CH3)3)3

Fig 48: Synthesis of the first known silicon porphyrins.[241]

Several more silicon porphyrins (**92-94**) , bearing octa-substitution on the periphery (see Fig 49), were synthesised in the early 1970s by Buchler *et al.*,[243,244] and analysed by fluorescence and phosphorescence spectroscopy.[245] Dichlorosilicon octaethylporphyrin was found to have a higher fluorescence lifetime in THF then other similar porphyrins bearing metals such as germanium, tin and lead.

Kadish *et al.* synthesised octa-substituted silicon porphyrins bearing alkyl and aryl substituents connected via an Si-C bond, and also converted these compounds to the mono-hydroxide derivatives via irradiation in a chloroform solution.[246]



92: X = Y = Cl
93: X = Y = OPh
94: X = Y = OMe

Fig 49: Structures of several axially-substituted silicon octaethyl porphyrins.[243,244]

The silicon tetraarylporphyrins were developed in much greater detail by Lemke *et al.* throughout the 1990s.[247-250] Initial attempts to form silicon tetra-*p*-tolylporphyrin dichloride (**95**) via the same metal insertion method used for the octa-substituted compounds (see above) proved unsuccessful, forming instead a protonated cationic derivative of the starting porphyrin (**96**).[247] The target compound (**95**) was arrived at by first synthesising the lithium derivative of the starting porphyrin,[251] and then reacting this with hydrochlorosilanes (the reaction with silicon tetrachloride was incomplete and low-yielding). Compound **95** was highly water-sensitive, reverting to the protonated cationic form (**96**) in solutions containing trace water. In addition, reaction of the compound with either antimony(III) fluoride, silver tetrafluoroborate or trimethylsilyl triflate gave the corresponding difluoride (**97**) and bis(triflate) derivatives (**98**) (see Fig 50). A crystal structure was also obtained for **98** (see Fig 51).

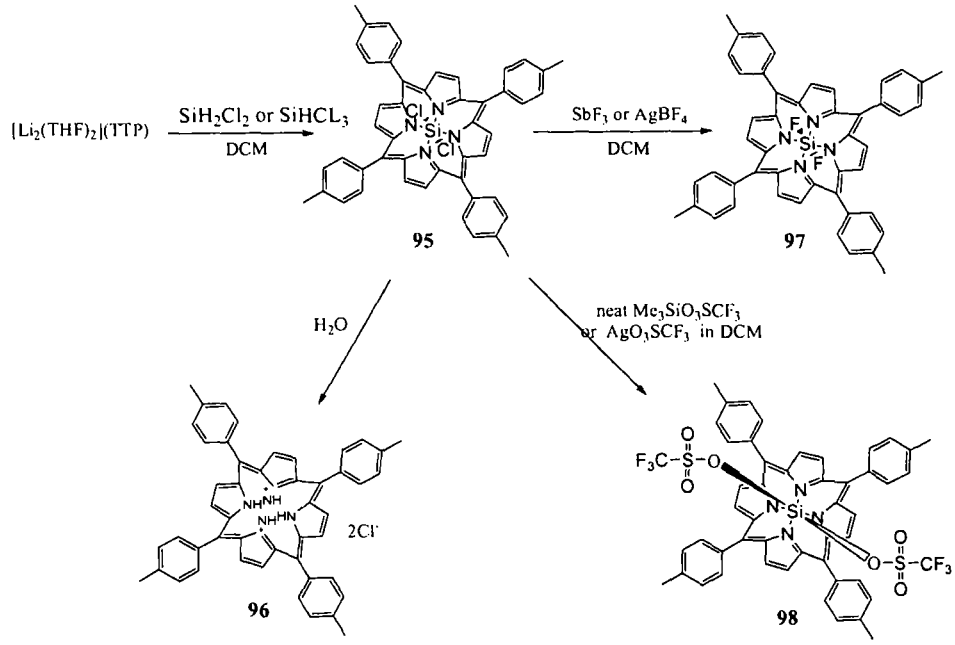


Fig 50: Synthesis of a series of axially-substituted silicon tetraarylporphyrins.[247]

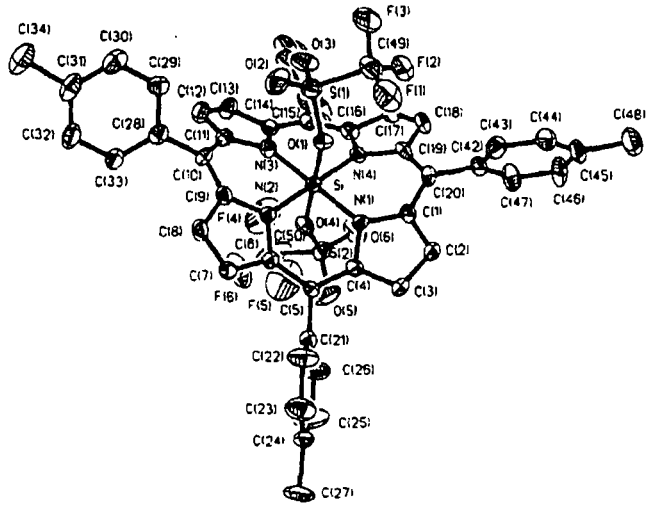


Fig 51: Crystal structure of silicon tetra-*p*-tolylporphyrin bis(triflate) (**98**), hydrogens omitted for clarity.[247]

Further work achieved the synthesis of the difluoride derivative of silicon tetrakis-[*p*-(trifluoromethyl)phenyl]porphyrin (**99**) (again a crystal structure was obtained, see Fig 52),[249] and the preparation of the analogous tetraphenylporphyrins and octaethylporphyrins via the same method.[250] Reaction of silicon tetraphenylporphyrin dichloride with a series of functionalised Grignard reagents to give axially substituted porphyrins has also been published.[252] One of these dialkyl silicon porphyrins was converted to a bis(ethyl peroxide) derivative via reaction with dioxygen in the absence of light.[253] The same phenomenon was also observed using nitroxy compounds as the reagent, and the reaction reaches an equilibrium via the switching on and off of light.[254]

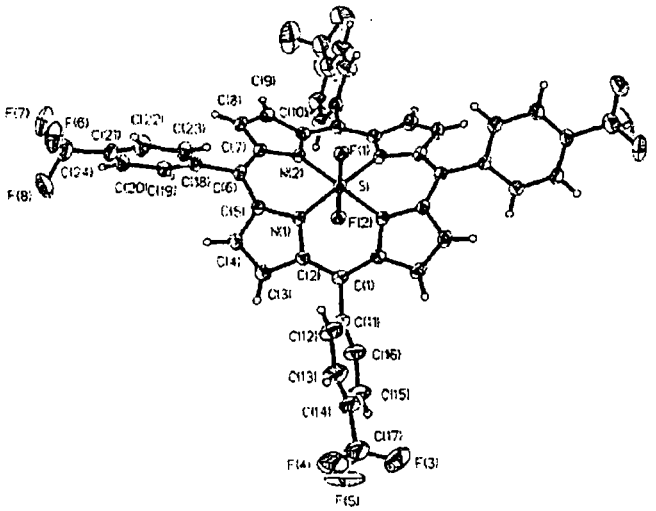
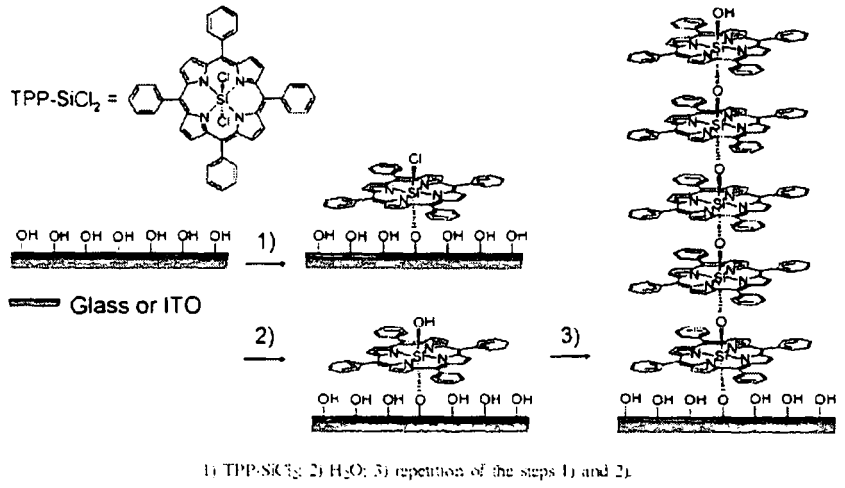


Fig 52: Crystal structure of silicon tetrakis[*p*-(trifluoromethyl)phenyl]porphyrin (**99**).[249]

Since the 1990s, several further examples of silicon porphyrins have been published, including; the synthesis of a new silicon porphyrin bearing axial siloxy derivatives,[255], silicon porphyrins tetra-substituted on the periphery by dodecylphenyl moieities,[256] formation of solvent-bearing silicon porphyrins via reduction in solution,[257] and the stepwise attachment of silicon tetraphenylporphyrin rings to either glass or indium-tin oxide (ITO) layers to form a cofacial porphyrin multilayer (see Fig 53),[258]



1) TPP-$SiCl_2$; 2) H_2O; 3) repetition of the steps 1) and 2).

Fig 53: Systematic construction of a cofacial silicon porphyrin multilayer.[258]

1.3.3 Zinc Porphyrins

Zinc-containing porphyrins have been known for over sixty years,[259,260] and the quenching effect of the zinc ion upon the porphyrin fluorescence is well documented.[261-263] The heavy-metal atom leads to an increased inter-system crossing from the excited singlet to excited triplet state relative to the free-base compounds, and therefore zinc porphyrins have a great deal of potential for use in photodynamic therapy. They have a much greater singlet oxygen yield from the triplet state, relative to analogous Pcs. However, this is balanced by the fact that porphyrin absorption does not extend as far into the near-IR region as for Pcs.[79,264]

Other current applications for zinc porphyrins include use in photoelectrochemical devices,[265] fluorescence sensors and switches,[266,267] photonic wires,[268] and chiral shift reagents.[269]

Zinc porphyrins bearing a wide range of peripherally-attached functional groups include the following recent examples. Sun *et al.* synthesised zinc porphyrins bearing pendant triphenylamine groups (**100-107**) (see Fig 54) via the corresponding substituted-

benzaldehydes and pyrrole using routes based on the methods of both Adler and Lindsey.[208,218,270] Their study indicated efficient energy transfer between the strongly electron-donating triphenylamine groups and the porphyrin core when the compounds were excited at a wavelength corresponding the triphenylamine absorption.

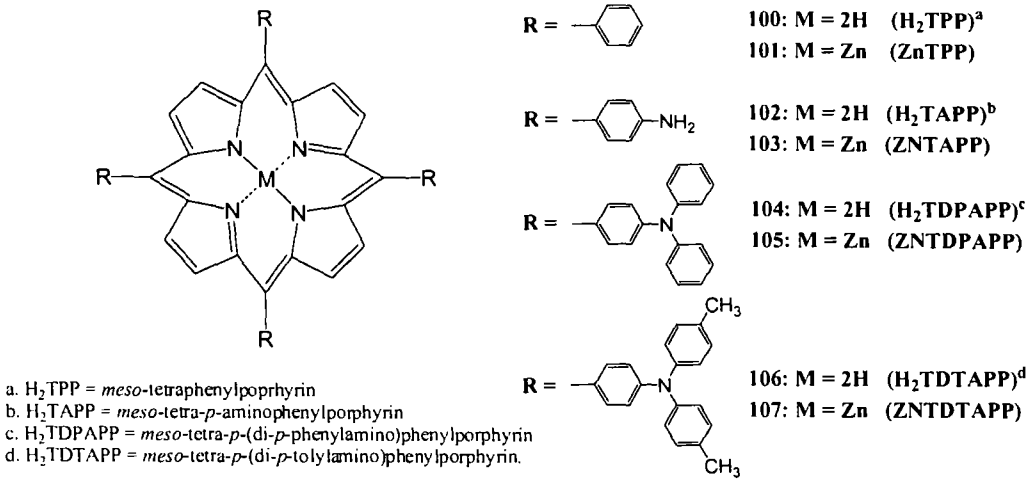


Fig 54: Synthesis of triphenylamine-bearing Zn porphyrins.[270]

Yen *et al.* studied analogous compounds where the triphenylamine moieties and the porphyrin core are separated by alkyne bonds.[271] The π-conjugation of the porphyrin core was shown to be significantly extended by the addition of the bridged triphenylamine moieties, giving large red shifts in the absorption spectra of the compounds. These types of molecules have potential for application as molecular wires, charge-transporters or in light-harvesting systems.

The synthesis of new fused five-membered porphyrin systems was achieved accidentally by Shen *et al.* when they attempted to activate a mono-brominated zinc tetraarylporphyrin by treating it with activated metallic zinc. Instead of the expected porphyrin-zinc reagent, they obtained an intramolecular cyclisation product.[272] This method was then applied to other brominated zinc porphyrins (**108-111**) (see Fig 55).

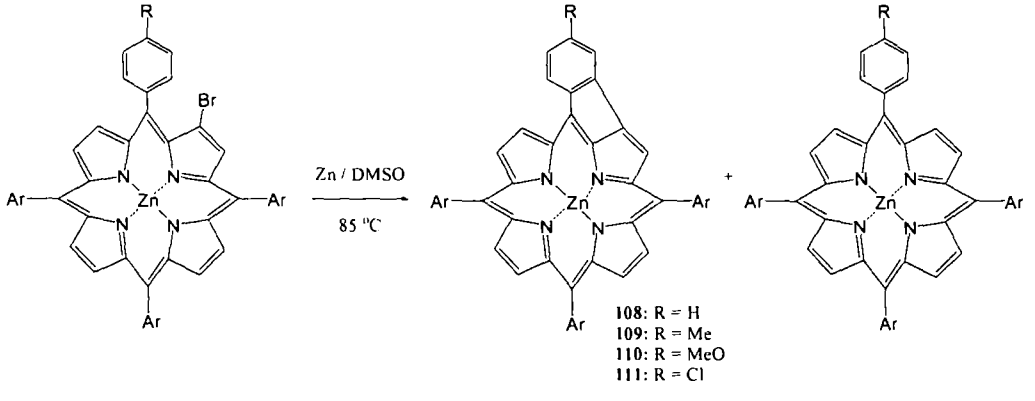


Fig 55: Intramolecular cyclisation of brominated zinc porphyrins.[272]

Other recent papers have detailed the synthesis of zinc porphyrins bearing groups such as pyridine derivatives,[273,274] triarylamines,[275] oligo(*p*-phenylene vinylene)s,[276] calixarenes,[277] quinones,[278] azulenes,[279] nitrothiophenyls,[280] and azobenzenes (**112**) (see Fig 56).[281] In the latter case, the peripheral azobenzene units were shown to suppress photoisomerization in the molecules.

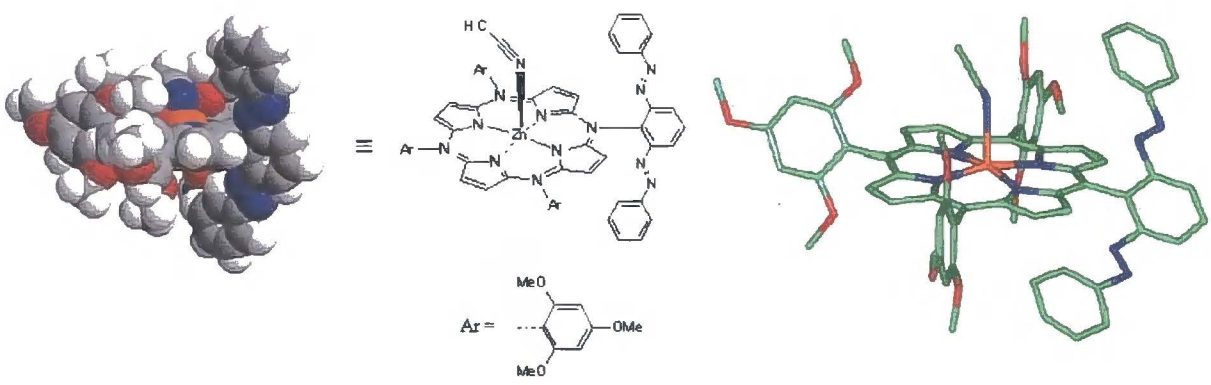
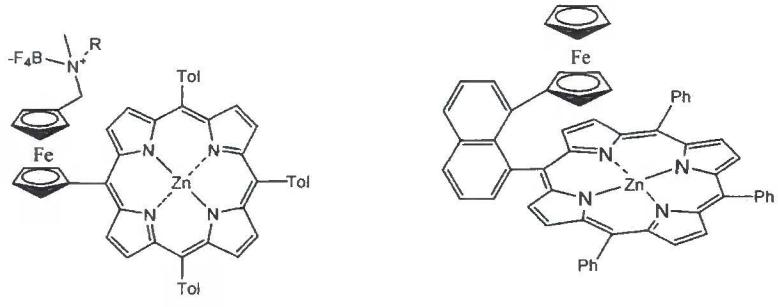


Fig 56: An azobenzene-confined porphyrin (**112**) and its crystal structure with coordinated acetonitrile solvent.[281]

In addition to this, three recent papers have dealt with the synthesis of compounds containing two or more linked metal complexes (**113-115**) (see Fig 57).[282-284]



113 **114**

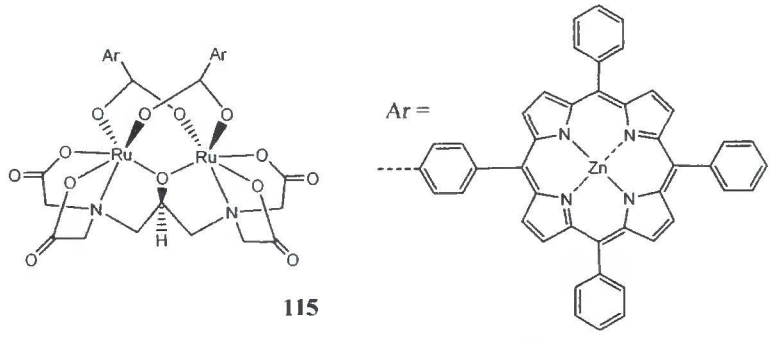


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Fig 57: Compounds of zinc porphyrins with other metal complexes.[282-284]

There is currently much interest in the chemistry of zinc porphyrin-fullerene conjugates and associated compounds for a variety of applications, including guest-entrapment[285] and photonic wires.[268,286-293] Fullerene has the characteristics of low reduction potential and low reorganization energy,[294] which make it an ideal component of donor-acceptor conjugates.[295-299] By combining the electron-accepting properties of the fullerene system with the strongly electron-donating properties of a porphyrin ring, intramolecular electron transfer can be realised and the use of a zinc-centred porphyrin results in both higher stability of the porphyrin moiety as well as a greater potential for electron transfer. Preliminary work on Zn porphyrin dyads concentrated on simple systems with a variety of spacer groups, including oligothiophenes,[287] alkyne chains,[286] bicyclic bridges,[300,301] and malonates (**116-121**) (see Fig 58).[302,303] More recently, this work has included triads comprising fullerene and two zinc porphyrins,[304-306] and also moieties other than fullerene as the electron-acceptor (**122** and **123**) (see Fig 59).[307-309]

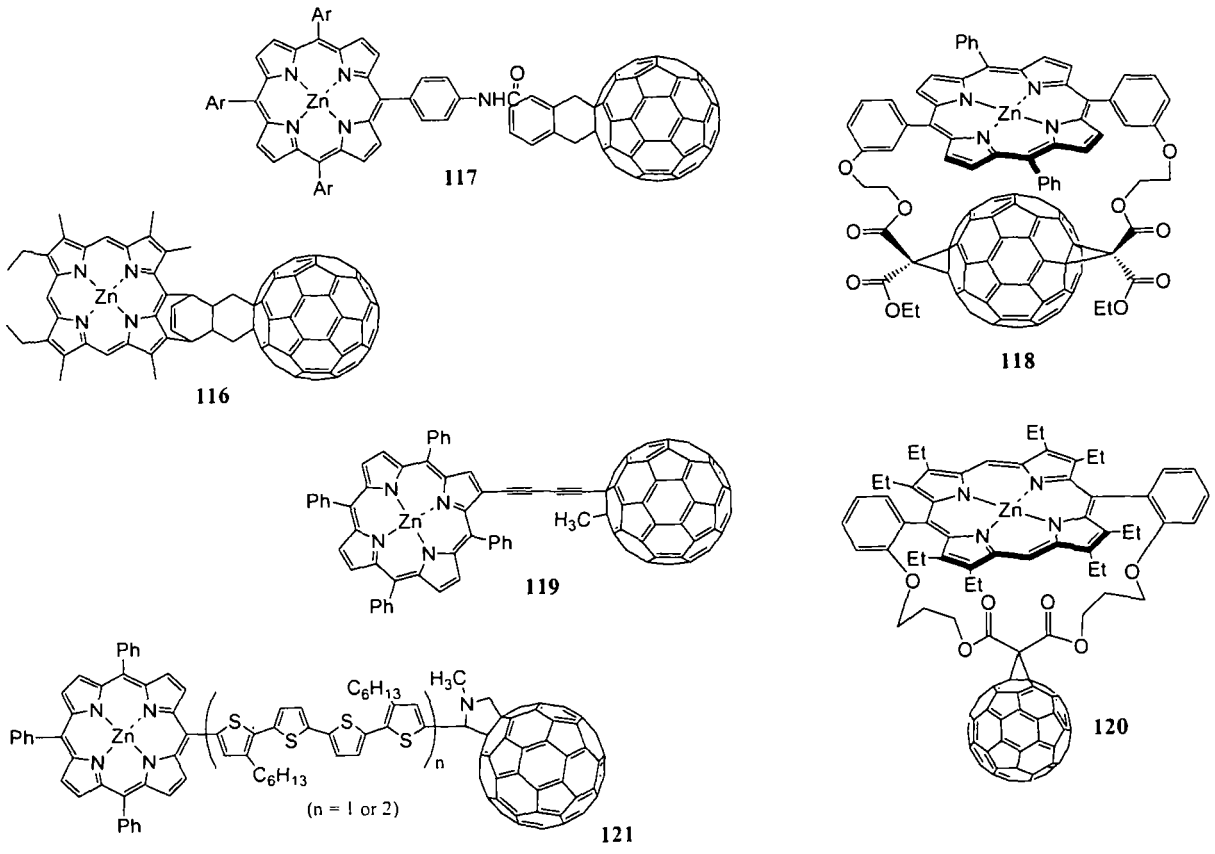
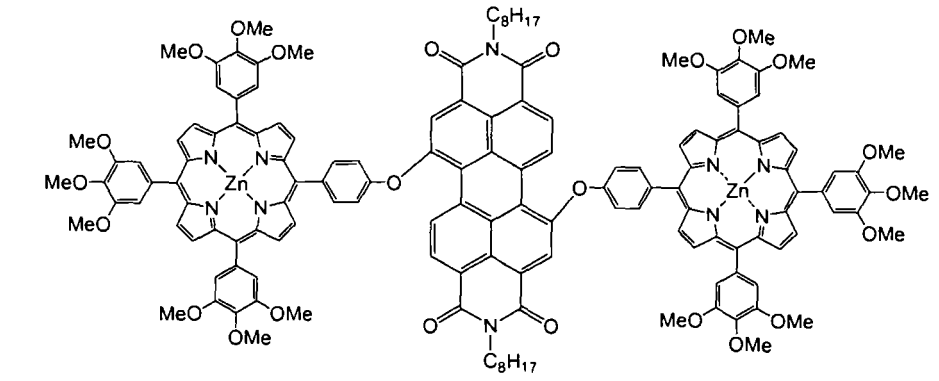


Fig 58: Structures of various synthesised Zn porphyrin-fullerene dyads.[286,287,300-303]



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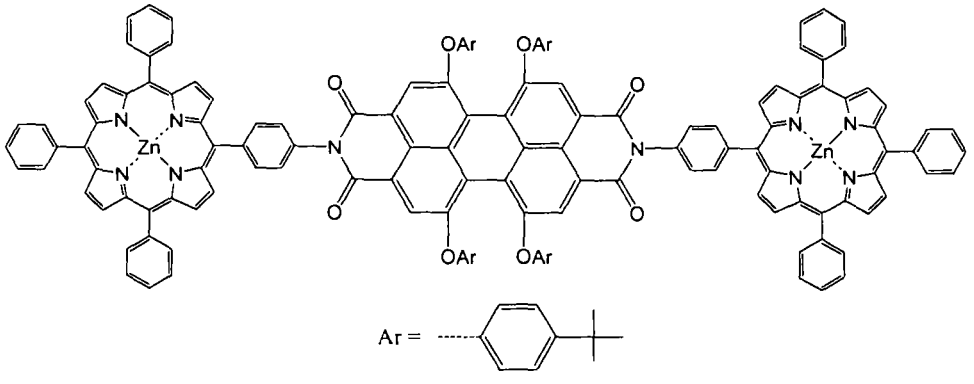

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Fig 59: Structures of two Zn porphyrin-perylenediimide dyads.[307,308]

As well as triads incorporating two zinc porphyrins, a variety of alternative arrangements for zinc porphyrin dimers have recently been published.

Cofacial dimers are attractive as precursors for multi-porphyrin arrays for use in fields such as light gathering, long-range energy relay and components of molecular photonic devices.[310,311] Yagi *et al.* synthesised a cofacial zinc porphyrin dimer (**124**) where the two porphyrin rings are connected peripherally via a diarylurea linkage (see Fig 60).[312] Kalita *et al.* used an imidazoyl group to connect the periphery of one zinc porphyrin to the axial site of another, thus forming a "slipped-cofacial" dimer.[313] Wu *et al.* have used two zinc porphyrins peripherally linked to form a foldamer (**125**), which functioned as "molecular tweezers" able to complex fullerene derivatives (see Fig 60).[314] To achieve a cofacial orientation, Kieran *et al.* connected the two macrocycles via two disulfide-bridges (**126**) (see Fig 60).[315] This work also encompassed the complexation of fullerene moieties within the centre of the dimer complex.[316]

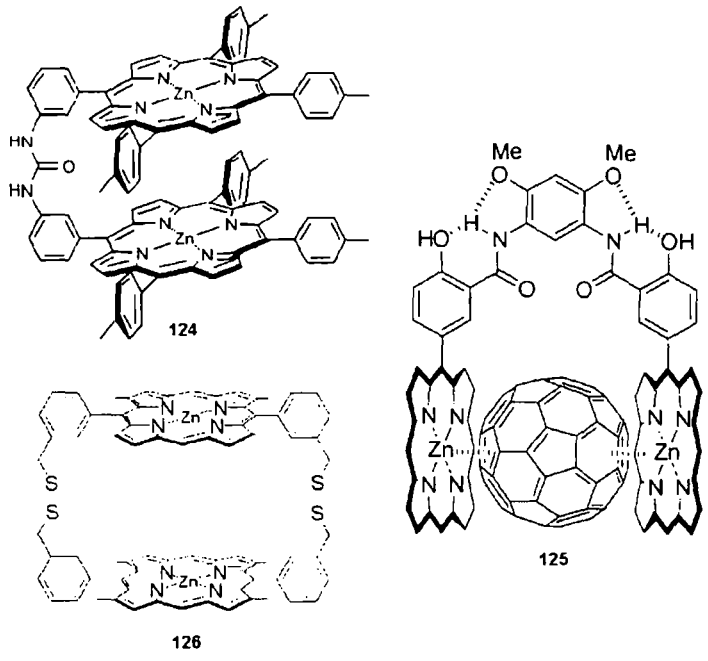


Fig 60: Structures of some recently synthesised cofacial zinc porphyrin dimers.[312,314,315]

Linearly-conjugated porphyrin oligomers are potentially useful for many of the same reasons as cofacial oligomers, including single-molecule conductivity and photon absorption. Drobizhev *et al.* recently constructed a series of conjugated porphyrin dimers, connected via alkyne chains, and these compounds showed greatly enhanced absorption and fluorescence properties (including strong two-photon absorption) relative to the analogous monomers (**127-132**) (see Fig 61).[317,318] The same group has also used a vinylene spacer-group, resulting in a staggered dimer.[319] Susumu *et al.* and Pettersson *et al.* independently produced similar alkyne-based compounds containing thiadiazole-based spacer units (**133**) (see Fig 62).[320,321] Wallin *et al.* utilised oligothiophene chains of various lengths to connect two tetraaryl zinc porphyrins (**134-135**) (see Fig 62) .[322]

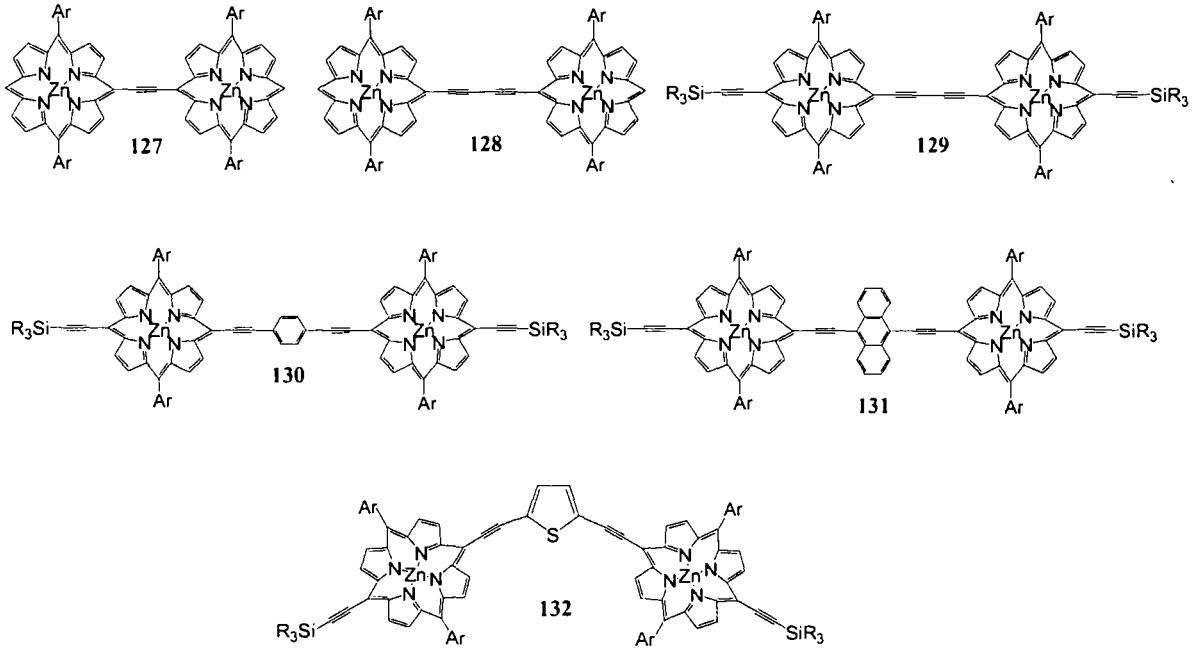


Fig 61: Structures of zinc porphyrin dimers connected via alkyne chains.[317,318]

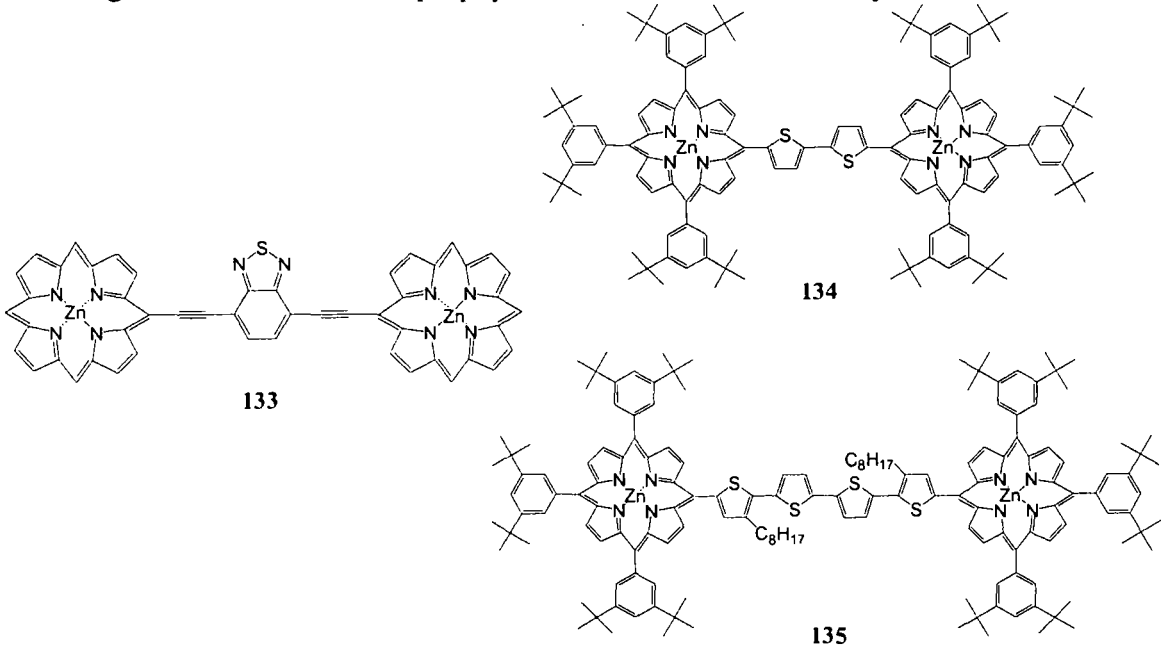


Fig 62: Structures of zinc porphyrin dimers connected via oligothiophenes or thiadiazole derivatives.[320-322]

Recent literature also contains several examples of more-complicated zinc porphyrin arrays,[323-328] including a triple-linked diporphyrin (formed from a dibenzo-fused porphyrin dimer (**136**) (see Fig 63),[329] a series of tetralactam macrocycles incorporating two zinc porphyrins in cofacial and twisted orientations relative to each other (**137**) (see Fig 63),[330] the formation of a hydrogen-bonded cyclic tetramer containing four porphyrin rings bearing a peripheral 2-ureido-4[1H]-pyrimidinone group (**138**) (see Fig 63) ,[331] and the

combination of both peripheral and axial spacer groups to create a ladder array of zinc porphyrins (**139**) (see Fig 63).[332]

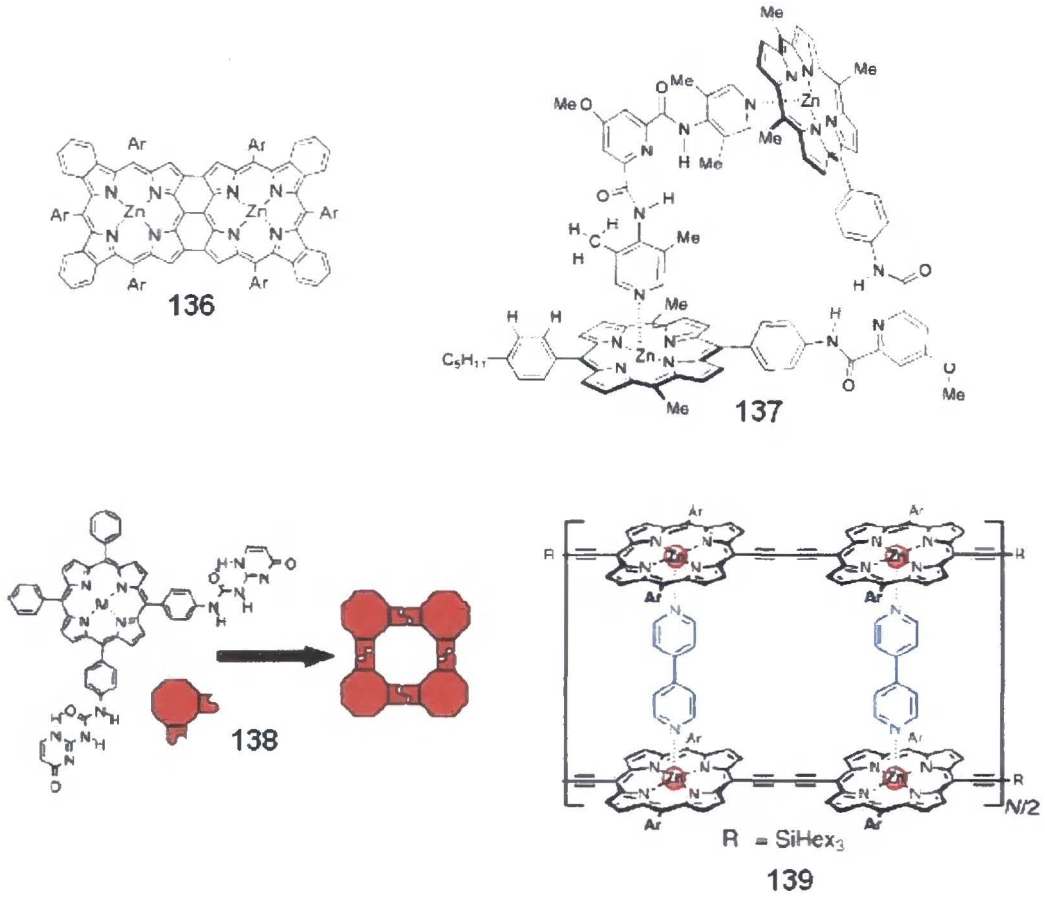


Fig 63: Structures of several unusual macrocyclic architectures based on zinc porphyrins.[329-332]

The use of porphyrins in dendrimer architectures is relatively new, the first examples of free-base porphyrin dendrimers,[333] and zinc porphyrin dendrimers,[334,335] appearing in the early 1990s. Porphyrin-core dendrimers generally have high fluorescence and/or phosphorescence due to the fact that large quenching molecules are unable to move close to the excited porphyrin core. Consequently, such molecules have very high potential for light-harvesting applications and also in photodynamic therapy where the exterior dendrimer architecture may be used to mimic biological compounds.[336,337] Recent examples with a zinc-porphyrin core include a phenylazomethine-based system by Imaoka *et al.*,[338] and the work of Oar *et al.* to incorporate fluorene moieties into a zinc porphyrin architecture, either directly to form star dendrimers (**140**) (see Fig 64)[339] or via attachment to the exterior periphery of a octa-substituted porphyrin dendrimer (**141** and **142**) (see Fig 65).[340]

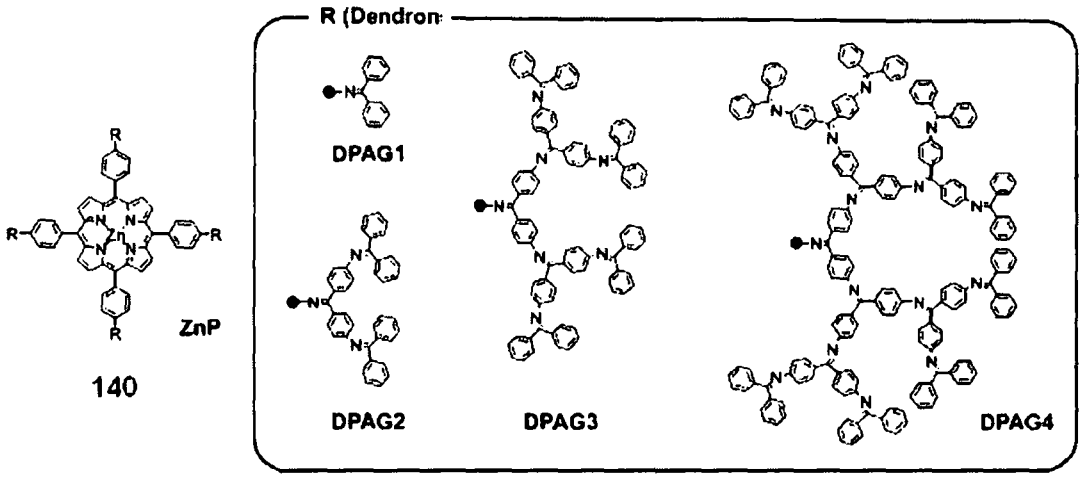
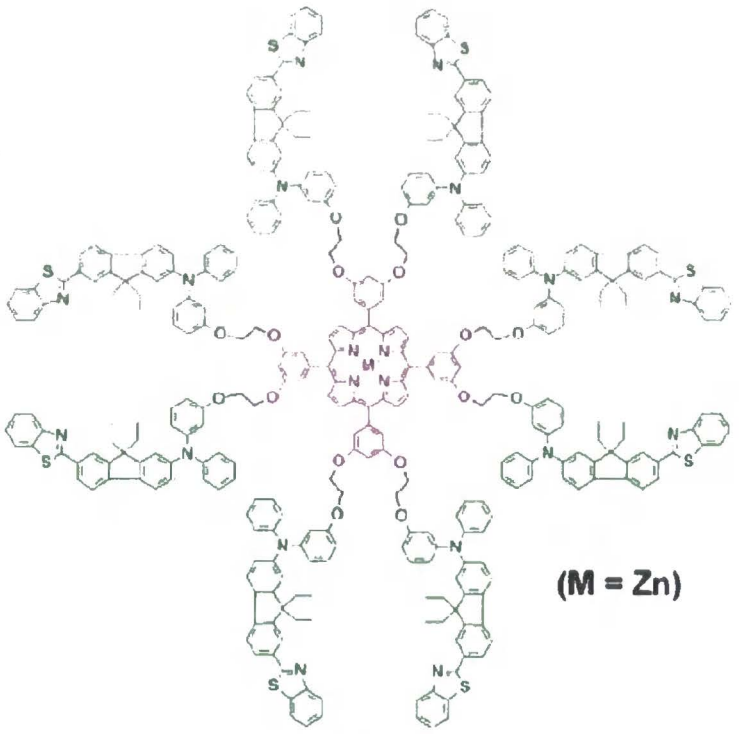


Fig 64: Some recently synthesised zinc porphyrin-core dendrimers.[339]



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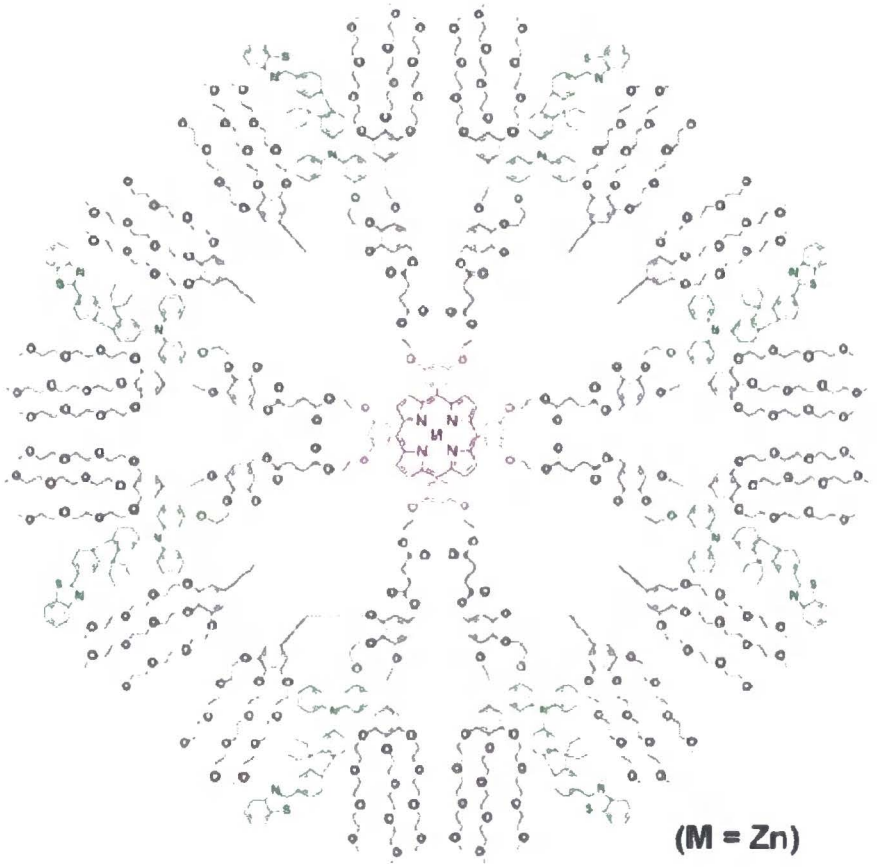

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Fig 65: Fluorene-containing zinc porphyrin-core dendrimers.[340]

The incorporation of multiple porphyrin rings within the hierarchy or at the periphery of a dendrimer is also attractive for light-harvesting and as photosynthetic mimics.[341] Recent examples include the work of Li *et al.* on a benzene-centred dendrimer with zinc porphyrins incorporated into the dendritic chains (**143**) (se Fig 66),[342,343] and the imine-based porphyrin dendrimers by Crossley *et al.* (**144**) (see Fig 67).[344,345]

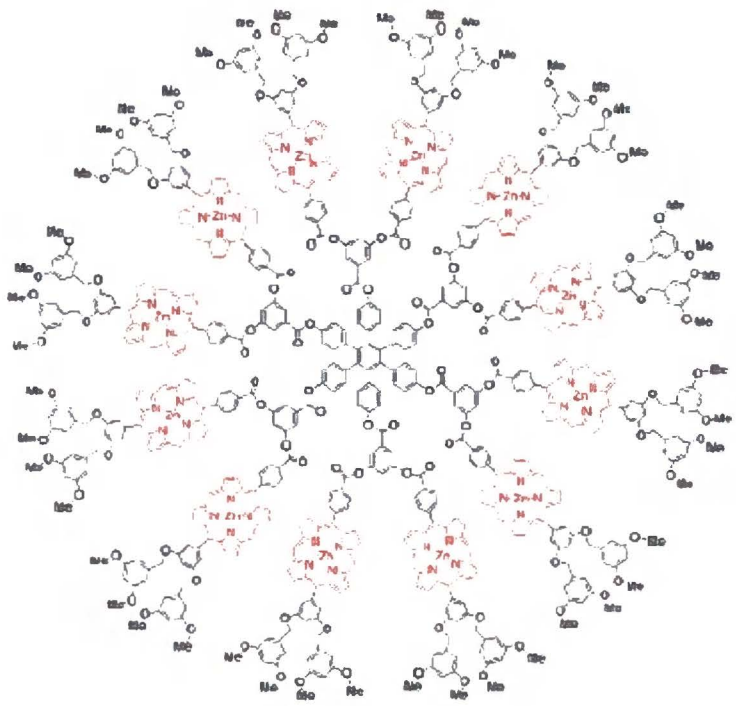

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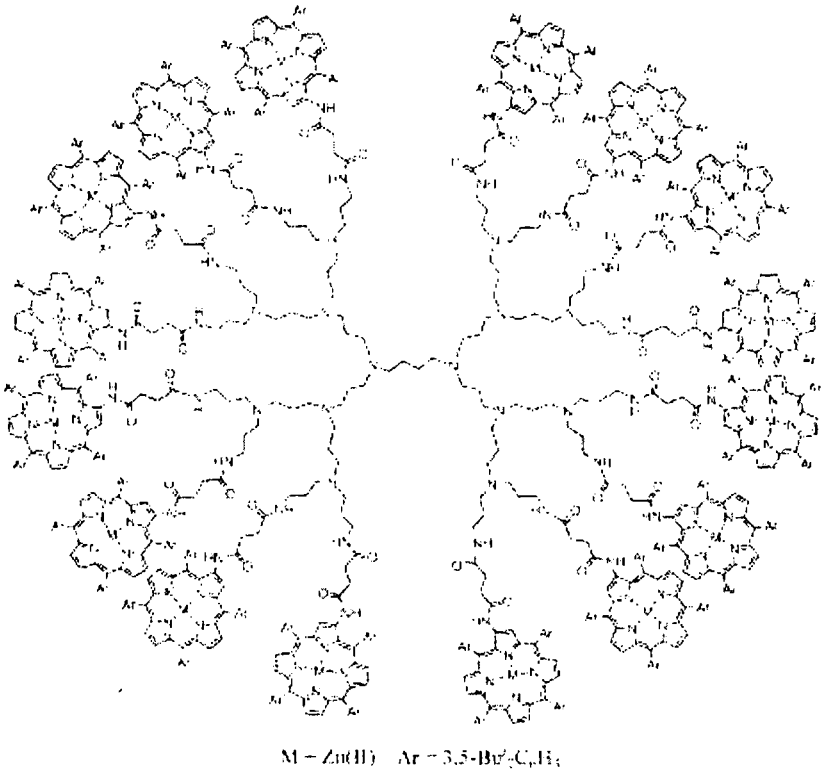
Fig 66: Recently synthesised zinc porphyrin-appended dendrimer based on a benzene core.[342]



144

Fig 67: Recently synthesised zinc porphyrin-appended dendrimer based on an imine core.[344]

The use of zinc porphyrins as components of polymer architectures is also known,[346-349] and two recent examples are the synthesis of conjugated polyacetylenes bearing pendant zinc tris(trimethoxyphenyl)porphyrin units,[350] and the incorporation of a functionalised tetraaryl zinc porphyrin into a series of soluble polyimides.[351]

The planar nature of porphyrins lends itself well to deposition onto surfaces, and examples of zinc porphyrin mono- and multi-layers tethered to a variety of materials are well known in the literature. Surfaces widely used include silicon(100), quartz, gold, and tin oxide, and potential applications include the production of hybrid molecular/semiconductor architectures to bridge the gap between the bulk and nanoscale dimensions, smart materials for use in photoinduced and electron transfer energy processes, organic films for use in optical devices (i.e. OLEDs) and solar cells.[352-359] An alternative method to surface deposition for these high-performance devices is that of film-formation from solutions of porphyrins, and such films have been previously formed using simple zinc-porphyrins bearing peripheral substituents.[360,361]

1.3.4 Other metalloporphyrins

Aside from the aforementioned zinc and silicon porphyrins, a wide variety of metalloporphyrins are well-known, incorporating metals including nickel,[362-367] iron,[368-374] cobalt,[375-379] manganese,[380-382] ruthenium,[383-386] rhodium,[384] aluminium,[387,388] magnesium,[389] copper,[390-393] chromium,[394] molybdenum,[395] palladium,[396] platinum,[397-399] vanadium,[400] rhenium,[401] tin,[402] and zirconium.[403] The synthesis of macromolecular arrays often involves two or more different metalloporphyrins.[404,405] In addition to this, examples of lanthanide-containing porphyrins are also known.[406-409] Phosphorus has also found use as a central atom in porphyrin structures.[410-412] A more detailed consideration of these metallophthalocyanines will not be included in this literature review.

1.3.5 Free-base Porphyrins

Since the first production of a free-base porphyrin by Fischer,[205] the occurrence of non-metallated porphyrins in the literature has remained high. A variety of routes to these compounds are employed, including the well-established protocols of Rothemund,[206] Adler,[208] Lindsey,[215] and MacDonald,[227] as well as alternative more modern methods such as the benzannulation of Fischer-carbene complexes,[413] and palladium-catalyzed coupling such as Suzuki and Heck reactions,[414-416] which are well suited to modifying the periphery of simply-functionalised porphyrins with more complex moieties.

Free-base porphyrins are often precursors to the corresponding metalloporphyrins. The following is a brief summary of recent literature articles, which detail the synthesis of free-base porphyrins and for the most part do not include the corresponding metalloporphyrins.

Two general strategies are employed in the synthesis of highly-functionalised free-base porphyrins: the first of these is to construct highly-functionalised precursor molecules, which are then cyclised to form the desired porphyrin.

Examples of tetra-substituted porphyrins synthesised via functionalised aryl-aldehyde derivatives are commonplace, and a wide range of groups have been employed in this fashion, including aryl halides,[417,418] alkoxides,[417,419-421] sulfone derivatives,[422,423] nitroxides,[424] amides,[417,425] anilines,[426,427] and alkynes.[413] In addition, alternative arenes such as thiophenes,[428-430] pyridines,[431-433] and furans,[222,417,434] have been employed.

Murtinho *et al.* synthesised tetraarylporphyrins bearing naphthalene (**145**), phenanthrene (**146**) and aryl halide (**147**) derivatives for potential use as sensitizers in the photooxidation of phenols (see Fig 68). The compounds produced gave higher yields in these reactions via the production of singlet oxygen and its subsequent addition to the phenol.[435] More recently, the same group has synthesised the water-soluble free-base, tin and zinc analogues of 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin in the same reaction.[436]

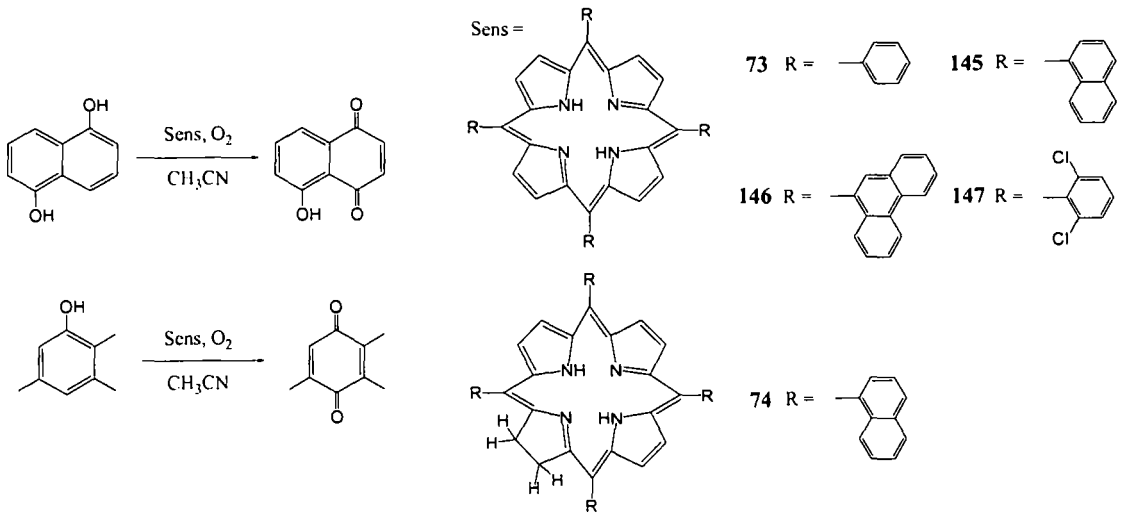


Fig 68: Use of substituted tetraarylporphyrins as photosensitizers.[435]

Shen *et al.* used phenylpropargylaldehyde with substituted pyrroles in a Rothemund condensation to obtain a series of phenylethynyl-substituted porphyrins (**148-150**) : crystal structures were obtained for all three systems (see Fig 69).[437]

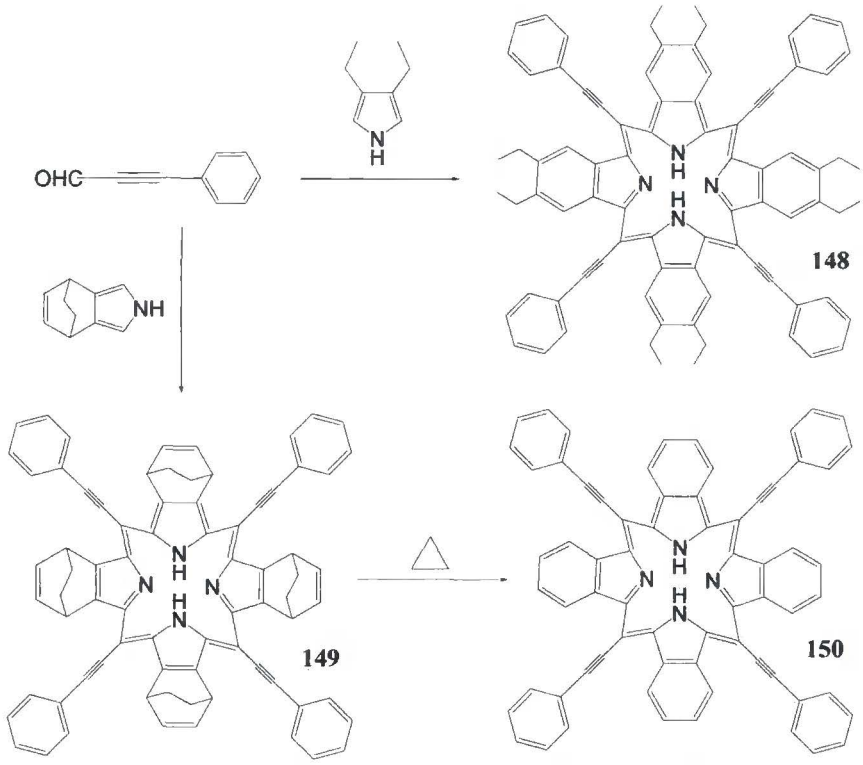


Fig 69: Synthesis of phenylethynyl-substituted porphyrins.[437]

A nano-sized π-conjugate molecule containing both a truxene and porphyrin moiety (**151**) was shown by Duan *et al.* to have a high fluorescence quantum yield due to efficient energy transfer between the antenna-like aryl groups and the porphyrin core (see Fig 70).[438]

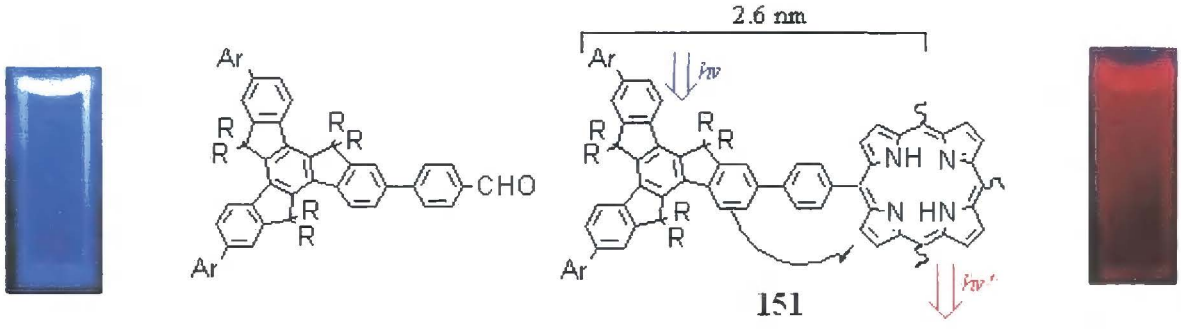


Fig 70: Comparison of emission from both the starting truxene molecule and the truxene-porphyrin conjugate. Change in emission wavelength demonstrates efficient energy transfer from truxene to porphyrin moiety.[438]

Some tetra-substituted porphyrins have also recently been synthesised by variations on the MacDonald "2 + 2" methodology.[227]

Ogura *et al.* synthesised 2,3-dimethoxyphenyldipyrromethane and then explored various routes to a symmetrical porphyrin via reaction with *p*-tolualdehyde.[439] The

conditions used by Lee and Lindsey for their synthesis of *trans*-substituted porphyrins,[440] resulted in a number of rearrangement products caused by the acidic medium.[441] However, a micellular reaction, *a la* Bonar-Law,[222] gave only the desired *trans*-substituted product (see Fig 71). The methoxy-substituted porphyrin was then converted to the hydroxy-substituted analogue and reacted with a molybdenum complex to form a dimetallic complex (**152**).

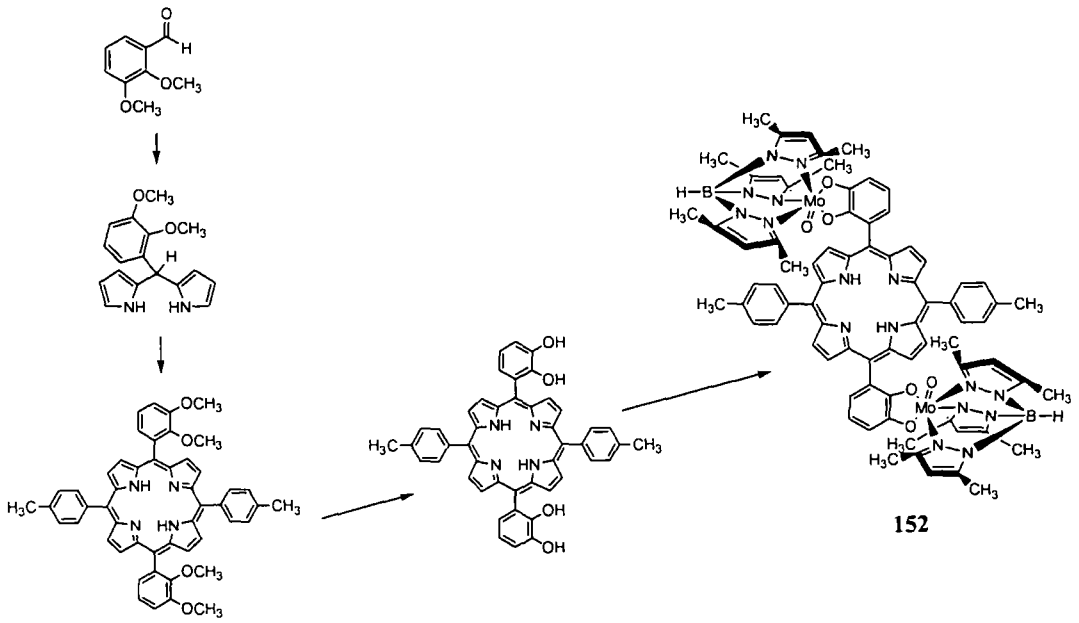


Fig 71: *Trans*-substituted porphyrin obtained by the MacDonald approach.[440]

Senge *et al.* instead utilised a dithianyl aldehyde as a starting point for the synthesis of a variety of substituted porphyrins via either conversion to the corresponding dipyrromethane and subsequent "2 + 2" cyclisation, or direct reaction with pyrrole in different conditions to give alternatively substituted porphyrins.[442]

As an alternative to functionalised aldehydes, functionalised pyrroles or dipyrromethanes allow the synthesis of tetra- and octa-substituted porphyrins. The pyrrole derivative must usually bear either a keto- or a carboxylic group in the 2 and/or 5 position(s), or alternatively an aldehyde can be used, resulting in a porphyrin bearing further substitution. Examples of porphyrins bearing simple groups attached to the pyrrole rings are well known, including halogens,[443-446] alkyl groups,[447-449] alkoxy groups,[450,451] thiols,[452] and nitro groups.[453] Ono *et al.* used 3,4-diarylpyrroles and aldehydes bearing a variety of aryl substituents to synthesise the corresponding dodecaarylporphyrins (**153-161**) via standard Lindsey conditions (see Fig 72).[454]

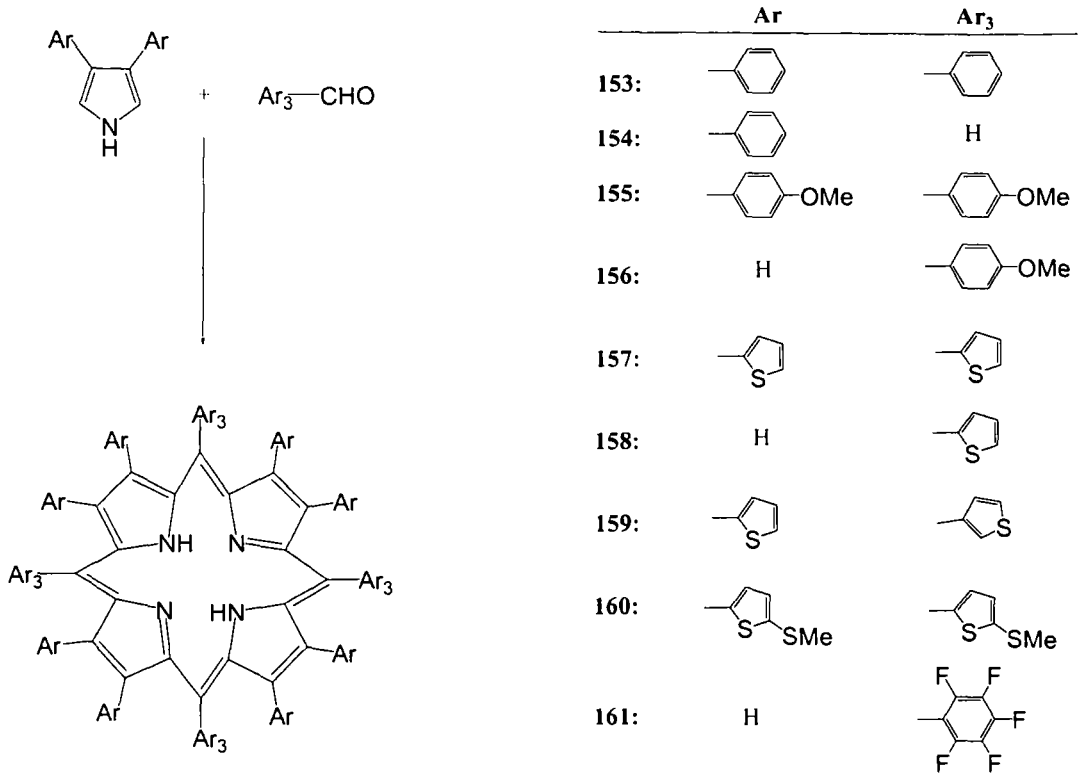
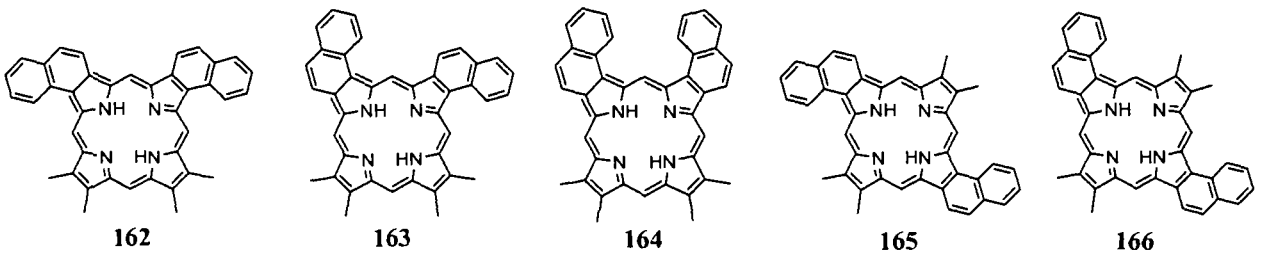


Fig 72: Synthesis of dodecylarylporphyrins.[454]

Porphyrins bearing aryl substituents fused directly to the pyrrole units are also well known. Lash *et al.* used a dihydronaphthopyrrole to form the corresponding naphthoporphyrin via a MacDonald "2 + 2" condensation followed by dehydrogenation with DDQ.[455] Porphyrins bearing more then one naphthalene moiety were synthesised by Manley *et al.* using naphtha[1,2-c]pyrrole and β-substituted pyrroles. Using these two units, a set of five isomeric dinaphthoporphyrin systems were produced (**162-166**) (see Fig 73), employing routes such as a MacDonald "2 + 2" condensation and the cyclisation of a,c-biladiene intermediates with copper(II) chloride.[234]



162 **163** **164** **165** **166**

Fig 73: Structures of isomeric dinaphthoporphyrin systems.[234]

Several rather more complex architectures are known incorporating such substituents as 9,10-dihydroanthracene (**167** and **168**) and bicyclic systems (**169**) (see Fig

74).[456-460] Li *et al.* used a pseudo-"3 + 1" approach to produce a novel TTF-porphyrin dyad (**170**) in which one TTF unit was fused directly to the porphyrin via a pyrrole ring. Though the species was almost non-fluorescent, it was shown that selective chemical oxidation of the TTF unit reduced electron transfer from the TTF unit to the porphyrin core, and fluorescence increased; hence the molecule functioned as a fluorescent switch (see Fig 75).[461]

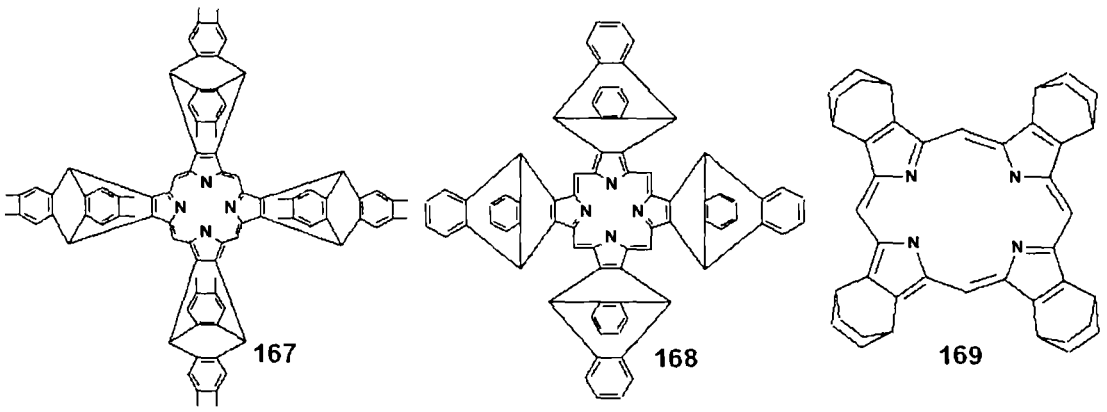


Fig 74: Structures of highly complex multicyclic porphyrins.[456,458-460]

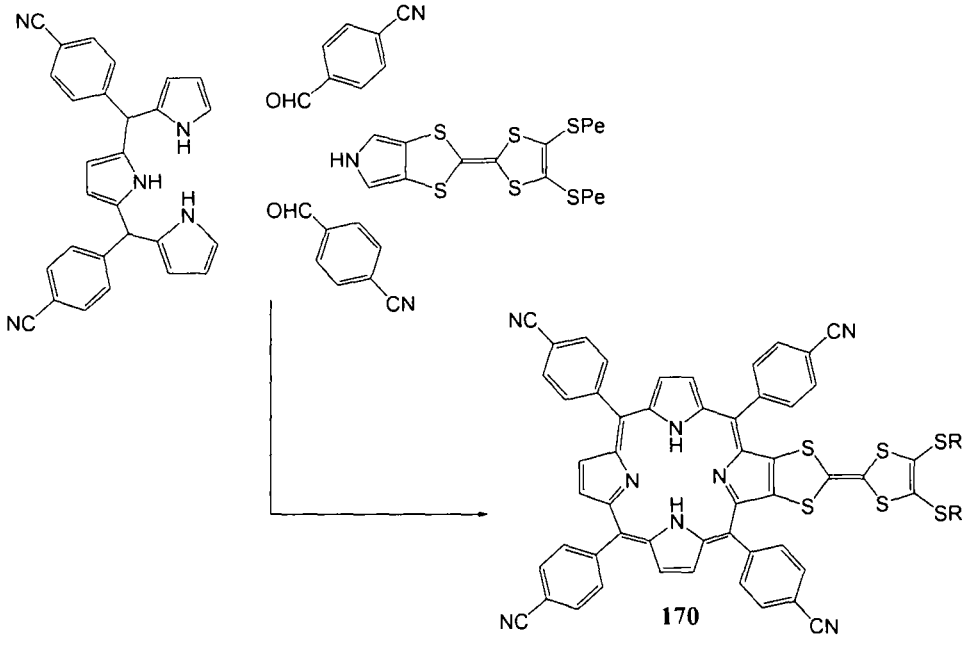


Fig 75: Synthesis of a mono-TTF-annulated porphyrin fluorescent switch.[461]

The second method for the synthesis of highly functionalised porphyrins is to perform a variety of coupling reactions on the existing macrocyclic system. These reactions more commonly involve attachment to a pre-existing group located at the *meso*-positions of the porphyrin, although attachment to the pyrrole rings is also known.[462-464]

Chan *et al.* synthesised of a series of quinonylporphyrins by two different methods.[413] The first was by Suzuki cross-coupling reactions of substituted phenyl boronic acids with porphyrins bearing either *meso*-aryl triflates or aryl bromides. The use of such palladium-catalysed reactions has become common in this form of macrocyclic system expansion.[328,465,466] The second route was much more unusual. Fischer-carbene complexes (**171**) are a stable and isolatable form of carbenoids, which usually contain either tungsten or chromium,[467] and Chan *et al.* reacted such compounds with a series of (alkynylphenyl)porphyrins, followed by an oxidative work-up to give porphyrin-monoquinones and –tetraquinones (**172-179**) (see Fig 76).

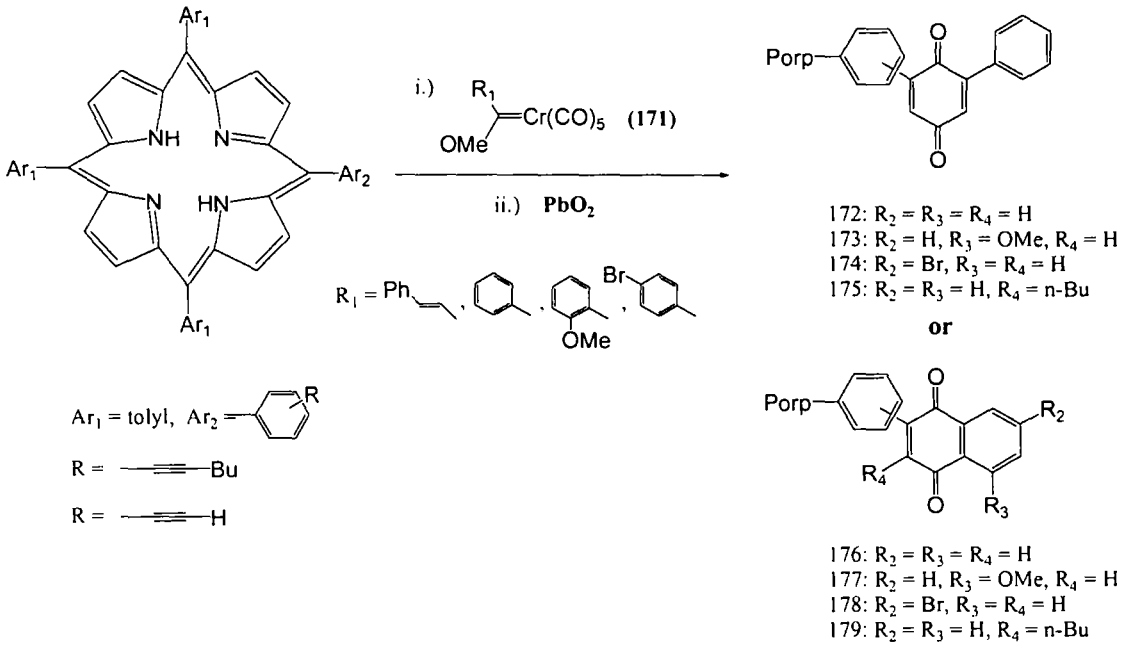


Fig 76: Synthesis of quinonylporphyrins via benzannulation of Fischer-carbenes.[413]

The Heck reaction has found widespread use in the synthesis of porphyrins bearing vinyl groups attached either directly to the porphyrin core, or to peripheral aryl substituents. In general, these reactions involve the palladium-catalysed reaction of substituted olefins with brominated porphyrins.[414,415,465,468-470] One interesting aspect of the reaction is the possibility of intramolecular cyclisation on the porphyrin periphery, and several examples of this involving metalloporphyrins have been published.[284,471] Other palladium-catalysed couplings include the formation of aryl- and alkylamino-substituted porphyrins, and the reaction of *meso*-brominated porphyrins with thiols by Gao *et al.*[472,473] Alternatively, it was found that organolithium reagents react with porphyrins giving substitution at the *meso*-positions.[474]

Much simpler coupling methods, without the need for metal catalysis are also regularly used to functionalise porphyrins. Recent work has included the synthesis of a series of porphyrin dyads and triads incorporating fullerenes, indolizines and pyrenes (**180**), with the objective of designing photonic switches (see Fig 77). The compounds were synthesised starting from a simple ester-substituted porphyrin via successive coupling reactions using amide and acid end-groups. Excitation of the porphyrin core gives a photoinduced electron transfer to one of the moieties, and by photoisomerising the second moiety (and thereby increasing its reduction potential), the direction of electron transfer and hence porphyrin fluorescence, can be controlled.[475-478]

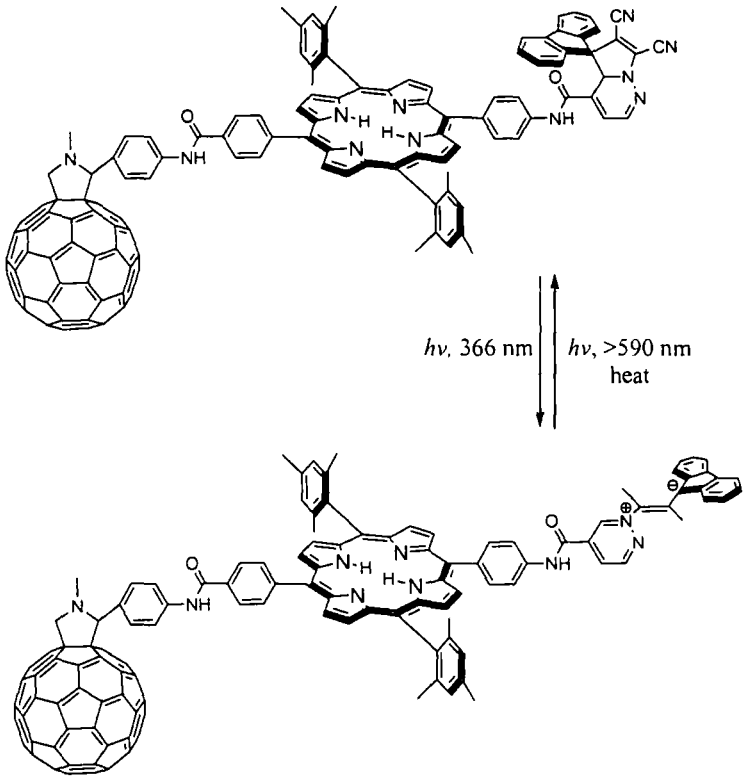
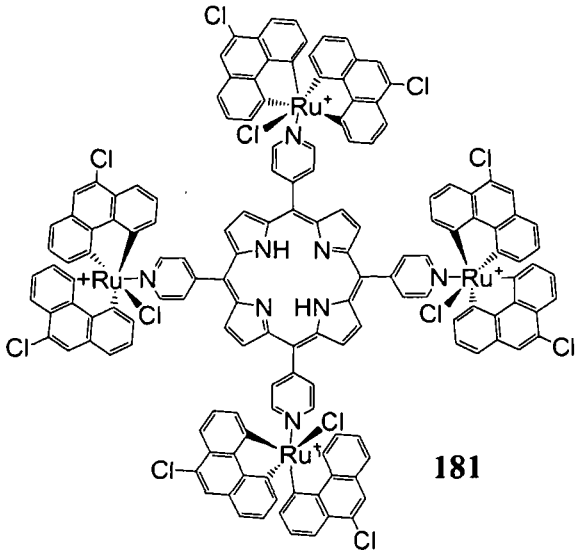


Fig 77: Structure of a porphyrin triad with potential as a photonic switch.[478]

Similar coupling reactions have been used to attach amino acids and oligonucleotides to acid-substituted porphyrins,[479-482] as well as in esterification reactions with aryl alcohols.[483] Water-soluble cationic porphyrins are of interest for binding to DNA molecules.[484-487] Reactions of acyl chloride-substituted porphyrins with amide-functionalised long-chain alkanes, alkynes and ketones are also known.[488,489]

The attachment of ruthenium complexes to *meso*-4'-pyridylporphyrins has recently been published by two different groups (see Fig 78). Winnischofer *et al.* attached a ruthenium phenanthrene complex to all four pyridyl units of *meso*-4'-pyridylporphyrin via reaction in an acidified mixture of methanol and DMF (**181**).[490] This material was shown to

be a highly active electrocatalyst for the oxidation of nitrite ions to nitrates. Gianferrara *et al.* performed a similar reaction using a ruthenium chloride-nitrosyl complex, refluxed in dichloromethane (**182**).[491] The anti-viral properties of this molecule are currently under investigation.



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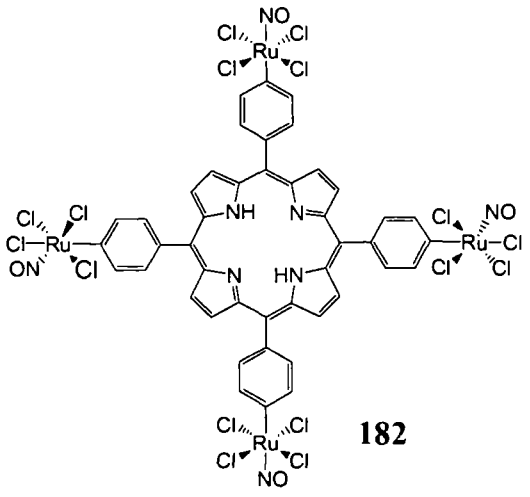
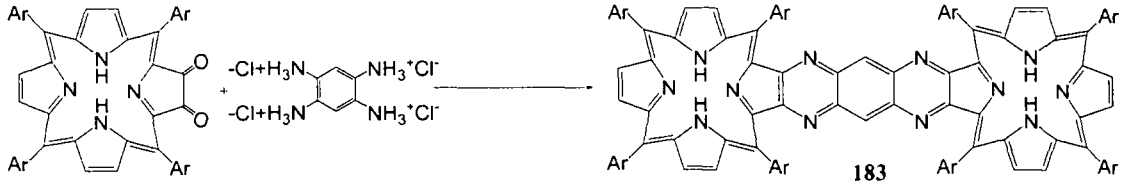


182

Fig 78: Structure of *meso*-4'-pyridylporphyrins bearing ruthenium complexes.[490,491]

Examples of free-base porphyrin dimer, trimers and oligomers containing a range of spacer groups can be found in the literature. Crossley *et al.* directly fused two dione-derivatised porphyrins via a condensation reaction with benzenetetraamine (see Fig 79),[492] and then expanded this reaction to the construction of a quasi-one-dimensional linearly conjugated poly-porphyrin molecular wire.[493] Other more recent free-base porphyrin dimers use diaza-crown ethers,[494] succinate based bridges,[495] and oxacalixarenes[496] as spacers. The use of diacyl chlorides produces cofacial dimers capable of guest-binding.[497]



183

Fig 79: Synthesis of a directly-fused free-base porphyrin dimer.[492]

Two-dimensional porphyrin arrays are of great interest as models for mimicking the natural photosynthetic system. Recent examples of the synthesis of such arrays are the use of a one-pot Suzuki polycondensation by Fei *et al.* (**184**),[498] and the acid-catalysed reaction of a benzaldehyde-substituted porphyrin with pyrrole by Inokuma *et al.* to form a star-like porphyrin oligomer (**185**) (see Fig 80).[499]

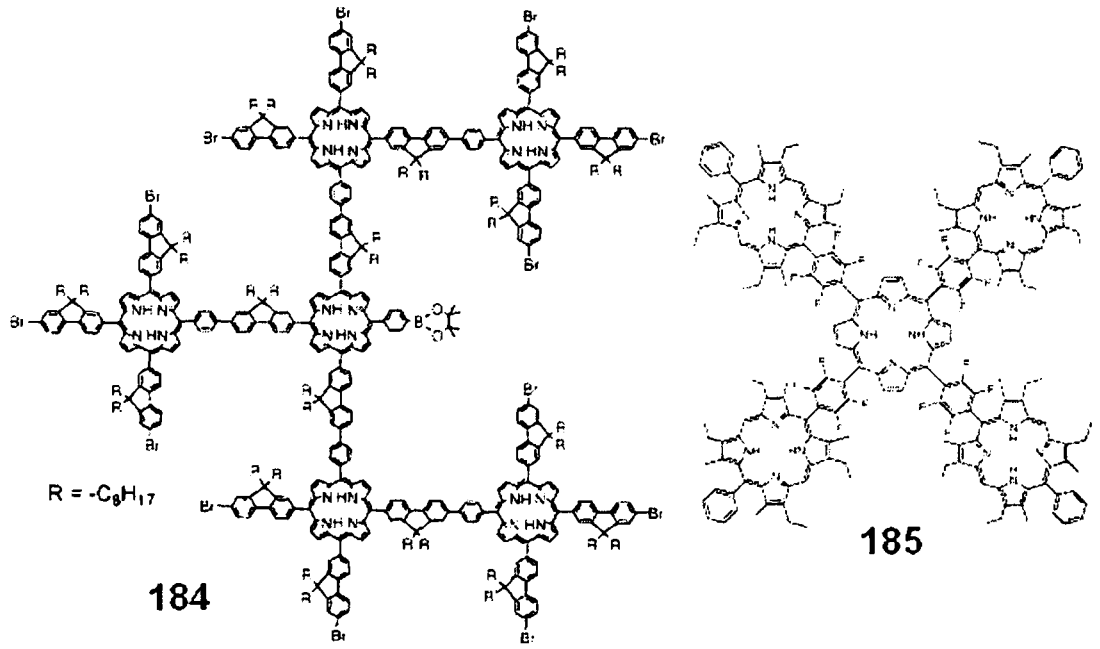


Fig 80: Free-base porphyrin arrays.[498,499]

Recent porphyrin-cored dendrimers have included the use of stilbene dendrons,[500] polyphenylene dendrons terminated with either dimethoxybenzene or benzoquinone end-groups,[501] and phenylazomethine dendrons.[502] The attachment of (poly)fluorene containing chains to the periphery of free-base porphyrins is currently being investigated by at least two groups. Li *et al.* have published work detailing the synthesis of star-like porphyrin dendrimers with four oligofluorene arms attached to the *meso*-positions. The syntheses involve either first producing oligofluorene aldehyde derivatives or by extending mono-fluorene substituted porphyrins via Suzuki coupling.[416,503] In contrast, Oar *et al.* reacted a (dihydroxyphenyl)porphyrin with a fluorene-containing moiety with a bromide eng-group.[339] Ballardini *et al.* produced a series of porphyrin-cored glycodendrimers via reaction of acyl chloride-substituted porphyrin with a number of protected glycopyranose amide derivatives. Once the dendrimers were formed, the sugar-protecting groups were removed to produce water-soluble dendrimers.[504]

Free-base porphyrin polymers can be found in the literature, including linear systems incorporating porphyrins into the polymer chain via the *meso*-positions (**186**) (see Fig 81),[505] polyporphyrin films formed from mercaptoporphyrins,[506] and the attachment of pendant porphyrins to already synthesised polymers.[507]

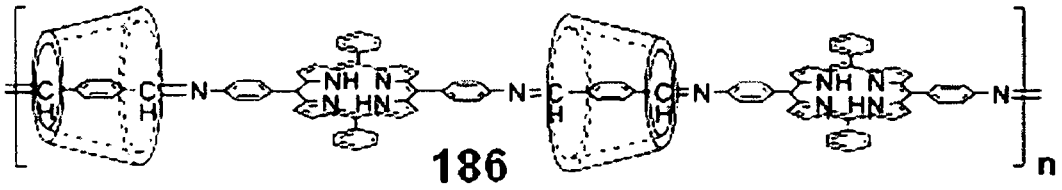


Fig 81: A porphyrin-containing polymer chain, cylinders represent cyclodextrin rings.[505]

This review chapter has sought to highlight the varied chemistry of phthalocyanines, pyrazinoporphyrins and porphyrins, with emphasis on recent developments and applications. The subsequent chapters of this thesis will describe the work we have carried out on specifically-functionalised derivatives of these macrocycles.

Chapter 2. Phthalocyanines

2.1 Introduction

The initial aim of this section of the work was to build on previous work in our laboratory by Farren *et al.*[58,508] Bis-substitution of silicon phthalocyanine dichloride $Si(Pc)Cl_2$ (**1**) at the *trans*-axial positions had been explored in some detail, with particular attention paid to ligands containing tetrathiafulvalene (TTF) units, as a possible route to redox-controlled fluorescence quenching of the macrocycle. The outcome of this work was the realisation that to facilitate a controllable quenching of this type, more direct control over the steric and electronic interactions between the phthalocyanine and axial substituents (TTF and others) was needed. This would involve either the use of more complex ligands to directly control the electronic interactions, or attaching only one ligand of this type. Both these methods require the prior incorporation of a simple alkyl or aryl group onto one of the *trans*-axial positions of the phthalocyanine. Such a group should not only limit the magnitude of ligand interaction but also allow the attachment of solubilising chains if needed. The exploration of these types of mono-substituted phthalocyanines has so far been very limited and the chemistry of phenyl silicon phthalocyanine chloride [PhSi(Pc)Cl] (**36**) is relatively unknown.[68,99,102]

2.2 Basic Strategy

Work began with the synthesis of PhSi(Pc)Cl (**36**) and its simple derivatives based on displacement of the chloride (with hydroxide, alkoxides and aromatic esters). However, once a range of these derivatives had been obtained (see below), it became clear that these systems based on **36** were much more problematic to work with than initially envisaged, and so further work to attach TTF-containing ligands was not undertaken. Furthermore, reactions to synthesise silicon phthalocyanines bearing groups other than the phenyl substituent were unsuccessful.

As a consequence of these initial findings, the emphasis of our phthalocyanine work switched to the synthesis of a range of new symmetrical bis-substituted silicon phthalocyanines, culminating in a thorough investigation of the fluorescence properties of

all the phthalocyanines produced from **36** and **1**, (see section 2.4). The effects of peripheral substitution of an electron-rich moiety upon the fluorescent properties of a free-base phthalocyanine were also briefly investigated.

During the course of this work, collaboration with Dr. Kataky's group in Durham allowed us to investigate the interactions of a number of these bis-substituted compounds with a surface of highly-ordered pyrolytic graphite (HOPG) (see section 2.5).

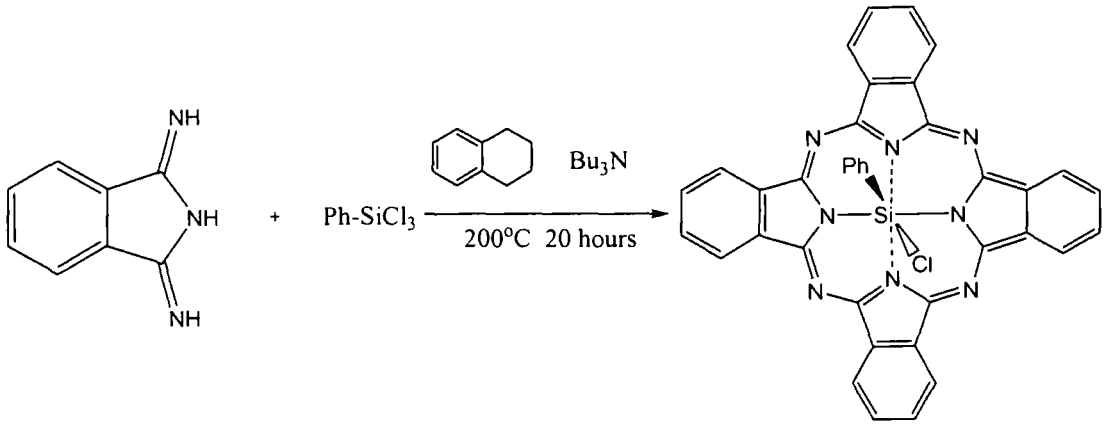
A reliable and relatively high-yielding synthesis of PhSi(Pc)Cl (**36**) was developed based on a modification of existing preparations.[68,99,102,107] Various routes to convert **36** to PhSi(Pc)OH (**37**) were attempted without success. Both **36** and **1** were reacted successfully with a range of different compounds to form new silicon phthalocyanine derivatives via displacement of the chloride(s) by reaction with the acid or alkoxide derivative of the ligands. Despite the use of a large range of potential ligands in these reactions, a relatively small number of novel compounds were obtained and this can be attributed to the problems encountered in the purification of these materials. Attempted syntheses of analogues of **36** incorporating both alkyl and aryl substituents were also unsuccessful. The synthesis of a peripherally substituted free-base phthalocyanine was achieved via attachment of two aryl substituents to the phthalonitrile starting material before the subsequent cyclisation to form the macrocycle.

2.3 Discussion

2.3.1 Synthesis of phenyl silicon phthalocyanine chloride (36)

Although the synthesis of **36** has already been documented more than once,[68,99,102] our initial attempts to synthesise this compound were unsuccessful. In a first attempt to synthesise **36**, 1,3-diiminoisoindoline and phenyltrichlorosilane were reacted together in a 1:1 molar ratio in quinoline, to produce an oily black substance containing a multitude of ^{1}H-NMR signals. This failure could be explained by the fact that compound **36** contains 4 indoline units for each silane unit. However, in all three literature routes to this material, the indoline and the trichlorosilane were reacted together in a 2:3 molar ratio, with the trichlorosilane, and not the indoline, being in excess.

The original source of information for the preparation of **36** was the work of Kraus *et al.*[102] in 1998 which in turn cited the work of Dirk *et al.*[107] This preparation was adopted and the indoline and silane reacted together in a 2:3 molar ratio, using quinoline as a solvent. In our hands, the use of quinoline was problematic, giving thick oily solutions which did not filter well after reaction and comprised mixtures of unreacted starting materials and unidentified products (NMR evidence).



36

Fig 82: Synthesis of phenyl silicon phthalocyanine chloride (**36**).

Tamao *et al.*[99] reported a mixture of tetrahydronaphthalene and tributylamine as the solvent system and we found that this gave a better quality product: washing the crude product with methanol was the key step, leaving **36** as a purple crystalline solid in 54% yield. Attempts to carry out the synthesis in tetrahydronaphthalene alone resulted in no

reaction between the starting materials, pointing to a base-catalysed process (the proposed mechanism of which is shown below). Furthermore, as tributylamine is a much better base then quinoline, the reaction proceeds more quickly.

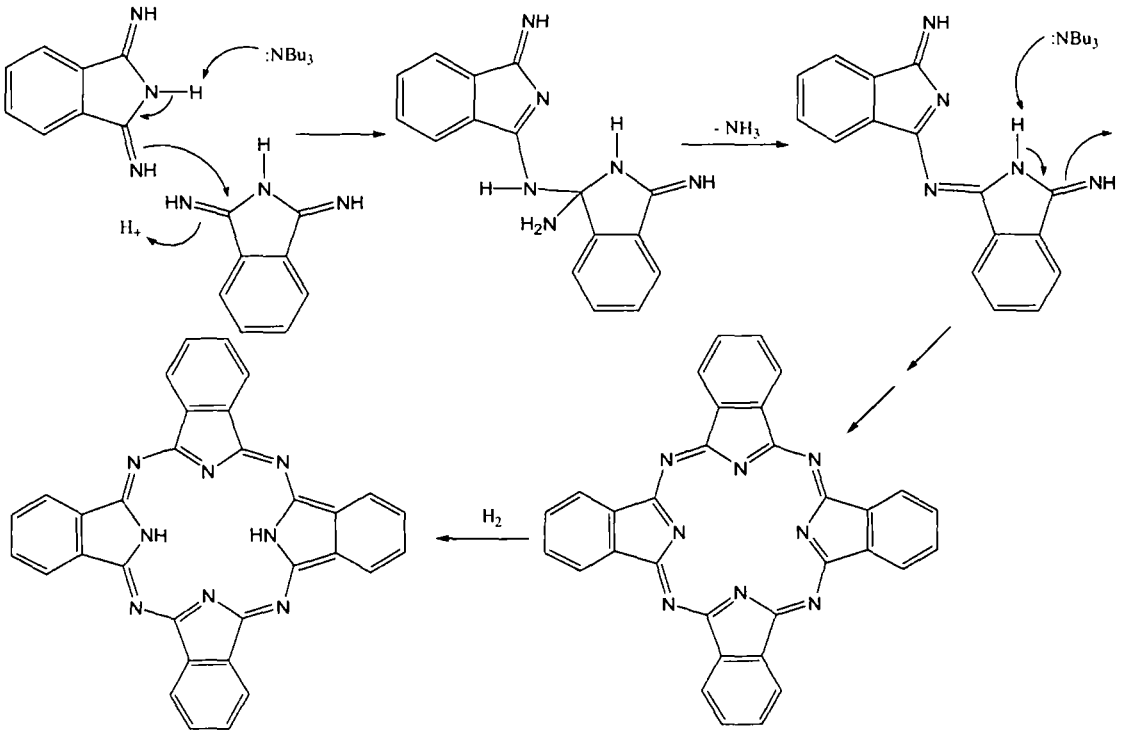


Fig 83: Proposed cyclisation mechanism for phthalocyanine synthesis.

The ^{1}H-NMR spectrum of **36** did not agree with the literature data for this compound.[102] We observe three separate peaks (of multiplicity 2:2:1) for the phenyl group at δ 1.56, 5.51, and 5.53 ppm, whereas Kraus *et al.* quoted a singlet peak at δ 6.81 ppm. The other two syntheses of **36** do not include any NMR data.[68,99]

Compound **36** is highly insoluble in most common solvents. Indeed ^{1}H-NMR spectra were obtained in DMSO-d_6 only after heating the solution and filtering excess solid. This insolubility proved to be a help in the purification of the solid and recrystallization from toluene gave yields of >90% based on the crude material and an overall yield of 54% for the reaction (which is considerably higher then the previously published preparations). In almost all the mass spectra obtained for **36**, the parent ion at m/z 653 was not observed: instead the $(M\text{-}Cl)^{+}$ peak at m/z 617 had the highest intensity. This is consistent with the labile nature of the Si-Cl bond and the high reactivity of **36** and **1** at the axial positions.

2.3.2 Attempted synthesis of phenyl silicon phthalocyanine hydroxide (37)

Although attachment of simple oxo-bridged ligands via reaction with **36** is feasible,[58,72,132,508,509] the synthesis of more complex bis-substituted Si(Pc) derivatives has previously been more easily achieved by reaction with the dihydroxy compound $Si(Pc)(OH)_2$ (**2**) .[61,68,72,102,127,509] Davison and Wynne achieved the basic hydrolysis of $Si(Pc)Cl_2$ (**1**) to **2** by using an excess of sodium hydroxide in a solution of pyridine and water[510] and this method was also utilised by Kraus *et al.* in their claimed synthesis of **37**.[102] However, in our hands this method gave only unreacted starting material with no evidence of an OH group in the product. Furthermore, the solid obtained was completely insoluble in methanol, despite the fact that the published preparation gives ^{1}H-NMR data of **37** in CD_3OD. This unreliable route was therefore abandoned.

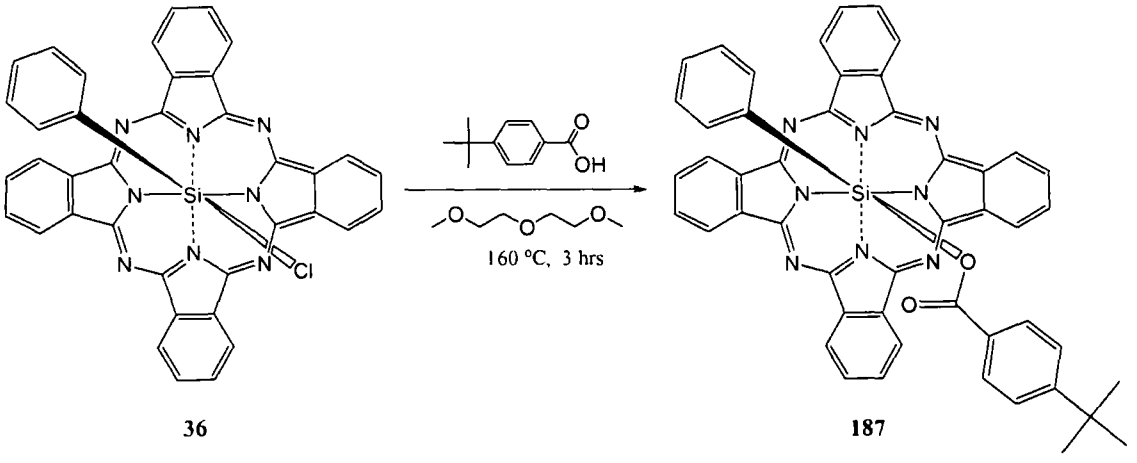
The alternative literature route to **2** by Sasa *et al.* is more chemically aggressive,[127] involving initial reaction of **1** with concentrated sulphuric acid, followed by washing with a water-acetone mixture before further reaction with concentrated ammonia solution. Applying this route to compound **36** produced a bright blue solid, suggesting a possible reaction. The solid was completely insoluble in chloroform and acetone but had high solubility in dimethyl sulphoxide. Both ^{1}H-NMR and ^{13}C-NMR spectra gave no peaks consistent with a Pc derivative and a mass spectrum showed no distinguishable peaks higher than m/z 335 and so this route was also abandoned. Attempts to react this blue solid with a number of carboxylic acids failed to give identifiable products.

The problems encountered with this conversion of **1** and **36** remain unresolved. The successful reactions of the chloride and dichloride with carboxylic acid or alkoxide derivatives of the ligand (see below) show that chloride displacement itself is not a problem. It may therefore be that extensive H-bonding or dimerisation/oligomerisation through Si-O-Si bonds (oxo-bridging) contributes to the problems we encountered.

2.3.3 Synthesis of phenyl silicon phthalocyanine (4-*tert*-butyl)benzoate (187)

Silicon phthalocyanine bis-(4-*tert*-butyl)benzoate (**4**) was synthesised by Farren *et al.*[508] as a reference compound. We therefore chose compound **187** as a comparable reference compound. The *tert*-butyl functionality provides an ideal ^{1}H-NMR marker for easy analysis of the product, and ensures good solubility.

The original synthesis of the bis-ester was achieved by reaction of **1** with a four-fold excess of 4-*tert*-butylbenzoic acid. A similar protocol using compound **36** produced a green solid, the ^{1}H-NMR of which showed the presence of both starting materials as well as possible product formation. After much experimentation, particularly with respect to product purification, a reproducible, high-yielding synthesis of **187** was developed. Recrystallization and a basic-wash were key steps in the workup. Thus, reaction of an equimolar mixture of 4-*tert*-butylbenzoic acid and **36** in 2-methoxyethyl ether at 160 °C for 3 h gave **187** as a green solid in 78% yield, after removal of some unreacted starting materials.



36 **187**

Fig 84: Synthesis of Compound **187**

The ^{1}H-NMR spectrum of **187** showed two doublets for the ring protons of the attached ligand at δ 4.96 ppm and 6.21 ppm. The *tert*-butyl group appeared at higher field shift (δ 0.71 ppm) relative to 4-*tert*-butylbenzoic acid (δ 1.35 ppm). This shift is expected due to the close proximity of these protons to the large macrocyclic ring current. The electrospray mass spectrum did not show the parent ion of **187** but as is common in these types of esters,[58,508] gave a peak at m/z 818.3 due to the $[M+Na]^+$ ion. Also present is a peak at m/z 617.3 due to the $[Si(Pc)Ph]^+$ ion (i.e. loss of the benzoate ligand). As expected,

this is the major peak and emphasises the fact that the carboxylate fragment is more stable then the alternative phenyl fragment.

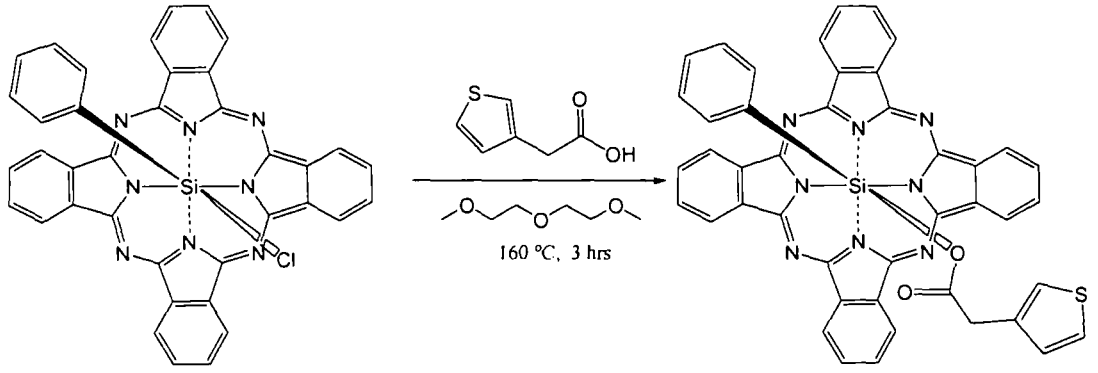
2.3.4 Attempted synthesis of phenyl silicon phthalocyanine (4-bromo)benzoate

The attachment of a bromine-substituted benzoate ligand was attractive as such a derivative might allow subsequent reactions, with the bromine acting as a reactive handle for attachment of further functional groups or even a second SiPc unit.

The reaction was attempted using both equimolar quantities of **36** and 4-bromobenzoic acid and a four-fold excess of the latter but without success. In both cases, ^{1}H-NMR analysis showed only the free bromobenzoic acid with no Pc peaks evident. Purification as for compound **187** gave a dark precipitate which was insoluble in solvents such as chloroform, dichloromethane or acetone and a ^{1}H-NMR spectrum in DMSO-d_6 showed only Pc peaks at δ 8.5 ppm and 9.65 ppm corresponding to the phthalocyanine unit. It appears that the products of this reaction are unstable to basic conditions. This may have led to a mixture of insoluble polymeric products, which may explain why no distinct Pc peaks were evident in the ^{1}H-NMR spectra of the original crude solid obtained. However other polymeric Pc-containing materials do not exhibit the same insolubility.[60,510] A similar attempt to obtain silicon phthalocyanine bis-(4-bromo)benzoate by analogous reaction with **1** also gave intractable products.

2.3.5 Synthesis of phenyl silicon phthalocyanine (3-thienyl)acetate (188)

Pc derivatives with peripheral thiophene substituents are known[27] and thiophene derivatives have previously been used in our laboratory as axial ligands[508]. The properties of the thiophene-containing ligand utilised differs from 4-*tert*-butylbenzoic acid in that the thiophene ring has a higher electron density, and additional flexibility of the ligand is afforded by the extra methylene linker.



36 **188**

Fig 85: Synthesis of compound **188**

By analogy with the synthesis of silicon phthalocyanine bis-(3-thienyl)acetate,[508] **36** and 3-thiophene-acetic acid gave **188** as a pure dark blue solid in 69% yield. ^{1}H-NMR analysis of the product gave a signal at δ 0.67 ppm due to the CH_2 group in the ligand. This is similar to the value of 0.65 ppm for the bis-substituted derivative.[74] The signals from the thiophene protons also agree with the values for the bis-substituted derivative [i.e. δ 4.43, 4.96 and 6.11 ppm; cf. δ 4.41, 4.94 and 6.06 ppm for silicon phthalocyanine bis-(3-thienyl)acetate]. No effect on the chemical shifts of the phenyl protons is evident compared with values for **36**. The electrospray mass spectrum was consistent with structure **188** with the presence of the $(M+Na)^+$ peak at m/z 781.1.

2.3.6 Attempted synthesis of phenyl silicon phthalocyanine (9,9-dihexyl-9H)-fluoren-2-ate

The attachment of fluorene units to the SiPc moiety was of interest as fluorene derivatives are widely used as electroluminescent materials.[511-515] Fluorene derivatives exhibit interesting chemical and physical properties and can often improve the solubility of polymers without increasing steric hindrance within the polymer backbone.[516] To our knowledge, although fluorene has been incorporated into materials and devices containing other related macrocycles such as porphyrin[416,503,517] there are to date no examples of Pc species containing fluorene components at the axial sites. As the high efficiency and thermal stability of fluorene polymers has led to their extensive use as blue-emitting materials,[517,518] the comparative optical properties of any Pc-fluorene hybrid would be of great interest due to the well-documented optical properties of phthalocyanine-containing polymers.[519,520] As the oxidation potential of the fluorene unit is higher than that of Pc (fluorene E_{ox} = 1.13 V[521], Pc E_{ox} = 0.78 V[58], vs. $Ag/AgNO_3$), the possibility of selective oxidation of the ligand in a hybrid of this type, and thereby creation of a "fluorescence switch"[21,58,267,461,522,523], is not feasible. The possibility does exist, however of attaching functional groups to the fluorene unit which would stabilise any radical cation formed via oxidation and hence perhaps lower the oxidation potential of the fluorene unit to a level below that of the Pc unit.

The synthesis of 9,9-dihexyl-9H-fluorene-2-carboxylic acid was, therefore, attempted first. The hexyl chains were chosen to provide extra solubility.

2-Bromo-9,9-dihexyl-9H-fluorene (**189**) (the immediate precursor to the acid derivative) was obtained by a dialkylation reaction on 2-bromofluorene.[524,525] Selective bromination at C(2) of a dialkylated fluorene of this type is unknown, the reaction having been performed only on unsubstituted fluorene.[514,526-528] The alternative route is to brominate first and then dialkylate the mono-brominated product.[514] Commercial 2-bromofluorene was used. The method of Anémian *et al.*[524] using potassium *tert*-butoxide was preferable to those of Koizumi *et al.*[529] and He *et al.*,[514] the dialkylated product being purified by a single column. The synthesis of 9,9-dihexyl-9H-fluorene-2-carboxylic acid is not known, although the dioctyl analogue has previously been reported,[512] and so our attempted synthesis was based on the procedure previously reported for the di-acid[511].

Compound **189** was dissolved in THF, cooled to -78 °C and reacted with an equimolar amount of n-butyllithium. Addition of dry carbon dioxide and standard work-up of the aqueous layer gave no product, and purification of the organic layer produced only starting material and alkylated reaction fragments.

The failure of this reaction is surprising as the synthesis of the di-acid is relatively facile via the same route.

Therefore the initial target mono-acid was abandoned in favour of the use of the more readily synthesised dicarboxylic acid.[511]

2.3.7 Reaction of phenyl silicon phthalocyanine chloride (36) with 9,9-dihexyl-9H-fluorene-2,7-dicarboxylic acid (193)

As a large stock of **189** had already been prepared for use in the attempted synthesis of the mono-acid, the conversion of this material into 2,7-dibromo-9,9-dihexyl-9H-fluorene (**190**), using the method for synthesis from 9,9-dihexyl-fluorene,[525] was first attempted. A 2:1 molar ratio of bromine to **189** gave **190** as the major product (37% yield).

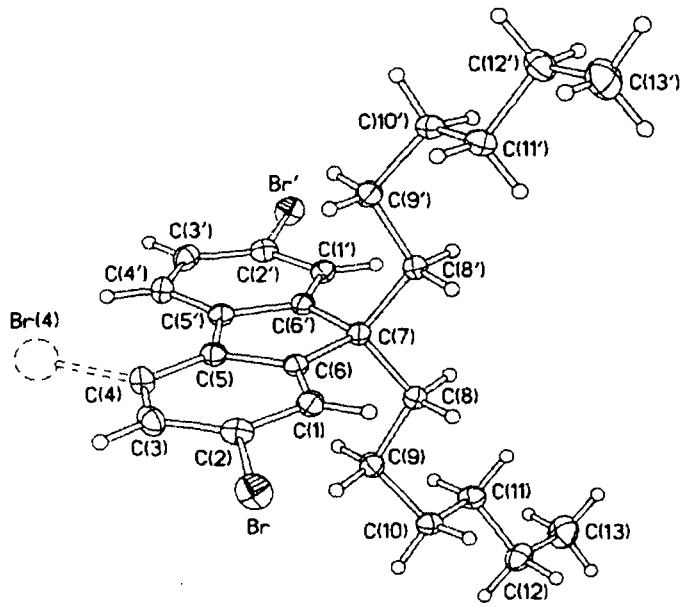


Fig 86: X-Ray crystal structure of compound **190**. Selected bond distances (Å): C(2)-Br 1.903(2), C(4)-Br(4) 1.967(1), C(7)-C(8) 1.546(2), C(7)-C(8') 1.546(3).

X-Ray crystallographic analysis revealed that a minor component (< 10%) was 2,4,7-tribromo-9,9-dihexyl-9H-fluorene. This data was further supported by an extremely minor higher weight mass peak in the EI mass spectrum at m/z 570.

In the crystal structure of **190** (Fig 86; general space group of C2/c), the bromine atoms at C(2) and C(7) occupy symmetrical positions so as to give equal bond angles with their adjacent carbon atoms (ca. 118°): the additional bromine atom attached to the C(4) carbon is slightly inclined away from the adjoining phenyl ring giving angles of 123° and 113° with its adjacent carbons, C(3) and C(5). This is most likely a result of minor steric hindrance from the C(4') hydrogen atom. In addition the C-Br bond length of the additional bromine is slightly elongated [1.967(1) Å *cf.* 1.903(2) Å for 2,7-dibromo-9,9-dihexyl-9H-fluorene], again most likely a result of steric hindrance.

After the discovery of this impurity, the original literature method for the synthesis of 2,7-dibromo-9,9-dihexyl-9H-fluorene was used, namely dibromination of 9,9-dihexyl-9H-fluorene (**191**) by the same method.[525]

Compound **191** was synthesised by the method of Anémian *et al.*[524] and identified by comparison of its NMR data with literature values obtained by Destri *et al.*[525] The product was obtained as yellow oil in high yield (96%) and showed a minor impurity by TLC corresponding to the mono-alkylated product. This product was used without further purification to give 2,7-dibromo-9,9-dihexyl-9H-fluorene (**192**) as a white crystalline solid in 40% yield. The EI mass spectrum of the product contained no evidence of higher weight fragments corresponding to synthesis of the tribromo analogue and the melting point was in agreement with the literature values.[525] In addition, a crystal structure was obtained (see Fig 87). Bond lengths and angles for the crystal were in general agreement with those found for **190**.

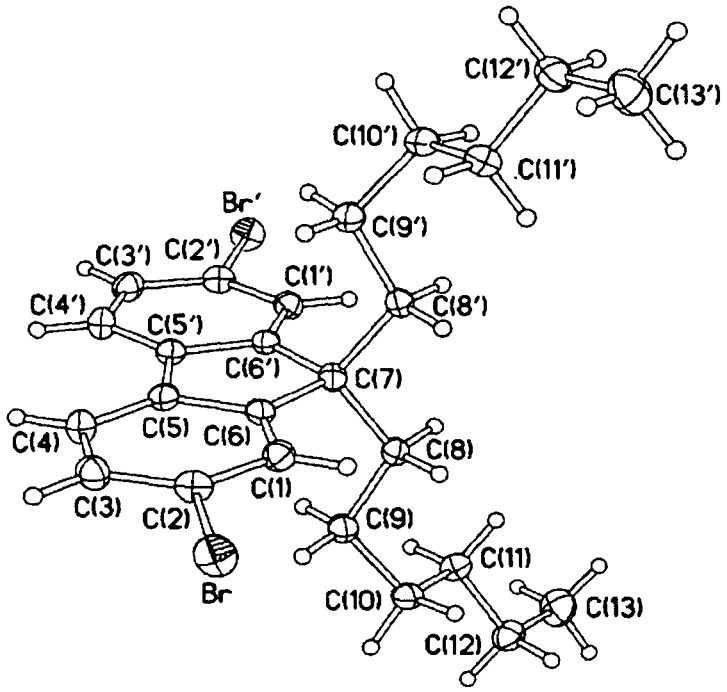


Fig 87: Crystal structure of compound **192**. Selected bond distances: C(2)-Br 1.904(8), C(7)-C(8) 1.549(2), C(7)-C(8') 1.549(2).

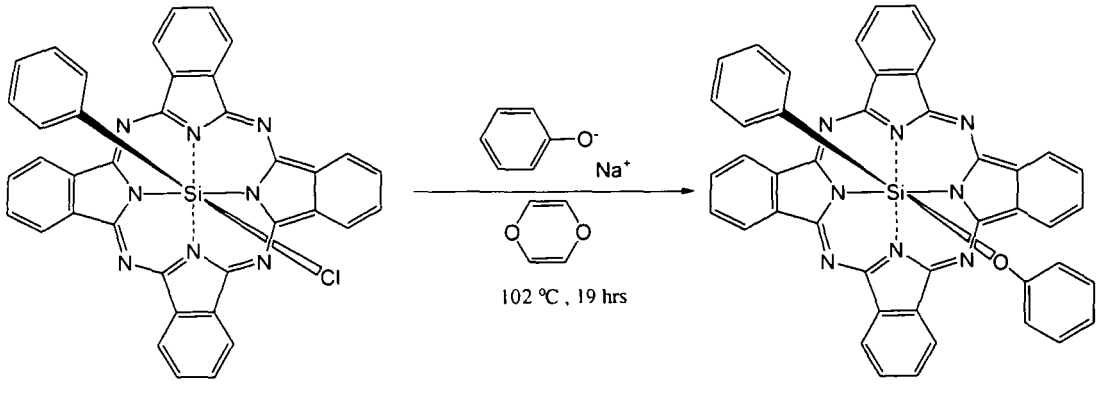
9,9-Dihexyl-9H-fluorene-2,7-dicarboxylic acid (**193**) was synthesised from **192** via the method of Oyston *et al.*[511] The attempted reaction of **193** with **36** followed the same protocol as for **187**. However, no pure products could be isolated. The ^{1}H-NMR of an isolated blue product showed peaks due to the fluorene unit and hexyl chains, together with very minor peaks corresponding to the Pc unit. An EI mass spectrum of the compound indicated only the presence of unreacted **193** and could not confirm the presence of a Pc unit. The product was most likely a mixture and reaction was, therefore, abandoned.

2.3.8 Synthesis of phenyl silicon phthalocyanine phenoxide (195)

Phthalocyanine alkoxides were also of more interest due to their fluorescent properties (see section 2.4). Previous work to produce phthalocyanine alkoxides has been mainly via the hydroxy derivative **2** [72,127,530] and not the chloride. Kenney *et al.* synthesised $Si(Pc)(OMe)_2$ from **1** using sodium methoxide in refluxing methanol[68] and so this method was adopted for the synthesis of **195**.

The method was modified to incorporate aspects of the work-up procedure used in the synthesis of $Si(Pc)(OEt)_2$ from **1** by Krueger *et al.*[72] Sodium phenoxide is commercially available only as the trihydrate form ($NaOPh{\cdot}3H_2O$) and so this reagent was used in the first attempt. An equimolar ratio of **36** and NaOPh·3H2O were refluxed in methanol for 4 h, cooled, quenched with water and filtered to produce a light green solid. The ^{1}H-NMR showed no presence of the desired product and contained a large methoxy signal, presumably from reaction of the solvent. Electrospray mass spectrometry also indicated the presence of PhSi(Pc)OMe.

Sodium phenoxide (**194**) was therefore synthesised directly from sodium and phenol, using the method of Saunders *et al.*[531] The synthesis of **195** was rerun in the same conditions using **194**. The two equimolar reagents were refluxed in dioxane at 105 °C for 19 h to give **195** in 71% yield after recrystallization from 1,2-dichlorobenzene.



36 **195**

Fig 88: Synthesis of compound **195**

The structure was first confirmed by the EI mass spectra. The phenoxide group gave two new sets of triplets at δ 6.78 and 7.19 ppm. The doublet for two of the protons in the phenoxide group was not evident, although this may be obscured by a solvent peak of

DMSO-d_6. The fluorescence properties of this compound are discussed in a later section of this chapter.

2.3.9 Attempted syntheses of phenyl silicon phthalocyanine substituted phenoxides

As a *tert*-butyl group had already been employed as a useful ^{1}H-NMR marker, an attempt was made to synthesise the substituted phenoxide, phenyl silicon phthalocyanine (4-*tert*-butyl)phenoxide. Sodium (4-*tert*-butyl)phenoxide (**196**) was synthesised via a modification of the method of Kissling *et al.* for production of sodium alkoxides.[532]

Compounds **36** and **196** were reacted together in equimolar proportions using 1,4-dioxane as a solvent, in a reaction analogous to that for the production of **195** (see above). The solid produced showed almost no product formation in the ^{1}H-NMR spectrum and so the reaction was repeated using a 4-fold excess of the alkoxide. The ^{1}H-NMR of this product still showed a minor amount of starting material. Attempted recrystallization in a variety of solvents (including 1,2-dichlorobenzene, chlorobenzene and toluene) led to gradual decomposition of the compound. Attempts at purification via column chromatography using both dichloromethane and methanol on both silica and alumina resulted in the product solidifying on the column. Although the desired product could not be obtained in a pure form, some information was obtained from the analysis. The singlet peak due to the *tert*-butyl group is shifted upfield compared with that of compound **187**. This is most likely due to the closer proximity of the group to the electron density of the macrocycle. The four protons in the phenyl ring of the phenoxide group are also at a higher field shift (δ 2.24 and 5.49 ppm *cf.* 6.46 and 6.97 ppm). The two protons nearest the macrocycle exhibit a much larger shift and hence the doublet is very similar in position to that of the directly bonded phenyl group. This demonstrates the ineffectiveness of the oxygen spacer to shield the phenyl group from the macrocycle. MALDI-TOF confirmed the mass peak at m/z 766.3 as well as containing minor peaks from loss of a phenyl group and loss of the *tert*-butylphenyl group respectively.

The 4-octylphenoxide derivative was explored in the hope that it would convey a greater solubility to the phthalocyanine moiety due to the long flexible carbon chain. Sodium 4-octylphenoxide (**197**) was synthesised via a method based on the already

mentioned work of Saunders *et al*[531] for synthesis of sodium phenoxide using THF as solvent. The proton NMR spectrum confirmed the structure of **197**, although the parent ion peak could not be seen in the electrospray mass spectrum. Elemental analysis was consistent with a solvated species, $C_{14}H_{21}ONa + 3THF$.

Compounds **36** and **197** were reacted together in either equimolar proportions or using a four-fold excess of the alkoxide in refluxing 1,4-dioxane. In both cases, ^{1}H-NMR spectra showed both starting material and product, which could not be separated by recrystallization or column chromatography. All fractions obtained were multi-component mixtures. The reaction was therefore abandoned. As mentioned previously, this tendency of phthalocyanine compounds to fragment in chromatographic systems has been observed throughout this work with Si-O bonded materials.

2.3.10 Attempted synthesis of octyl silicon phthalocyanine chloride

As octyltrichlorosilane is commercially available, the synthesis of OcSi(Pc)Cl was attempted. Not only would solubility of this compound be increased compared to **36**, but having an alkyl substituted phthalocyanine would provide a good contrast molecule. The route first attempted was identical to that for **36** (i.e. octyltrichlorosilane and 1,3-diiminoisoindoline were reacted together in a 3:2 molar ratio in a refluxing mixture of tetrahydronaphthalene and tributylamine). This method has already been claimed to yield OcSi(Pc)Cl][99] (though no analytical details of the product were given) but we were unable to reproduce the results. In our hands a dark oily product contaminated with tributylamine was obtained which could not be purified. Similar results were obtained using 1,4-dioxane as the solvent.

Triethylamine (bp 89 °C) was used in place of tributylamine (bp 216 °C) in the hope that purification would be easier. However, the reaction remained pale green in colour and a white precipitate formed over time. ^{1}H-NMR analysis indicated that the desired product was not formed and that a preferential reaction between the base and octyltrichlorosilane had occurred. Other commercial amines (*e.g.* diisopropylamine and disopropylethylamine and isopropylamine) behaved similarly and the silane unit was not incorporated into the Pc structure, perhaps as a consequence of the steric hindrance caused by the alkyl chain. Only the free-base Pc was recovered.

2.3.11 Attempted synthesis of (4-*tert*-butyl)phenyl silicon phthalocyanine chloride

1,3-Diiminoisoindoline and 4-*tert*-butylphenyl-trichlorosilane (obtained from reaction of 4-*tert*-butylphenyl bromide and tetrachlorosilane in THF) were reacted in the usual 2:3 molar ratio using tetrahydronaphthalene and tributylamine as solvents. Elemental analysis of the resulting dark blue solid obtained by recrystallization from toluene confirmed the compound as the free-base phthalocyanine.

2.3.12 Attempted synthesis of (4-*tert*-butyl)silicon phthalocyanine chloride

1,3-Diiminoisoindoline and 4-*tert*-butyltrichlorosilane were reacted together in a 2:3 ratio in the usual solvents and conditions but after refluxing of the solution for almost 24 h, unreacted 1,3-diiminoisoindoline precipitate was obtained upon cooling. The filtrate contained no phthalocyanine product (^{1}H NMR data).

The reason why this reaction fails to form any phthalocyanine material at all, whereas the analogous reaction with (4-*tert*-butyl)phenyl-trichlorosilane gives free-base phthalocyanine as a product, is not clear. It may be that the sterically bulky *tert*-butyl group hinders the approach of other indoline groups to initially coordinated species and so prevents further reaction.

2.3.13 Attempted synthesis of (9,9-dihexyl-9H-fluoren-2-yl)-silicon-phthalocyanine chloride

The attempted synthesis of (9,9-dihexyl-9H-fluorene-2-yl)-silicon trichloride from **189**, *via* lithiation with 1 equiv of nBuLi and reaction with tetrachlorosilane failed to give the desired product. The EI mass spectrum showed evidence of higher molecular weight fragments (probably difluorenyl species) as well as silicon species bearing multiple fluorene substituents. Multi-substitution at the silicon atom could be favoured by the electron-rich fluorene substituent on the initially-formed Fl-$SiCl_3$ species (Fl = fluorenyl) favouring loss of a second chloride ion (see Fig 89).

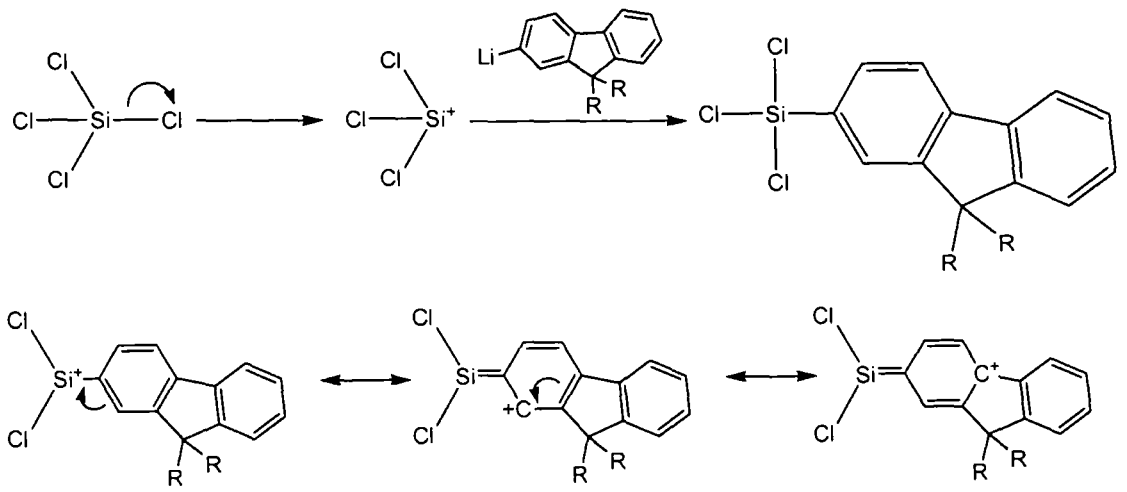


Fig 89: Proposed SN2 mechanism and resonance structures for attempted synthesis of (9,9-dihexyl-9H-fluoren-2-yl)-silicon trichloride.

2.3.14 Synthesis of silicon phthalocyanine dichloride (1)

$Si(Pc)Cl_2$ was synthesised in 20% yield via the method of Tamo *et al.*[99] In contrast to the commercially available product, we obtained **1** as a highly insoluble purple solid. The elemental analysis of this solid confirmed the identity of **1**, however we elected to use the commercial material in all subsequent reactions.

2.3.15 New syntheses of silicon phthalocyanine bis-(4-*tert*-butyl)benzoate (4) and silicon phthalocyanine bis-(3-thienyl)acetate (198)

Before synthesising new bis-substituted silicon phthalocyanine derivatives, two derivatives previously reported within our group by Farren *et al.*,[508] *viz* silicon phthalocyanine bis-(4-*tert*-butyl)benzoate (**4**) and silicon phthalocyanine bis-(3-thienyl)acetate (**198**) were re-synthesised for use as model compounds. The reaction conditions were the same as used previously (*i.e.* reaction of **1** with 4-tert-butylbenzoic acid or thiophene-3-acetic acid) although a modified purification procedure was used (based on purification of the Si(Pc)Ph derivatives), comprising a recrystallization from toluene (to remove unreacted **1**) and the filtrate being washed once with a dilute sodium hydroxide solution (5 wt.% in H_2O) and then several times with water before being dried and the solvent removed *in vacuo*. Though it was hoped that the different purification would increase the yields obtained, the final yields were 16 and 13% for **4** and **198**, respectively. Analytical and spectroscopic data showed that **4** was identical to that previously synthesised.[508]

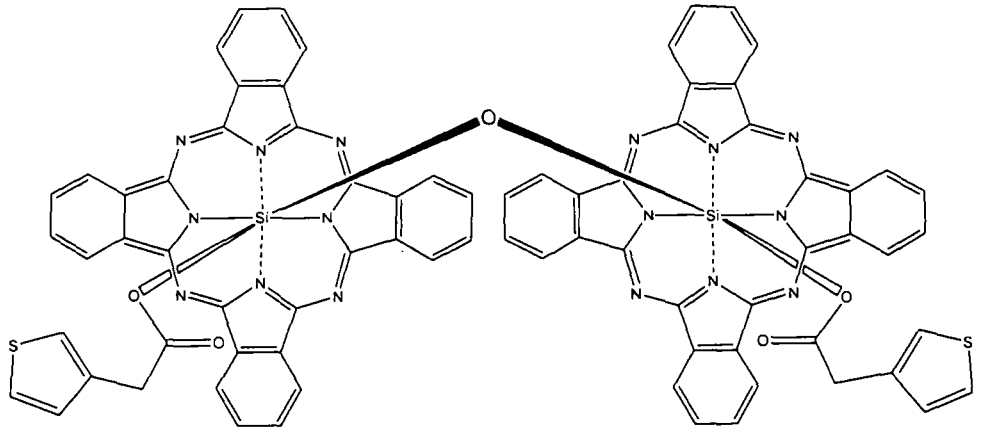


Fig 90: Oxo-bridged dimer of compound **198**

For compound **198**, analysis was mostly consistent with the published data for this compound[508] with an additional peak in the MALDI-TOF mass spectrum at m/z 1337 suggesting the formation of an μ-oxo-bridged dimer from the original compound (see Fig 90). Dimerisation of axially substituted phthalocyanines is well documented, sometimes as an unwanted side-reaction alongside substitution reactions.[60,68,118,509,533-535] This phenomenon was also observed in the MALDI-TOF spectra for several of the new bis-substituted silicon phthalocyanines synthesised and may be a result of the

heat generated by the laser used in the MALDI-TOF analysis (temperatures of >200 °C are possible during the experiment.)

The most interesting outcome of this alternative synthesis of **198** was the growth of crystals which proved to be a new polymorph of this compound with a crystal structure (see Fig 93) which is distinctly different from the one previously reported.[508] The X-ray structure was solved by Dr. A. S. Batsanov.

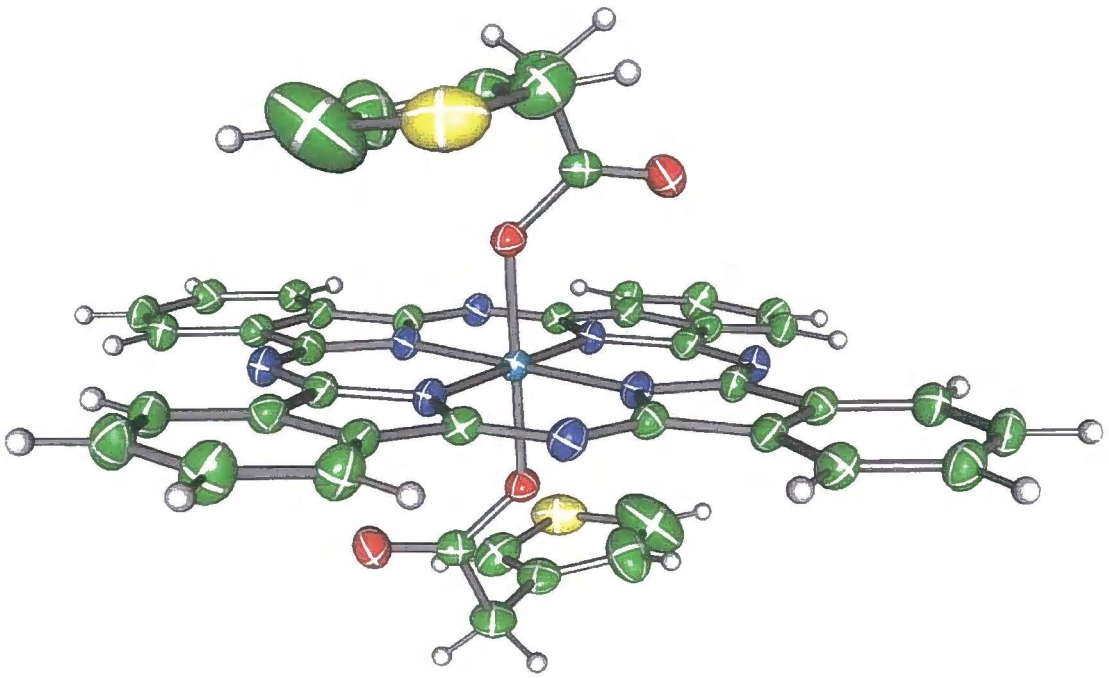


Fig 91: Original α-polymorph obtained for silicon phthalocyanine bis-(3-thienyl)acetate.[508]

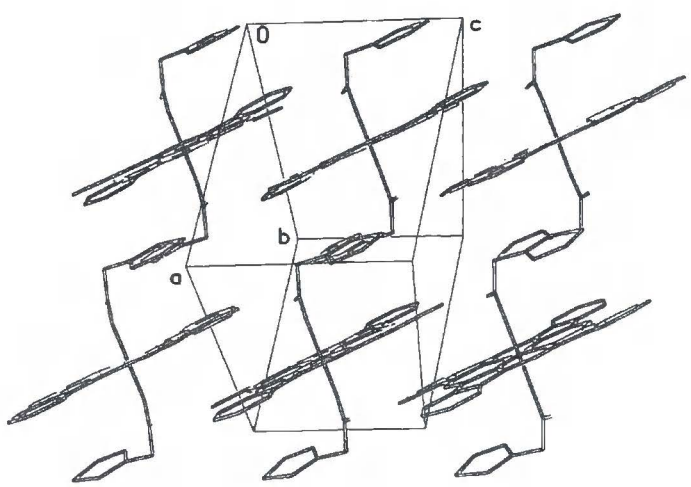


Fig 92: Crystal packing of the original α-polymorph.[508]

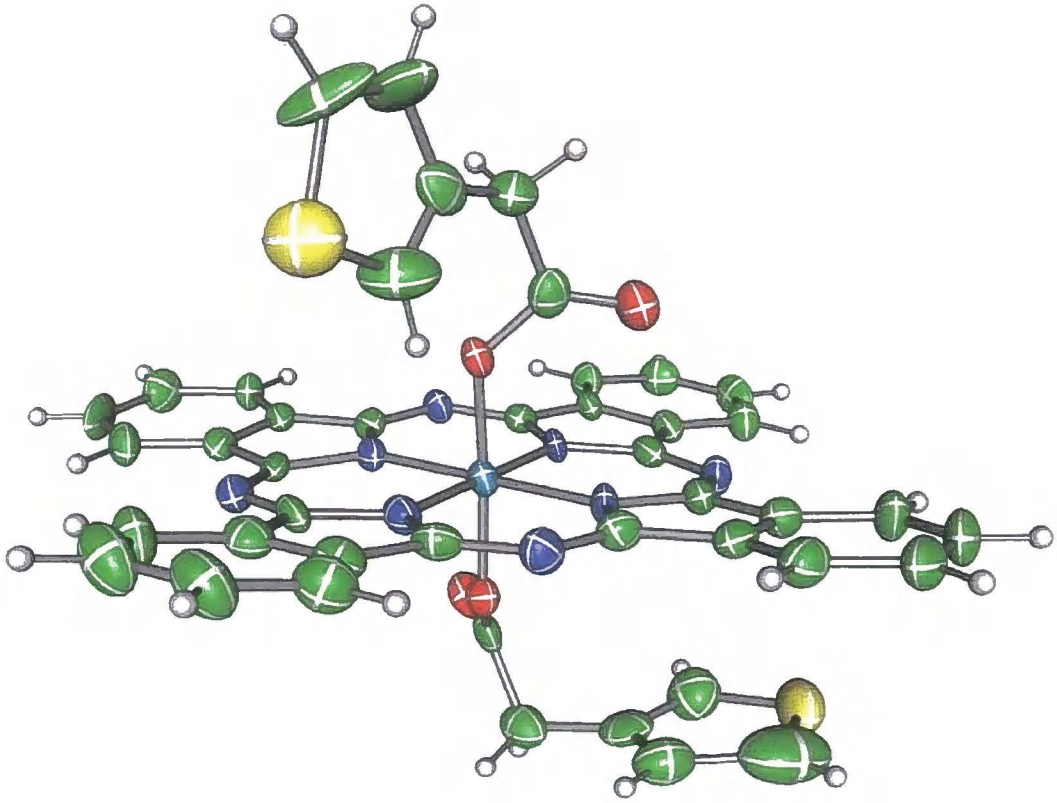


Fig 93: New β-polymorph obtained for compound **198**

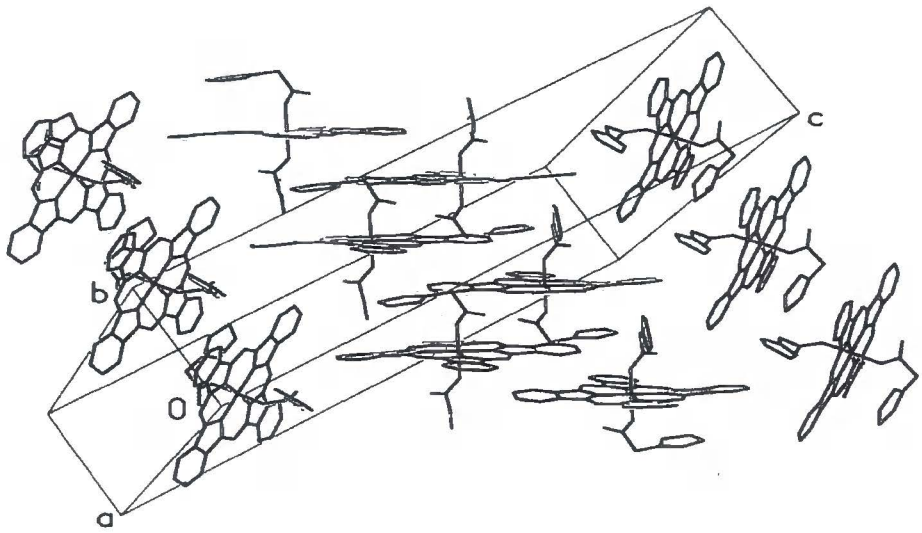


Fig 94: Crystal packing of the new β-polymorph of compound **198**.

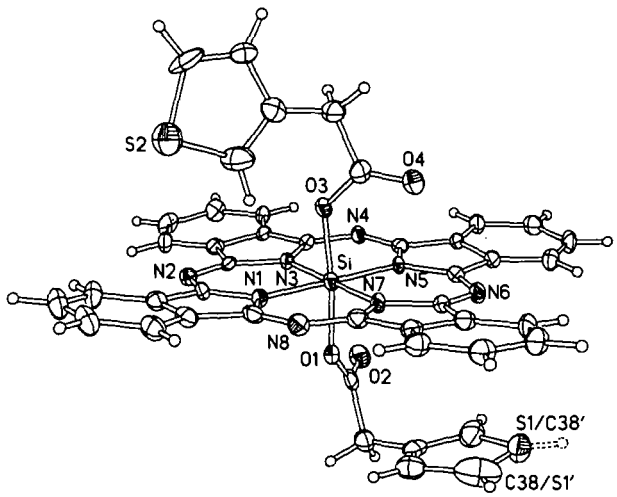


Fig 95: Labelling scheme for selected atoms of the new β-polymorph (198). Selected bond distances (Å): Si-N(1) 1.911(3), Si-N(3) 1.899(3), Si-N(5) 1.900(3), Si-N(7) 1.907(3), Si-O(1) 1.756(3), Si-O(3) 1.778(3).

Both structures are monoclinic. In the earlier α-polymorph the silicon atom lies at a crystallographic inversion centre in the space group $P2_1/c$, whereas in the β–polymorph the molecule occupies a general position in the space group $C2/c$ (see Fig 93). The coordination polyhedron of the silicon atom in the β-polymorph is an octahedron compressed along an O...O axis. The Si-N distance of 1.904(5) Å is the same as in the α-polymorph (1.909(3) Å) and other $(Pc)Si(O_2CR)_2$ compounds[65,76,508,536] (1.900-1.914 Å) but shorter than in (Pc)Si without axial ligands (1.946 and 1.965 Å).[537] The SiN_4 coordination in the β-polymorph is perfectly planar, but the (Pc)Si system as a whole is puckered: the average deviation of the 41 non-H atoms from their mean plane is 0.11 Å and the maximum deviation is 0.28 Å (*c.f.* 0.06 and 0.14 Å, respectively, in the α-polymorph), interplanar angles between the four 'isoindole' moieties vary from 5 to 12° (*cf.* 0 to 6° in the α-polymorph). The carboxy moieties O(1)O(2)C(33)C(34) and O(3)O(4)C(39)C(40) are inclined to the SiN_4 plane by 73 and 83° (*c.f.* 75° in the α-polymorph), which is usual for $(Pc)Si(O_2CR)_2$ molecules. However, in other respects the molecular conformations in the two polymorphs are quite different. In the α-polymorph, and all other $(Pc)Si(O_2CR)_2$ structures, the carboxy groups have a *trans* orientation with respect to the O-Si-O axis, irrespective of whether or not the Si atom occupies an inversion centre. In the β-polymorph however, the carboxy groups are in a *gauche* orientation, with an O(2)···O(1)···O(3)···O(4) torsion angle of 92°. In the α-polymorph, the thienyl rings

are stacked to the phthalocyanine moiety (interplanar angle 11°). Such a conformation has been observed previously in all $(Pc)Si(O_2CR)_2$ molecules which had the rotational freedom to adopt it. In the β-polymorph, one thienyl ring is near-parallel and the other near-perpendicular to the phthalocyanine moiety; the dihedral angles to the SiN_4 plane being 8° and 82° respectively. The Si-O bond lengths in the β-polymorph differ by 0.02 Å, whereas in its analogues these distances are equal within experimental error, if not symmetrically equal (in the range 1.742 to 1.758 Å). The 'parallel' thienyl ring in the β-polymorph (as in the α-polymorph) is disordered by a 180° rotation around the C(34)–C(36) bond, with silicon and carbon atoms statistically mixed in a 3:2 ratio. The reason for this alternate polymorph is most likely due to the degree of rotational freedom afforded to the thienyl groups by the additional methylene spacer not present in other axially substituted phthalocyanine-esters.

2.3.16 Synthesis of silicon phthalocyanine bis-thiophen-2-carboxylate (199) and silicon phthalocyanine bis-thiophen-3-carboxylate (200)

The new isomeric bis(thienyl) analogues **199** and **200**, which lack the methylene spacer of **198**, were synthesised by reaction of **1** with 5 molar equivalents of thienyl-2-carboxylic acid or thienyl-3-carboxylic acid in refluxing 2-methoxyethyl ether. The products were obtained in 26 and 17% yields, respectively (see Fig 96).

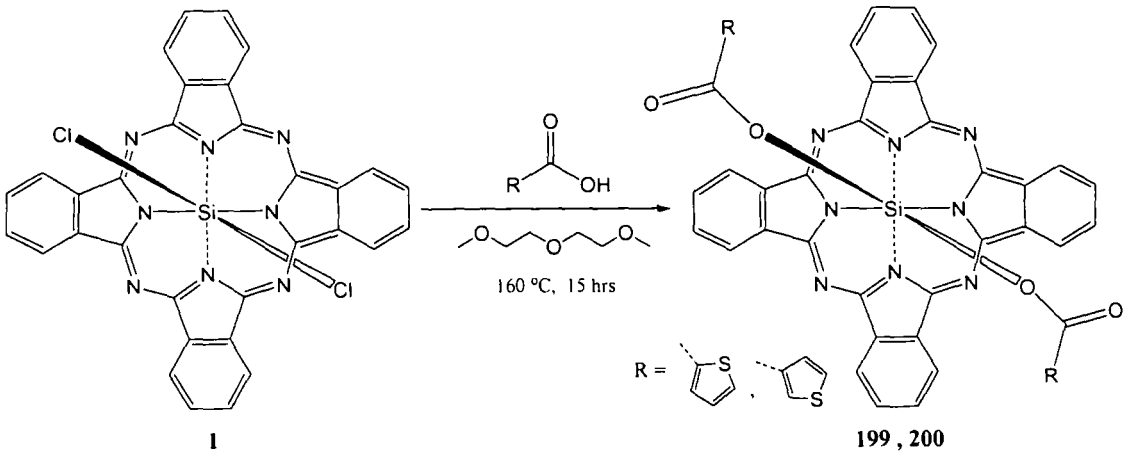


Fig 96: Synthesis of compounds **199** and **200**

For compound **199**, the three different thienyl hydrogens of the thiophene rings gave three distinct peaks at δ 5.26, 5.94 and 6.37 ppm, which are significantly

downfield of the corresponding protons (δ 4.41, 4.94 and 6.06 ppm) in compound **198**. This suggests that removal of the methylene spacer group has indeed reduced the thiophene rings' freedom of rotation, most likely resulting in them adopting a position which is more perpendicular to the plane of the Pc (see Fig 97). This in turn would reduce their proximity to the large Pc ring current, hence the resonances of **199** are at a higher frequency then in **198**.

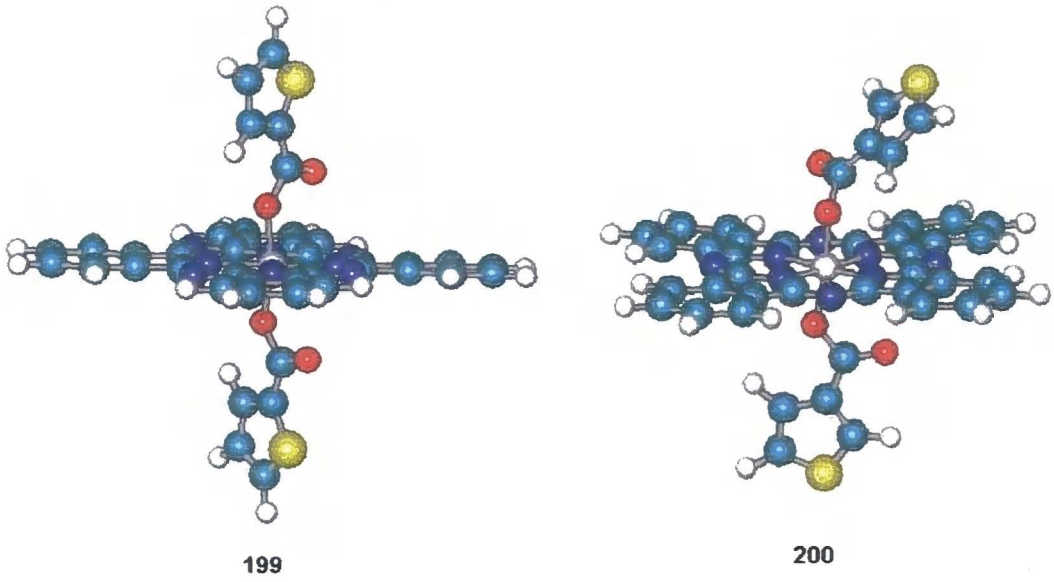


Fig 97: Two minimum energy conformations of **199** and **200,** modelled in Hyperchem 6.0 (AM1 semi-empirical calculation)

The ^{13}C-NMR spectra of **199** and **200** were of much poorer quality than those obtained for both **4** and **198** in that the peaks due to the Pc carbons of both species were not visible. This is most likely a consequence of the reduced distance of the electron-rich thiophene rings from the plane of the macrocycle, resulting in a longer relaxation time for the atoms within the phthalocyanine core. A MALDI-TOF analysis of **199** in chloroform showed the parent ion (m/z 794), and as with **198**, higher weight peaks were also evident indicating some form of dimerisation. For compound **200,** the parent ion was clearly visible in the EI mass spectrum along with secondary peaks due to the sequential loss of each ligand. A MALDI-TOF analysis was therefore not performed.

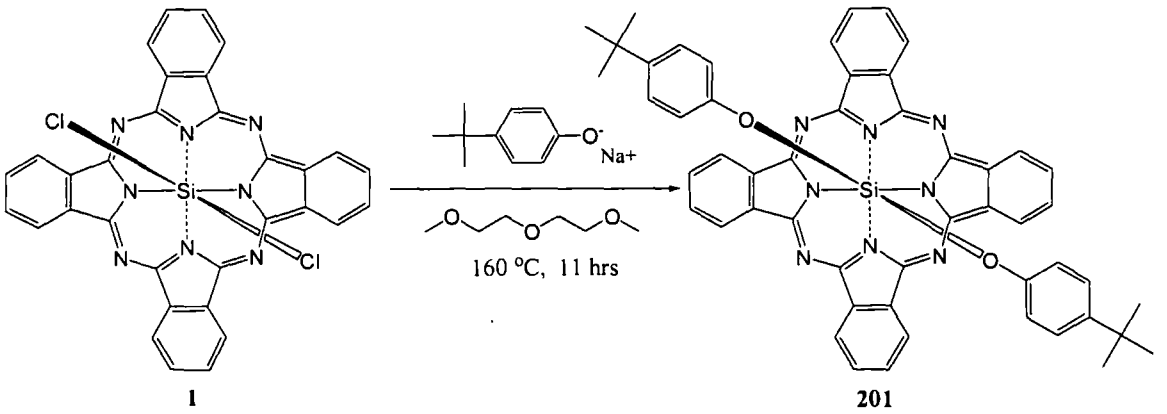
For compound **200**, the thienyl protons are shifted upfield (δ 4.98, 5.14 and 6.12 ppm) relative to **199**, which can be rationalised by a consideration of the ligand conformation (see Fig 97). The thiophene ring is oriented into a position where the sterically bulky sulphur atom is at the furthest possible distance from the plane of the

phthalocyanine. This results in a reduced shielding effect by the sulphur atom of the aromatic hydrogen atoms and so they experience a much larger upfield shift caused by the Pc ring current.

Attempted crystal growth of **199** and **200** from a variety of solvents was unsuccessful. The fluorescence properties of both compounds are discussed in a later section of this chapter.

2.3.17 Synthesis of silicon phthalocyanine bis-(4-*tert*-butyl)phenoxide (201)

We successfully prepared the bis(4-*tert*-butyl)phenoxide derivative **201** in 20% yield by reaction of **1** with **196** in refluxing 2-methoxyethyl ether. The hydrogen atoms of the (4-*tert*-butyl)phenyl group in **201** show substantial upfield shifts (δ 0.56, 2.35 and 5.53ppm) relative to **196** (δ 1.23, 6.46 and 6.97 ppm), due to the Pc ring current. It is likely that the phenyl protons nearest to the Pc ring give rise to the peak at 2.35 ppm, showing the greatest shift, whereas the singlet from the *tert*-butyl group, being the furthest away from the Pc, shows the least perturbation. A higher quality ^{13}C-NMR was obtained for the compound than for the corresponding ester **4**, most likely as a result of the ligand having a lesser effect on the relaxation time of the phthalocyanine core carbon atoms (the ligand π-system is not in a favourable orientation relative to the plane of the phthalocyanine).



1 201

Fig 98: Synthesis of compound **201**

In contrast to the spectra of the Pc esters, the MALDI-ToF spectra of **201** contained a sequence of higher weight peaks (1337.28, 1245.42, 1113.23, 1096.23,

1082.25) related to the sequential fragmentation of the μ-oxo-bridged dimer (see Fig 99), beginning with the loss of a *tert*-butyl group (see Fig 100). The fluorescence properties of this compound are discussed in a later section of this chapter.

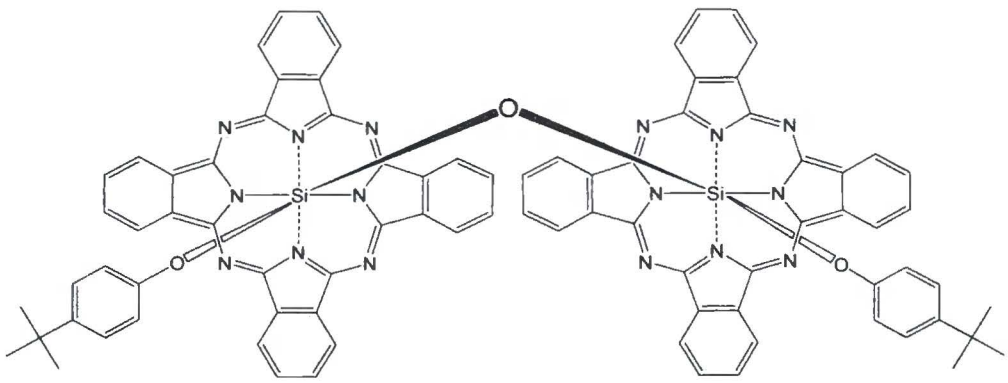


Fig 99: Suggested structure of μ-oxo-bridged dimer of compound **201**.

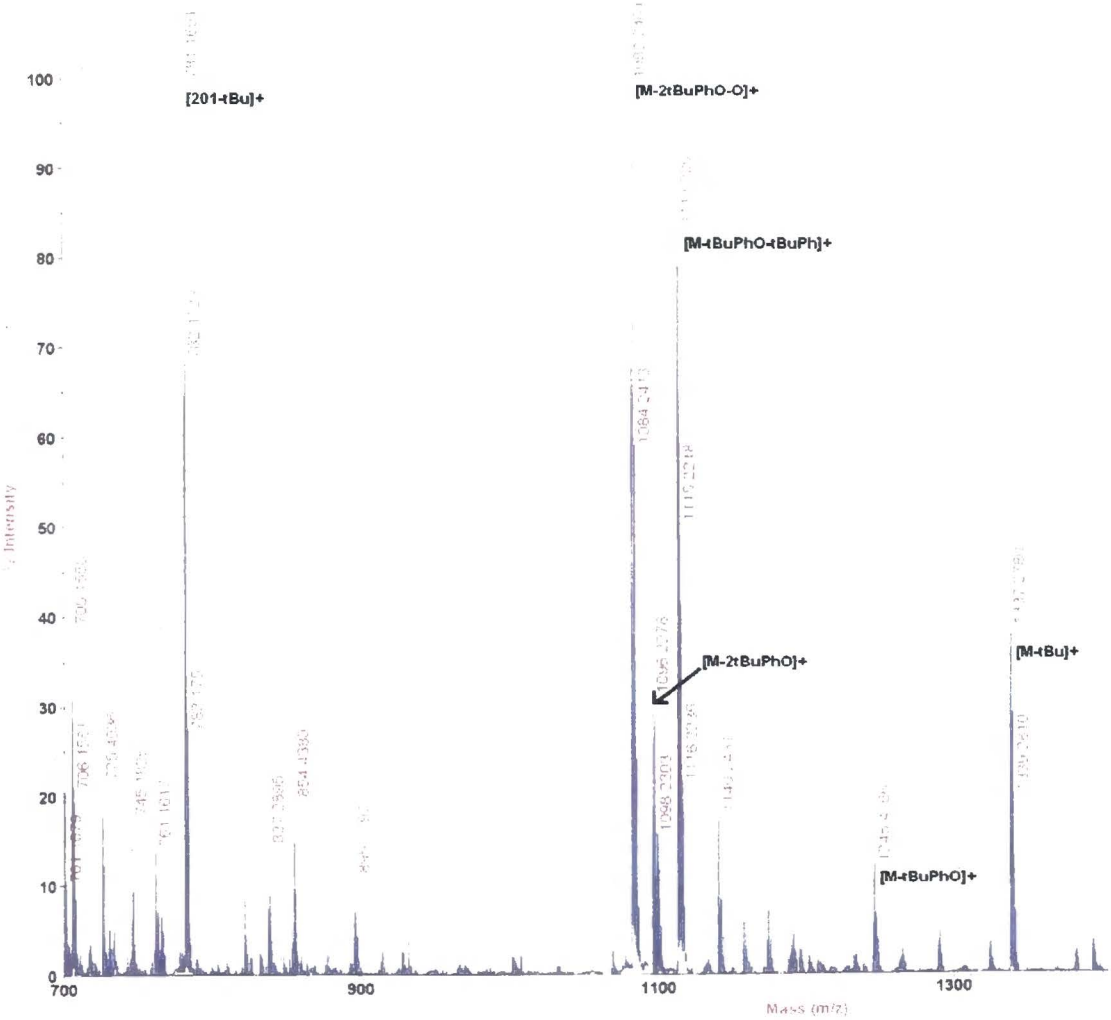
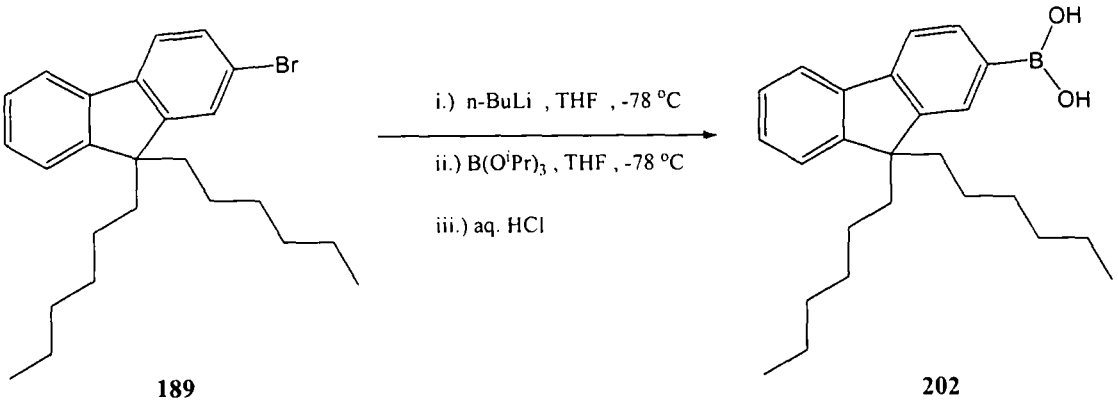


Fig 100: MALDI-ToF spectrum of compound **201**.

2.3.18 Attempted synthesis of silicon phthalocyanine bis-[4-(9,9-dihexyl-9H-fluoren-2-yl)]benzoate

After the failure to synthesise 9,9-dihexyl-9H-fluorene-2-carboxylic acid, and the problems encountered during the reaction of **36** with the corresponding di-acid **193**, a different strategy was adopted for producing a mono-carboxylic acid derivative containing a fluorene unit. The target was an analogue of 9,9-dihexyl-9H-fluorene-2-carboxylic acid, with a phenyl spacer group between the fluorene and acid moieties. It was hoped that by avoiding the possibility of formation of oligomeric materials, greater control would be gained over the reaction with any Pc derivative. Suzuki coupling presented a facile way of synthesising this ligand.

9,9-Dihexyl-9H-fluorene-2-boronic acid (**202**) was synthesised from the bromide precursor **189** using the method reported by Ding *et al*[512] for the synthesis of the dioctyl analogue. Thus reaction of **189** with triisopropylborate using n-butyllithium gave **202** as a white solid in 63% yield (see Fig 101). X-Ray analysis of the product established a boroxin structure, formed by dehydrative cyclisation of three molecules of the boronic acid (see Fig 102). This structure did not refine well due to the powdery nature of the crystals. This structure explains why no signal is observed in the proton NMR due to the $B(OH)_2$ protons, which would be expected at *ca.* δ 6.0 ppm.



189 **202**

Fig 101: Synthesis of compound **202**

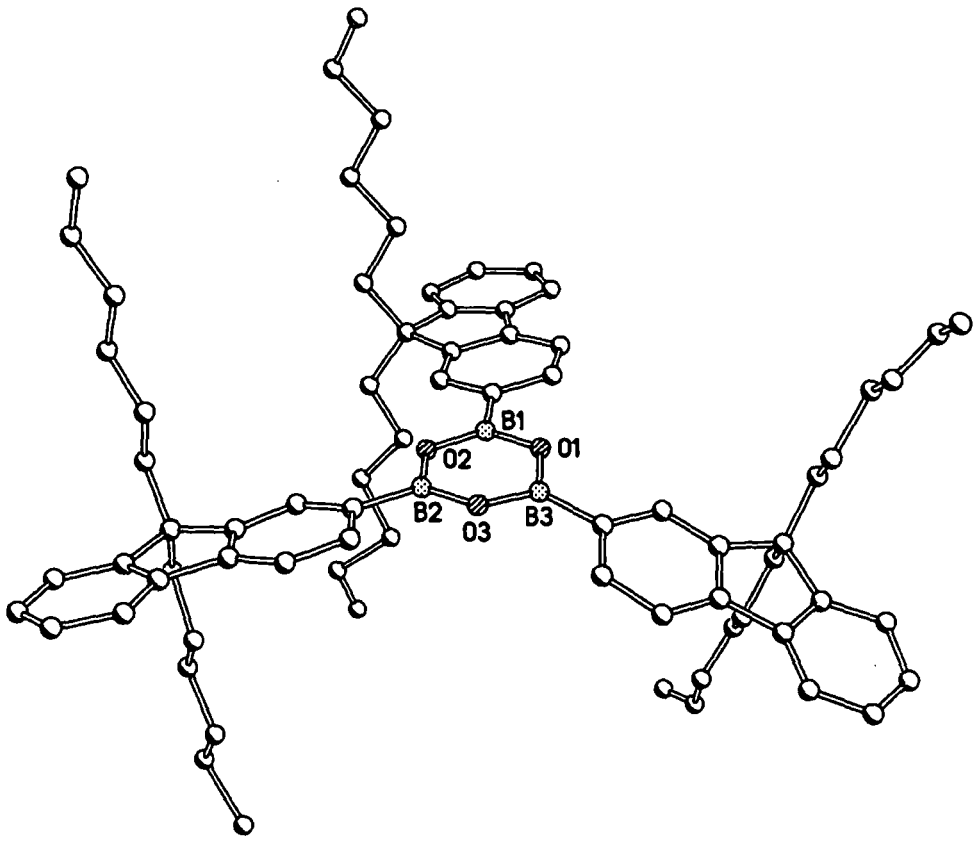


Fig 102: Low refinement X-ray crystal structure of 2,4,6-tri(9,9-dihexyl-9H-fluoren-2-yl)-boroxin obtained from **202**.

Reaction of **202** with 4-bromobenzoic acid in a 1 : 1.1 molar ratio, using dichlorobis(triphenylphosphine)palladium(II) as a catalyst, yielded 4-(9,9-dihexyl-9H-fluoren-2yl)benzoic acid (**203**) as a white solid in 22% yield (see Fig 103). The inclusion of a catalytic amount of tri(*tert*-butyl)phosphine[538,539] resulted in a slight increase in yield but complicated the purification to the extent that a second purification via column chromatography became necessary.

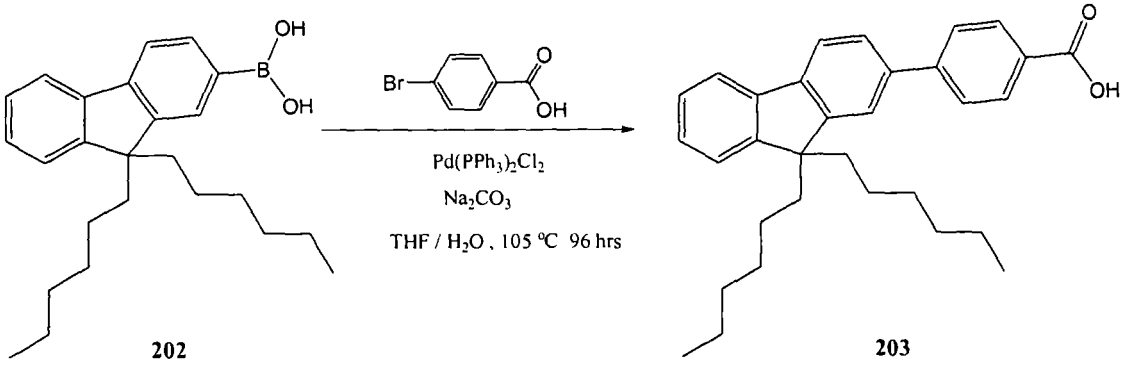


Fig 103: Synthesis of compound **203**

The attempted reaction of **1** with **203** proceeded as described previously for reaction of **1** with **193**, to produce a light blue solid, which was not a Pc derivative (by its ^{1}H-NMR spectrum) and a blue product obtained from the filtrate showing extremely weak multiplets at δ ~8.35 and ~9.60 ppm, which were dwarfed by those from the dialkylfluorene-phenyl unit. Attempted purification by column chromatography appeared to decompose this material so the reaction was not taken further.

2.3.19 Attempted synthesis of silicon phthalocyanine bis-[5,2`-thienyl]thiophen-2-carboxylate

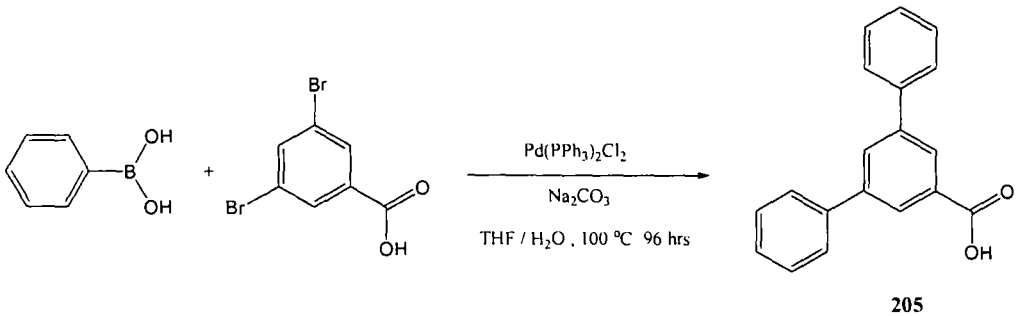
After the successful synthesis of silicon phthalocyanine bis-thiophen-2-carboxylate (**198**), the synthesis of silicon phthalocyanine bis-[5,2`-thienyl]thiophen-2-carboxylate was attempted in order to evaluate the effect on the Pc fluorescence of the addition of subsequent thiophene moieties to the ligand structure.

[2,2']Bithienyl-5-carboxylic acid (**204**) has been previously synthesised both from bithiophene (via reaction of a lithiated intermediate with carbon dioxide)[540-543] and the 5-methyl and 5-carboxaldehyde derivatives[544]. We chose a new route, namely Suzuki cross-coupling between thiophene-2-boronic acid and 2-bromothiophene-5-carboxylic acid (1:1.1 molar ratio, dichlorobis(triphenylphosphine)palladium(II) as a catalyst in THF / water at 105 °C) to give **204** in 35% yield. Variation of the reaction temperature, solvents and reactant ratios later showed this to be the optimum yield.

Compound **204** was then reacted with **1** using a 5 : 1 molar ratio in the usual manner, producing a blue solid after quenching with water and subsequent filtration of the precipitate. However, the same problems found with the purification of silicon phthalocyanine bis-[4-(9,9-dihexyl-9H-fluoren-2-yl)]benzoate were evident here. The ^{1}H-NMR spectrum of the crude solid was dominated by signals from the thiophene groups. Toluene recrystallization removed a dark blue solid which gave only rough aromatic signals and the remaining blue filtrate showed both thiophene and extremely weak phthalocyanine signals. Attempts to purify this filtrate via a basic extraction of impurities were unsuccessful, and TLC analysis of the material in DCM showed a blue baseline with more than ten other fluorescent spots on the plate. The reaction was therefore abandoned.

2.3.20 Synthesis of silicon phthalocyanine bis(3,5-diphenyl)benzoate (206)

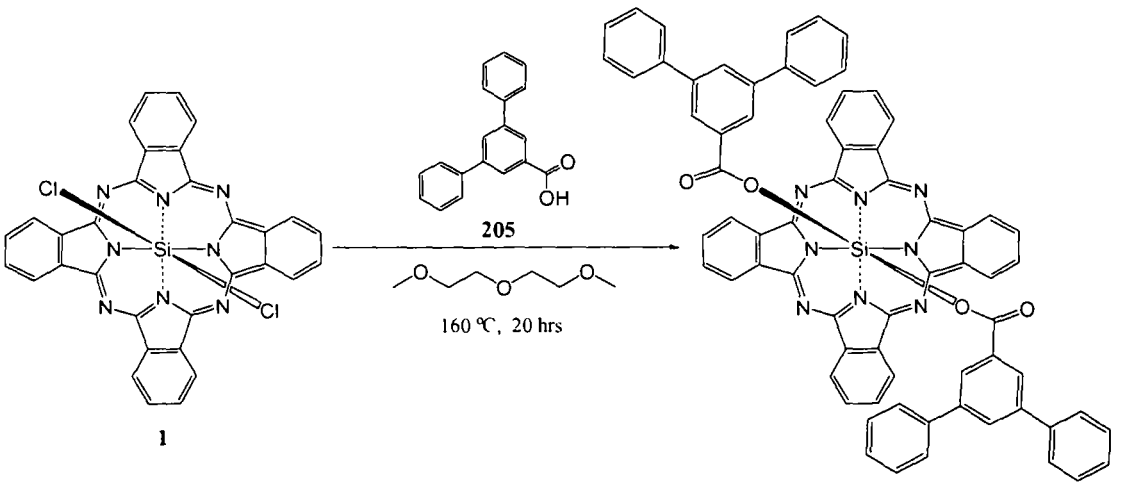
This compound was targeted as a derivative not only for photophysical studies but also for studies of its thin films on highly-ordered-pyrolytic-graphite (HOPG) (see section 2.5). The two-fold Suzuki reaction of 3,5-dibromobenzoic acid and benzeneboronic acid provided a novel approach to a functionalised terphenyl derivative (**205**) in 47% yield. Previous syntheses of 3,5-diphenylbenzoic acid (**205**) have used either 1-methyl-3,5-diphenyl-benzene[545] or alkyl- and aryl-ester derivatives[546] as starting points for the conversion to the carboxylic acid.



205

Fig 104: Synthesis of **205** via two-fold Suzuki coupling.

Reaction of **1** with **205** in a 1 : 5 molar ratio in refluxing 2-methoxyethyl ether gave the desired bright blue product (**206**) in 28% yield. Interestingly, although the MALDI-ToF spectrum did contain some higher weight fragment peaks, their relative intensities were negligible when compared with the monomeric species. This resilience of compound **206** to dimerisation during ionisation in the spectrometer can be attributed to the size of the ligand preventing interaction at the Si-O bond.



1 **206**

Fig 105: Synthesis of compound **206**.

2.3.21 Attempted synthesis of silicon phthalocyanine bis(3,5-dithien-2-yl)benzoate

The successful synthesis of compound **206** and the apparent increased stability of a SiPc unit bearing bulkier ligands prompted the attempted preparation of the analogue with two thiophene rings replacing the two outer phenyl rings of the ligand. In theory, the electron-rich thiophene rings should give fluorescence properties similar to those of **206**.

The synthesis of 3,5-dithien-2-yl-benzoic acid was therefore attempted via the same Suzuki coupling route used for **205**. Thiophene-2-boronic acid and 3,5-dibromobenzoic acid were refluxed together in a 2.1 : 1 molar ratio with dichlorobis(triphenylphosphine)palladium(II) as a catalyst in THF / water at 105 °C. Some red crystals were isolated which gave a signal in the ^{31}P NMR spectrum at 54.9 ppm. (They were clearly not $Ph_3P{=}O$, which is a common by-product: δ_P *ca.* 27 ppm). X-ray analysis showed the crystals to be a chlorine-bridged dimer of the palladium catalyst (see Fig 106). Dimeric structures of this type are already well-known in the literature.[547-550]

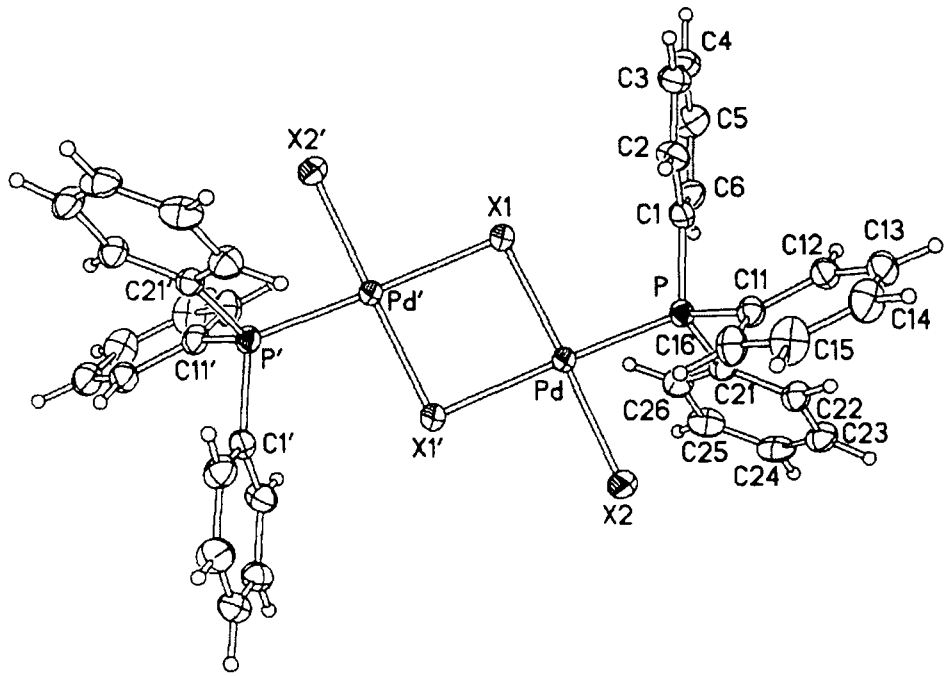


Fig 106: Dimer formed from dichlorobis(triphenylphosphine)palladium(II), X1 and X2 both represent Cl.

Other products isolated were bithiophene (formed by "homo-coupling" of the boronic acid) and unreacted 3,5-dibromobenzoic acid, both identified by NMR and MS data. No yields were calculated for these materials. The Suzuki coupling was repeated using palladium(II) acetate as an alternative catalyst, but the same two major products were obtained again. The formation of bithiophene as a by-product of Suzuki couplings utilising thiophene-2-boronic acid has been previously reported.[551-553] Homo-coupling of boronic acids is well-documented in Suzuki reactions but it is unusual to observe this to the exclusion of cross-coupled product.[554-556] We did not consider it worth pursuing further catalysts/reaction conditions as other aspects of the project took precedence.

2.3.22 Synthesis of silicon phthalocyanine bis(1-pyreneacetate) (207) and silicon phthalocyanine bis(1-pyrenebutanoate) (208)

The final structural variation was to synthesise two pyrenyl derivatives **207** and **208** as shown below (Fig 107), from the corresponding commercial carboxylic acids. The presence of the large pyrenyl groups in both compounds resulted in an increased solubility such that both products could be purified via column chromatography. Yields for **207** and **208** were 32% and 3% respectively and product structures were confirmed by NMR and mass spectrometry.

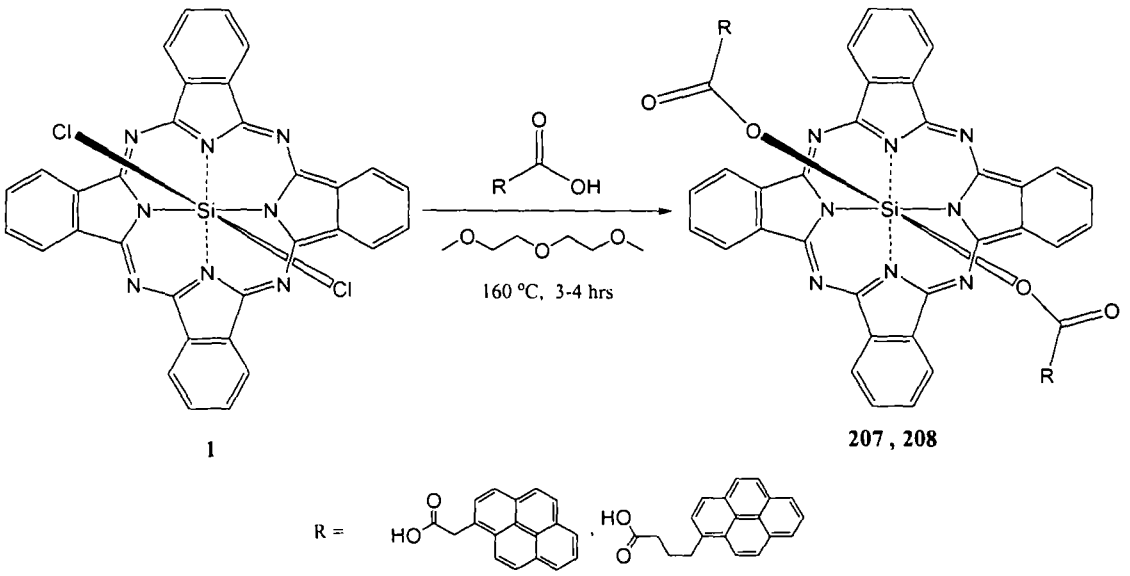


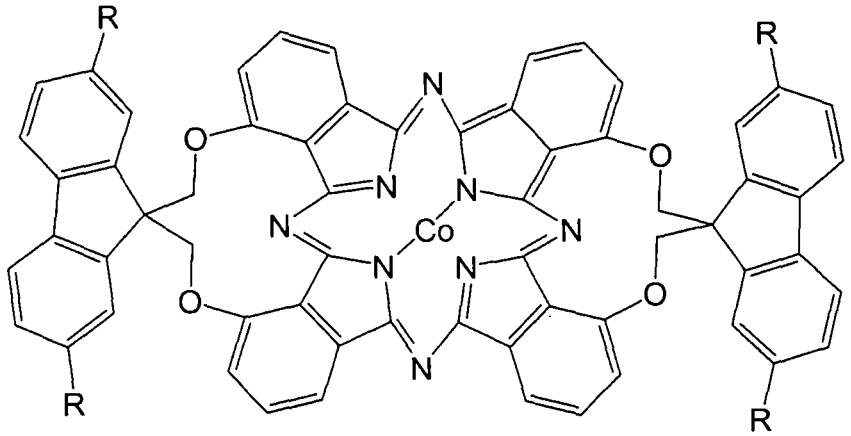
Fig 107: Synthesis of compounds **207** and **208**.

The yield of **208** is noticeably lower than the other SiPcs and may be a consequence of the greater flexibility afforded to the bulky pyrene groups by the carbon chain spacer group. The attachment of one ligand may sterically hinder the attachment of a second unit. Alternatively, the increased length of spacer group may simply result in a decreased stability towards loss of the axial substituents. The fluorescence properties of both compounds are discussed in a later section of this chapter.

2.3.23 Synthesis of 2,3,9,10,16,17,23,24-octakis(9,9-dihexyl-9H-fluoren-2-yl)-29H, 31H-phthalocyanine (214)

Although all previous attempts to attach one or more fluorene units to a SiPc at the axial sites had failed, the synthesis of a Pc-fluorene hybrid was still a desirable goal. Once the successful synthesis of a range of axially substituted SiPcs had been completed, the chemistry of the fluorene unit was revisited. The attachment of fluorene units to peripheral sites on a Pc core could be expected to enhance Pc fluorescence.

A precedent was recent work by Lyubimtsev *et al.* with fluorene substituted phthalonitriles which led to new cobalt monophthalocyanine complexes (**209**) containing intramolecular bridges with perpendicular fluorenyl substituents of the general structure shown in see Fig 108.[557]



209

Fig 108: General structure of fluorene-bridged cobalt phthalocyanines.[557]

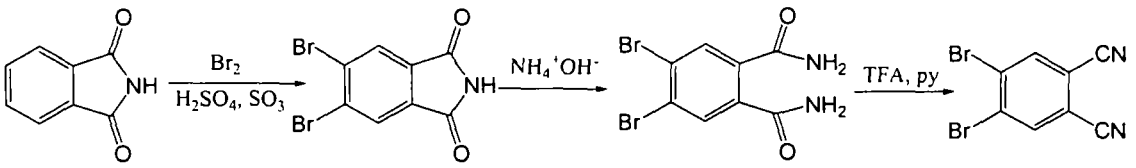
The initial impetus behind this work was a novel approach to prevention of phthalocyanine aggregation in solution and a subsequent study of physical and catalytic properties of the products. Only preliminary spectroscopic absorption data were reported, the three compounds synthesised displaying typical absorption maxima between λ_{max} 680 and 693 nm in toluene solutions. Therefore, the Pc-fluorene hybrid (**214**) synthesised here stands as the first example of a free-base octa-substituted phthalocyanine containing eight fluorene units directly conjugated to the π-system of the central Pc core, whose fluorescent properties have been thoroughly investigated.

One reason why there are far more numerous examples of peripherally substituted Pcs in the literature than axially substituted metal-centred derivatives is

the ease of purification of the former.[41,146,150,156,558] In the case of the peripherally substituted Pcs, the cyclisation to form the Pc core is usually the final step in a series of reactions, therefore only one Pc product is present in the crude product mixture, and as the properties of such macrocycles are often very different from those of smaller molecules present, purification is much simpler.

The synthesis of **214** was achieved as follows:

After failing to produce a 4,5-dihalogenated phthalonitrile species by a variety of routes, we adopted the synthetic route to 4,5-dibromophthalonitrile (**212**) of Leznoff *et al.*[559]



210 **211** **212**

Fig 109: Synthetic route to 4,5-dibromophthalonitrile (**212**) adopted from the literature.[559]

Even with the use of oleum, the first step of the reaction proved extremely difficult and Leznoff's procedure gave an impure mixture of 4-bromophthalimide and 4,5-dibromophthalimide (characterised by ^{1}H-NMR) which could not be purified further by recrystallization or column chromatography. The impure product was therefore used in the next step.

After purification of the crude phthalamide product, via washing with ice-cold water and methanol, no further traces of impurity were noted and a pure sample of **211** was obtained in 34% yield based on the impure starting material. The ^{1}H-NMR of the product differed from that in the literature in that the three peaks appeared in a different order. A high resolution EI mass analysis gave a peak at m/z 319.8799 corresponding to the M^+ ion and the obtained melting point was in agreement with the literature value. The conversion to **212** gave the product as a pure white solid in 63% yield (verified by NMR, MS and EA data). The overall yield for this conversion of phthalimide into **212** was only 6%, compared with an overall yield of 49% in the literature. The incomplete dibromination of phthalimide had the greatest effect on the yield.

Attachment of two fluorene units to the phthalonitrile compound was achieved by a two-fold Suzuki reaction (see Fig 110). The high yield of 87% is notable although Suzuki couplings are quite tolerant of sterically demanding substrates.[560] The presence of not one but two electron-withdrawing cyanide groups on the aryl dibromide activates the compound, making it more receptive to oxidative addition from the palladium catalyst and numerous examples exist in the literature of Suzuki couplings with aryl bromides containing both meta-substitution[561-564] and para-substitution[561,565-567] by cyanide groups.

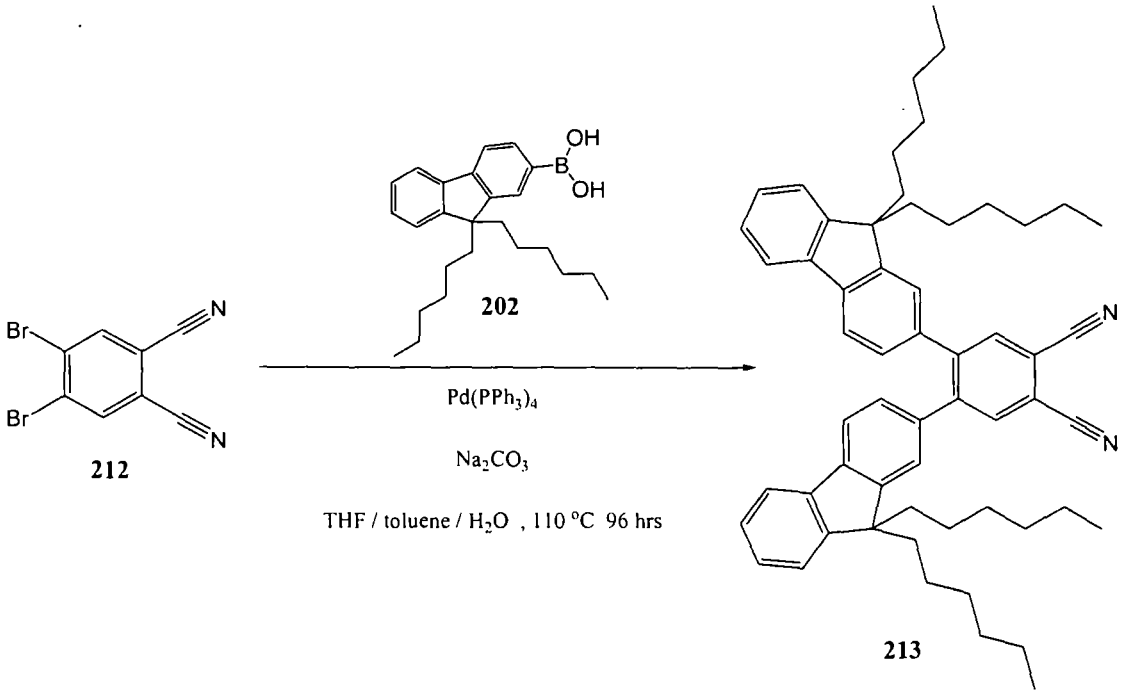
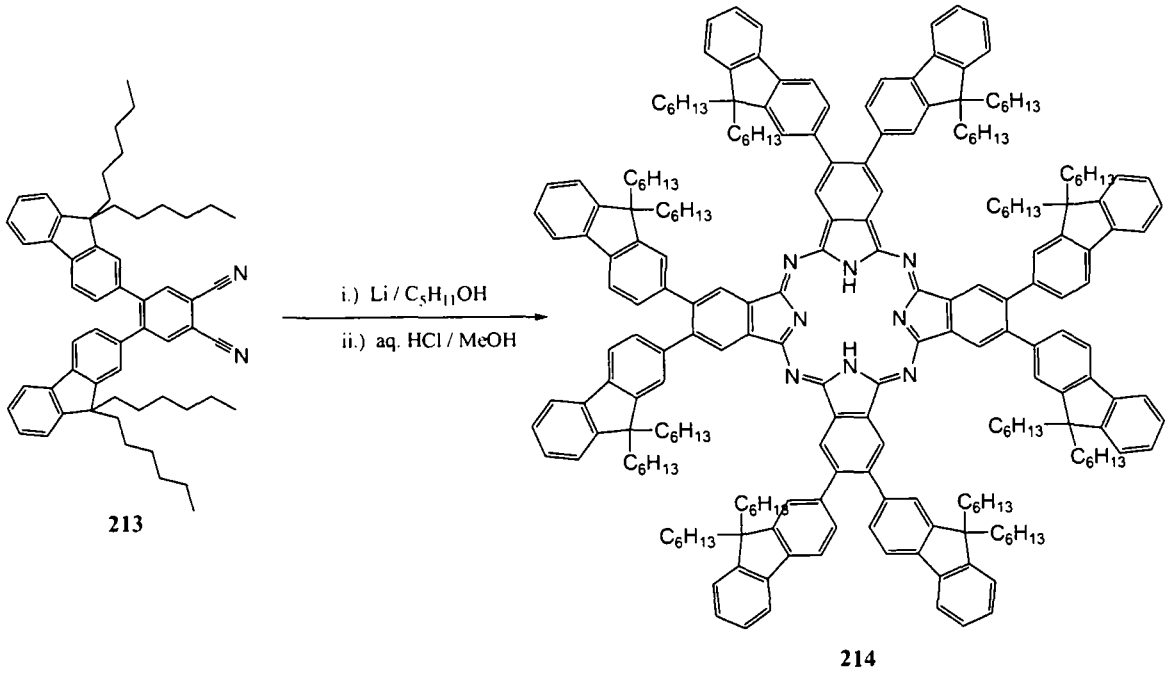


Fig 110: Synthesis of **213** via a two-fold Suzuki coupling.

The preparation of compound **214** from the substituted phthalonitrile **213** was based on known syntheses for free-centre octa-substituted Pcs[136,162,559,568] utilising lithium metal in a solution of 1-pentanol. The target compound was obtained as a bright green solid in 11% yield (see Fig 111). The Pc protons gave a broad singlet at δ 9.64 ppm due to extensive shielding by the peripheral ligands. The signals from the aromatic ligands were not sufficiently resolved to differentiate the phenyl ring and the fluorene unit. The central N-H protons were not observed between 0 ppm and -5 ppm, most likely due to effective shielding from the fluorene units and hexyl chains. No higher weight peaks were observed in the mass spectrum. The observed melting point of 128-130 °C is comparable with values in the literature for other octa-substituted

free-centre phthalocyanines.[569] The fluorescence properties of this compound are discussed in a later section of this chapter.



213

214

Fig 111: Synthesis of compound **214**.

2.4 Fluorescence Properties of Synthesised Phthalocyanines

2.4.1 Introduction

Before giving a detailed account of the fluorescent properties of the novel Pcs synthesised, it is first necessary to introduce the relevant nomenclature for the various features of the associated photophysics.

Metal-centred Pcs typically give a sharp intense absorption peak in the UV-Visible spectrum between 650 - 700 nm, denoted as the 'Q band'. In contrast, in the absorption spectra of free-centre phthalocyanines, this band becomes split into two distinct peaks, denoted Q_x and Q_y. This splitting is a result of the removal of the metal ion and its subsequent replacement by two central hydrogen atoms, causing a change in the overall symmetry of the molecule from D_{4h} to D_{2h}.[570] A second much broader peak is present in both types of Pc species, typically between 300 - 400 nm, and this is denoted the 'B band' or 'Soret band' (see Fig 112).

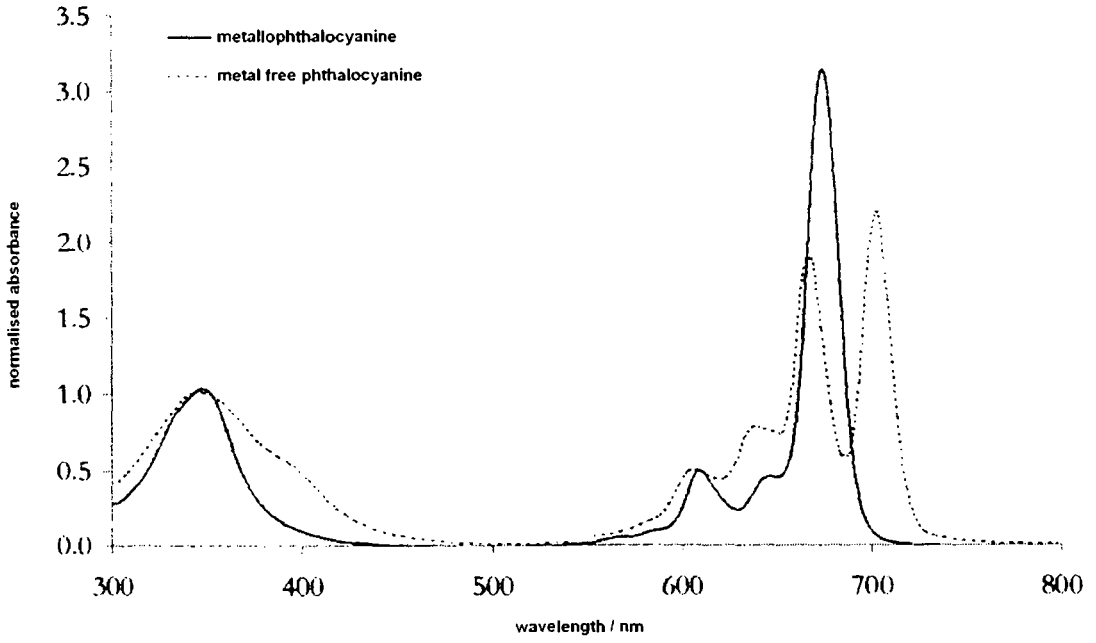


Fig 112: Variations in UV-visible absorption spectra for typical monomeric metal-centre and free-base Pcs.[571]

Three more lower energy bands exist for Pcs, denoted by the letters N, L and C.[572] However these peaks are generally obscured by the solvent absorption in solution

state spectra and as all measurements on our compounds were performed in solution, these additional bands will not be discussed.

The fluorescent properties of Pcs are strongly dependent upon the nature of the interactions between individual molecules when in solution where a common problem is their tendency to aggregate. This phenomenon has been known for some time[573,574] and continues to be extensively studied in metallated and non-metallated phthalocyanines.[35,158,557,575-577] Such interactions between the π-systems of the individual macrocycles also occur in related species such as the porphyrins (though generally to a lesser extent).[578,579] Aggregation of Pcs most commonly gives a co-facial stacked arrangement. The degree of aggregation is affected by variables such as solvent[142,162,580-582], temperature[583] and the nature of substituents attached to the macrocycle,[584,585] as well as the presence of various ions in solution.[586,587] Where aggregation occurs, the UV-visible absorption spectrum contains additional peaks, which may appear either blue- or red-shifted relative to monomeric species. A number of theories can explain these changes, including the exciton theory which are not discussed here.

The photophysical behaviour of monomeric Pcs is highly dependent on the nature of the central atom within the macrocycle. Elements such as Al and Zn, commonly utilised in the synthesis of metalloPcs,[28,139,559,588] increase the triplet yield of the Pc, resulting in a reduction of the quantum yield and lifetime of the compound. Paramagnetic ions such as Cu and Cr act as electron acceptors to the macrocycle and hence quench the Pc emission, resulting in extremely short triplet lifetimes and compounds which are often non-fluorescent. In contrast to these metalloPcs, SiPcs typically possess higher quantum yields and longer fluorescent lifetimes. In the case of the axially-substituted SiPcs, a reduction in the degree of aggregation is also observed.

2.4.2 Results and Discussion

The photophysical data for all Pc compounds prepared are collated in Table 1.

Table 1: Spectroscopic Data for all Phthalocyanine compounds.

Compound	λ_{max}(abs)/nm	λ_{max}(em)/nm	Φ_f[a]	τ_{f1}/ns[b]	τ_{f2}/ns[b]
187	685	691	0.55	7.1 (99%)	1.1 (1%)
188	688	696	0.52	6.9 (99%)	1.0 (0%)
195	685	692	0.31	5.8	-
4[74]	685	691	0.62	6.7	-
198[74]	685	691	0.39	6.7	-
199	686	689	0.48	6.2 (88%)	2.1 (12%)
200	684	689	0.58	6.3 (86%)	2.4 (14%)
201	680	683	0.06	0.5 (94.7%)	5.4 (5.3%)
206	685	691	0.69	6.4 (96.4%)	1.7 (4.6%)
207	691	696	0.84	6.9 (99.6%)	0.1 (0.4%)
208	684	691	0.81	6.4 (99.6%)	1.9 (0.4%)
214	696, 729	737	0.88	4.66	-

[a] ±10%, λ_{ex} = 615 nm, λ_{em} = 630-850 nm, 293 K, dichloromethane.

[b] ±0.1 ns, λ_{ex} = 635 nm, λ_{em} = 690 nm, 293 K.

All of the Si-Pcs show very sharp electronic absorption transitions in the concentration range 10^{-4}–10^{-7} M (Table 1 and Figures 113 and 114 for compound **195** and **208** in DCM) which are characteristic of monomeric Si-Pc derivatives.[589]

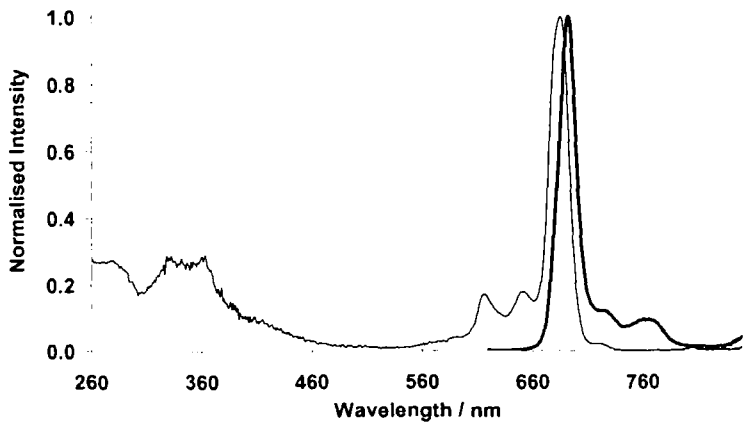


Figure 113: Normalised absorption (thin line) and emission spectra (thick line) of compound **195** in DCM (λ_{ex} = 615 nm, same conditions as stated in Table 1).

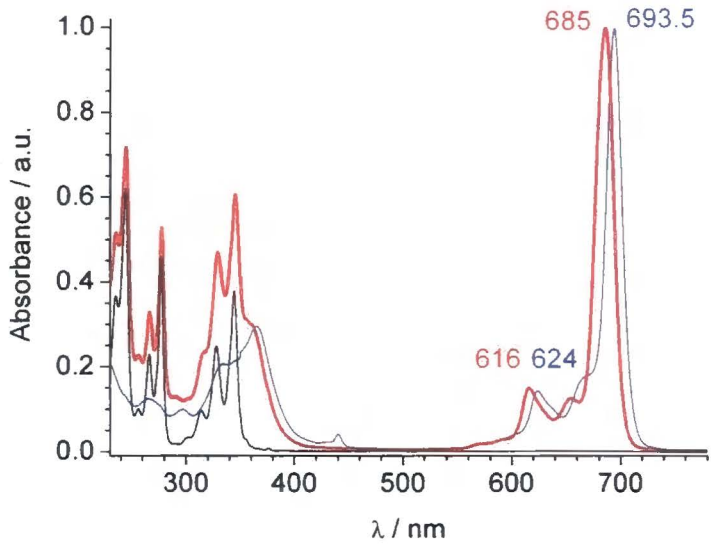


Figure 114: Normalised absorption spectra of compound **208** (thick red line), **1** (thin blue line) and 1-pyrenebutyric acid (thin black line) in DCM.

The retention of monomeric behaviour even at 10^{-4} M demonstrates that the axial ligands are very effective at sterically isolating the chromophoric Pc rings, by preventing intermolecular interactions between the macrocycles. All the axial derivatives (**4**,**187**,**188**,**195**,**198-201**,**206-208**,**214**) show small hypochromic shifts of their long-wavelength maxima compared to **1** (by 2–14 nm, Table 1, Figure 113). As an example, Figure 114 compares the electronic absorption spectra of compound **208** with **1** and 1-pyrenebutyric acid, demonstrating that the spectrum of **208** combines the spectral features of both the silicon phthalocyanine and the ligand. The molar extinction coefficients determined for compounds **4**, **206** and **207** in DCM are of the order of ~ 2×10^5 mol dm^{-3} cm^{-1} at λ_{max} and are consistent with those values found for monomeric phthalocyanines.

Analysis of the emission data in Table 1 shows that the electronic energy levels for the axially substituted silicon phthalocyanines are relatively unaltered by changing the axial substituents and all of the compounds have a very small Stokes shift of less than 10 nm. In general, the fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ_{fl}) values are high, with the exception of compounds **195**, **198**, **199** and **201**, and are typical of SiPcs.[15,590,591] The presence of the lighter Si atom in the macrocycle leads to lower rates of inter-system crossing (ISC) than those observed

in other metallo-Pcs *e.g.* zinc derivatives.[592] The high Φ_f (> 0.5) and long lifetimes (> 6 ns) are indicative of efficient fluorescent emission and a fairly small non-radiative decay constant. Compounds **206**, **207** and **208** have the most bulky substituents and possess the highest Φ_f values due to their ability to prevent intermolecular interactions and show no evidence of ligand-macrocycle quenching. As may be expected, the slightly larger and more flexible pyrenyl ligands in compound **208** are more effective at preventing intermolecular interaction then those in compound **207**. However the rigidity of the large pyrene units may be the reason for compounds **207** and **208** having increased quantum yields when compared with compound **206**, containing the more flexible terphenyl ligands.

The axial ligands in compounds **198** and **199** contain thiophene and also possess significantly lower Φ_f values. The electron-rich thiophene group may quench the excited state by an electron transfer mechanism resulting in a lower value for Φ_f.[27,40,593-595]

As shown in Figure 95, if a thiophene ring is allowed to lie close (*i.e.* parallel) to the Pc macrocyle then electron transfer is more facile. Unusually the lifetimes of **198** and **199** are not reduced by this quenching. The calculated rate constants of fluorescence k_f (= Φ_f/τ_f) are 5.8×10^7 and 7.7×10^7 s^{-1} for compounds **198** and **199**, respectively, in comparison to that of 7.7×10^7 s^{-1} for compound **187**.

Compounds **195** and **201** also have low Φ_f and τ_f values. The axial phenoxy substituents lead to significant quenching of the Pc fluorescence, again possibly *via* an electron transfer process. The replacement of the carboxyl spacer group with a single oxygen-bridge between the macrocycle and the aromatic component of the ligand may reduce the separation between the two moieties and hence make any electron transfer process more favourable. Although several examples of silicon and germanium Pc bis-ethers containing aromatic ligands are known,[66,68,73,596,597] fluorescence quantum yields and lifetimes have not been obtained for these compounds. Flora *et al* synthesised bis-ethers using alkylated siloxy ligands but these compounds show little or no quenching of the Pc fluorescence.[598]

Compound **214** displays an extremely high fluorescence quantum yield (0.88) and PLQY values of this magnitude have been observed in other highly conjugated peripherally substituted free-base Pcs.[140] The fluorescence lifetime is similar to those obtained for a series of free-base Pcs bearing peripheral alkoxy substituents,[599] demonstrating the small magnitude of effect the peripheral substituents have on the fluorescence lifetime of the Pc core.

In addition to the fluorescence lifetime observed at an excitation of 620 nm, excitation of **214** at 300 nm produced a second component to the fluorescence lifetime corresponding to an emission at ~500 nm, assigned to emission from the fluorene substituents. To verify this hypothesis, excitation spectra were run, monitoring at both 500 and 760 nm, and showed that the emission band at ~500 nm was due entirely to the fluorene ligands. Specific excitation of the fluorene units produces emission from the fluorene units, along with emission from the Pc core. Therefore **214** demonstrates efficient and rapid energy transfer between the peripheral fluorene units and the Pc core. The spectroscopic data for **214** are summarised in Fig 115.

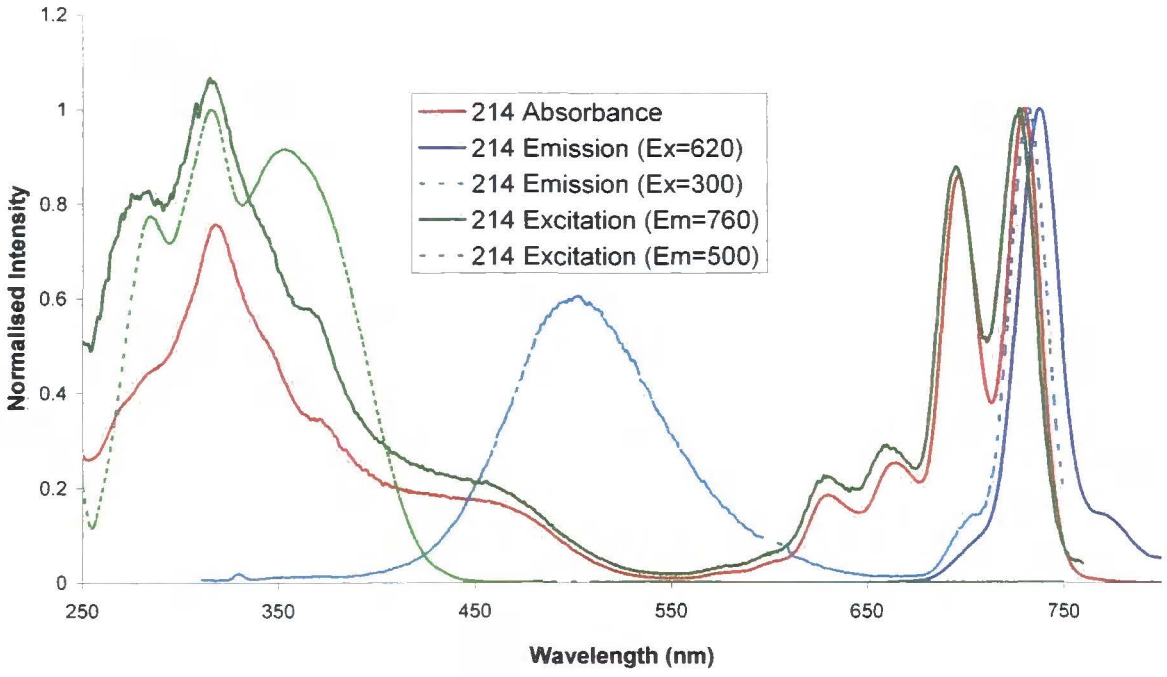


Fig 115: Fluorescence spectra of **214** in DCM at 298K.

2.5 Surface Chemistry of Selected Phthalocyanine Compounds

2.5.1 Introduction

A combined electrochemical, scanning Kelvin nanoprobe (SKN), atomic force microscopy (AFM) and molecular modelling study was undertaken, in conjunction with Dr. Kataky's group within our department, on the various surface properties of the SiPc derivatives **4**, **198** and **206**). The properties of these compounds were compared against a free-base reference compound, 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine. All films of these materials were prepared by Aidan Rhodes and Alan Massey in Dr. Kataky's group. The AFM and SKN measurements were carried out by Aidan Rhodes, and the electrochemical work was conducted by both Aidan Rhodes and Alan Massey.

2.5.2 Scanning Probe Techniques

Scanning probe microscopy (SPM) first appeared in 1982, after its discovery by Binnig *et al.* and their subsequent invention of the scanning tunnelling microscope (STM).[600-604] Since then, the number of similar techniques has grown substantially to enable analysis of surface properties such as composition and topography as well as structural and mechanical properties.[605] All SPM methods are based upon the principle of obtaining an image of a surface by mechanically moving a probe in a "raster scan" across the surface line by line. The interaction between the probe and surface is then measured and recorded as a function of position. The various methods differ in the manner of interaction between probe and surface.

2.5.2.1 Atomic Force Microscopy (AFM)

AFM is the most commonly used scanning probe method, first invented by Binnig *et al.* in 1986.[606] The high-resolution scanning technique employs a probe consisting of a sharp tip (usually silicon based) mounted onto a flexible cantilever, which can interact with the surface in one of several ways.

During 'contact mode', the tip is moved so as to give a light contact with the surface and then scanned in a raster pattern. The scan is performed at a constant height so that changes in height of the surface cause a deflection in the cantilever. This deflection is measured by a sensitive optical sensor, comprising a laser diode which reflects back from the cantilever onto a photodiode. The position of this reflection is therefore monitored (see Fig 116).

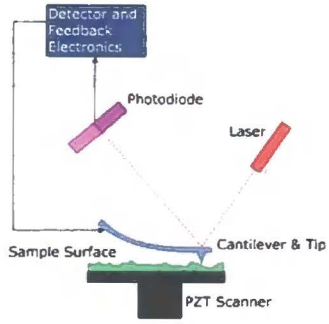


Fig 116: Method of action of atomic force microscopy.

In 'constant force' mode, a feedback mechanism connected to the optical sensor is employed in order to keep a constant deflection between the probe and the surface. The movement required to maintain this constant force is then mapped to give information about the surface topography (see Fig 117).

'Non-contact (or tapping) mode' is a 'dynamic' method alternative to the above 'static' methods in which the tip is held at a small distance (~5 nm) above the surface and oscillated close to its resonance frequency using a piezo-electric modulator attached to the cantilever. Proximity of the tip to the surface changes the frequency of this oscillation and gives information which is then used to maintain a constant distance between the tip and surface. Hence, a measure of surface topography is again achieved. The advantage of this method is that soft surfaces, which may be damaged by contact with the probe tip, can be safely scanned.[605,607]

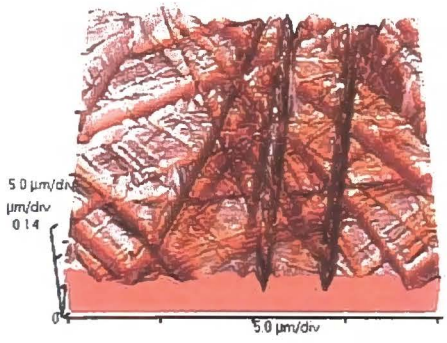


Fig 117: An example of a 3D surface image obtained by AFM.

2.5.2.2 Scanning Kelvin Force Microscopy

Kelvin probe force microscopy (KPFM) is a non-contact form of AFM invented by Nonnenmacher *et al.* in 1991.[608] A conducting cantilever (usually metal-coated silicon or silicon nitride) is scanned across the surface whilst maintaining a constant height above the surface, and applying both an AC and DC potential. The frequency of the AC signal matches the natural mechanical resonance of the cantilever and the cantilever oscillates due to variation in electrostatic force with the surface. By again employing a feedback circuit connected to the DC signal, the DC potential is used to minimise movement of the cantilever and hence produce a mapping of the work-function of the surface (see Fig 118).

The work function of the surface gives information about the local composition and local electronic states of the surface. This relates to many properties of the surface including catalytic activity, doping and band-manipulation of semi-conducting materials, corrosion and charge trapping.

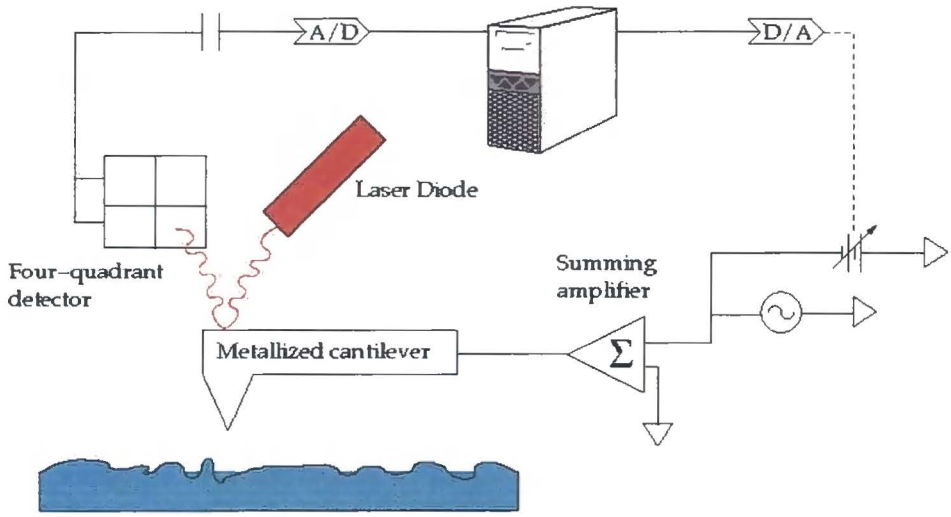


Fig 118: Schematic of a Kelvin Probe Force Microscope.

2.5.3 Previous Work

Thin films of phthalocyanines have been studied on various substrates by several groups.[609-614] Cook and coworkers have reported the formation of thin films of Pcs with one or two trichlorosilyl alkylchains on glass and silicon,[610] and the self-assembly of the thiol and disulfide-derivatized Pcs on gold surfaces.[611] Infrared

reflection–absorption spectroscopy (IRRAS) and evanescent wave-excited fluorescence emission studies suggested that the orientation of the Pc ring of the molecule depended on the length of the spacer between the ring and the gold surface. Huc and coworkers reported that ruthenium Pc can be grafted onto gold substrates by axial ligation using isonitriles as spacers between the metal and the Pc.[612] Li and coworkers have reported the formation of self-assembled monolayers (SAMs) of thiol-tethered, octasubstituted, and axially ligated SiPcs.[613] Sampath and his group have reported the molecular film formation of 2,9,16,23-tetraamino metalloPcs [metal = Co(II), Cu(II)and Fe(III)] on gold and silver surfaces.[614] The properties of these films investigated by cyclic voltammetry, impedance, and FT-Raman spectroscopy suggested that the tetra-amino cobalt Pc was adsorbed as a monolayer with an almost complete coverage. The blocking behaviour of the films toward oxygen and $Fe(CN)_6^{3-/4-}$ redox couple followed by cyclic voltammetry and impedance measurements lead to an estimate of the coverage of about 85% in the case of copper and the iron analogues. FT-Raman studies showed characteristic bands around 236 cm–1 revealing the interaction between the metal substrate and the nitrogen of the amino group on the phthalocyanine molecules.

2.5.4 Experimental details

For all experimental details of cyclic voltammetry and other electrochemical investigations, atomic force microscopy, Kelvin nanoprobe investigations and molecular modelling please refer to the main experimental section (see section 5.2).

2.5.5 Results and Discussion

2.5.5.1 Kelvin Probe studies:

Scanning Kelvin Nanoprobe (SKN) measurements enable non-invasive interrogation of the work function of materials and can differentiate energy levels between molecular components and electrodes which influence the electron transfer

rates in metal-organic hybrids.[615] In this work we used SKN to probe the integrity and formation of a thin film of monolayer dimensions.

The work function of an electronic conductor is defined as the difference between the Fermi energy and Volta Energy (Equation 1):

$$\phi = -e\psi - E_F \qquad (1)$$

where ϕ is the work function, ψ the Volta potential, e the unit charge, and E_F the Fermi energy within the solid. The Volta potential is the potential at *ca.* 10 nm from the surface where surface (image) forces do not affect the unit charge e (Fig. 119). The Volta energy is unit charge × the Volta potential ($-e\psi$). The electrical potential at infinity is assumed to be zero.[616] When two conductors with work functions ϕ_1 and ϕ_2 and Fermi levels E_{F1} and E_{F2} are contacted, the flow of charge allows the Fermi levels to equalize giving rise to a potential difference called the contact potential difference, V_c (Equation 2).

$$V_c = \Delta\phi = (\phi_1 - \phi_2) \qquad (2)$$

The application of a backing potential of equal and opposite sign to V_c, negates the surface charges and this potential is equal to the work function difference between the materials (Equation 2). To enable repeated measurements of V_c, a vibrating capacitance probe is used. Combining the equations for capacitance and the sinusoidal movement of the probe at equilibrium, an equation for the Kelvin current is derived as (Equation 3):

$$i_t = \frac{dQ}{dt} = (V + V_0)\frac{\varepsilon\omega d_1 A\omega t}{(d_0 + d_1\cos\omega t)^2} \qquad (3)$$

where d_0, and V_0 represent the rest position and voltage of the probe, d_1 represents the amplitude of vibration, V denotes the voltage at equilibrium between the probe and the sample, ε the permittivity of the material, ω the angular frequency of vibration and A the area of the electrode.[617] At equilibrium, when the contact potential is compensated by the backing potential, no current flows in the system and this null condition is

detected in the SKN. In our work we used a scanning Kelvin nanoprobe (SKN) microscope with a tungsten nanotip probe of diameter 100 nm developed by Thompson *et al.*, the details of which have been published previously.[618-620]

When a dielectric material is deposited on the sample, the Volta potential and the corresponding work function of the sample and material change, giving the relationship (Equation 4):

$$\Delta\phi_{TFS} = \phi_{TF} - \phi_S = -e(\psi_{TF} - \psi_S) \qquad (4)$$

where ϕ_{TF} and ϕ_S are the work functions of the substrate with the thin film material, and the substrate, $\Delta\phi_{TFS}$, difference, respectively. Ψ_{TF} and Ψ_S are the Volta potentials of the substrate with the thin film and the substrate, respectively. The difference in work function, therefore, arises from the change in the Volta potential when a film is deposited on the surface.

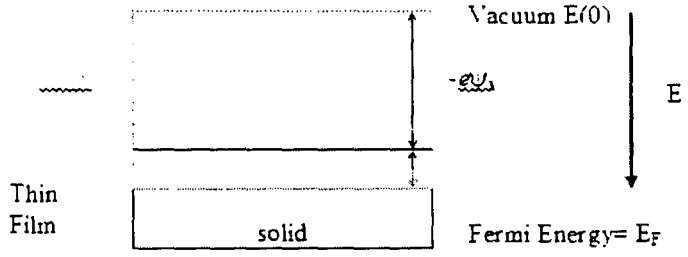


Fig. 119: Figure showing the difference in Volta Energies ($-e\Psi$) of a bare gold substrate and a substrate with a thin film.

SKN images were used to monitor the formation of a thin film of **206** on the electrode surface. The image profiles (Fig. 120) of the bare gold electrode (Fig. 120a) and the filmed electrode (Fig. 120b) showed a change in the CPD (contact potential difference) of the bare gold electrode area from –1.06 (±0.01) V, (V_{C1}) to –0.98 (±0.01) V, (V_{C2}), for the modified electrode, resulting in an overall CPD change of 80 mV. Furthermore, the CPD of the dielectric material surrounding the gold electrode, also changed from 0.09 (±0.01) V to –0.07 (±0.01) V giving an overall change of +0.16 mV. Additionally, the 3D surface maps of a *ca.* 10 μm^2 area of the modified surface, intact (Fig. 120c) and with a scratch made by the tungsten probe tip on the film (Fig 120d) measured a contact potential difference, V_{C1}= –1.08 (±0.01) V for the bare gold

electrode substrate and a contact potential difference V_{C2} = –0.99 (±0.01) V for the filmed electrode, which is approximately the same as the CPD differences observed in the image profiles. The shoulder observed at the bottom of the scratch (Fig 120d) may be due to the edge of a basal plane in the HOPG surface.

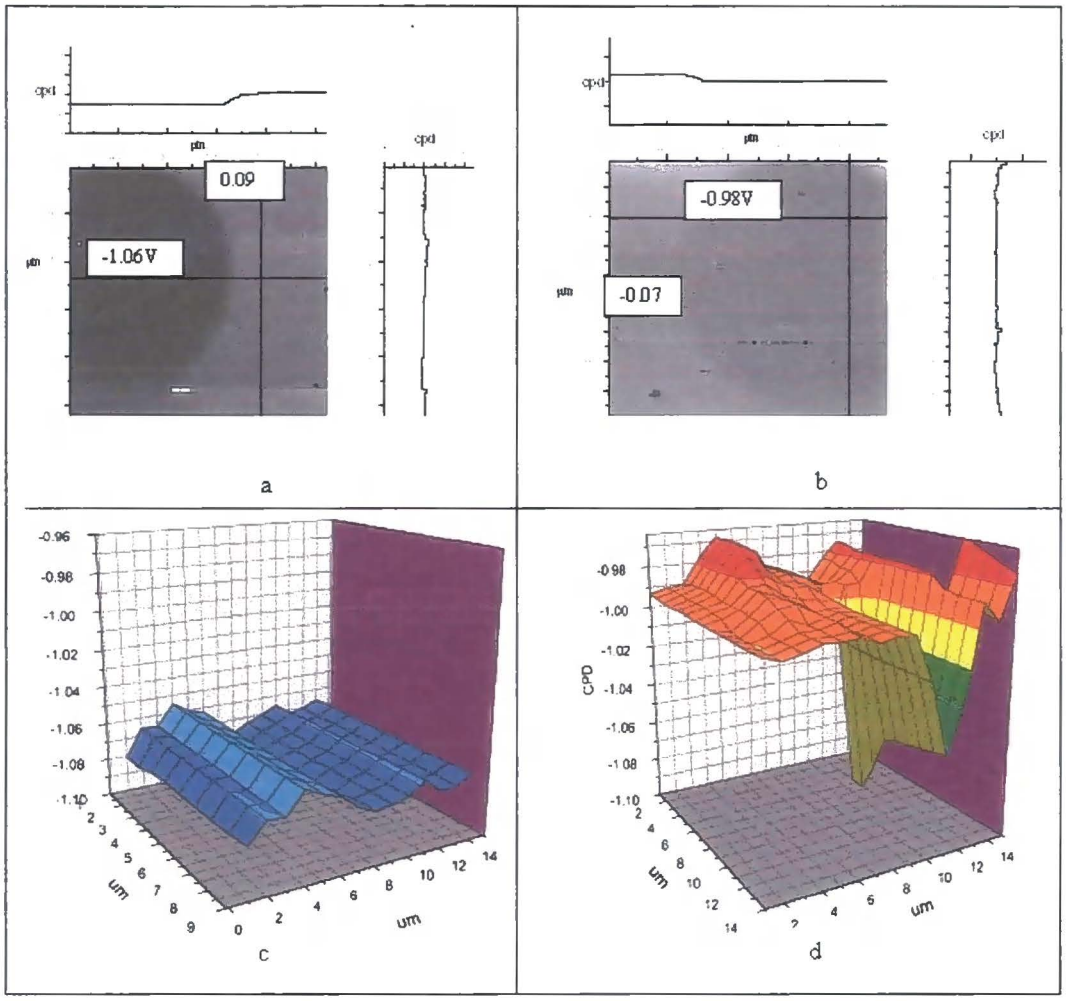


Fig 120: SKN image profiles of a.) bare gold electrode and b.) filmed electrode and 3D surface maps of c.) intact modified surface and d.) modified surface with a scratch.

The change in the CPD of the dielectric material in the vicinity of the conducting gold electrode surface suggests a leakage of the Pc solution which increases the permittivity and results in a decrease in the CPD value. The SKN measurements proved a reliable method of ensuring the formation of films of reproducible thickness and integrity.

2.5.5.2 AFM Studies:

Figure 121 shows the obtained AFM images obtained from $CHCl_3$ solutions of compounds **4**, **198** and **206** evaporated onto freshly cleaned surfaces of highly ordered pyrolytic graphite (HOPG).

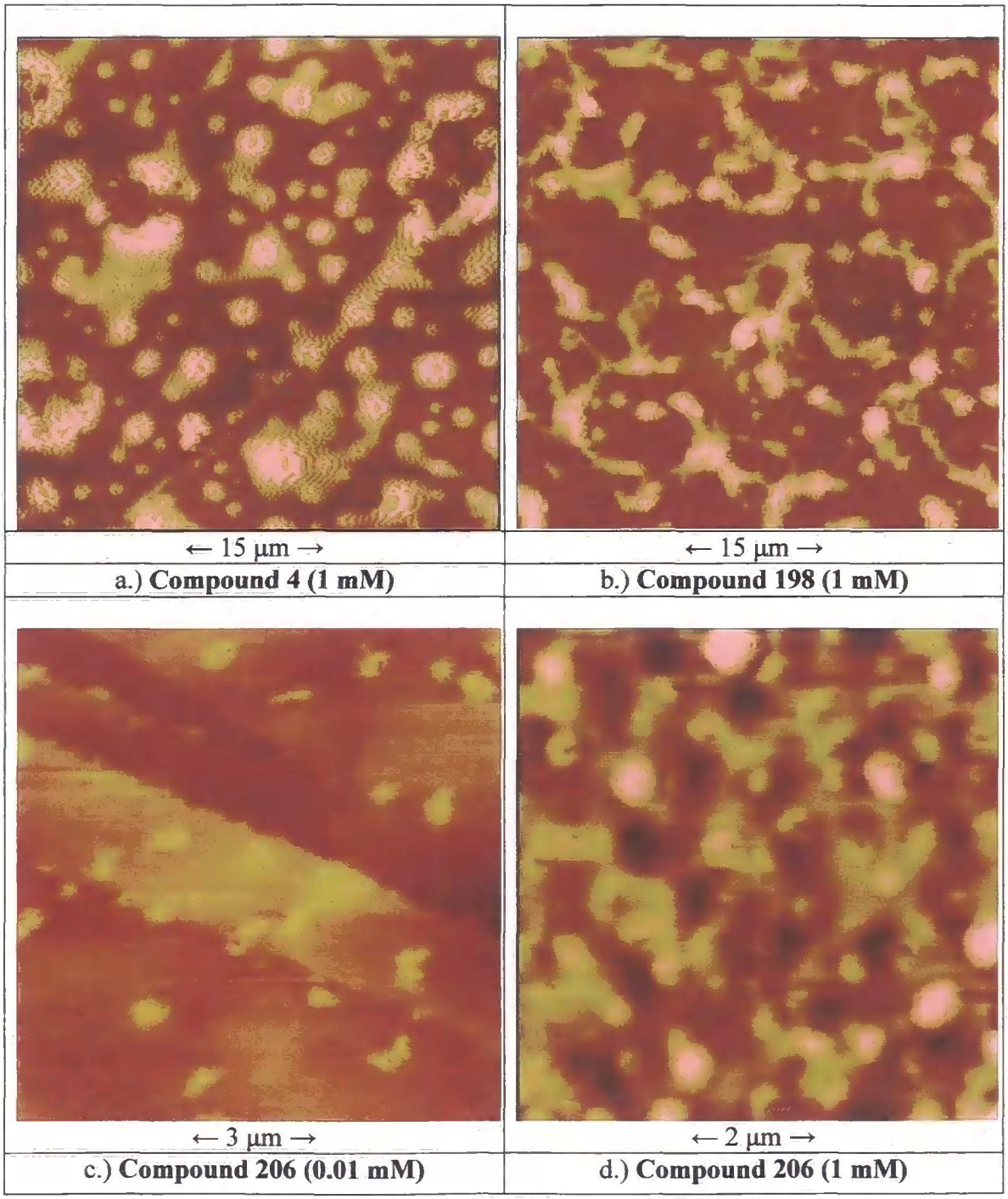


Fig 121: AFM images (15 x 15 μm) of HOPG surfaces coated with compounds **4**, **198**, and **206**, using solution concentrations of either 1 mM or 0.01mM.

The surfaces obtained from solutions of **4** and **198** are much less ordered than the surface obtained from a solution of **206** at the same concentration. This is presumably due to a greater degree of interaction between the axial ligands and the HOPG surface in the case of **206** and supports the findings of the molecular modelling simulations (see section 2.5.5.4). In figures 121a and 121c the edge of the basal planes of the HOPG surface can be seen. An attempt was made to estimate the surface thickness of the phthalocyanine layer of **206** via an AFM sectional analysis (see Fig 122), and average value of 12-13 nm was obtained. However, as a second sectional analysis of an untreated HOPG surface showed that the height of the basal planes varied by as much as 10nm (see Fig 122), no information about the surface thickness could be reliably obtained. The large troughs observed in the sectional analysis of **206** (see Fig 122) have diameters in the order of 200-500 nm and therefore are far too large to be interstices within the ordered phthalocyanine surface (see section 2.5.5.4). It is likely that these sharp changes in surface height are due to changes in the height of the underlying HOPG surface and are unrelated to the deposited phthalocyanine layer.

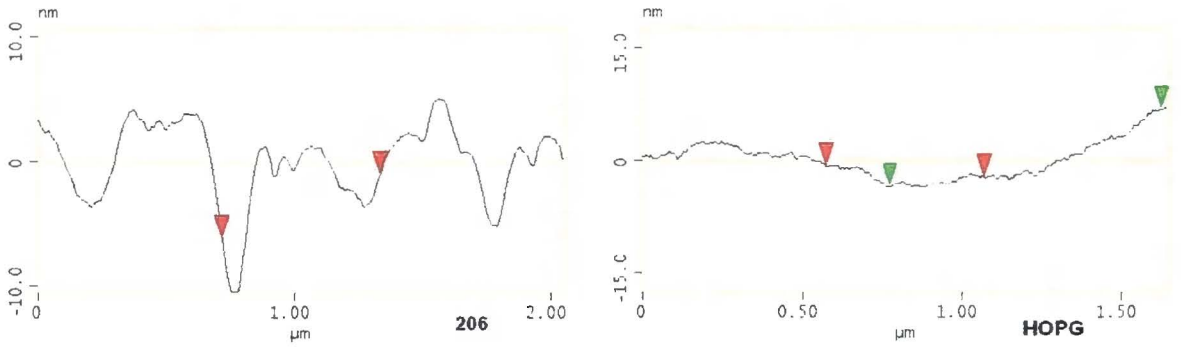


Fig 122: AFM sectional analysis of thin film of compound **206** and of untreated HOPG.

2.5.5.3 Electrochemical Studies:

Electrochemical investigations of the porosity of the film was carried out using probes of varying size and charge, *viz.* $[Ru(NH_3)_6]3^+$, $[Fe(CN)_6]^{3-}$ and $[Fe(di\text{-}SO_3\text{-batho-phen})_3]^{4-}$ (with diameters of 0.6 nm, 0.6 nm and 2.4 nm respectively) and *para*-benzoquinone (0.3×0.5×0.6 nm) and dopamine (0.3×0.6×0.8 nm) (see Fig 123).[621,622]

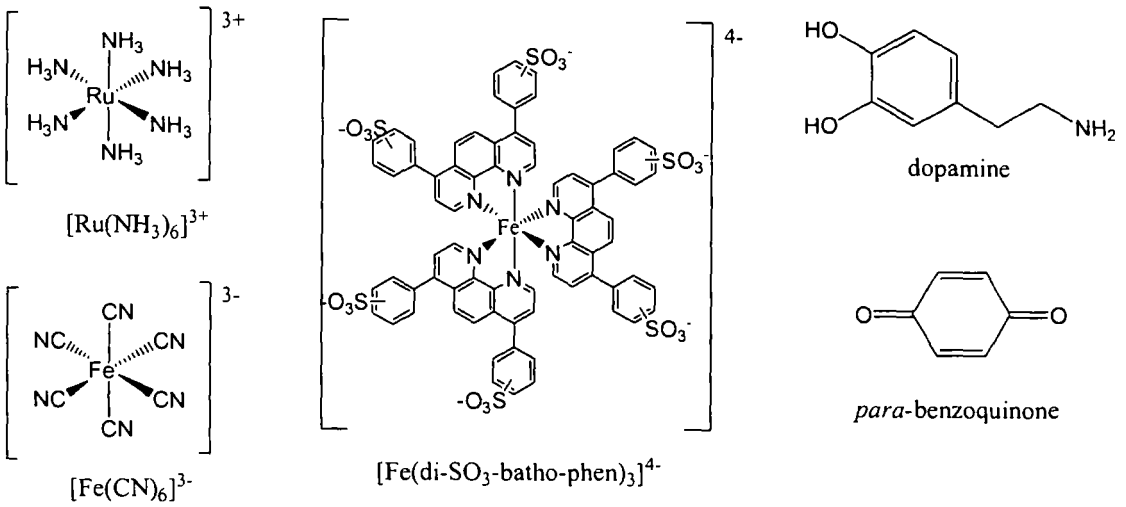


Fig 123: Structures of various probe molecules used.

DigiElch (Version 2.1), a software for the digital simulation of electrochemical reactions using the standard Butler Volmer equation (equation 5), was used to evaluate the heterogeneous rate constants (k_s) based on the obtained chronoamperometric measurements for the films (see Table 3).

$$i = i_o\left[\exp\left(\frac{\alpha_A nF}{RT}\eta\right) - \exp-\left(\frac{\alpha_C nF}{RT}\eta\right)\right] \qquad (5)$$

where i_o = exchange current density
η = overpotential (= $E - E_o$)
n = number of electrons
α_A = anodic transfer coefficient
α_C = cathodic transfer coefficient
F = Faraday constant (96,500 C/mol)

Table 2: Results of chronoamperometric measurements on compounds **4**, **198** and **206**.

Probe	Bare electrode		**4**		**198**		**206**	
	k_s (cm s^{-1})	D (cm^2 s^{-1})	k_s (cm s^{-1})	D (cm^2 s^{-1})	k_s (cm s^{-1})	D (cm^2 s^{-1})	k_s (cm s^{-1})	D (cm^2 s^{-1})
$[Ru(NH_3)_6]3^+$	6.0E-02	7.1E-06	1.0E-04	7.0E-06	1.0E-04	6.9E-06	2.0E-04	6.6E-06
Benzoquinone	5.0E-02	6.6E-06	3.0E-02	6.3E-06	4.2E-02	6.3E-06	1.4E-02	5.7E-06
Dopamine	5.1E-02	8.0E-06	-	-	5.0E-05	6.5E-06	3.0E-04	5.2E-06
$[Fe(CN)_6]^{3-}$	3.2E-04	5.0E-07	0	0	0	0	0	0
$[Fe(di\text{-}SO_3\text{-}batho\text{-}phen)_3]^{4-}$	3.2E-04	5.0E-07	0.0	0	0.0	0	0.0	0

The results shown in Table 2 suggest that all three of the phthalocyanine layers are both size and charge selective with respect to the probe molecules used. For all three Pcs, benzoquinone was found to have the highest rate constant of the probe molecules. Neither the ferricyanide ion or the $[Fe(di\text{-}SO_3\text{-}batho\text{-}phen)_3]^{4-}$ ion showed any penetration of the phthalocyanine layers, and this may be due to a charge repulsion effect between the anionic probe molecules and the electron-rich phthalocyanine layer. In the case of compound **206**, the electron transfer rates were higher for both uncharged probe molecules with no charge effects present. The slightly larger dopamine molecule showed a much lower k_s value than benzoquinone, which is not surprising considering that the molecular dimensions are approaching that calculated for the interstices using Hyperchem (see section 2.5.5.4). Despite being of a similar size to benzoquinone, the ruthenium hexamine ion has a lower k_s value then benzoquinone, and this may be due to an attractive electronic interaction as the cationic probe molecule approaches the phthalocyanine layer.

Chronoamperometric measurements for **206** based on the Cottrell equation (see eq. 6) using the ruthenium hexammonium ion probe molecule and the appropriate diffusion coefficient showed that the electrode coverage was *ca.* 68%.

$$I = nFAC_o\sqrt{\frac{D}{\pi t}} \qquad (6)$$

n = number of electrons transferred per molecule.
F = Faraday constant (96,500C/mol)
A = electrode area (cm2)
Co = concentration of species in solution (mol/cm3)
D = diffusion coefficient of probe (cm2 / s))

Assuming an intermolecular nanocavity of 0.9 nm diameter (see Fig 126) on the electrode surface of area 0.07 cm^2, a surface density of 2.8E+06 cavities is expected. This would give an electroactive area of ca. 0.025 (±0.005) cm^2.

Figure 124 shows the cyclic voltammograms for two electrodes modified with **206** and **4** respectively, using the ruthenium hexammonium and $[Fe(di\text{-}SO_3\text{-}batho\text{-}phen)_3]^{4-}$ probe molecules.

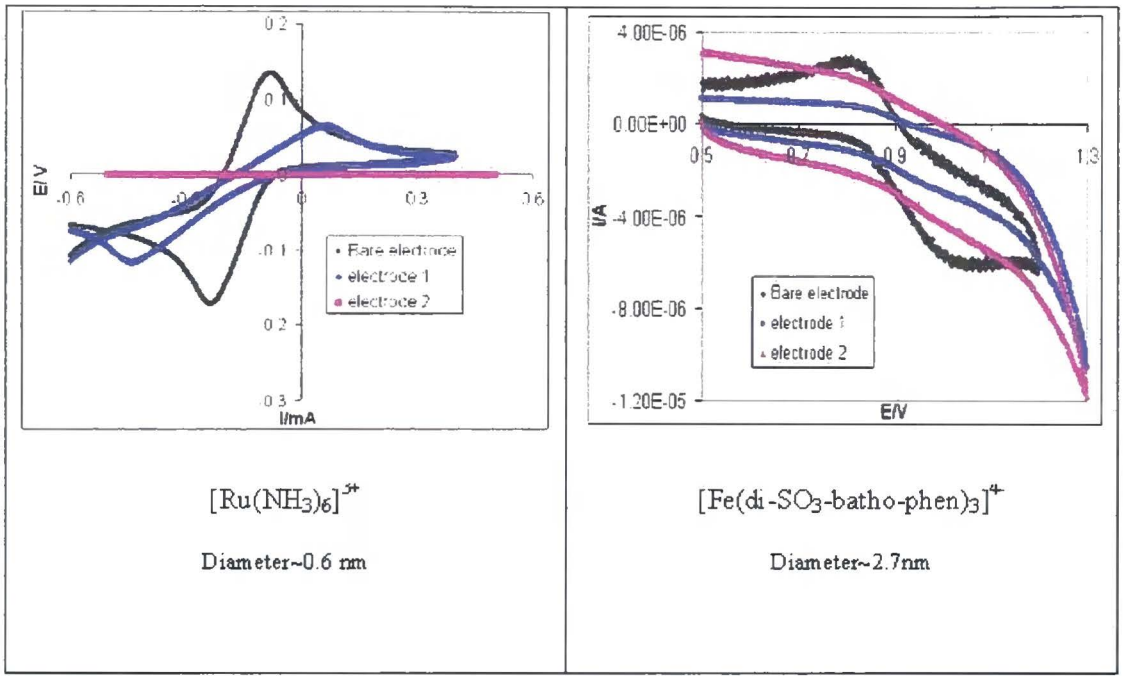


Fig 124: Cyclic voltammograms for a bare electrode, electrode 1 modified with a thin film of **206**, and electrode 2 modified with a thin film of **4** using two redox-active probe molecules.

The bare electrode showed the expected redox cyclic voltammograms for the probe molecules (see Fig 124). Whereas electrode 2 coated with **4** showed a complete blockage of the electrode surface with $[Ru(NH_3)_6]^{3+}$, electrode 1 coated with **206** showed CVs with separated anodic and cathodic peaks (Fig. 124). The results with the larger $[Fe(di\text{-}SO_3\text{-betho-phen})_3]^{4-}$ anion were interesting. With both electrodes 1 and 2, rectangular CVs characteristic of pseudocapacitive behaviour were observed, with electrode 1 showing very limited electron transfer and electrode 2 showing larger capacitive behaviour. These results indicate that the smaller probe molecules are able to penetrate through the 0.9 nm diameter intermolecular cavities in the film of **206** (electrode 1) but not the film of **4** (electrode 2). The larger $[Fe(di\text{-}SO_3\text{-batho-phen})_3]^{4-}$ anion is hindered and the pseudocapacitive behaviour reflects the formation of a capacitive layer caused by a π-π interaction between the modified electrode 1 and the probe anion, which is induced by the electrode potential.

In conclusion, this study demonstrates that well-ordered porous nanocavities were formed with a judiciously designed phthalocyanine on an electrode surface. Additionally, SKN microscopy combined with traditional electrochemical techniques provided excellent tools for interrogating the thickness of thin films on electrode surfaces and their porosity.

2.5.5.4 Molecular modelling for compounds 4, 198 and 206:

Construction of the Pc structure required the adoption of arbitrary valence for the central silicon atom, allowing an octahedral geometry to be assumed.
For each compound, two geometry optimisations were run using the AM1 semi-empirical method. In each case, the first of these optimisations was performed on the unrestrained molecule so as to find a local minimum for the structure in the gas phase.

Two torsional restraints were then applied between the silicon atom and the two ligands in order to force the aromatic rings in the ligands into a more parallel orientation with respect to the Pc plane. A second geometry optimisation was run on these restrained structures and an energy difference between the two orientations was then calculated for each compound (see Fig 125 & Table 3).

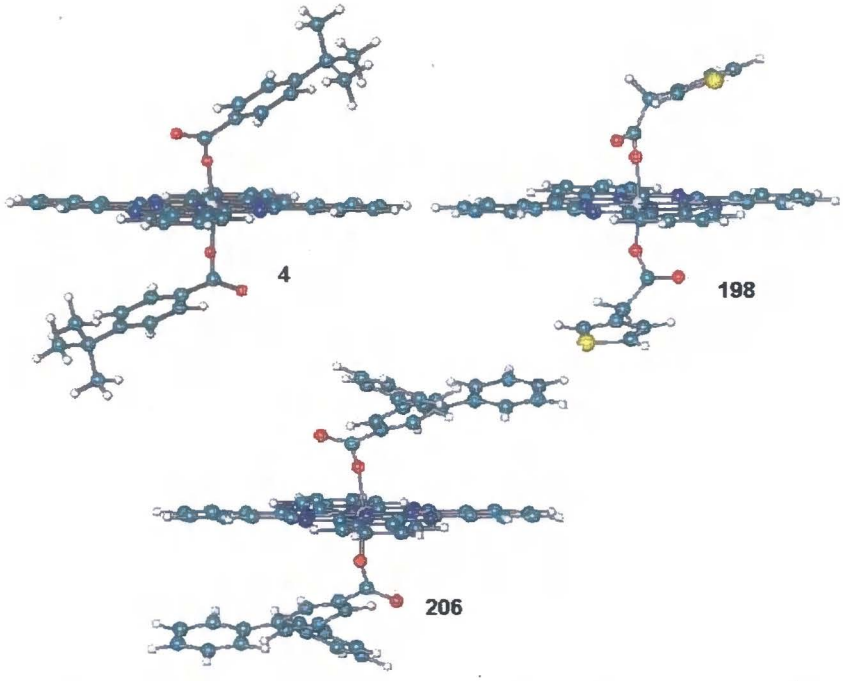


Fig 125: Minimum energy conformations for the restrained structures of **4**, **198**, and **206**, modelled in Hyperchem 6.0.

Table 3: Calculated energy values and differences for all phthalocyanine structures.

Compound	Total energy of unrestrained structure (kcal/mol)	Total energy of restrained structure (kcal/mol)	Calculated energy difference (kcal/mol)
4	-242356.874	-242347.256	9.62
198	-216692.231	-216690.796	1.44
206	-289527.137	-289518.044	9.09

These energy calculations act as a guide to explaining the observed surface properties of the different Pc derivatives. It is therefore important to note that two assumptions must be taken into account when considering these optimised structures:-

- The calculated energy differences will not take into account the possibility of an energy maximum between the two structures which would represent a greater energy barrier. However, it can be said that the values of these energy differences are sufficiently low that these geometrical changes can be achieved when molecules are ordered on the surface.
- Ordering of the molecules upon the surface of the high order pyrolytic graphite (HOPG) takes place in solution and not in the gas phase; therefore the actual energy differences between these structures may be lower due to solvation effects.

As expected, compound **4** gives the largest energy difference between the two optimised structures due to the sterically bulky *tert*-butyl groups and this compound displays the least ordering upon the graphite surface. Irrespective of the angle between the ligands' aromatic rings and the Pc plane, the butyl groups result in a poor interaction between the compound and the surface.

The energy difference for compound **206** is not noticeably lower than that for compound **4**. The high degree of ordering of the molecule upon the graphite surface is most likely due to both the increased number of aromatic rings in the axial ligands giving a better electronic interaction with the graphite, and the favourable orientation afforded by the degree of rotation of the additional phenyl rings.

The main consequence of the additional methylene spacer in compound **198** is that a much smaller rearrangement energy is ne

eded to adopt a favourable orientation for interaction with the graphite surface. The torsional strain placed on the ester linkage is therefore reduced and the observed energy difference is noticeably lower.

The fact that **206** gives the highest degree of ordering on the graphite surface indicates that the overriding factor in the ordering of these films is the number of aromatic moieties within the ligand, and not the degree of rotational freedom within the ligands.

An energy minimization of four molecules of **206** was performed via the Polak-Ribiere method (with an RMS gradient of 0.1) and suggested the formation of nanoporous sieve-like structures with the four molecules arranged in a cross-like formation with an interstice of *ca.* 0.9 nm diameter (see Fig 126).

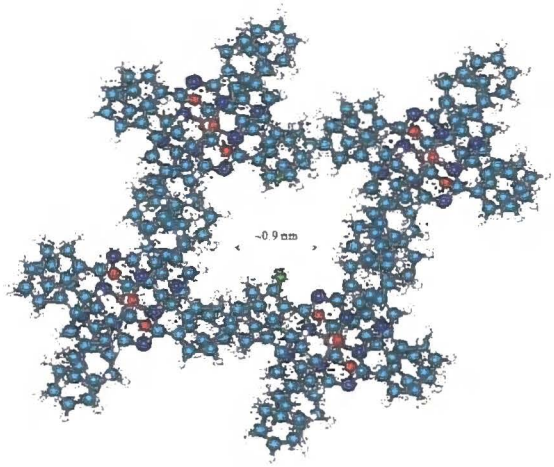


Fig 126: Aggregate structure of **206**, derived from Hyperchem calculations.

2.6 Summary

After initial difficulties encountered with both the synthesis and purification of novel phenyl silicon phthalocyanine derivatives, a reliable method of purification was developed which avoided the need for the previously unsuccessful column chromatography method. Once it became clear that alkoxide derivatives of these compounds were much more difficult to purify, emphasis was switched to the synthesis of new bis-substituted silicon phthalocyanine esters. In addition to this, one novel free-base phthalocyanine (**214**) bearing fluorene moieties, has also been prepared.

This range of new silicon phthalocyanine derivatives possessing axial substituents, effectively prevent aggregation of the Pc chromophores as shown by the very sharp transitions in their visible absorption and emission spectra. Altering the axial substituents does not significantly change the λ_{max} values. The luminescence properties are characterised by long lifetimes and high quantum yields, except for compound **201** where the two axial phenoxy substituents lead to siginificant quenching of the Pc fluorescence, possibly via an electron transfer process. The luminescence properties of **214** are typical of other octa-substitued free-base phthalocyanines and include a relatively high quantum yield. Efficient electron transfer from the fluorene moieties to the phthalocyanine core has been demonstrated.

Thin films of three bis-ester derivatives (**4**, **198** and **206**) were produced on highly-ordered pyrolytic graphite, and these surfaces were then probed using several techniques including Kelvin Nanoprobe Microscopy, AFM and cyclic voltammetry. The films formed by compound **206** were shown to be highly ordered, with those formed by compounds **4** and **198** showing a much lesser degree of ordering. This is presumably due to a reduced interaction between the axial ligands and the graphite surface when compared with the interactions for compound **206**. Some simple molecular modelling simulations of compound **206** suggested an interstice of approximate diameter 0.9 nm, between four phthalocyanine units. This value was in agreement with the data obtained by electrochemically probing the surface with a variety of charged and neutral probe molecules.

Chapter 3. Porphyrins

3.1 Introduction

Originally intended as a set of compounds for direct comparison with the previously synthesised axial SiPcs, the route to novel axially-substituted silicon porphyrins began with the attempted synthesis of 5,10,15,20-tetra-*para*-tolyl-porphyrinato-silicon dichloride (**95**). The choice of the tolyl-substituted porphyrin ring over the more common 5,10,15,20-tetraphenyl-porphyrin (TPP) (**73**)[207] was motivated by the relative ease of product identification by proton NMR spectroscopy, the methyl protons giving a characteristic downfield signal relative to starting materials.

Problems encountered in reproducing the literature synthesis of **95**[247] led us to turn instead to a number of peripherally-substituted free-base porphyrins for the purpose of a thorough study of their fluorescent properties.

3.2 Basic Strategy

A variety of pathways were used to synthesise free-base porphyrins. The classical route to *meso*-tetraphenyl-porphyrin (**73**), used by Rothemund *et al.* over seventy years ago,[623] has been extensively modified over the years and many of these routes were adopted for our targets.[208,214,215,220,222-224,417,624-626] Of particular note is the condensation method developed by Lindsey *et al*[215], which allows the facile production of porphyrins under equilibrium conditions and continues to be widely employed in the synthesis of substituted porphyrins.[420,438,627-629] The Lindsey condensation was of great use for structurally more complex starting materials.

The other main method which was successfully employed in these reactions was the use of an anionic micelle medium, pioneered by Bonar-Law.[222] Despite its simplifying effect upon the purification of the crude products, surprisingly this method appears to have found only limited use as a route to free-base porphyrins.[439]

3.3 Discussion

3.3.1 Synthesis of 5,10,15,20-tetra-*para*-tolyl-porphyrin (TTP) (215)

The successful synthesis of 5,10,15,20-tetra-*para*-tolyl-porphyin (**215**) was based on the simplified method for the production of **73** developed by Adler *et al.*[208] Pyrrole and *para*-tolualdehyde were reacted together in an equimolar ratio in refluxing propionic acid for 1 hour to give **215** as a purple crystalline solid in 22% yield. This yield is similar to that reported for **73** via this method,[208] but is lower than for some of the more modern syntheses of **215**.[221,630-632] However, optimisation of the yield of **215** was not a priority, so different methods were not explored.

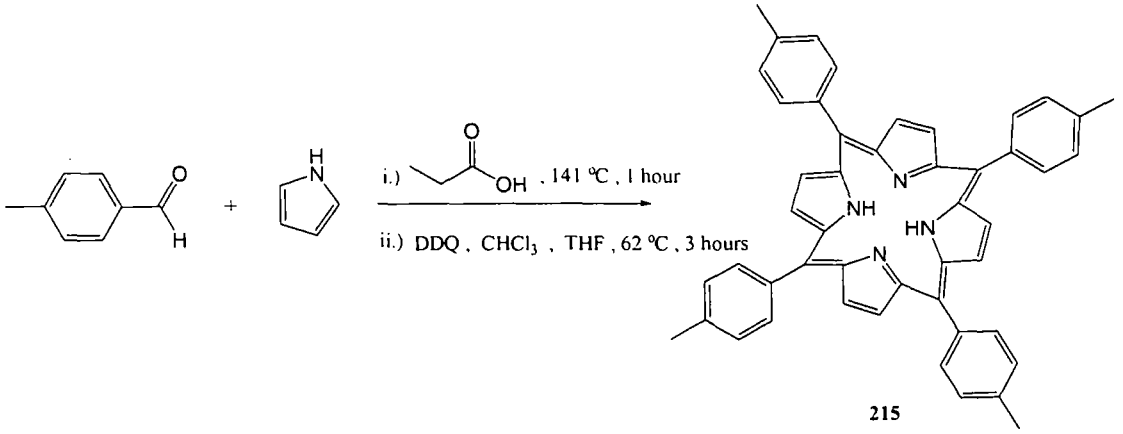


Fig 127: Synthesis of compound **215**

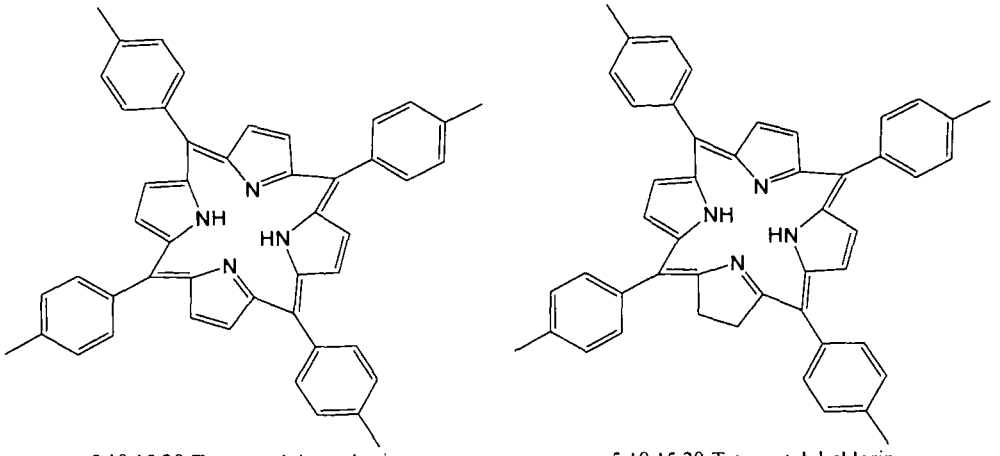


Fig 128: Structures of tolyl-porphyrin and chlorin impurity.

The visible absorption spectrum of the crude material showed no evidence of the presence of **216** (see Fig 128) as a minor impurity (enhanced absorption at long wavelength caused by superposition of the chlorin band upon that of **215**) but purification via the method developed by Barnett *et al.* used for **73** was performed as a precaution:[214] transformation of any residual chlorin to the porphyrin being effected by refluxing a mixture of DDQ and the crude material in chloroform. This gave **215** in an overall yield of 19% compared with 24% for the phenyl derivative (**73**).[214] Compound **215** was used as a reference in the fluorescence studies discussed in a later section of this chapter.

3.3.2 Attempted synthesis of 5,10,15,20-tetra-*para*-tolylporphyrinato-silicon dichloride (TTP)$SiCl_2$ (95)

Several attempts were made to synthesise (TTP)$SiCl_2$. Kane *et al.*[247] wrongly claimed that prior to their work, silicon tetra-aryl-porphyrins did not exist in the literature, the only previous examples of silicon-centred porphyrins were those with eight alkyl chains attached to the periphery.[241,245,246,633] However silicon tetra-aryl-porphyrins had previously been synthesised by Buchler *et al* via the reaction of the free-base porphyrin with silicon tetrachloride in a mixture of methanol and pyridine.[244,634] Although further examples of axially-substituted silicon porphyrins are published,[253,254] no additional synthetic routes to (TTP)$SiCl_2$ are known and so the Kane methodology was adopted.

In contrast to the work of Buchler *et al.*, Kane *et al.* found that reaction of **215** with silicon tetrachloride in anhydrous pyridine did not produce the desired product but instead gave a protonated porphyrin after acidic aqueous workup. This result was also observed by Kane *et al* upon attempts to repeat the work of Gouterman *et al,*[245] and it became clear that the silicon porphyrin species was highly sensitive to water. The alternative route then devised involved reacting the free-base porphyrin (**215**) with lithium bis-(trimethylsilyl)amide in tetrahydrofuran to form a lithio-porphyrin intermediate which is then converted to the silicon porphyrin product by reaction with trichlorosilane in dichloromethane. Given the contrasting reports in the literature, a fresh investigation into the various routes to (TTP)$SiCl_2$ (**95**) was undertaken.

We first attempted the novel method of adding silicon tetrachloride during the cyclisation step to see if a template effect occurred. An equimolar ratio of *para*-tolualdehyde and pyrrole was reacted with silicon tetrachloride using both propionic acid and dichloromethane (containing a catalytic amount of trifluoroacetic acid) as solvents. In both cases, dilution with methanol and filtration gave a brown highly insoluble solid which could not be analysed or purified. The likely reason is that cyclisation to form the porphyrin did not occur in this case.

Our second route was identical to the lithium intermediate method in the literature, except that silicon tetrachloride was used in place of trichlorosilane. Kane *et al.* reported that $SiCl_4$ in tetrahydrofuran or toluene gave incomplete reaction and only small amounts of the desired product,[247] whereas Buchler *et al.* reported that $SiCl_4$ was used successfully.[244] In our hands the reaction of (TTP) with an excess of freshly-prepared lithium bis(trimethylsilyl)amide in anhydrous tetrahydrofuran at 60 ^{o}C for 12 hours produced identical results to the literature, giving a green solution which was evaporated to dryness. Anhydrous dichloromethane was added, followed by $SiCl_4$ and after work-up as described[247] and passage through a short celite column, in addition to the green band mentioned in the literature, a second red band was observed. Effective separation could not be achieved. Instead of the purple product described in the literature, dark green solids were obtained. ^{1}H-NMR analysis showed that the singlet due to the porphyrin aromatic hydrogen atoms was shifted upfield relative to the free-base porphyrin (**215**), and could not be resolved from the second doublet due to the phenyl rings. This spectrum (containing peaks at δ 2.78, 7.81, 8.50 and 8.53 ppm) did not correspond to that in the literature (δ 2.65, 7.56, 7.98 and 9.03 ppm); however the solid did show the same sensitivity to water. A green solution of the solid in dichloromethane changed immediately to red upon the addition of water and a ^{1}H-NMR spectrum of the purple solid obtained was identical to that of **215**. The compound was unstable; consequently, mass spectral analysis showed only the free-base porphyrin. A ^{29}Si-NMR spectrum of the compound gave no signal at -217 ppm (as in the literature). Therefore, the unstable product obtained may simply be unreacted lithium intermediate.

The reaction was repeated using trichlorosilane to give a dark green solution after filtration through a celite column (there was no evidence of a second red band) and evaporation of the solvent gave a purple solid. A ^{1}H-NMR spectrum of this solid showed the presence of more than one porphyrin species, giving multiple signals in

the aromatic region, and so the crude material was reacted with a second batch of trichlorosilane in an attempt to complete the reaction. Again the same impure mixture of porphyrins was obtained. The ^{29}Si-NMR spectrum of the solid showed an extremely broad signal at approximately -215 ppm, corresponding to the signal obtained for **95** in the literature. Attempted purification via column chromatography (eluent dichloromethane or more polar solvents) gave only a red band, which was shown to be the free-base porphyrin (**215**) by proton NMR and mass spectrometry.

The failure to achieve a reliable synthesis of (TTP)$SiCl_2$, which was a proposed starting material for novel axially-substituted silicon porphyrins led to the study of free-base porphyrins bearing peripheral substitution.

3.3.3 Synthesis of 5,10,15,20-tetra-(9,9-dihexyl-9H-fluoren-2-yl)-porphyrin (218)

This choice of derivative was motivated by our successful synthesis of the fluorene-substituted free-base Pc (**214**) as the two compounds would provide an interesting comparison between the macrocyclic systems. Although there are numerous examples of octa-substituted free-base porphyrins bearing aromatic substituents,[454,460,635-638], we recognised that the attachment of eight 9,9-dihexyl-9H-fluorene units to the periphery of a porphyrin could prove difficult due to extreme steric hindrance. Therefore, our porphyrin target was **218**. The advantage of the tetra-substituted compounds is that they require only the synthesis of the corresponding aldehyde and avoid the need for the often more difficult synthesis of a 3,4-disubstituted pyrrole, as with the octa-substituted compounds.[639-641]

The aldehyde precursor, 9,9-dihexyl-9H-fluorene-2-carbaldehyde (**217**) was synthesised in 73% yield by a modified literature route from 2-bromo-9,9-dihexyl-9H-fluorene (**189**) (the synthesis of **189** has been discussed in section 2.3.6).[514]

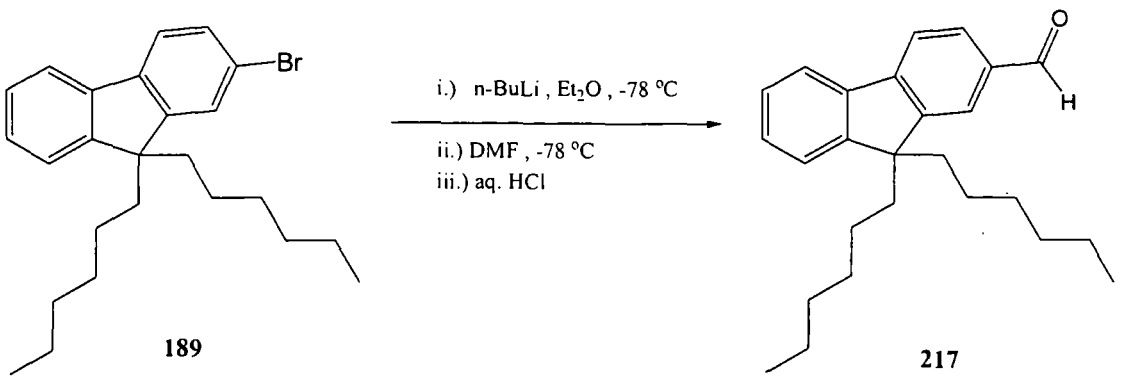
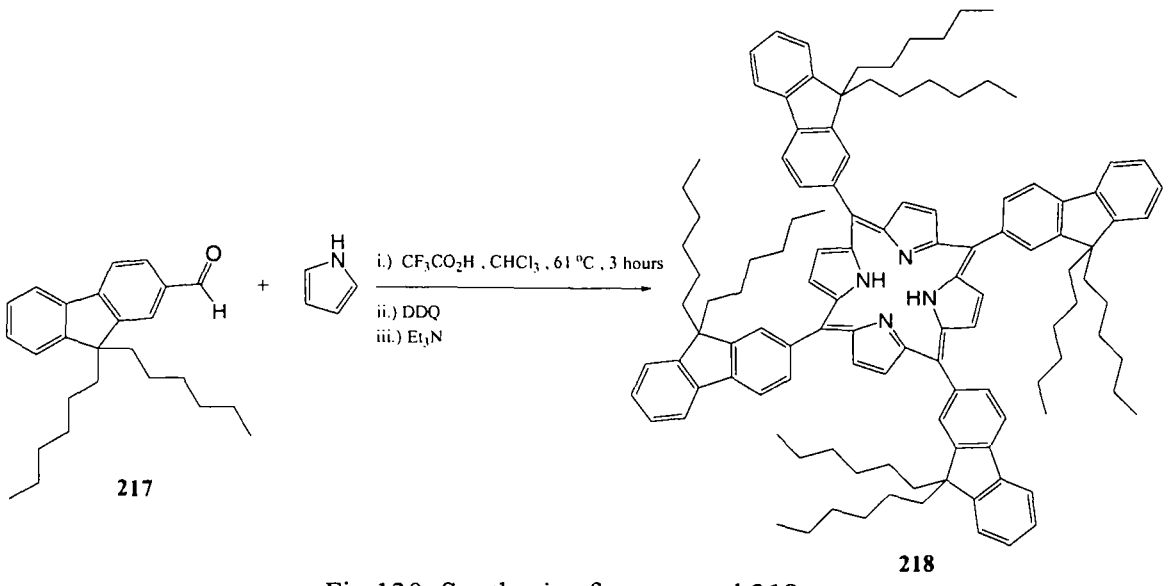


Fig 129: Synthesis of compound **217**

In the conversion to **217**, the 1.4 molar excess of n-butyllithium stated in the literature was considered unnecessarily high and 1.1 equivalents were employed instead.[512] Similarly the use of a five-fold excess of N,N-dimethylformamide was reduced to ~2.5 equivalents. It was noticed that **217** appears to undergo some form of reaction with acetone as mass spectra of **217** in acetone appeared different to those in other solvents, containing only higher weight peaks (m/z 439.4 and 453.4) and no evidence of the parent ion.

At this point in our work, the synthesis of an almost identical porphyrin to **218** (bearing octyl chains instead of hexyl chains) was published.[416] Nonetheless we completed the synthesis of **218**. A standard Lindsey condensation[215,624] was employed, trifluoroacetic acid being added to a solution of 9,9-dihexyl-9H-fluorene-2-carbaldehyde (**217**) and pyrrole in degassed anhydrous chloroform. As for compound **215**, DDQ was used to remove any chlorin impurities. Our target, (**218**), was obtained as a purple solid in 13% yield.



217 218

Fig 130: Synthesis of compound **218**

The ^{1}H-NMR spectrum of **218** gave an integration pattern of 3:1:1:2 for the fluorene aromatic hydrogens which is in general agreement with data for 5,10,15,20-tetra-(9,9-dioctyl-9H-fluoren-2-yl)-porphyrin.[416] One point of note is the change in peak order for the alkyl chains. In all the previous dihexylfluorene species in this work (compounds **189-193**, **202,203**, **213**, **214** and **217**), the two hexyl chains gave four peaks with an integration of 4:6:12:4 going from high to low field. However for **218**, the integration pattern has changed to 6:4:12:4 with the triplet due to the methyl group protons now shifted upfield relative to the other chain peaks. A comparison between the ^{1}H-NMR data of **218** and **217** shows that in both compounds the position of the triplet peak due to the methyl groups is about the same (δ 0.740-0.742 ppm). The methylene groups in **218** experience a shielding effect from the large porphyrin ring current and hence the signals are shifted downfield, to give the new integration pattern. The methyl protons, being the furthest distance from the macrocycle are relatively unaffected. An alteration of the alkyl integration pattern in hexyl chains attached to porphyrins has been observed previously in the literature, in systems where the hexyl chain is attached to the porphyrin ring either directly or by an oxygen or aromatic spacer group.[472,642-644] The fluorescence properties of this compound are discussed in a later section of this chapter.

Since the conclusion of this synthesis three more examples of a fluorene-substituted porphyrin have been published. Paul-Roth *et al.* attached four non-alkylated fluorene units to a porphyrin as part of work to produce new polymer

systems for catalytic carbene transfer. A derived network polymer was obtained. No fluorescence data for the respective monomers was reported.[383] Hou *et al.* have prepared copolymers based on fluorene and tetraphenyl-porphyrin-platinum(II) complexes which display complete quenching of the fluorescence emission and instead are intense red emitters from the triplet state.[645] Oar *et al.* have synthesised a porphyrin centred dendrimer based on tetrakis(3',5'-dihydroxyphenyl)porphyrin via reaction with an AF-343 derivative to form a star-shaped porphyrin containing eight fluorene-derivatised moieties.[339] In addition a porphyrin-centred dendrimer with fluorene units incorporated into the periphery of the dendritic chains has also been produced.[340]

3.3.4 Synthesis of 5,10,15,20-tetra-(thien-2-yl)-porphyrin (219)

The chemistry and fluorescence properties of both TPP (**73**) and TTP (**215**) are well known.[208,263,387,623,646] However, although the spectra of **219** had been recently recorded,[428,429,454,484] the fluorescence lifetime and quantum yield were unknown at the time this synthesis was undertaken. Sun *et al.* have subsequently reported a series of *meso*-tetra-thienyl-porphyrins, including 5,10,15,20-tetra-(thien-2-yl)-porphyrin.[430] Our initial attempt to prepare the compound was via the Lindsey condensation method, using 2-thiophene-carbaldehyde and pyrrole as described above for **218**. A mixture of dark coloured products was obtained which could not be purified. Okada *et al.*[484] used the alternative route developed by Adler *et al*[208] for their synthesis of 5,10,15,20-tetra-(thien-2-yl)-porphyrin although no purification details were given. Our attempts to follow this route were unsuccessful.

We then turned to a different route based on work by *Bonar-Law* with anionic micelle solutions to synthesise a range of sensitive polar *meso*-substituted porphyrins.[222] The yields reported for these compounds were between 10-48% and offered a simplistic route to certain less-stable porphyrins which avoided the need for protecting groups required when using the previously available route pioneered by Adler[208] and Lindsey.[215,624] The basic theory behind the employment of micelles is that the two organic reagents, not being soluble in the aqueous phase become concentrated within the non-polar interior of the micelles, thereby biasing the equilibrium of condensation so as to favour synthesis of the porphyrinogen

intermediates. This coupling reaction eliminates water and so increases the hydrophobicity of the growing chain, drawing it further into the micellular compartment, hence continuing to promote further reaction. Though not generally considered a sensitive porphyrin, **219** had been successfully synthesised by this route in modest yield (24%) and so the micelle route was adopted for our next attempt.

The reaction of 2-thienyl-carbaldehyde and pyrrole in the presence of acid and sodium dodecyl sulphate (SDS) led to a gradual colour change of the solution from yellow to red, consistent with observations from the literature. The decision to utilise TCQ as the oxidant in these reactions was arrived at in the literature, as more powerful oxidising agents such as DDQ and ammonium nitrate gave lower yields of the more functionalised porphyrins. As TCQ is only slightly soluble in the micelle solution, the oxidant is pre-dissolved in a small amount of THF so as to allow its incorporation into the reaction solvent.

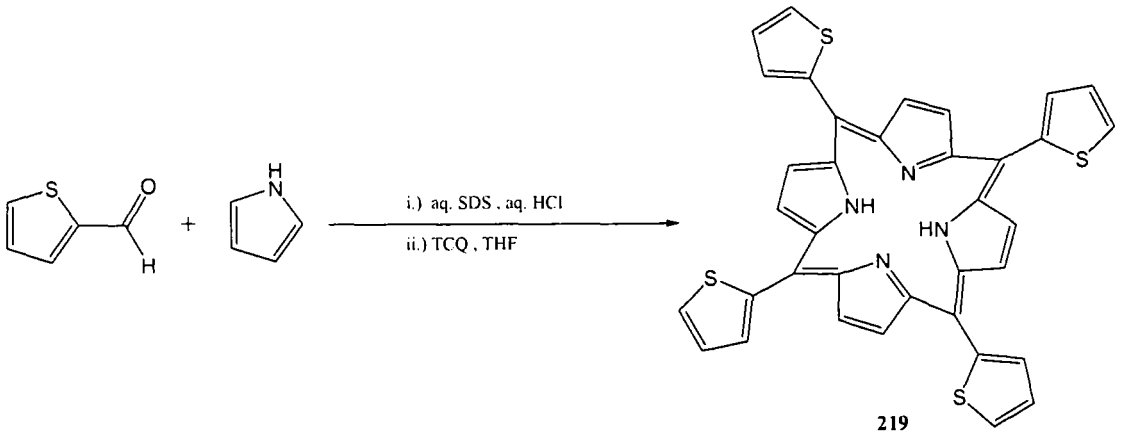


Fig 131: Synthesis of compound **219**.

The 18 % yield obtained for **219** was similar to that in the literature (24%). Melting point, ^{1}H-NMR and MALDI-ToF analysis of the purple product were consistent with data from the literature. The ^{13}C-NMR spectrum was also consistent with the product though no literature data could be found for comparison. The fluorescence properties of this compound are discussed in a later section of this chapter.

3.3.5 Attempted synthesis of 5,10,15,20-tetra-([2,2']bithienyl-5-yl)-porphyrin

Following the successful synthesis of **219**, the bithienyl analogue was chosen as a target compound. A comparison of the fluorescent properties of these two porphyrins would give a quantitative evaluation of the effect of the sequential addition of thiophene rings onto the porphyrin ring system. Shimidzu *et al.*[410] reported the production of the free-base porphyrin, 5,10,15,20-tetra-([2,2']bithienyl-5-yl)-porphyrin, from [2,2']-bithienyl-5-carbaldehyde via the method of Adler *et al.*,[208] although only scant details were given. The fluorescence properties of the compound were not studied, as the aim of the work was to synthesise conducting one-dimensional and two-dimensional polymers consisting of porphyrin units linked by molecular wire-like oligothiophene chains.

The only other example of bithiophene-substituted porphyrin rings is the work of Yamashita *et al.* who prepared stacked porphyrin trimers via Lindsey condensation of the alkyl-substituted [2,2']bithienyl-5-carbaldehyde species with dipyrrolomethane.

As both these literature routes were based on the use of a pre-synthesised bithiophene species, we needed to synthesise [2,2']-bithienyl-5-carbaldehyde (**220**). We synthesised **220** by the Vilsmeier reaction method of Raimundo *et al.*[647] in 69% yield. We also synthesised **220** by the novel method of Suzuki cross-coupling of thiophene-2-boronic acid with 5-bromo-thiophene-2-carbaldehyde in a 1 : 1.01 ratio using dichlorobis(triphenylphosphine)palladium(II) as a catalyst. However, the yield by this method was only 29% and well below that of alternative methods. Analysis of the product was identical to that obtained previously. An X-ray crystal structure of **220** is shown in Fig 133.

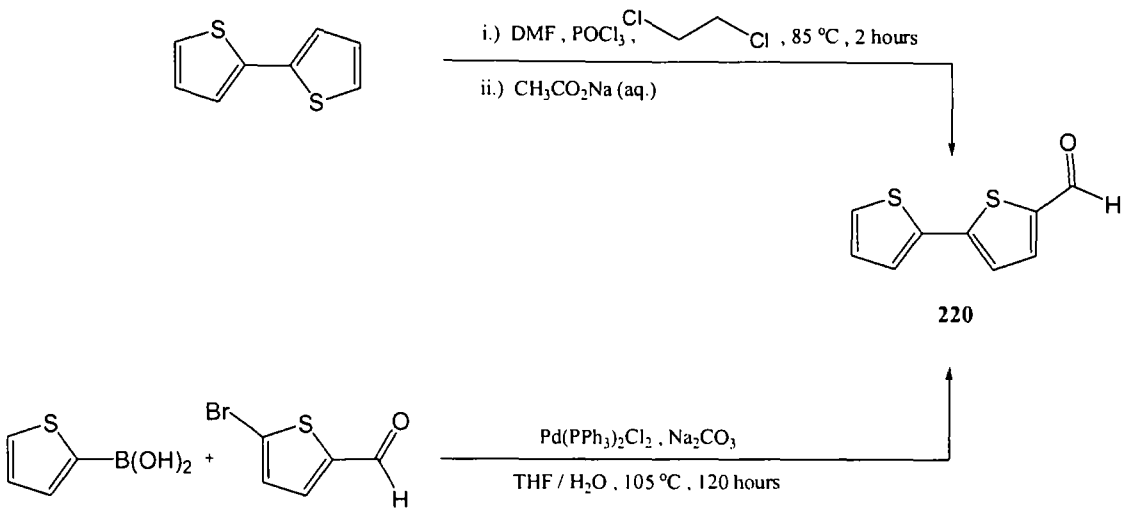


Fig 132: Alternative routes to compound **220**.

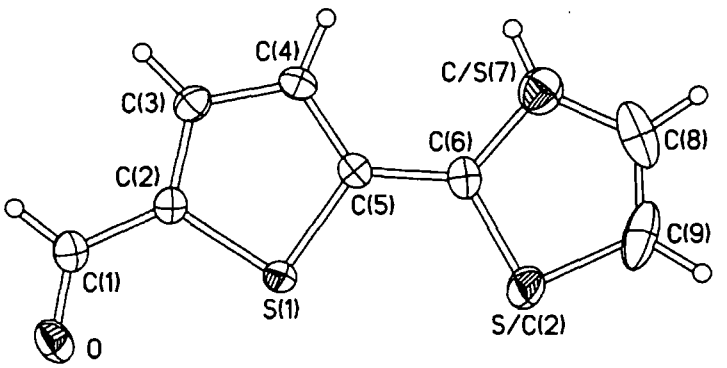


Fig 133: Crystal structure of compound **220**.

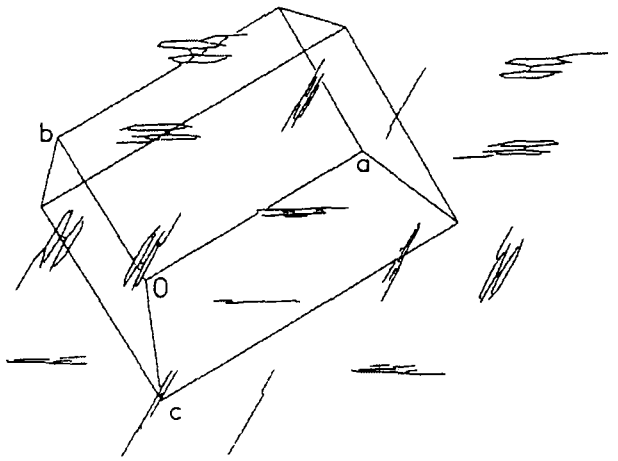


Fig 134: Crystal packing diagram for compound **35**.

The compound showed a predominantly cis-conformation of the two thiophene rings, which is consistent with data previously obtained for the compound.[648] The dominant

cis-orientation is also supported by the additional coupling seen in the proton NMR spectrum of the compound.

The already proven micelle route to tetra-substituted porphyrins was employed in the attempted synthesis of 5,10,15,20-tetra-{[2,2']bithienyl-5-yl}-porphyrin. It was noted that the solid **35** did not separate in the micelle solution as well as the liquid 2-thiophene-carbaldehyde had done previously. However, once the solution was acidified, reaction proceeded readily, as indicated by the rapid colour change from yellow to red. After work-up, the NMR spectra for the products obtained (4-5 multiplets between δ 6.4-7.8 ppm) were inconsistent with the data reported in the literature for 5,10,15,20-tetra-{[2,2']bithienyl-5-yl}-porphyrin.[410] Repeating the reaction gave a single red product, the ^{1}H-NMR of which showed five major multiplets (δ 6.39, 7.00, 7.19, 7.20 and 7.53 ppm) whose general pattern and integration were similar to that of **220**. These peaks were at noticeably higher-field than those reported in the literature for compound **219**, and in addition, no peak at δ ~9.0 ppm corresponding to the porphyrin ring (β-pyrrolyl) was observed. MALDI-ToF mass spectra of the compound in chloroform were equally inconclusive; no molecular ion peak corresponding to 5,10,15,20-tetra-{[2,2']bithienyl-5-yl}-porphyrin was seen. The elemental analysis of the solid (Found: C, 56.68, H, 4.22, N, 7.69%) was also inconsistent with the desired product ($C_{52}H_{30}N_4S_8$ requires C, 64.56, H, 3.13, N, 5.79%) and suggested complexation of additional ions into the porphyrin core. Attempts made to convert any metal complex present to the free-base porphyrin by acidification,[649-651] were unsuccessful and the compound produced showed only weak broadband absorbance bands compared with the previously synthesised **219** (see Fig 135). Its structure is unknown and although the high weight peaks in the mass spectra (m/z 923.2, 988.2) confirmed formation of the macrocycle, negligible emission was observed for this unknown compound.

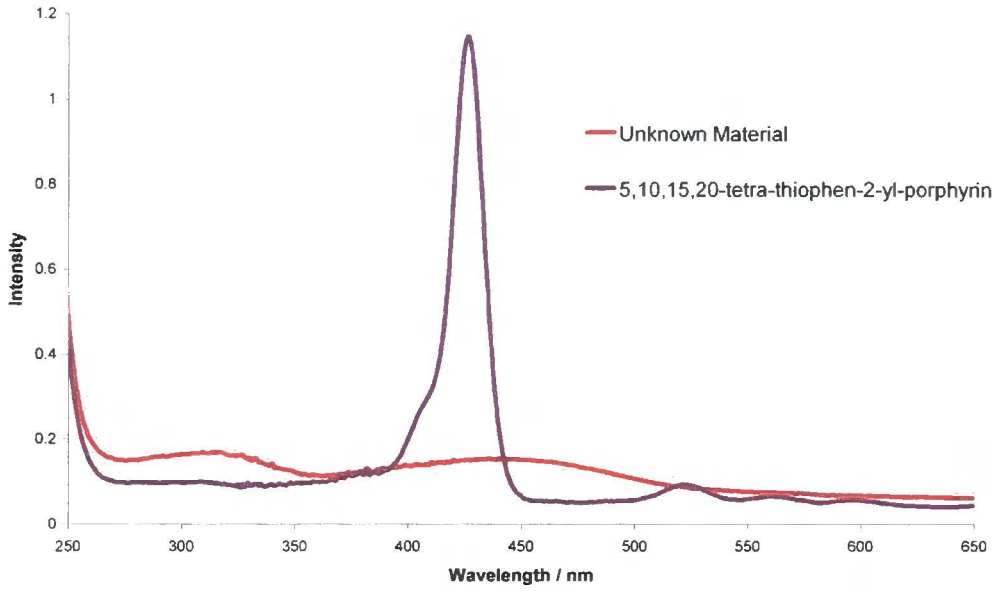


Fig 135: Comparative absorption of crude product with previously synthesised porphyrin **219**.

Attachment of aromatic groups directly to the porphyrin ring has been performed with both aromatic boronic acids[468,652-656] and porphyrin boronic acids.[323,416,501,657-660] As the synthesis of 5,10,15,20-tetra-(4-bromophenyl)-porphyrin is well known,[661] we attempted to prepare the thiophene analogue, 5,10,15,20-tetra-(5-bromothien-2-yl)-porphyrin (**221**) via the method of Mamane *et al.*[208] The route is similar to Adler's route to *meso*-tetraphenylporphyrin,[222] involving the use of an acidic solvent to catalyse the reaction, giving the product as a precipitate directly from the reaction mixture. 5-Bromothiophene-2-carbaldehyde and pyrrole were reacted together in an equimolar ratio via the micelle route developed by Bonar-Law.[360] The synthesis of compound **221** has since been published, using standard Lindsey conditions.[501,637]

Using this method, **221** was successfully synthesised in 15% yield. In contrast to previous thiophene-substituted porphyrins, purification of the compound via column chromatography did not require the use of either methanol or pyridine, the product eluting readily in dichloromethane. The porphyrin proton peak in the ^{1}H-NMR spectrum of the product was downfield shifted (δ 9.11 ppm) relative to the peak for the 4-bromothienyl-substituted species (δ 8.67 ppm), whereas the two thiophene doublets were upfield shifted (δ 7.49 and 7.66 ppm *c.f.* 8.17 and 8.29 ppm).[430] In

addition to the molecular ion peak, the MALDI-ToF analysis also showed a fragment peak due to the loss of a bromide ion. The fluorescence properties of this compound are discussed in a later section of this chapter.

The attempted conversion of compound **221** to 5,10,15,20-tetra-{[2,2']-bithienyl-5-yl}-porphyrin was based on a standard Suzuki cross-coupling protocol used successfully to synthesise 5,10,15,20-Tetrakis[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-porphyrin (**224**) (see section 3.3.6). Compound **221** was refluxed with a four-fold excess of thiophene-2-boronic acid in PhMe/THF for 2 days with $Pd(PPh_3)_4$ as the catalyst and aqueous Na_2CO_3 as base. However, only unreacted **221** (95% yield) was isolated. This complete lack of reaction of **221** is surprising, given literature precedents with 5,10,15,20-tetra-(4-bromo-phenyl)-porphyrin which used only slight molar excesses of the aryl boronic acid (between 4.4:1 and 6:1).[538,539] The electron-withdrawing effect of the porphyrin ring should activate the aryl halide substituents to oxidative addition by the palladium catalyst, and the yields for porphyrin tetra-couplings of this type are generally high (between 60–80%). Compound **221** may be less reactive due to the electron-rich thiophene rings. The next logical step would be to repeat the reaction using a much larger excess of thiophene-2-boronic acid and to vary the catalyst, however time constraints prevented us from pursuing this further.

3.3.6 Synthesis of 5,10,15,20-tetra-[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-porphyrin (224)

A tetra-substituted porphyrin with a phenyl spacer group between the porphyrin and fluorene units was an attractive analogue of **218** to probe the effect of increasing the distance between the fluorene and porphyrin sub-units whilst also increasing the overall conjugation of the molecule. The precursor aldehyde, 4-(9,9-dihexyl-9H-fluoren-2-yl)benzaldehyde (**222**), was synthesised via a Suzuki coupling method similar to that used previously for 4-(9,9-dihexyl-9H-fluoren-2-yl)benzoic acid (**203**) (see chapter 5). $Pd(PPh_3)_4$ proved to be an effective catalyst after the use of $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ resulted in either no evidence of reaction or < 1% yield, respectively. The modest yield of **222** (60%) achieved could not be improved by incorporation of tri(*tert*-butyl)phosphine into the reaction,[501] the addition of the ligand reagent serving only to complicate product purification.

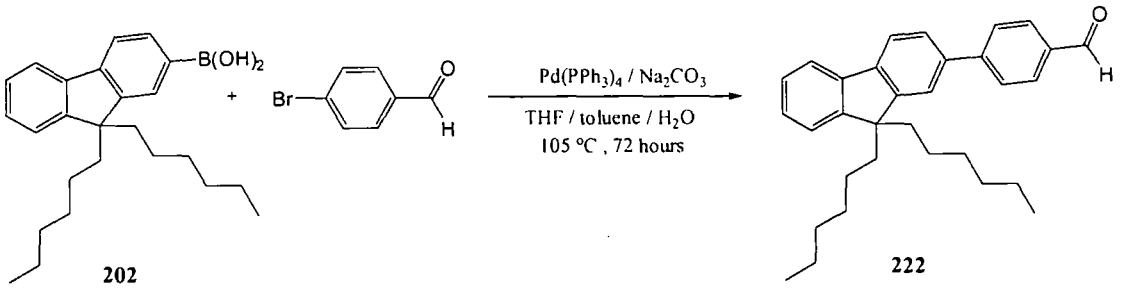


Fig 136: Synthesis of compound **222**.

The corresponding porphyrin (**224**) could not be obtained using the micelle route of Bonar-law:[222] viscous aldehydes such as **222** are highly problematic in this reaction. Analysis of the organic layer after work-up showed no clear evidence of porphyrin formation and this route was abandoned.

An alternative method was successful. The Suzuki cross-coupling reaction of 9,9-dihexyl-9H-fluorene-2-boronic acid (**202**) with 5,10,15,20-tetra-(4-bromo-phenyl)-porphyrin (**223**) gave **224** in 72% yield, which is efficient for a four-fold reaction. Compound **223** is well known in the literature and its synthesis was based on work by Capitosti *et al.*[662] The fluorescence properties of compound **224** are discussed in a later section of this chapter.

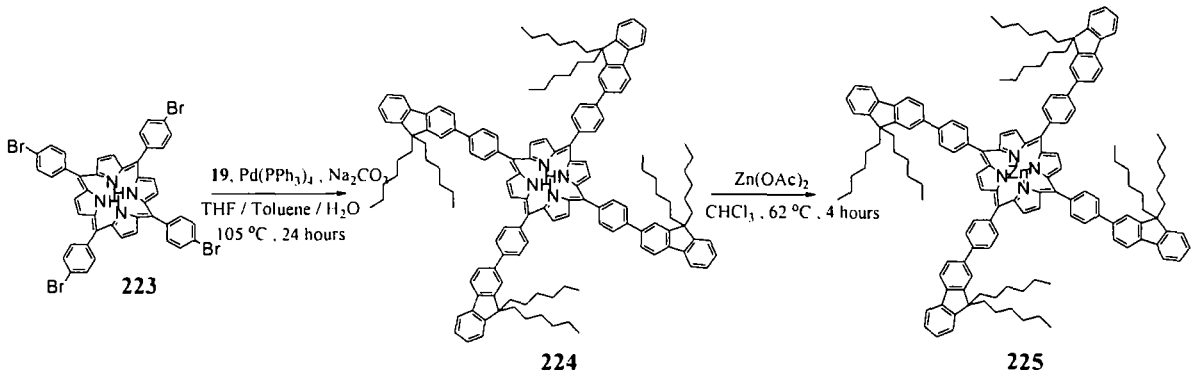


Fig 137: Synthesis of compounds 224 and 225.

The zinc derivative (**225**) was also prepared via direct reaction of the free-base porphyrin with zinc acetate, following the literature precedents.[663-665] The zinc derivative differed from **224** in that the melting point was slightly higher and a slight down-field shift of the porphyrin hydrogen atoms was observed in the ^{1}H-NMR spectra. The effect of metallation, upon the fluorescent properties of the molecule, are discussed in a later section of this chapter.

3.3.7 Synthesis of 5,10,15,20-Tetrakis-{[9,9-bis(6-carbazol-9-yl-hexyl)-9H-fluoren-2-yl]phenyl}-porphyrin (228)

The quenching of Pc fluorescence via through-space electron transfer has given some interesting results in derivatives bearing a variety of flexible and elongated chain-type ligands (see previous chapter). The possibility of similar interactions in porphyrin species was therefore, considered.

The previously synthesised 5,10,15,20-tetra-[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-porphyrin species (**224** and **225**) contain peripheral conjugated chains which are unlikely to adopt conformations where intramolecular electron transfer of this type can proceed. However, attachment of an electron-rich aromatic group to the hexyl chains might provide enough flexibility for the aromatic groups to move close enough to the porphyrin unit to affect its fluorescence properties.

The route to the target compound (**228**) began with the synthesis of the complex borolane precursor (**227**) from the corresponding iodide (**226**) using trimethyl borate. Attachment of the carbazole moieties to 2-iodofluorene was achieved by base-catalysis in the presence of a crown ether. Suzuki coupling of **227** with **223** gave **228** in 52% yield.

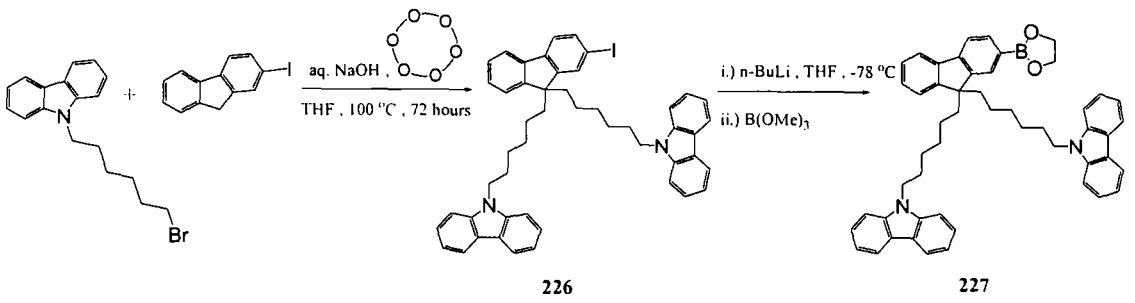


Fig 138: Synthesis of compound **226** and **227**.

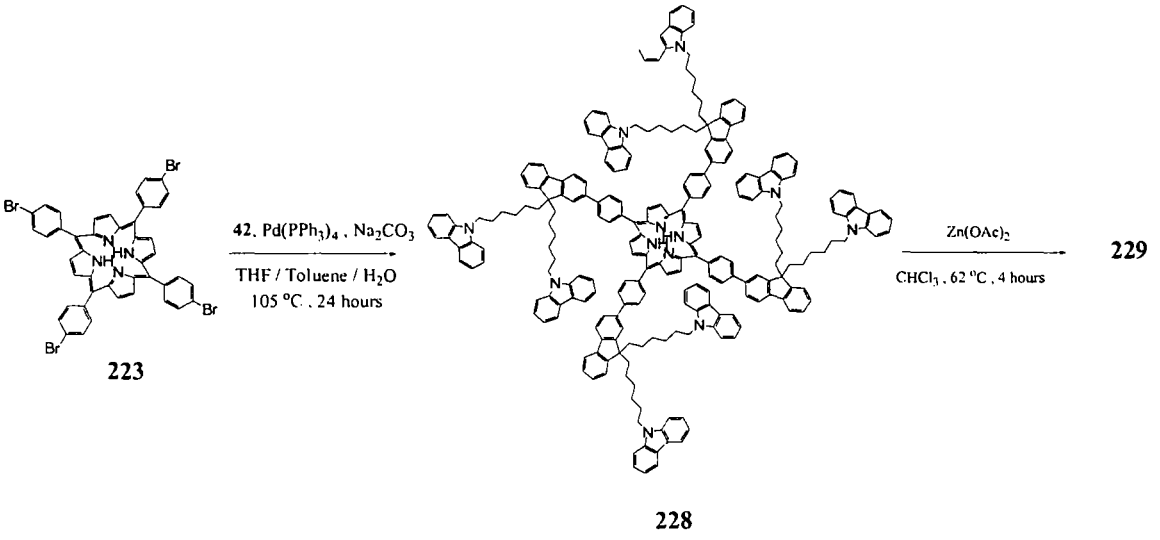


Fig 139: Synthesis of compounds **228** and **229**.

As for **224**, the zinc derivative (**229**) of compound **228** was readily obtained. The fluorescent properties of **228** and **229** are discussed in a later section of this chapter.

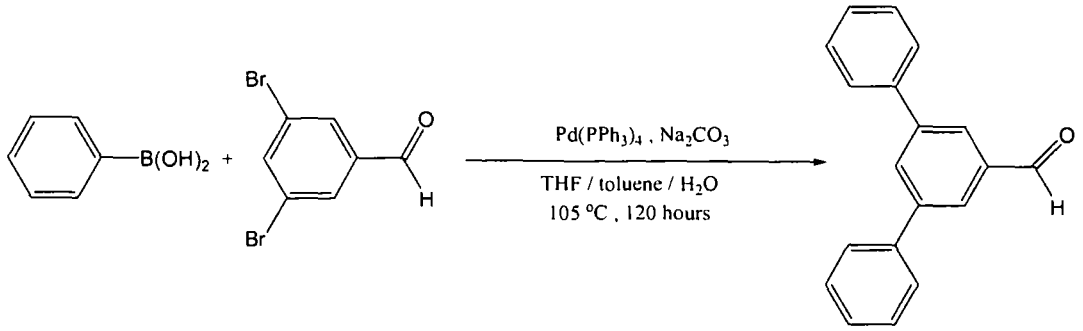
3.3.8 Synthesis of 5,10,15,20-tetra(3,5-diphenylbenzyl)-porphyrin (231)

Porphyrins bearing branched aromatic chain substituents have potential for use as functional dendrimers where the active component lies at the dendritic core. Many of the porphyrin-centred dendrimers previously synthesised are based on dendrons containing saturated links (particularly ether linkages) between the branching points,[338,438,500] whereas fewer fully conjugated dendrimers of this type are known.[501,666]

Porphyrins bearing polyphenylene dendrimers may be synthesised in one of two ways. Both methods begin by sequentially building up the dendron units via successive coupling reactions. Then the dendron may be converted to an aldehyde and reacted to form the porphyrin directly, or the dendron may be attached to a premade halogenated porphyrin via a coupling reaction.[501]

Although Capitosti *et al.* have produced large highly conjugated porphyrins in this manner,[501] the synthesis of smaller branched porphyrins via this method has not been explored. The comparatively simple tetra-substituted porphyrin, 5,10,15,20-tetra(3,5-diphenylbenzyl)-porphyrin (**231**), has previously been synthesised by the cyclisation of (1H-pyrrol-2-yl)-[1,1',3',1"]terphenyl-5'-yl-methanol in acidic conditions: a full analysis of the compound's fluorescent properties has not been reported, with only the absorption spectra published to date.[222] Compound **231** was therefore synthesised via the alternative aldehyde precursor (**230**) so as to obtain values for the fluorescence lifetime and quantum yield. The aldehyde was synthesised via a Suzuki coupling reaction.

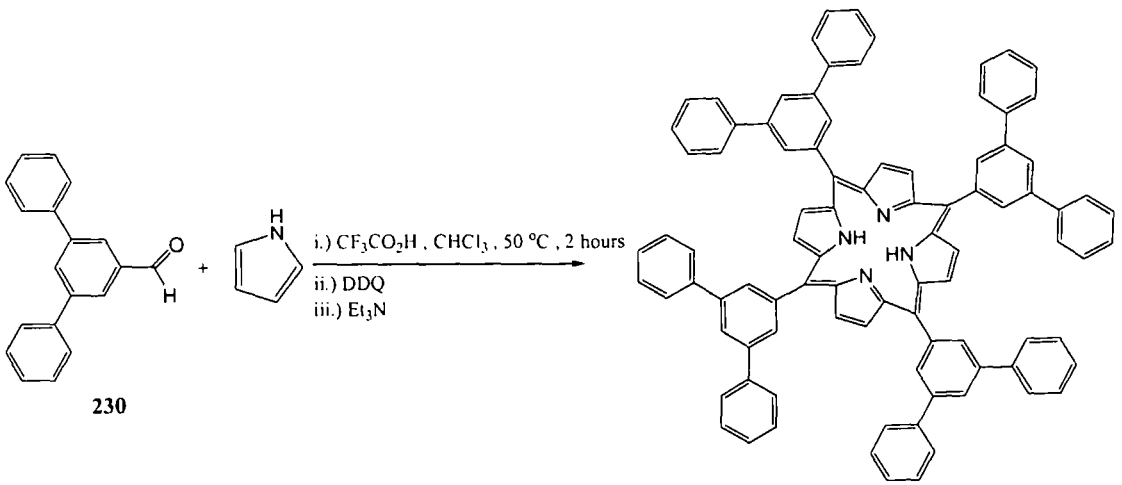
3,5-Diphenylbenzaldehyde (**230**) was obtained in 98% yield from phenyl-boronic acid and 3,5-dibromo-benzaldehyde, the only other product obtained from the purification being unsubstituted terphenyl.



230

Fig 140: Synthesis of compound **230**.

The synthesis of **231** was attempted without success using the micelle route,[222] probably due to insolubility problems with the aldehyde similar to those experienced with 4-(9,9-dihexyl-9H-fluoren-2-yl)-benzaldehyde (**222**). Even with heating of the solution at 80 °C for several hours, reaction seemed incomplete. Standard Lindsey condensation conditions in anhydrous chloroform, with trifluoroacetic acid as catalyst gave a deep purple-red product which was a mixture of two porphyrin components (by ^{1}H-NMR). Purified **231** was obtained in 14% yield and its fluorescence properties are discussed in the next section of this chapter.



230 **231**

Fig 141: Synthesis of compound **231**.

3.4 Fluorescence Properties of the Synthesised Porphyrins

3.4.1 Introduction

Porphyrins typically display a strong transition to the second excited state ($S_0 \rightarrow S_2$) at about 400-470 nm (the 'Soret' or 'B' band) in their electronic absorption spectrum. In addition, a weak transition to the first excited state ($S_0 \rightarrow S_1$) at about 550 nm (the 'Q' band) is also observed. As internal conversion from the S_2 to S_1 state is rapid, fluorescence is only detected from the S_1 state, giving rise to an emission band around 500-700 nm. Both the Soret and Q bands arise from π- π^* transitions and can be rationalised using the 'four orbital model' proposed by Gouterman.[667]

Transitions between two HOMOs and two LUMOs in the porphyrin system give rise to their absorption bands, and the relative energies of these transitions are affected by the presence of metal centres within the porphyrin ring as well as substituents on the ring itself. Mixing of these states gives rise to a higher energy state, responsible for the Soret band, and a lower energy state, responsible for the Q-band.

As with the Pcs, removal of a metal ion from the macrocyclic core results in a change in the overall symmetry of the molecule and splits the Q band into two separate bands, denoted as Q_x and Q_y. In the case of metalloporphyrins, the photophysical behaviour of the macrocycle is highly dependent on the identity of the central metal ion, as with metallophthalocyanines (see previous chapter). In particular, metalloporphyrins incorporating heavy metal ions such as zinc, cadmium and palladium have a reduced fluorescence lifetime and increased phosphorescence lifetime relative to their free-base analogues. This is due to an increased intersystem crossing rate from the excited singlet state to the excited triplet state, via a new spin-orbital coupling pathway. This pathway arises from the conjugation of the metal d_{xz} and d_{yz} π orbitals with the first pair of antibonding π^* orbitals of the porphyrin.

3.4.2 Results and Discussion

The photophysical data for all porphyrin compounds prepared are collated in Table 4 and Figures 142 and 143.

Table 4: Spectroscopic Data for all Porphyrin compounds.

Compound	λ_{max}(abs)/nm	λ_{max}(em)/nm	Φ_f[a]	τ_{f1}/ns[b]	τ_{f2}/ns[b]
215	420	656 (721)	0.11	8.6	-
218	427	660.5 (725)	0.21	8.2	-
219	426	675 (730.5)	0.016	1.2	-
221	430	677 (sh)	0.021	1.1 (83%)	5.6 (17%)
224	426	659 (724)	0.21	8.3	-
225	427	603.5 (651)	0.088	1.6	-
228	427	659.5 (725)	0.21	8.4	-
229	427	603 (650.5)	0.088	1.6	-
231	424	657 (715.5 br)	0.23	7.3	-

[a] ±10%, λ_{ex} = 430 nm, λ_{em} = 600-850 nm (525-815 nm for 40 & 44), 293 K, dichloromethane. [b] ±0.1 ns, λ_{ex} = 400 nm, λ_{em} = 655-700 nm (600-650 nm for 40 & 44), 293 K.

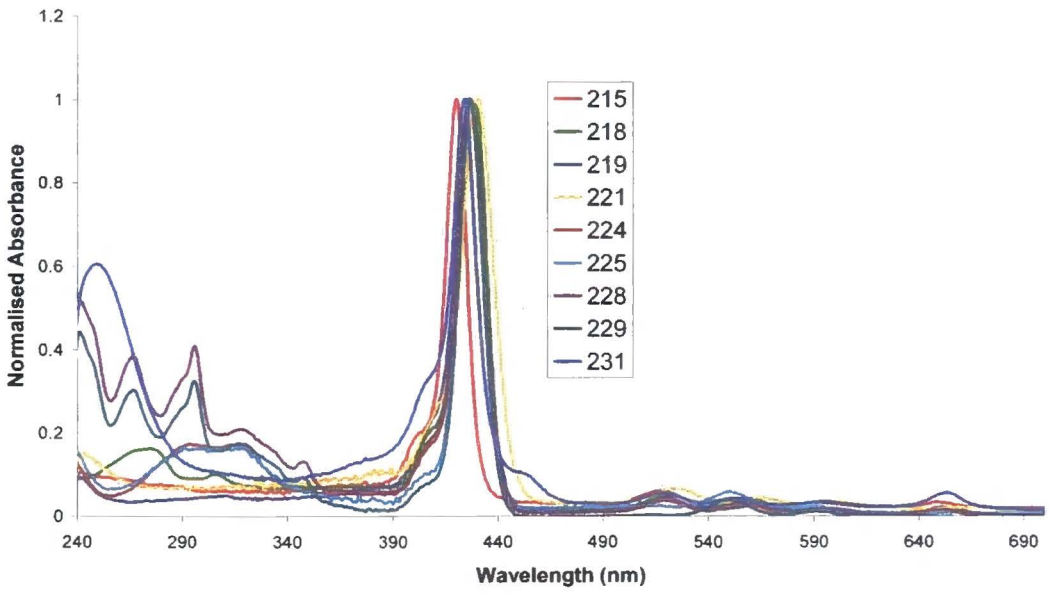


Fig 142: Normalised absorption spectra of porphyrins in DCM at 298K.

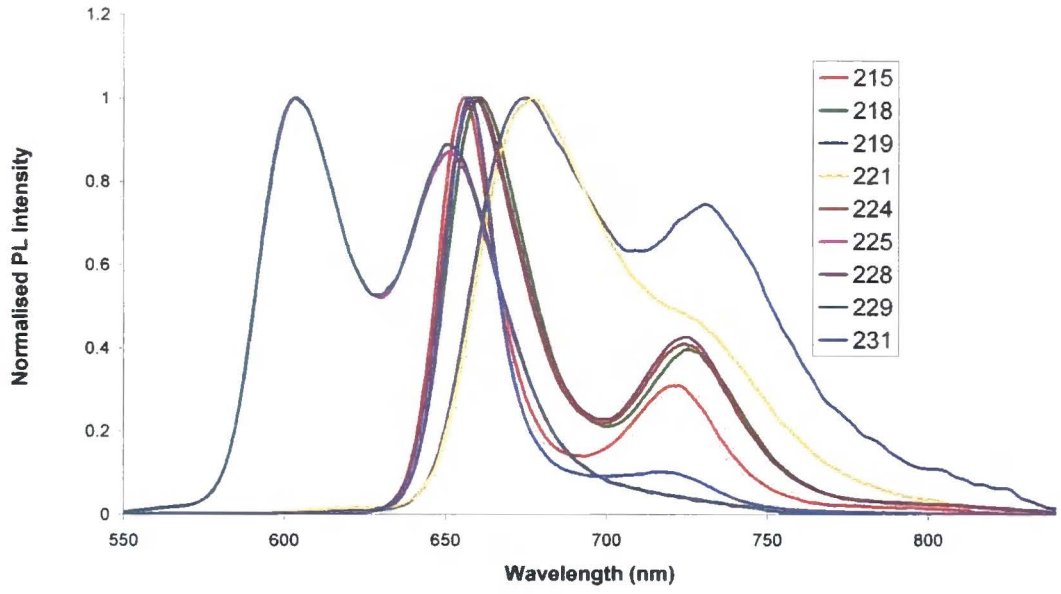


Fig 143: Normalised emission spectra of porphyrins in DCM at 298K.

All the free-base porphyrins studied display absorption and emission profiles characteristic of free-base tetraarylporphyrins.[417,418,421,428,434,435,646,668,669]

The value of 0.11 for the fluorescence quantum yield of **215** (synthesised as a reference compound) agrees well with the literature values of 0.11-0.13 for both 5,10,15,20-tetra-tolylporphyrin and 5,10,15,20-tetra-phenylporphyrin.[263,387,504,670] The observed value of 8.6 ns for the fluorescence lifetime is slightly lower than that of 9.40 ns in the literature; however our value was obtained in a different solvent mixture than that of the literature.[387,504]

The uniform fluorescence quantum yield (0.21) of compounds **218**, **224** and **228** is slightly higher than that of an analogous compound (5,10,15,20-tetra[9,9-dioctyl-9H-fluoren-2-yl]-porphyrin) in the literature,[416] obtained in a different solvent. In contrast the value of 0.23 obtained for compound **231** is greatly reduced compared to that of 5,10,15,20-tetra[3,5-di(4-*tert*-butylphenyl)benzyl]-porphyrin in the literature,[666] and this may be attributed to increased aggregation in the absence of the four bulky *tert*-butyl groups. As no lifetimes were given in the literature, there are no direct comparisons for compounds **218**, **224**, **228** and **231** but the obtained values do not differ significantly from those obtained for similar highly conjugated tetraarylporphyrins.[339,435,500,501]

Both the quantum yield and fluorescence lifetime, obtained for compound **219,** are in good agreement with recently published literature values of 0.013 and 1.11 ns.[430] In the case of compound **221**, the analogous compound, 5,10,15,20-tetra-(4-bromothien-2-yl)-porphyrin, displays similar values of 0.018 and 1.20 ns, respectively.[430] A poor fit was obtained for the raw data of compound **221** and a second component with a much longer lifetime (5.6 ns) was observed. A second component was also observed for 5,10,15,20-tetra-(4-bromothien-2-yl)-porphyrin, however its lifetime was much shorter than that of compound **221**.

The zinc-centred compounds, **225** and **229**, display a blue-shifted emission as well as greatly reduced fluorescence quantum yields and fluorescence lifetimes compared with the free-base porphyrins. These values are characteristic of zinc porphyrins in general,[671] and demonstrate the effective reduction of fluorescence from the porphyrin via inter-system crossing to the excited triplet state.

By comparing the observed values for compounds **218**, **224**, **225**, **228** and **229**, it appears that the highly mobile carbazole moieties in compounds **228** and **229** are unable to orient themselves in such a way as to quench the porphyrin fluorescence via intramolecular through-space transfer. In addition, increasing the conjugation of compound **218** with an additional phenyl spacer group has no appreciable effect on the fluorescence properties of the porphyrin core.

3.5 Summary

Our attempts to synthesise a silicon porphyrin derivative via a variety of methods were unsuccessful. The failure to replicate the work of Kane *et al.*[247] is possibly due to the instability of the target compound (silicon porphyrin dichloride) with respect to moisture and temperature. Further attempts to produce this compound would therefore require more stringent reaction conditions (possibly involving the use of a glove-box).

A series of free-base porphyrins bearing a variety of peripheral functional groups have been successfully synthesised. These compounds possess typical luminescence properties when compared with other porphyrins bearing similar aromatic substituents and show no evidence of aggregation effects in their fluorescence spectra. A number of porphyrins bearing four fluorenyl-based substituents were synthesised and it was shown that the variations between the luminescence properties of these compounds was small. Increasing either the number of fluorenyl groups per ligand or the flexibility of the fluorene groups within the ligands appeared to have very little effect upon the fluorescence of the porphyrin core.

Two zinc-centred porphyrin derivatives (**225** and **229**) were also prepared from the aforementioned fluorenyl-based systems and the emission from these compounds is significantly blue-shifted. The Φ_f and τ_f values are greatly reduced compared to their free-base precursors **224** and **228**, respectively, demonstrating the effective reduction of fluorescence from the porphyrin via inter-system crossing to the excited triplet state.

Chapter 4. Pyrazinoporphyrazines

4.1 Introduction

Selected pyrazinoporphyrazines were targeted for comparison with Pc and porphyrin derivatives synthesised in the previous chapters. The differences in the component atoms of the macrocycle relative to phthalocyanines and porphyrins may influence the interaction between the inner core and the peripheral aromatic units, resulting in changes to the overall fluorescent properties of the molecule.

4.2 Basic Strategy

The general route to these peripherally substituted pyrazinoporphyrazines began with the synthesis of either a diketone or an unsubstituted pyrazine, which was then reacted further to produce the desired bis-substituted pyrazine bearing carbonitrile moieties. The porphyrazine was then produced by a cyclisation reaction using a lithium reagent.

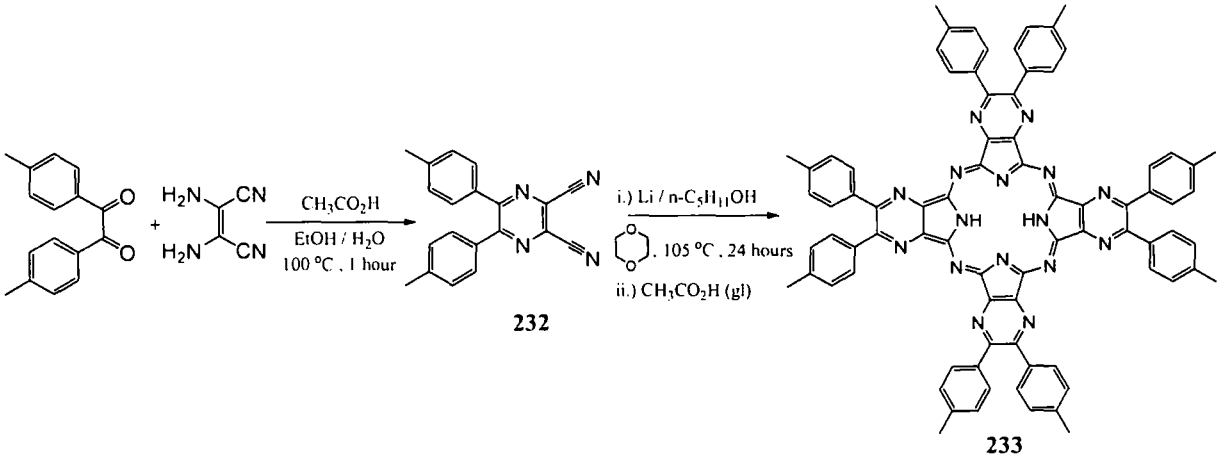
Synthesis of the silicon derivative was attempted by a variety of methods based on previous work within this field.[173,175] Metallation was attempted both during and after cyclisation but without success.

4.3 Discussion

4.3.1 Synthesis of 2,3,9,10,16,17,23,24-octakis-(*para*-tolyl)-29H,31H-tetrapyrazino-porphyrazine (233)

The choice of a tolyl-substituted derivative was motivated by our previous successful use of *para*-substituted aromatic substituents in reference compounds **187** and **215** (Chapters 2 and 3).

Our overall route to the novel compound **233** was based on the work of Wang *et al.* to produce a range of metal-centred and free-base pyrazinoporphyrazines bearing peripheral tetrathiafulvalene (TTF) units.[173] This route required the prior synthesis of 5,6-*para*-tolyl-pyrazine-2,3-dicarbonitrile (**232**) from the readily available precursors, 4,4-dimethylbenzil, and diaminomaleonitrile, previously carried out by Popp.[672] The initial reaction gave a considerably higher yield of **232** than that published (77% *cf.* 50%). Scaling up the reaction gave yields of ~80% and a product which required a much greater amount of drying under vacuum to remove remaining solvent. Only the melting point and elemental analysis of **232** had been previously reported and so **232** was additionally characterised by NMR and mass spectrometry.



232 233

Fig 144: Synthesis of compounds **232** and **233**.

Cyclisation of **232** to form the porphyrazine (**233**) was achieved by reaction with lithium pentoxide, produced by direct reaction of lithium metal with a solution of 1-pentanol. The active lithium species was freshly prepared for each reaction although samples had a usable shelf-life of 1-2 weeks (storage at 0-4 °C). As with the literature

materials,[173] the dark green product obtained by precipitation in ethanol could not be purified via column chromatography. Purification was achieved by filtration of the crude material through a short celite column to remove any inorganic impurities. No unreacted pyrazine was observed in the fractions collected.

Identification of the product via ^{1}H-NMR and ^{13}C-NMR analysis was not possible due to line-broadening, presumably caused by aggregation of the planar compound in solution. This was not a problem with the porphyrin analogue (**215**) suggesting that the pyrazine rings of **233** favour aggregation. However, the mass spectrum and elemental analysis were entirely consistent with a unimolecular structure for **233**. The yield of the reaction was optimised at 14%, which is somewhat lower than for other octa-substituted pyrazinoporphyrazines of a similar size.[188,673-675] The fluorescence properties of this compound are discussed in a later section of this chapter.

4.3.2 Attempted synthesis of 2,3,9,10,16,17,23,24-octakis-(*para*-tolyl)-29H,31H-tetrapyrazino-porphyrazino-silicon dichloride

Synthesis of the silicon-centred derivative of compound **233** was first attempted based upon the previous incorporation of zinc(II) and copper(II) atoms into the cores of TTF-substituted pyrazinoporphyrazines by Wang *et al*[173] via reaction of an equimolar amount of silicon tetrachloride with the lithiated derivative of **233** in chloroform.

A highly insoluble black solid was obtained which could not be purified by column chromatography. The MALDI-ToF spectrum showed the parent ion for the free-base compound as well as a number of higher weight peaks which did not correspond to the desired product. In addition, the elemental analysis was inconclusive and showed the material to be gaining weight. The reaction was rerun using a four-fold molar excess of silicon tetrachloride to give another black highly insoluble solid. The MALDI-ToF spectra of this compound showed only the free-base derivative and this was confirmed by the elemental analysis. It is therefore likely that metallation by this insertion method is unsuccessful.

An alternative route to the target compound involved incorporating the silicon reagent into the cyclisation reaction, based on the production of a peripherally

unsubstituted silicon pyrazinoporphyrazine by Kudrevich *et al.*[175] Reaction of compound **232** with silicon tetrachloride in the presence of urea, using a mixture of quinoline and tributylamine as solvent gave a dirty grey solid which was completely insoluble in common organic solvents. In contrast to the silicon derivatives characterised in the literature procedure, there was no Si-Cl band at ~480 cm^{-1} in the IR spectrum.[175] Reaction of this crude material with a number of aromatic carboxylic acids, in an attempt to effect axial substitution, was unsuccessful. The same insoluble material was obtained from other attempted reactions and we therefore turned to peripheral substitution of the free-base pyrazinoporphyrazine.

4.3.3 Attempted Synthesis of 2,3,9,10,16,17,23,24-octakis-(thien-2-yl)-29H,31H-tetra-pyrazinoporphyrazine (237)

Thiophene-2-carboxaldehyde was the starting material from which the diketone derivative **235** was obtained by a Benzoin self-condensation, followed by oxidation of the hydroxy-ethanone intermediate (**234**). Several examples of this reaction already exist in the literature[676-681] and we chose to follow the precedent of Lee *et al.*, using 3-benzyl-5-(hydroxyethyl)-4-methylthiazolium chloride as the catalyst.[677] The reaction produced an oily mixture of two products. In our hands, the respective yields of 2-hydroxy-1,2-dithien-2-yl-ethanone (**234**) and 1,2-dithien-2-yl-ethane-1,2-dione (**235**) (55% and 6%) were strikingly different to those in the literature (20% and 55%). The conversion of the intermediate species (**234**) to **235** was achieved via the method of Lukeš *et al.*,[676] by oxidation using bismuth oxide in 95% yield. Full analysis of both yellow solids (**234** and **235**) was consistent with that in the literature.[676]

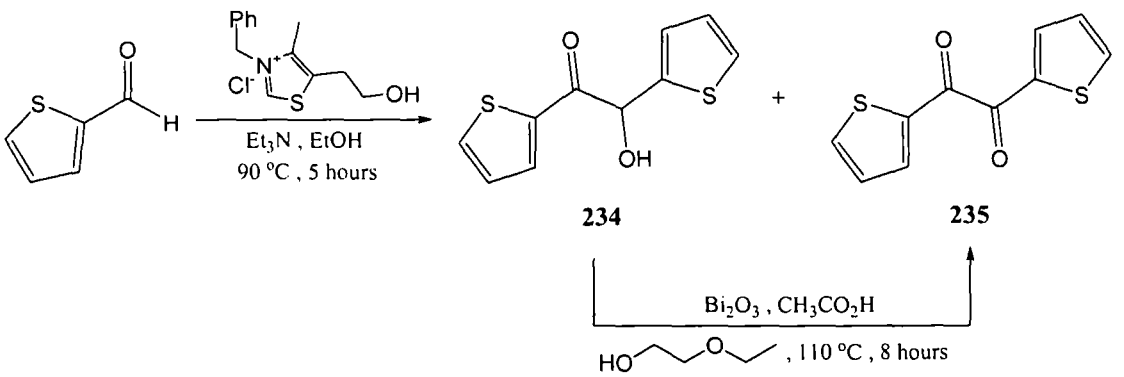
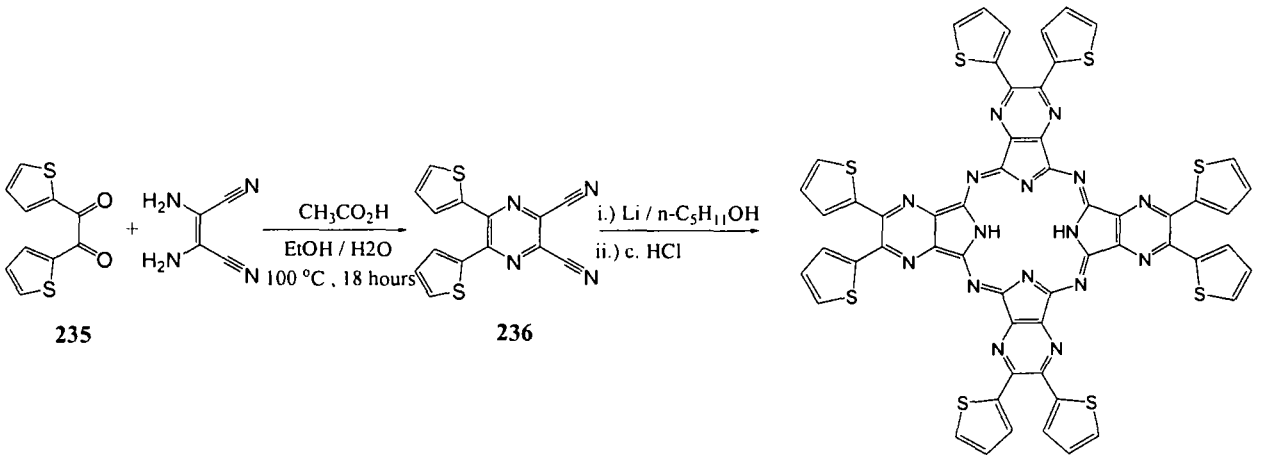


Fig 145: Synthesis of compounds **234** and **235**.

The formation of 5,6-dithien-2-yl-pyrazine-2,3-dicarbonitrile (**236**) via the acid-catalysed cyclisation of **235** and diaminomaleonitrile has been previously published by Mørkved *et al.*[682] and we modified this reaction by the addition of a mixture of ethanol and water, based on the previous synthesis of **47**.[672] This procedure led to **236** precipitating directly from the reaction solution in 82% yield. Analysis of the compound was consistent with that in the literature (see chapter 4).



235 **236** **237**
(Speculative structure)

Fig 146: Synthesis of compounds **236** and **237**.

The free-base pyrazinoporphyrazine derivative has supposedly been synthesised previously from the pyrazine precursor (**236**),[190] although no details of the reaction method or characterisation data were reported. A metal-centred derivative of the compound, containing magnesium, has also been synthesised by Mørkved *et al.* by using magnesium propoxide, generated *in situ*.[682] Taking this method into account, we attempted to synthesise the free-base macrocycle using the analogous lithium pentoxide route already utilised to produce **48**. We found that the use of an additional solvent (1,4-dioxane) resulted in an unwanted reaction producing a red solution, which showed no evidence of the macrocyclic product. Therefore, the lithium pentoxide was produced *in situ*. Again a red colouration was seen; however acidification of the solution and dilution with methanol yielded a small amount of dark blue solid (**237**). This insoluble blue material could not be characterised and further work with this material was not undertaken.

4.3.4 Attempted synthesis of 2,3,9,10,16,17,23,24-octakis(9,9-dihexyl-9H-fluoren-2-yl)-29H,31H-tetrapyrazinoporphyrazine

As with the previous work with both phthalocyanines and porphyrins, the attachment of electron-rich fluorene units to the periphery of the pyrazinoporphyrazine unit was attractive as a method for increasing the fluorescence of the macrocyclic core. The synthesis of 9,9-dihexyl-9H-fluorene-2-carbaldehyde (**217**) from its bromide precursor has been discussed in Chapter 3 (see section 3.3.3) and we attempted to produce 1,2-bis-(9,9-dihexyl-9H-fluoren-2-yl)-ethane-1,2-dione via the Benzoin self-condensation of **217**.

The conditions were identical to those previously employed for the successful synthesis of compounds **234** and **235** [namely the use of 3-benzyl-5-(hydroxyethyl)-4-methylthiazolium chloride as a catalyst in a mixture of triethylamine and ethanol]. No evidence of reaction was observed, despite changing the catalyst to potassium cyanide and employing stronger bases such as sodium hydride. The fact that no reaction with the solvent was observed in this case suggests that the aldehyde group of **217** is unreactive to chemistry of this type. We therefore decided to synthesise a 1,2-dihalogenated pyrazine with the aim of then attaching the fluorene units via Suzuki coupling methodology.

Our first target was 2,3-dibromo-5,6-dicyanopyrazine, which to our knowledge is not known in the literature. For its synthesis we followed the preparation of the dichloride analogue[683,684] (see Fig 147).

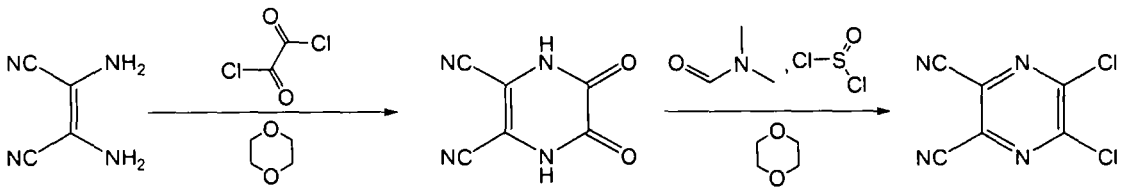
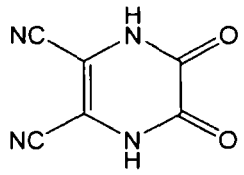
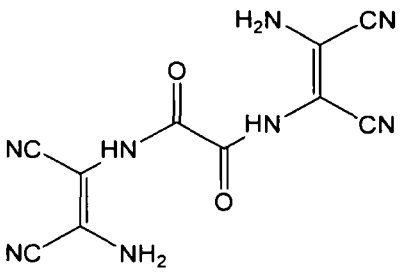


Fig 147: literature route to 2,3-dichloro-5,6-dicyanopyrazine.[684]

We repeated the literature procedure to produce 5,6-dicyano-2,3-dioxo-1,2,3,4-tetrahydropyrazine using oxalyl chloride. In our hands, a procedure identical to that used by Suzuki *et al.*,[684] employing an equimolar ratio of reagents, produced a brown insoluble material which appeared to contain amine units, from the ^{1}H-NMR spectrum. It is likely that this unwanted product is *N,N'*-bis[(Z)-3-amino(dinitrilo)but-2-en-2-yl]oxamide (see Fig 148), as reported by Mørkved *et al.* when they attempted to repeat the same procedure.[683]



5,6-Dicyano-2,3-dioxo-1,2,3,4-tetrahydropyrazine



N,N'-Bis-([(Z)-3-amino(dinitrilo)but-2-en-2-yl]oxamide

Fig 148: Possible products from the reaction of oxalyl chloride with diaminomaleonitrile

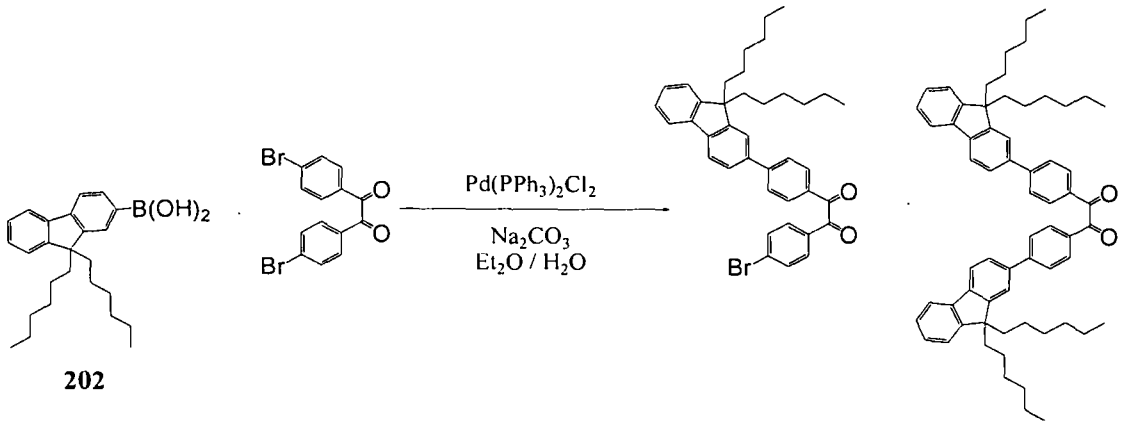
We therefore altered the conditions of our reaction to match that successfully performed by Mørkved *et al.* However, we found that work-up of the crude material, obtained from a number of reactions, consistently gave the desired product along with *N,N'*-bis[(Z)-3-amino(dinitrilo)but-2-en-2-yl]oxamide in a *ca.* 4:1 molar ratio. As this crude material was only soluble in water, purification by column chromatography was not possible and attempted recrystallization from water had no effect on the purity of the material. Reaction of the impure mixture with thionyl bromide in a procedure analogous to that in the literature produced a yellow solid. Purification of this material yielded several fractions, none of which showed any evidence of cyanide groups in the ^{13}C-NMR spectra. It is therefore possible that thionyl bromide is not a suitable reagent for the reaction. The synthesis and further use of 5,6-dichloro-pyrazine-2,3-dicarbonitrile was not undertaken due to time constraints.

4.3.5 Synthesis of 2,3,9,10,16,17,23,24-octakis[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-29H,31H-tetrapyrazinoporphyrazine (240)

Following the failure to synthesise a pyrazine derivative bearing directly-bonded fluorene units, we utilised an alternative strategy to obtain a fluorene-pyrazine hybrid. Dibromobenzil is a commercial material and we attempted to synthesise 1,2-bis[4-(9,9-dihexyl-9H-fluoren-2-yl)-phenyl]-ethane-1-2-dione via a Suzuki coupling with 9,9-dihexyl-9H-fluorene-2-boronic acid (**202**).

Dibromobenzil and **202** were reacted in a 1:2 molar ratio, using $Pd(PPh_3)_2Cl_2$ as catalyst in a mixture of diethyl ether and water. TLC analysis of the crude yellow

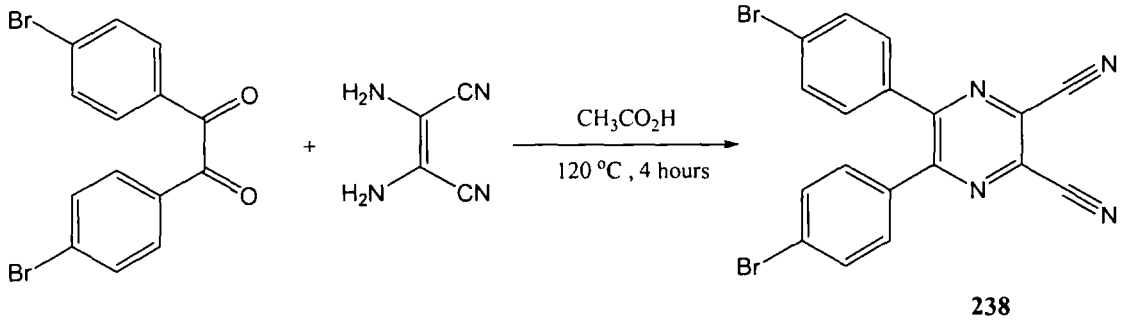
product revealed two spots with almost no separation in all solvent combinations. Efforts to separate these two compounds via column chromatography, preparatory TLC and recrystallization were all unsuccessful. It is likely that the two compounds are both 1,2-diketones with similar polarity (see Fig 149).



202

Fig 149: Reaction scheme for two-fold Suzuki coupling of **202** and dibromobenzil.

The synthesis of 5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile (**238**) was achieved by a modification of the literature method.[685] Dibromobenzil was reacted with an excess of diaminomaleonitrile in acidic conditions to yield the product in 77% yield after purification by column chromatography.



238

Fig 150: Synthesis of compound **238**.

The phenyl carbon atoms appeared as a single peak in the ^{13}C-NMR spectrum. An X-ray crystal analysis confirmed the structure of **238** (see Figs 151 and 152).

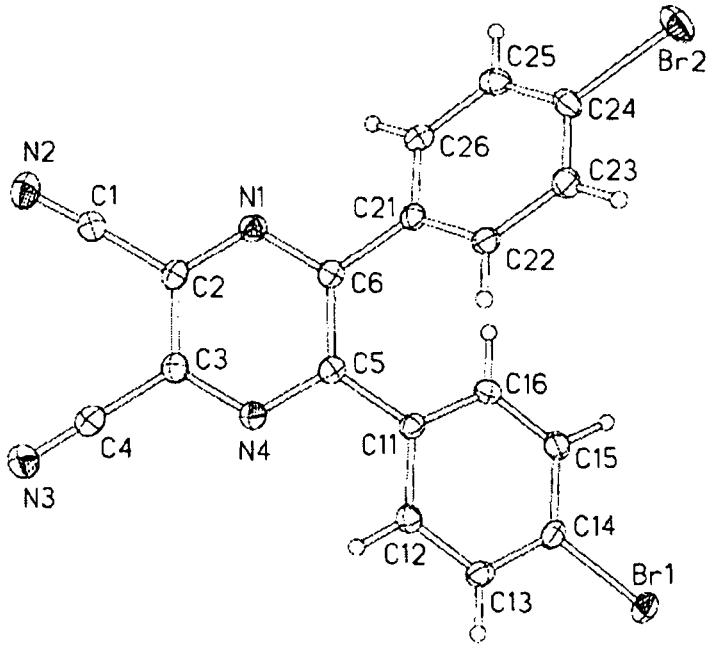


Fig 151: Labelled scheme for the crystal structure of **238**.

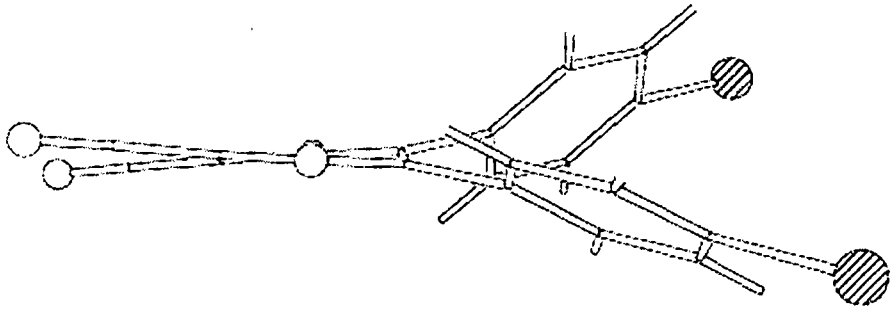


Fig 152: Side-on view of crystal of **238**.

A molecular modelling of **238** using Hyperchem 6.0 gave a torsional angle of 13.15°, which was in good agreement with the crystal structure obtained. This model was therefore used as the basis for the modelling of **239** (see Fig 155).

The use of $Pd(PPh_3)_2Cl_2$ as a catalyst in the subsequent Suzuki coupling of **238** with **202** gave a multitude of products which were difficult to isolate. However, $Pd(PPh_3)_4$ resulted in the desired product (**239**) being produced in a much higher yield. The crude material obtained from the reaction was a bright yellow two-component mixture colour with a high degree of fluorescence. Purification by column chromatography (eluent 50% DCM in hexane) separated the two major products from

the other minor products, and the mono-substituted impurity and the di-substituted product (**239**) were then isolated from one another by a second column.

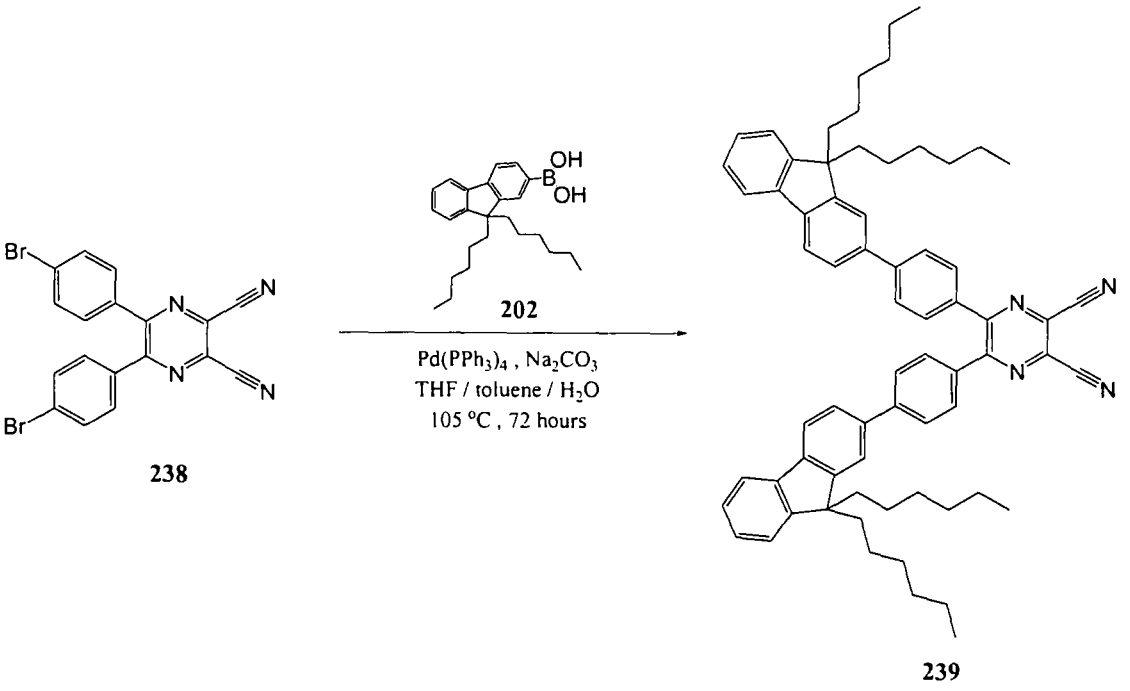


Fig 153: Synthesis of compound **239**.

The NMR spectra of **239** were highly complex and the assignment of individual aromatic peaks in both the ^{1}H-NMR and ^{13}C-NMR spectra was not possible. The compound showed good stability in solution: the MALDI-ToF mass spectrum containing only the parent ion peak (*m/z* 946.5).

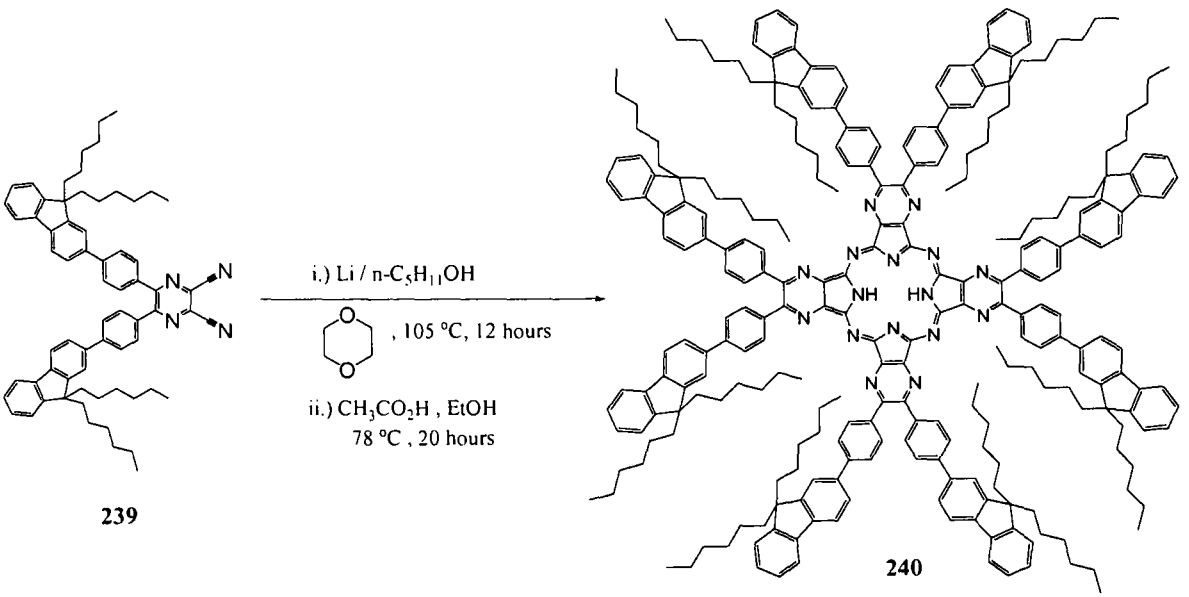


Fig 154: Synthesis of compound **240**.

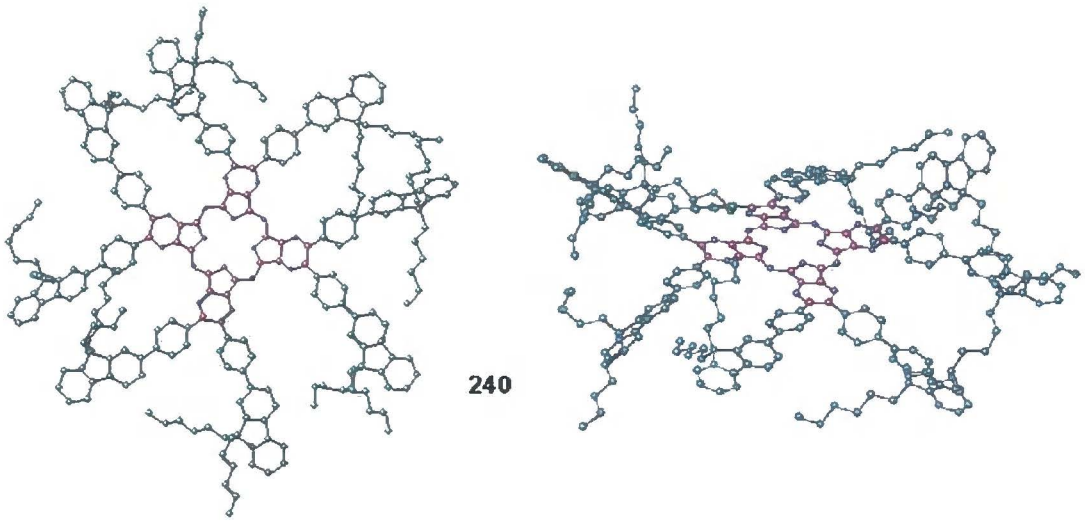


Fig 155: Minimum energy conformation of **240**, modelled using Hyperchem 6.0 (MM+ molecular mechanics calculation) with pyrazinoporphyrazine core highlighted in red and blue.

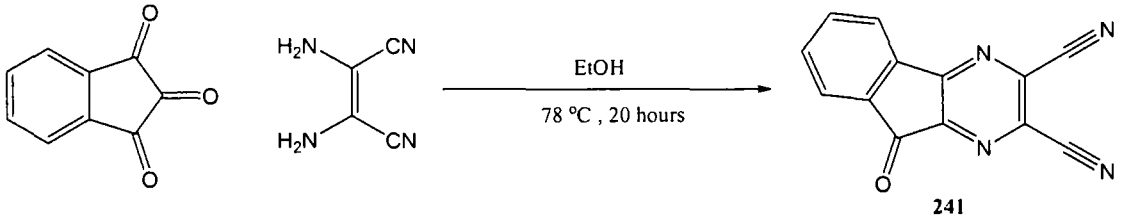
Cyclisation of **239** to form the corresponding pyrazinoporphyrazine (**240**) was based on a literature route to analogous compounds of a similar size containing TTF units.[173] The crude material contained several minor impurities, which were removed by flash chromatography. As with the pyrazine precursor, the macrocycle showed good stability in solution, demonstrated by the lack of fragmentation in the MALDI-ToF mass spectrum. As with the other pyrazinoporphyrazines synthesised, NMR analysis of the compound provided limited information, the peripheral aromatic groups producing only broad unresolved peaks in the ^{1}H-NMR spectra (although the quality was considerably better than that for compounds **233** and **237**). This was disappointing as it was initially hoped that the presence of numerous hexyl chains on the periphery of the macrocycle would hinder aggregation of the compound and hence decrease line broadening in the ^{1}H–NMR spectrum sufficiently to resolve all peaks. Structural assignment was therefore based on mass spectrometry and elemental analysis. The fluorescence properties of **240** are discussed in a later section of this chapter.

4.3.7 Attempted synthesis of Tetra(5-oxo-2,3-pyrazino-[2,3-b]indeno)-porphyrazine

The formation of indenopyrazine derivatives from diaminomaleonitrile and indano-ketone derivatives provides an alternative method for extending the conjugation of a pyrazinoporphyrazine using fused ring systems. In theory, macrocycles of this type would have increased fluorescence properties and increased stability relative to the peripherally octa-substituted pyrazinoporphyrazines already synthesised.

Ninhydrin was chosen as a starting reagent for reaction with diaminomaleonitrile based upon its availability. Ideally we would have liked to use indan-1,2-dione, however this compound is not readily available and would require several synthetic steps.[686,687] The much easier alternative was to synthesise 9-oxo-9H-indeno[2,1-b]pyrazine-2,3-dicarbonitrile (**241**) using ninhydrin and then to attempt reduction of the compound to its deoxygenated form.

Our synthesis of **241** was based upon a simplification of the literature method.[688] In contrast to the literature, we found that reaction of equimolar quantities of ninhydrin and diaminomaleonitrile in refluxing ethanol gave a pure product after cooling of the solution and addition of water to form a precipitate. Therefore recrystallization of the material was not necessary.



241

Fig 156: Synthesis of compound **241**.

Analysis of **241** was consistent with that in the literature, though the obtained melting point was slightly higher then previously recorded. In addition to the literature data, we also obtained NMR data for the compound. The ^{1}H-NMR spectrum of **241** shows little effect on the phenyl hydrogens by the cyclisation reaction. The ^{13}C-NMR spectrum contained a single strong signal for the cyanide groups and individual peaks for all other carbon atoms.

We attempted reduction of **241** by a variety of methods, the main problem being the instability of the cyanide groups to harsh reaction conditions. The use of a modified Wolff-Kishner reaction based on the reduction of fluorenone and similar hetarenoindanones by Kashulin *et al*[689] was unsuccessful. The product failed to precipitate in the work-up and an attempted layer separation gave an organic phase which contained only hydrazine and minor impurities. A similar reaction utilising ethylene glycol as a solvent with an acidic catalyst was also unsuccessful.[690] The NMR analysis confirmed removal of the carbonyl group, however the cyanide groups also appeared to be removed during the reaction.

Conversion to the porphyrazine macrocycle was therefore attempted using **241**. Cyclisation via the usual route of a lithium pentoxide reagent was unsuccessful, the porphyrazine not being formed. One other example of an indoloporphyrazine exists in the literature, and a second attempt to make the porphyrazine was based on this route.[199] 1,8-Diazabicyclo[5.4.0]undec-7-ene was used as a catalyst and the reaction was refluxed in ethanol for 20 hours. The solvent was removed *in vacuo* and the residue redissolved in DCM and water. The layers were separated and the organic layer dried over anhydrous magnesium sulphate before being evaporated to dryness. The crude material was purified via column chromatography (eluent 10% methanol in DCM) giving three fractions. The MALDI-ToF mass spectra of these fractions showed no evidence of porphyrazine formation and the synthesis of the macrocycle was therefore abandoned.

4.4 Fluorescence Properties of Synthesised Pyrazinoporphyrazines

4.4.1 Introduction

The fluorescent properties of pyrazinoporphyrazines are almost identical to that of phthalocyanines, displaying two sharp intense peaks in the UV-visible absorption spectra between 650-700 nm, denoted as the 'Q bands', Q_x and Q_y. As with the Pcs, incorporation of a metal ion into the macrocyclic core results in a single Q band peak due to a change in the molecular symmetry. A second much broader peak is present in both types of pyrazinoporphyrazines species, typically between 300 - 400 nm, and this is denoted the 'B band' or 'Soret band'. As with Pcs, aggregation in solution is often a common problem and the use of bulky peripheral substituents can reduce the quenching. (For further details see section 2.4).

In contrast to the Pcs however, very little fluorescence data is available for pyrazinoporphyrazines,[200] reflecting the fact that these macrocycles are often much more sparingly soluble compared to their Pc analogues.

4.4.2 Results and Discussion

The photophysical data for all pyrazinoporphyrazine compounds successfully prepared are collated in Table 5.

Table 5: Spectroscopic Data for the Pyrazinoporphyrazine compounds.

Compound	λ_{max}(abs)/nm	λ_{max}(em)/nm	Φ_f[a]	τ_{f1}/ns[b]	τ_{f2}/ns[b]
233	669	676.5	0.22	7.0 (75%)	3.6 (25%)
240	681 (654)	684	0.019	4.0 (60%)	1.5(40%)

[a] ±10%, λ_{ex} = 615 nm, λ_{em} = 630-850 nm, 293 K, dichloromethane.

[b] ±0.1 ns, λ_{ex} = 635 nm, λ_{em} = 685 nm, 293 K.

Both compounds display absorption and emission maxima typical of octa-aryl substituted pyrazinoporphyrazines,[177,673,674] as well as small Stokes shifts indicating very little molecular rearrangement in the excited state. Compound **240** was also

strongly absorbing in the region 300-400 nm, corresponding to the peripheral fluorenyl-substituents. Several excitation spectra were run at varying emission wavelengths (see Fig 157), confirming that the majority of energy is absorbed by the peripheral substituents and then transferred to the macrocyclic core.

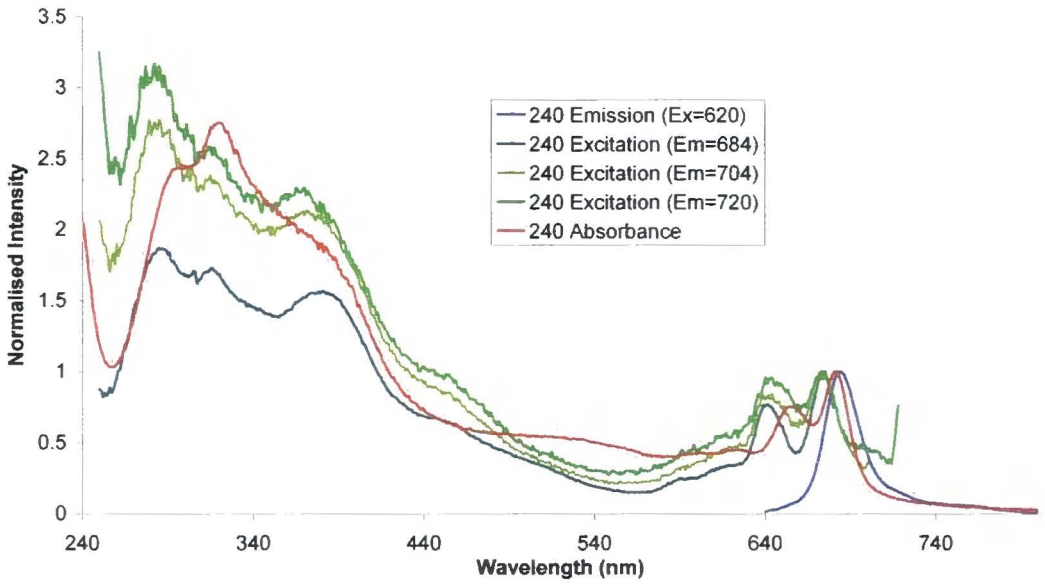


Fig 157: Excitation spectra of **240** in DCM at 298K.

The quantum yields are extremely low, compared with peripherally-substituted free-base Pcs.[140] The only available values for pyrazinoporphyrazine fluorescence quantum yields and lifetimes in the literature are for magnesium and zinc-centred derivatives.[200]

Both compounds **233** and **240** displayed a large secondary component to the fluorescence lifetime, which may be the result of some form of electron transfer within the molecule. No additional peaks were visible in the emission spectra of either compound, though the possibility of some minor aggregation cannot be ruled out. After running an absorption spectrum, a DCM solution of **55** was left in direct sunlight for several days before rerunning the absorption spectrum (see Fig 158), however no appreciable change in the spectrum (which might have indicated compound breakdown) was observed. In addition, a MALDI-ToF analysis of this solution also showed no evidence of compound breakdown, displaying a single peak due to the $[M]^+$ ion.

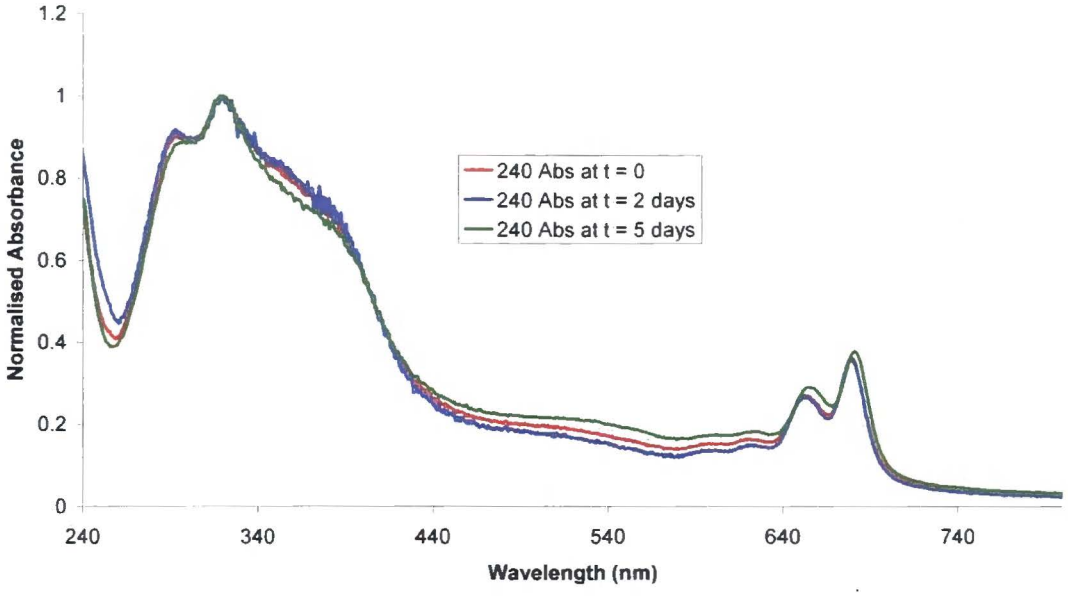


Fig 158: Absorption spectra of **24** **0** over several days in DCM at 298K.

4.5 Summary

As with our work with the porphyrins, all attempts to produce a silicon pyrazinoporphyrazine derivative proved unsuccessful, resulting in a highly insoluble solid which could not be adequately characterised.

Although the synthesis of several free-base pyrazinoporphyrazines was attempted using a variety of methods, only two compounds were successfully prepared. Both compounds displayed a much lesser degree of fluorescence then the associated phthalocyanine and porphyrin compounds, and this is typical of macrocycles of this type. Compound **240**, bearing eight peripheral fluorene-based substituents showed intense absorption at wavelengths corresponding to absorption by the fluorene moieties and it was shown that efficient energy transfer occurs from the peripheral groups to the macrocyclic core, with the majority of emission coming from the porphyrazine centre.

Both the synthesised compounds showed a second component in their fluorescence lifetimes, and the source of this is currently unknown. Further work is required in order to obtain a complete picture of the electron transfer processes occurring within these molecules.

Chapter 5. Experimental

5.1 General Procedures

All reagents and solvents were of commercial quality and where necessary, were dried using a Pure-Solv 400 Solvent Purification System. Unless otherwise stated, reactions were performed under an inert atmosphere of argon dried via passage through a column of phosphorus pentoxide. Commercial chemicals were purchased from Aldrich and Lancaster chemical supplies and used without any further purification. NMR solvents were purchased from GOSS Scientific and used without any further purification. Column chromatography was carried out using Fluorochem silica gel (70-230 mesh). Analytical Thin Layer Chromatography (TLC) was performed on Merck DC-Alufolien Silica gel, 60 F_{254} 0.2 mm thickness or Merck DC-Alufolien Aluminium Oxide neutral (Type E), 60 F_{254} 0.2 mm thickness precoated TLC plates. Solvents for chromatography were used as supplied. All glassware was pre-dried before use.

5.2 Instrumentation

^{1}H-NMR spectra were obtained on a Varian Mercury 200, a Varian Unity 300 or a Varian VXR400S spectrometer operating at 200, 300 or 400 MHz respectively. ^{13}C-NMR spectra were obtained on either a Varian VXR400S or a Varian Inova 500 spectrometer operating at 100 and 125 MHz respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the high frequency positive convention, and J values are given in Hz. $CDCl_3$ and DMSO-d_6 were used as NMR solvents. The abbreviations s, bs, d, t, q and m are used in listing NMR spectra, denoting singlet, broad singlet, doublet, triplet, quartet and multiplet, respectively.

Electron Impact (EI) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70eV with the ionisation mode as indicated. Electrospray (ES) mass spectra were recorded on a Micromass LCT spectrometer using

electrospray ionisation. MALDI mass spectra were recorded on an Applied Biosystems Voyager-DE STR BioSpectrometry Workstation, using dithranol as a matrix unless otherwise stated. A few of the mass spectra were obtained via the EPSRC National Mass Spectrometry Service, University of Wales, Swansea, using the following instruments: Applied Biosystems Voyager-DE-STR (for MALDI-TOF) and Finnigan MAT 900 XLT (for HRMS).

IR spectra were obtained either in nujol, mounted between NaCl disks or dissolved in the stated solvents. In all cases, either a Perkin Elmer 1600 FTIR spectrometer, operated from a Grams Analyst 1600, or a Perkin-Elmer Spectrum 100 FT-IR Spectrometer (connected to a PC running Windows XP) were used. In the case of the Spectrum 100, all spectra were processed using the accompanying Spectrum program, version 6.0.2.

Melting Points were determined in open-end capillaries using a Stuart Scientific SMP3 apparatus at a ramping increment of 1.5 °C/min without calibration.

CHN microanalyses were obtained using an Exeter Analytical CE-440 elemental analyser.

Cyclic voltammetry data were recorded using either a BAS CV50 electrochemical analyser with internal resistance compensation or a Princeton Applied Research VMP four-channel potentiostat.

In the case of the CV50, experiments were performed in a one-compartment cell with a platinum disc working electrode, a platinum counter electrode and an aqueous $Ag/AgNO_3$ electrode as reference. The experiments were carried out using a solution of the active species in an anhydrous and degassed 0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane or acetonitrile.

The Princeton Applied Research VMP multichannel potentiostat was connected to a standard PC running Windows XP and the latest version of the potentiostat software. For the phthalocyanine measurements, a BAS MF-2013 platinum working electrode with a 1.6mm diameter active surface was used. For the probe measurements, two BAS MF-2012 glassy carbon working electrodes with 2.0mm active working surfaces were used, one coated with film and the other left bare. The

other electrodes in the electrochemical cell were a standard Ag/AgCl aqueous reference electrode. and a counter electrode prepared by the departmental glassblowers consisting of a $0.5cm^2$ square of Pt connected to a conducting wire. The cell contents were stirred using a conventional magnetic stirrer bead. All experimental solutions were originally prepared with a 1×10^{-3} M solution of the probe molecules dissolved in distilled water – when the concentration of probe was found to be insufficient to give a strong distinctive signal, as with the $Fe(di\text{-}SO_3\text{-}batho\text{-}phen)_3^{4-}$, then the concentration was increased to 5×10^{-3} M. All chemicals except the phthalocyanine derivatives were sourced from Sigma-Aldrich. The phthalocyanine thin-films were prepared using 5×10^{-3} M concentrations of the phthalocyanine derivative dissolved in chloroform deposited on the electrode surface and allowed to evaporate in a solvent-rich environment.

Kinetic parameters were evaluated using Digielch, a free program for the simulation and curve-fitting of cyclic voltammograms, created by Manfred Rudolph of the Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena in Germany (www.digielch.de).

Atomic Force Microscopy (AFM) studies were conducted on a Digital Instruments Multimode SPM, managed by a Nanoscope IV controller. Experiments were carried out using the instrument's Tapping Mode, on phthalocyanine-coated SPI-2 grade HOPG substrates, sourced from SPI Supplies (www.2spi.com). Data for both conventional topography and phase mapping to determine surface elasticity was collected.

The films were prepared using chloroform as the solvent, due to its relatively high volatility and the phthalocyanine derivatives high solubility in chloroform. The phthalocyanine derivatives were made up in 1×10^{-5} M and 1×10^{-3} M concentrations, in order to investigate the optimal concentration for the thin films. The substrates were cleaned beforehand using acetone and purified water, before being left in an oven at 80 °C for 30 minutes. Using a Gilson micropipette, 5 μL of a derivative solution was taken and deposited on the substrate. The substrate was then either left in a stoppered test-tube filled with a small quantity of chloroform or immediately spin-evaporated. The samples left to naturally evaporate were stored for several hours or overnight in the tube.

The Kelvin probe instrument in use at Durham is a prototype instrument developed by Professor Michael Thompson and his research group at the University of Toronto. This instrument has unprecedented sensitivity and precision for a Kelvin probe, being able to measure lateral features of less then 100nm and vertical structures of less then 1nm. This is made possible by the probe tip, constructed of tungsten and with a diameter of less then 50nm.

The films used were prepared in a method identical to that for the AFM experiments detailed above. Samples to be scanned were mounted on a piezoelectrically-controlled table capable of moving in three dimensions. The table was kept at a constant potential (usually 2V), and this potential must be communicated to the sample, either through direct contact, or, if the sample is mounted on an insulating surface, by means of a conducting clamp.

The tip is moved close to the substrate by manual control until a Kelvin current is found by means of a virtual oscilloscope. The control is then given over to the computer, which moves the piezoelectric table closer to the tip in tiny increments, until the contact potential difference is between two manually set bounds. The probe then commences scanning, waiting until it finds an average CPD value at each point. This means that in variable or difficult to scan surfaces, the scan time can be very long, from 20-30 minutes for a 200-point scan to a full day for a detailed 5000-point scan.

Fluorescence spectra were recorded with a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. The spectra of dilute solutions, with an absorbance of <0.1 in the range 190-900 nm, were recorded by using conventional 90° geometry, and a front-face geometry was used to study highly absorbing solutions. Both the excitation and emission spectra were fully corrected by using the manufacturers' correction curves for the spectral response of the excitation and emission optical components. A spectral band-pass of 2.5 nm was used for both the excitation and emission monochromators.

The technique of time-correlated single-photon counting[592,691] was used to record fluorescence lifetimes of the macrocycles. All the solutions under study were prepared with a concentration which gave a maximum absorbance at the Q-band absorption of not greater than 0.05 in order to eliminate the effects of re-absorption. The excitation source consisted of a pulsed 635 nm diode laser (IBH NanoLED

Model-02) providing output pulses of 200 ps at a repetition rate of 1 MHz. The fluorescence emission was collected at 90° to the excitation source, and the emission wavelength was selected using a monochromator (Jobin Yvon Triax 190). The fluorescence was detected using a photomultiplier tube (IBH Model TBX-04) linked to a time-to-amplitude converter (Ortec 567) and a multi-channel analyzer (E.G. & G. Trump Card and Maestro for Windows v. 5.10). The instrument response function (IRF) of the apparatus was measured using a dilute suspension of milk powder in water as a scattering medium, giving an IRF with duration of 450 ps full width at half maximum. All fluorescence decays were recorded to a minimum of 10,000 counts in the peak channel of the pulse height analyzer. The data were transferred to the computer and analyzed using the standard method of iterative re-convolution and nonlinear least squares fitting in a Microsoft Excel spreadsheet. The quality of the calculated fits was judged using statistical parameters, including the DurbinWatson parameter, reduced x2, random residuals and autocorrelated residuals.

Quantum yields were determined by the comparative method of Williams *et al.*,[692] measurements being taken using several dilutions of each sample to negate concentration effects. Disulfonated aluminium Pc (Φ_f = 0.4) and *meso*-tetraphenylporphyrin (Φ_f = 0.11 in toluene / 0.07 in DCM)[263] were used as standards.

Molecular modelling for compounds **4**, **198**, **199**, **200**, **206** and **240** was carried out using the Hyperchem molecular modelling package (version 6.0). Calculations for compounds **4**, **198**, **199**, **200** and **206** were run using the AM1 semi-empirical method with a convergence limit of 0.001 and the convergence criterion of the geometry optimisations was 0.01 kcal/(Å mol). Calculations for compound **240** were run using the MM+ molecular mechanics method. In all cases, the macrocyclic core was first minimized using the Polak-Ribiere gradient optmizer with an RMS gradient of 0.001. The peripheral or axial substituents were then added and the molecule again energy minimized using the same method, with between 1000 and 10000 cycles, depending on the size of the molecule. In the case of peripheral dihexl-fluorenyl substituents, manual rotation of these units was necessary in order to achieve a minimum energy conformation for some compounds.

5.3 Synthesis

Phenyl silicon phthalocyanine chloride (36).

1,3-Diiminoisoindoline (10 g, 68.9 mmol) and phenyltrichlorosilane (17.5 cm^3, 109 mmol) were stirred in a mixture of tetrahydronaphthalene (175 cm^3) and tributylamine (75 cm^3) at 215 °C for 20 h. The resultant mixture was allowed to cool and then methanol (100 cm^3) was added. Filtration of the precipitate followed by copious washing with methanol and diethylether gave **36** as a purple solid (6.1 g, 54%) after recrystallisation from toluene: mp >400 °C. (Found: C, 69.90; H, 3.25; N, 17.16%; $C_{38}H_{21}N_8ClSi$ requires C, 69.88; H, 3.24; N, 17.16%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 1.56 (2H, d, ^3J = 7.8 Hz, *o*-Ph**H**), 5.13 (2H, dd, ^3J = 7.5 Hz, *m*-Ph**H**), 5.53 (1H, t, ^3J = 6.6 Hz, *p*-Ph**H**), 8.53 (8H, m, Pc**H**), 9.68 (8H, m, Pc**H**); IR (Nujol): 2926, 2856, 1464, 1380, 1336, 1286, 1164, 1124, 1080, 908, 727; MS (ES^+): *m/z* 617, 618, 619 ($[M - Cl]^+$), 652, 653, 654 ($[M]^+$)

Phenyl silicon phthalocyanine (4-*tert*-butyl)benzoate (187).

A mixture of 4-*tert*-butylbenzoic acid (0.055 g, 0.31 mmol) and **36** (0.20 g, 0.31 mmol) were stirred in 2-methoxyethyl ether (8 cm^3) at 160 °C for 3 h. Quenching of the reaction mixture in water (25 cm^3), followed by filtration of the resulting precipitate gave an impure green solid. Unreacted **36** was removed by recrystallisation from toluene and the filtrate was combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the solvent *in vacuo* to dryness gave **187** as a green solid (0.19 g, 78%): mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.71 (9H, s, C**H**$_3$), 1.82 (2H, d, ^3J = 6.9 Hz, *o*-Ph**H**), 4.96 (2H, d, ^3J = 8.7 Hz, Ar**H**), 5.16 (2H, dd, ^3J = 7.2, 7.2 Hz, *m*-Ph**H**), 5.60 (1H, t, ^3J = 7.0 Hz, *p*-Ph**H**), 6.21 (2H, d, ^3J = 8.7 Hz, Ar**H**), 8.35 (8H, m, Pc**H**), 9.66 (8H, m, Pc**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 29.06 (**C**H$_3$), 41.30 (**C**Me$_3$), 124.36, 131.51, 133.33, 136.35, 150.32, 172.63 (**C**O$_2$) [some Pc and Ph peaks were not seen in ^{13}C-NMR spectrum]; IR (DCM): 3054, 2988, 2367, 2340, 1420, 1270, 900, 742, 711; MS (ES^+): *m/z* 817, 818, 819 ($[M + Na]^+$). HRMS found 794.2573, calcd. for $C_{49}H_{34}N_8O_2Si$ 794.2574.

Phenyl silicon phthalocyanine (3-thienyl)acetate (188)

A mixture of thiophene-3-acetic acid (0.044 g, 0.31 mmol) and **36** (0.20 g, 0.31 mmol) were stirred in 2-methoxyethyl ether (8 cm^3) at 160 °C for 3 h. Quenching of the reaction mixture in water (25 cm^3), followed by filtration of the resulting precipitate gave an impure blue solid. Unreacted **36** was removed by recrystallisation from toluene and the filtrate was then combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the solvent *in vacuo* to dryness gave **188** as a blue solid (0.16 g, 69%): mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.67 (2H, s, C**H**$_2$), 1.73 (2H, d, ^3J = 8.1 Hz, *o*-Ph**H**), 4.43 (1H, d, ^3J = 3.6 Hz, thiophene-5H), 4.96 (1H, s, thiophene-2H), 5.10 (2H, dd, ^3J = 8.3, 7.0 Hz, *m*-Ph**H**), 5.56 (1H, t, ^3J = 7.2 Hz, *p*-Ph**H**), 6.11 (1H, d, ^3J = 3.7 Hz, thiophene-4H), 8.35 (8H, m, Pc**H**), 9.63 (8H, m, Pc**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 36.34 (**C**H_2), 112.59, 120.31, 123.60, 124.30, 126.41, 128.78, 131.50, 132.86, 135.88, 136.34, 150.20, 164.54 (**C**O_2) [one peak was not seen in ^{13}C-NMR spectrum]; MS (MALDI-ToF): *m/z* 781, 782, 783 ($[M + Na]^+$).

2-Bromo-9,9-dihexyl-9H-fluorene (189)[524]

1-Bromohexane (27.1 cm^3, 193 mmol) was added dropwise to a stirred solution of 2-bromofluorene (12.5 g, 51.0 mmol) in degassed anhydrous THF (120 cm^3) and the mixture was then cooled to 0 °C in an ice-bath. To this was added dropwise a solution of potassium *tert*-butoxide (13.1 g, 117 mmol) in degassed anhydrous THF (120 cm^3) over the course of 1 h. The reaction mixture was stirred for a further 3 h at 0 °C and then allowed to warm to room temperature and stirred for 16 h at this temperature. Filtration of the reaction mixture and removal of the solvent *in vacuo* gave a crude yellow oil, which, after column chromatography over silica gel (eluent 40/60 pet. ether) gave **189** as a colourless oil (20.4 g, 97%). (Found: C, 71.92, H, 7.94%; $C_{25}H_{33}Br$ requires C, 72.63, H, 8.05%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.57-0.59 (4H, m, CH_2), 0.77 (6H, t, ^3J = 6.8 Hz, CH_3), 1.03-1.05 (12H, m, CH_2), 1.93-1.95 (4H, m, CH_2), 7.31 (3H, m, Ar**H**), 7.46 (2H, m, Ar**H**), 7.54 (1H, d, ^3J = 7.2 Hz, Ar**H**), 7.66 (1H, m, Ar**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.11 (**C**H_3), 22.65 (**C**H_2), 24.33 (**C**H_2), 30.02 (**C**H_2), 32.04 (**C**H_2), 40.07 (**C**H_2), 55.96 (CH_2**C**CH_2), 120.02, 121.50,

121.72, 123.62, 126.33, 127.78, 128.01, 130.05, 140.04, 140.08, 150.07, 153.64; IR (Nujol): 2954, 2925, 2947, 2881, 1746, 1464, 1406, 1238, 1062, 876, 821, 773, 736; MS (EI): *m/z* 243, 244, 245 ($[M\text{-}2hexyl+H]^+$), 327, 328, 329 ($[M\text{-}hexyl]^+$), 412, 413, 414 ($[M]^+$).

9,9-Dihexyl-9H-fluorene (191)

Compound **191** was obtained following the published procedure of Anémian *et al.*[524] using diethyl ether as a solvent, instead of dimethylformamide. The product was identified by comparison of its NMR data with literature values.[525]

2,7-Dibromo-9,9-dihexyl-9H-fluorene (192)

Compound **192** was synthesised based on the literature route[525] but with a different purification procedure.

The reaction was carried out in the dark to avoid bromination of the aliphatic chains. Anhydrous ferric chloride (74 mg, 0.456 mmol) and bromine (3.21 cm^3, 62.65 mmol) were added to a stirred solution of **191** (10.0 g, 29.89 mmol) in degassed anhydrous chloroform (75 cm^3) at 0 °C and the solution was then allowed to warm to room temperature and stirred for 20 h. The resultant red solution was then poured into water (200 cm^3) and sodium thiosulphate was slowly added until the colour of the organic phase changed to yellow. The layers were separated and the aqueous phase extracted with chloroform (2 x 100 cm^3). The organic layers were combined, dried over anhydrous magnesium sulphate and the solvent removed *in vacuo* giving a pale yellow oil. Purification by column chromatography (eluent hexane) gave 2,7-dibromo-9,9-dihexyl-9H-fluorene **192** as a white solid (5.84 g, 40%): mp 67.2-71.0 °C; (lit. 67.5-68.5 °C). (Found: C, 60.82, H, 6.58%; $C_{25}H_{32}Br_2$ requires C, 60.99, H, 6.55%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.58-0.60 (4H, m, C**H**$_2$), 0.77 (6H, t, ^3J = 6.9 Hz, C**H**$_3$), 1.03-1.11 (12H, m, C**H**$_2$), 1.88-1.93 (4H, m, C**H**$_2$), 7.437 (2H, d, ^4J = 1.5 Hz, Ar**H**), 7.461 (2H, d, ^4J = 1.2 Hz, Ar**H**), 7.158 (2H, d, ^3J = 9.0 Hz, Ar**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.11 (**C**H$_3$), 22.85 (**C**H$_2$), 23.98 (**C**H$_2$), 29.92 (**C**H$_2$), 31.96 (**C**H$_2$), 40.05 (**C**H$_2$), 55.99 (CH$_2$**C**CH$_2$), 121.56, 121.60 , 126.12, 130.04,

139.22, 152.43; MS (EI): *m/z* 321, 323, 325 ([M-2hexyl+H]$^+$), 405, 407, 409 ([M-hexyl]$^+$), 490, 492, 494 ([M]$^+$).

9,9-Dihexyl-9H-fluorene-2,7-dicarboxylic acid (193)

Compound **193** was prepared following the literature route.[511] A 2.5 M solution of n-butyllithium in hexane (4.4 cm^3, 11.00 mmol) was added dropwise to a stirred solution of **192** (2.5 g, 5.08 mmol) in degassed anhydrous THF (100 cm^3) at -78 °C. The reaction was stirred at this temperature for 4 h and then carbon dioxide gas (dried through a P_2O_5 column) was continuously bubbled through the stirred mixture for 1.5 h. The reaction was allowed to warm slowly to room temperature and water (100 cm^3) was added. The solution was acidified (pH ca. 1) using 37% aq. HCl, the layers were then separated and the aqueous phase was then extracted with diethyl ether (2 x 50 cm^3). The combined organic layers were extracted with 5% NaOH solution (2 x 50 cm^3), the combined alkaline solution then being acidified with conc. HCl and extracted with ethyl acetate (2 x 50 cm^3). The solvent was removed *in vacuo* and the resultant crude white solid was recrystallised from EtOH-H_2O to give **193** as a white solid (0.81 g, 38%): mp 245-249 °C (lit mp 249.0-250.4 °C). (Found: C, 76.70, H, 8.22%; $C_{27}H_{34}O_2$ requires C, 76.74, H, 8.11%).

Sodium phenoxide (194).[693]

Sodium (1.22 g, 53.1 mmol) was stirred in ethanol (50 cm^3) until completely dissolved. Phenol (5.0 g, 53.1 mmol) was dissolved in ethanol (25 cm^3) and added dropwise to the solution. Stirring was continued for 1h before cooling and removal of the solvent *in vacuo* gave **194** as a white crystalline solid (5.99 g, 97%): mp >350 °C. (Found: C, 62.29, H, 4.59%; C_6H_5NaO requires C, 62.07, H, 4.34%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 6.05 (1H, t, ^{3}J = 7.2 Hz, Ar**H**), 6.26 (2H, d, ^{3}J = 8.1 Hz, Ar**H**), 6.81 (2H, dd, ^{3}J = 7.8, 7.4 Hz, Ar**H**); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 110.95 (s, **C**HCHCHCO) 118.76 (s, **C**HCHCO), 129.92 (s, **C**HCO), 168.69 (s, **C**O); MS (ES$^+$): *m/z* 139 ([M + Na]$^+$), 255 ([2M + Na]$^+$), 371 ([3M + Na]$^+$), 487 ([4M + Na]$^+$).

Phenyl silicon phthalocyanine phenoxide (195).

Sodium phenoxide (**194**) (0.036 g, 0.31 mmol) and **36** (0.20 g, 0.31 mmol) were stirred in 1,4-dioxane (25 cm^3) at 102 °C for 19 h. Quenching of the reaction mixture in water (25 cm^3), followed by filtration of the resulting precipitate gave **195** as a dark blue solid (0.15 g, 71%) after recrystallisation from 1,2-dichlorobenzene: mp >400 °C. (Found: C, 73.78, H, 3.97, N, 16.11%; $C_{44}H_{26}N_8OSi$ requires C, 74.35, H, 3.69, N, 15.76%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 1.55 (2H, d, ^3J = 8.1 Hz, *o*-Ph**H**), 5.13 (2H, dd, ^3J = 7.8, 6.9 Hz, *m*-Ph**H**), 5.52 (1H, t, ^3J = 6.8 Hz, *p*-Ph**H**), 6.78 (2H, d, ^3J = 7.8 Hz, Ar**H**), 7.19 (1H, t, ^3J = 7.9 Hz, Ar**H**), 8.53 (8H, m, Pc**H**), 9.68 (8H, m, Pc**H**) (2H, ArH obscured by DMSO peaks); IR (DCM): 3058, 2992, 2367, 2310, 1389, 1270, 900, 746, 711; MS (MALDI-ToF): *m/z* 633, 634, 635 ([M – Ph]$^+$), 710, 711, 712 ([M]$^+$). HRMS found 710.1997, calcd. for $C_{44}H_{26}N_8OSi$ 710.1999.

Sodium (4-*tert*-butyl)phenoxide (196).[532]

Sodium (0.153 g, 6.66 mmol) was stirred in 1,4-dioxane (25 cm^3) at 102 °C until almost completely dissolved. 4-*tert*-Butylphenol (1.0 g, 6.66 mmol) was dissolved in 1,4-dioxane (20 cm^3) and added dropwise to the solution. Stirring was continued at 102 °C for 0.5 h before cooling and removal of the solvent *in vacuo* to give **196** as a white solid (1.12 g, 98%): mp >350 °C. (Found: C, 64.91, H, 8.42%; $C_{10}H_{13}ONa.C_4H_8O_2$ requires C, 64.60; H, 8.13%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 1.23 (9H, s, C**H**$_3$), 6.46 (2H, d, ^3J = 8.4 Hz, Ar**H**), 6.97 (2H, d, ^3J = 8.4 Hz, Ar**H**); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 32.46 (**C**H$_3$), 34.02 (**C**Me$_3$), 116.34 (**C**HCO), 126.01 (**C**HCHCO), 136.97 (**C**CMe$_3$), 161.62 (**C**O); MS (ES$^-$): *m/z* 149, 150 ([M – Na]$^-$).

Sodium (4-octyl)phenoxide (197).

Sodium (0.112 g, 4.85 mmol) was stirred in THF (30 cm^3) at 100 °C until completely dissolved. 4-Octylphenol (1.0 g, 4.85 mmol) was dissolved in THF (20 cm^3) and added dropwise to the solution. Stirring was continued at 100 °C for 0.5 h before cooling and removal of the solvent *in vacuo* to give **197** as a white solid (1.07 g, 97%): mp >350 °C. (Found: C, 70.14, H, 10.46%; $C_{14}H_{21}ONa.3C_4H_8O$ requires C,

70.23, H, 10.20%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 0.87 (3H, t, ^{3}J = 6.45 Hz, C**H**$_3$), 1.28 (10H, s, C**H**$_2$), 1.50 (2H, m, C**H**$_2$), 2.40 (2H, t, ^{3}J = 7.35 Hz, C**H**$_2$), 6.49 (2H, d, ^{3}J = 8.1 Hz, Ar**H**), 6.79 (2H, d, ^{3}J = 8.4 Hz, Ar**H**); MS (ES$^-$): *m/z* 205.5 ([M-Na]$^-$).

Silicon phthalocyanine dichloride (1).[99]

1,3-Diiminoisoindoline (10.0 g, 68.9 mmol) and silicon tetrachloride (11.8 cm^3, 103 mmol) were stirred in a mixture of tetrahydronaphthalene (175 cm^3) and tributylamine (75 cm^3) at 215 °C for 20 h. The resultant mixture was allowed to cool and then methanol (100 cm^3) was added. Filtration of the precipitate followed by copious washing with methanol and diethylether gave **1** as a dark purple solid (2.14 g, 20%) after recrystallisation from toluene: mp >400 °C. (Found: C, 62.63; H, 2.65; N, 18.30%; $C_{32}H_{16}N_8Cl_2Si$ requires C, 62.85; H, 2.64; N, 18.32%).

Silicon phthalocyanine bis-(4-*tert*-butyl)benzoate (4).[74]

4-*tert*-Butylbenzoic acid (0.20 g, 1.12 mmol) and **1** (0.20 g, 0.32 mmol) were stirred together in 2-methoxyethyl ether (2 cm^3) at 160 °C for 3 h. Quenching of the reaction mixture in water (25 cm^3), followed by filtration of the resulting precipitate gave an impure green solid. Unreacted **1** was removed by recrystallisation from toluene and the filtrate combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the solvent *in vacuo* to dryness gave **4** as a blue solid (0.047 g, 16%): mp >400 °C. (Found: C, 71.98, H, 4.62, N, 12.88%; $C_{54}H_{42}N_8O_4Si$ requires C, 72.46, H, 4.73, N, 12.52%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.73 (18H, s, C**H**$_3$), 5.07 (4H, d, ^{3}J = 8.8 Hz, Ar**H**), 6.25 (4H, d, ^{3}J = 8.7 Hz, Ar**H**), 8.37 (8H, m, Pc**H**), 9.70 (8H, m, Pc**H**), ^{13}C-NMR (125 MHz, $CDCl_3$) δ 30.55 (**C**H$_3$), 34.21 (**C**Me$_3$), 123.90, 124.33, 125.49, 127.55, 130.07, 131.50, 135.83, 150.48, 159.17 (**C**O$_2$); MS (EI): *m/z* 557 ([M-^{t}BuPhCO$_2$]), 894, 895, 896 ([M]$^+$).

Silicon phthalocyanine bis-(3-thienyl)acetate (198).[74]

Thiophene-3-acetic acid (1.16 g, 8.16 mmol) and **1** (1.00 g, 1.64 mmol) were stirred together in 2-methoxyethyl ether (25 cm^3) at 160 °C for 6 h. Quenching of the

reaction mixture in water (100 cm^3), followed by filtration of the resulting precipitate gave an impure blue solid. Unreacted **1** was removed by recrystallisation from toluene and the filtrate combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the solvent *in vacuo* to dryness gave **198** as a blue solid (0.17 g, 13%): mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.65 (4H, s, C**H**$_2$), 4.41 (2H, d, ^3J = 5.0 Hz, thiophene-5H), 4.94 (2H, s, thiophene-2H), 6.06 (2H, m, thiophene-4H), 8.31 (8H, m, Pc**H**), 9.58 (8H, m, Pc**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 34.97 (**C**H$_2$), 118.94, 122.84, 122.99, 125.04, 130.15, 131.49, 134.51, 148.83, 163.20 (**C**O$_2$); MS (EI^+): *m/z* 557 ([M-2(ThCH$_2$CO$_2$)+O]$^+$), 681 ([M-ThCH$_2$CO$_2$]$^+$), 822 ([M]$^+$).

Crystals for X-ray analysis were grown by a slow diffusion of hexane into a solution of **198** in DCM.

Silicon phthalocyanine bis-thiophen-2-carboxylate (199).

2-Thiophene-carboxylic acid (0.21 g, 1.64 mmol) and **1** (0.2 g, 0.33 mmol) were stirred together in 2-methoxyethyl ether at 160 °C for 15h. Quenching of the reaction mixture in water (100 cm^3) followed by filtration of the resulting precipitate gave an impure dark blue solid. Unreacted **1** was removed by recrystallisation from toluene and the filtrate was then combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the solvent *in vacuo* to dryness gave **199** as a blue solid (0.068 g, 26%): mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.26 (2H, d, ^3J = 3.0 Hz, thiophene-3H), 5.94 (2H, dd, ^3J = 4.4, 4.4 Hz, thiophene-4H), 6.37 (2H, d, ^3J = 4.2 Hz, thiophene-5H), 8.39 (8H, m, Pc**H**), 9.71 (8H, m, Pc**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 124.45, 130.45, 131.73, 135.85, 150.57 (**C**O$_2$) [no Pc peaks were seen in ^{13}C-NMR spectrum]; IR (DCM): 3054, 1592, 1527, 1389, 1336, 1270, 1068, 817, 746, 707; MS (MALDI-ToF): *m/z* 667, 668, 669 ([M – (ThCO$_2$)]$^+$), 794, 795, 796 ([M]$^+$). HRMS found 794.0976, calcd. for $C_{42}H_{22}N_8O_4S_2Si$ 794.0975.

Silicon phthalocyanine bis-thiophen-3-carboxylate (200).

3-Thiophene-carboxylic acid (0.21 g, 1.64 mmol) and **1** (0.2 g, 0.33 mmol) were reacted together as above. Quenching of the reaction mixture gave **200** as a blue solid (0.045 g, 17%) after removal of **1** by recrystallisation from toluene and evaporation of the filtrate solvent *in vacuo*: mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.98 (2H, m, thiophene-5H), 5.14 (2H, s, thiophene-2H), 6.12 (2H, m, thiophene-4H), 8.40 (8H, m, Pc**H**), 9.71 (8H, m, Pc**H**) [thienyl-2,4 proton peaks could not be cleanly resolved and are listed as multiplets]; MS (ES^+): *m/z* 667, 668, 669 ([M – ($ThCO_2$)]$^+$), 794, 795, 796 ([M]$^+$). HRMS found 794.0975, calcd. for $C_{42}H_{22}N_8O_4S_2Si$ 794.0975.

Silicon phthalocyanine bis-(4-*tert*-butyl)phenoxide (201).

Sodium (4-*tert*-butyl)phenoxide (0.22 g, 1.27 mmol) and **1** (0.20 g, 0.33 mmol) were stirred together in 2-methoxyethyl ether (20 cm^3) at 160 °C for 11 h. Quenching of the reaction mixture in water (75 cm^3) followed by filtration of the resulting precipitate gave **201** as a blue solid (0.056 g, 20%): mp >400 °C. (Found: C, 71.88, H, 4.88, N, 13.58%; $C_{52}H_{42}N_8O_2Si.2H_2O$ requires C, 71.37, H, 5.30, N, 12.81); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.56 (18H, s, C**H**$_3$), 2.35 (4H, d, ^{3}J = 8.4 Hz, Ar**H**), 5.53 (4H, d, ^{3}J = 8.7 Hz, Ar**H**), 8.32 (8H, m, Pc**H**), 9.60 (8H, m, Pc**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 31.88 (**C**H_3), 34.42 (**C**CH_3), 115.06 (**Ar**H), 126.78 (**Ar**H), 143.86 (**Ar**H), 153.46 (**Ar**H) [all the Pc peaks were not seen in the ^{13}C-NMR spectrum]; IR (DCM): 3054, 2988, 2305, 1389, 1266, 896, 751, 707; MS (MALDI-ToF): *m/z* 781, 782, 783 ([M – ^{t}BuH]$^+$), 838, 839, 840 ([M]$^+$). HRMS found 838.3200, calcd. for $C_{52}H_{42}N_8O_2Si$ 838.3200.

9,9 Dihexyl-9H-fluorenyl-2-boronic acid (202)

Compound **202** was synthesised by a modification of the literature route.[524] A 2.5 M solution of n-butyllithium in hexane (5.9 cm^3, 14.75 mmol) was added dropwise to a solution of **189** (5.58 g, 13.50 mmol) in degassed anhydrous diethyl ether (100 cm^3) at -78 °C, maintaining the temperature at <-70 °C. The solution was stirred at this temperature for 30 min before being allowed to warm to room temperature and stirred for a further 1 h. The solution was then cooled to -78 °C and a solution of triisopropylborate (9.32 cm^3, 40.4 mmol) in degassed anhydrous diethyl ether (50 cm^3) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred for 20 h. A solution of 2 M aq. HCl (50 cm^3) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with diethyl ether (50 cm^3) and the combined organic layers washed with water (100 cm^3), dried over magnesium sulphate and evaporated to give a crude white solid (3.62 g). Purification of this solid by column chromatography over silica gel (eluent 30% ethyl acetate in hexane) and subsequent recrystallisation from hexane gave **202** as a white solid (3.22 g, 63%): mp 92-98 °C. (Found: C, 82.98, H, 9.34%; $C_{75}H_{99}B_3O_3$ requires C, 83.33, H, 9.23%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.64-0.66 (4H, m, C**H**$_2$), 0.73-0.75 (6H, m, C**H**$_3$), 1.03-1.07 (12H, m, C**H**$_2$), 1.28-1.29 (4H, m, C**H**$_2$), 7.37-7.40 (3H, m, Ar**H**), 7.75-7.77 (1H, m, Ar**H**), 7.90 (1H, d, ^3J = 7.8 Hz, Ar**H**), 8.21 (1H, s, Ar**H**), 8.35 (1H, d, ^3J = 7.7 Hz, Ar**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.49 (**C**H$_3$), 22.63 (**C**H$_2$), 24.09 (**C**H$_2$), 29.66 (**C**H$_2$), 31.63 (**C**H$_2$), 40.80 (**C**H$_2$), 55.08 (CH$_2$**C**CH$_2$), 119.49, 120.77, 123.56, 127.50, 128.13, 129.03, 133.65, 141.24, 143.06, 149.57, 151.27; IR (Nujol): 2854, 2852, 2725, 2661, 1608, 1561, 1461, 1377, 1307, 1209, 1155, 1064, 997, 967, 915, 885, 833, 757, 740, 722, 618, 572; MS (EI): *m/z* 165, 166 ([M-B(OH)$_2$-2hexyl]$^+$), 178, 179,180 ([M-B(OH)$_2$-2hexyl+CH$_2$}$^+$), 249, 250, 251 ([M-B(OH)$_2$-hexyl]$^+$), 334, 335, 336 ([M-B(OH)$_2$]$^+$).

4-(9,9-Dihexyl-9H-fluoren-2-yl)benzoic acid (203).

Compound **202** (0.50 g, 1.32 mmol), 4-bromobenzoic acid (0.29 g, 1.44 mmol), dichlorobis(triphenylphosphine)palladium(II) (102 mg, 0.145 mmol) and sodium carbonate (0.27 g, 2.55 mmol) were stirred together in a degassed mixture of THF (50 cm^3) and water (10 cm^3) at 105 °C for 96 h. The reaction mixture was then allowed to cool to room temperature and the solvent removed *in vacuo*. The residue was redissolved in diethyl ether and water and the layers were separated. The organic phase was extracted with water (2 x 50 cm^3) and the combined aqueous phase was acidified (pH ca. 1) with 37% aq. HCl and left to stand for 3 h. Filtration gave an impure grey solid which after purification by column chromatography (eluent 20% ethyl acetate in hexane) gave **203** as a white solid (132 mg, 22%): mp 175-177 °C. (Found: C, 83.79, H, 8.46%; $C_{32}H_{38}O_2$ requires C, 84.54, H, 8.42%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.58-0.60 (4H, m, C**H**$_2$), 0.69 (6H, t, ^3J = 6.75 Hz, C**H**$_3$), 0.99-1.05 (12H, m, C**H**$_2$), 1.97-1.99 (4H, m, C**H**$_2$), 7.27-7.29 (3H, m, Ar**H**), 7.53-7.55 (2H, m, Ar**H**), 7.60-7.63 (2H, m, Ar**H**), 7.69 (2H, d, ^3J = 8.4 Hz, Ph**H**) 8.14 (2H, d, ^3J = 8.4 Hz, Ph**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.03 (**C**H$_3$), 22.31 (**C**H$_2$), 23.98 (**C**H$_2$), 29.64 (**C**H$_2$), 31.78 (**C**H$_2$), 40.06 (**C**H$_2$), 55.67 (CH$_2$**C**CH$_2$), 120.06, 120.09, 122.03, 123.34, 126.52, 127.21, 127.35 (**Ph**H), 127.64, 127.98, 131.53 (**Ph**H), 139.02, 140.84, 141.99, 147.91, 151.87, 152.03, 171.96 (**C**O$_2$); MS (EI): *m/z* 285, 286, 287 ([M-2hexyl]$^+$), 369, 370, 371 ([M-hexyl]$^+$), 454, 455, 456 ([M]$^+$).

[2,2']Bithienyl-5-carboxylic acid (204)

Compound **204** was synthesised by an alternative route to previous literature procedures.[540-544] Thiophene-2-boronic acid (0.60 g, 4.69 mmol), 2-bromothiophene-5-carboxylic acid (1.00 g, 4.83 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.34 g, 0.484 mmol) and sodium carbonate (1.00 g, 9.43 mmol) were stirred together in a degassed solution of THF (150 cm^3) and water (40 cm^3) at 105 °C for 72 h. The reaction mixture was then allowed to cool to room temperature and the solvent removed *in vacuo*. The residue was redissolved in diethyl ether and water and the layers were separated. The organic layer was extracted with water (50 cm^3) and the combined aqueous layers were acidified (pH ca. 1) with 37% aq. HCl and left to stand for 3 h. Filtration gave an impure brown solid which after purification by column chromatography (eluent 25% ethyl acetate in hexane) gave **204** as a pale yellow solid (347 mg, 35%): mp 173-176 °C. (Found: C, 51.91, H, 3.09%; $C_9H_6S_2O_2$ requires C, 51.41, H, 2.88%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.18 (1H, dd, ^3J = 4.2, 4.8 Hz, thiophene-4`H), 7.39 (1H, d, $^3J$ = 3.9 Hz, thiophene-3`H), 7.53 (1H, d, ^3J = 3.6 Hz, thiophene-3H), 7.67 (1H, d, ^3J = 5.1 Hz, thiophene-5`H), 7.70 (1H, d, ^3J = 3.6 Hz, thiophene-4H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 125.53, 126.45, 128.02, 129.93, 133.36, 135.44, 136.57, 143.91, 163.88 (**C**O_2); MS (EI): *m/z* 165, 166, 167 ([M-$CO_2H]^+$), 193, 194, 195 ([M-OH]$^+$), 210, 211, 212 ([M]$^+$).

3,5-Diphenyl-benzoic acid (205).

Benzene boronic acid (1.00 g, 8.20 mmol), 3,5-dibromobenzoic acid (1.10 g, 3.92 mmol), $Pd(PPh_3)_2Cl_2$ (0.58 g, 0.83 mmol) and degassed anhydrous THF (100 cm^3) were stirred at room temperature for ca. 30 min. Degassed aqueous Na_2CO_3 solution (15 cm^3) was added and the mixture was stirred for 96 h at 100 °C. The solvent was evaporated *in vacuo*, ethyl acetate (100 cm^3) was added and the reaction was washed with water (2 x 100 cm^3). The layers were separated and the aqueous layer was acidified (pH ca. 1) with 37% aq. HCl. The resultant brown precipitate was filtered and placed in a Soxhlet extractor for 95 h (solvent ethyl acetate). Removal of the solvent *in vacuo* gave **205** as a light brown solid (0.512 g, 47%): mp 246 °C. (Found: C, 82.92, H, 5.11%; $C_{19}H_{14}O_2$ requires C, 83.19, H, 5.14%); ^{1}H-NMR (200 MHz,

$CDCl_3$) δ 7.44 (2H, m, Ar**H**), 7.50 (4H, m, Ar**H**), 7.67 (4H, m, Ar**H**), 8.05 (1H, t, ^4J = 1.8 Hz, Ar**H**), 8.32 (2H, d, ^4J = 1.8 Hz, Ar**H**), 11.24 (1H, s, O**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 127.63, 128.03, 128.33, 129.34, 130.47, 131.52, 140.32, 142.63, 170.50 (**CO_2**); IR (DCM): 3062, 2820, 2658, 2592, 2520, 1694, 1597, 1504, 1468, 1437, 1402, 1339, 1292, 1265, 1243, 948, 894, 738, 699, 643; MS (MALDI-ToF): *m/z* 229, 230 ($[M - CO_2H]^+$), 274, 275, 276 ($[M]^+$).

Silicon phthalocyanine bis-(3,5-diphenyl)benzoate (206).

A mixture of **205** (0.40 g, 1.64 mmol) and **1** (0.20 g, 0.33 mmol) was stirred in 2-methoxyethyl ether (20 cm^3) at 160 °C for 20 h. Quenching of the reaction mixture in water (100 cm^3) followed by filtration of the resulting precipitate gave an impure bright blue solid. Unreacted **1** was removed by recrystallisation from toluene, and the filtrate was then combined with a 5% NaOH solution (150 cm^3). After separation of the layers and washing of the organic layer with water, removal of the organic layer *in vacuo* gave **206** (0.10 g, 28%) as a bright blue solid: mp > 400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.68 (8H, m, Ar**H**), 7.07 (12H, m, Ar**H**), 7.54 (2H, m, Ar**H**), 7.72 (2H, m, Ar**H**), 8.28 (2H, m, Ar**H**), 8.41 (8H, m, Pc**H**), 9.74 (8H, m, Pc**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 124.55, 125.77, 126.65, 127.50, 128.75, 131.81, 135.89, 139.60, 140.44, 150.62, 159.70, 168.07; IR (DCM): 3050, 2362, 2340, 1390, 1270, 896, 746, 711; MS (MALDI-ToF): *m/z* 1086, 1087, 1088 ($[M]^+$). HRMS found 1086.3099, calcd. for $C_{70}H_{42}N_8O_4Si$ 1086.3098.

Silicon phthalocyanine bis(1-pyreneacetate) (207).

1-Pyreneacetic acid (510 mg, 1.96 mmol) and **1** (300 mg, 0.49 mmol) were stirred together in 2-methoxyethyl ether (3.0 mL) at 160 °C for 4 h. The solvent was then removed *in vacuo* and the residue was filtered through a short silica gel column (eluent DCM). The solvent was removed *in vacuo* and the residue was purified by column chromatography (eluent DCM) to give **207** as a dark blue solid (160 mg, 32%); mp > 400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.33 (4H, s, C**H_2**), 5.38 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 5.52 (2H, d, ^3J = 9.3 Hz, pyrene-**H**), 6.75 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 6.79 (2H, d, ^3J = 9.3 Hz, pyrene-**H**), 7.67 (2H, d, ^3J = 8.8 Hz, pyrene-**H**),

7.92 (2H, d, ^3J = 7.3 Hz, pyrene-**H**), 8.07 (2H, d, ^3J = 9.3 Hz, pyrene-**H**), 8.09-8.16 (10H, m, Pc**H** + pyrene-**H**), 8.31 (2H, d, ^3J = 7.3 Hz, pyrene-**H**), 8.97 (8H, m, Pc**H**); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 39.68 (**C**H_2), 123.20, 123.48, 123.66, 124.26, 124.67, 125.06, 125.45, 125.48, 126.32, 126.45, 126.89, 126.98, 127.58, 129.24, 130.43, 130.53, 131.35, 134.70, 149.12, 164.14 (**C**O_2); MS (MALDI ToF): *m/z* 799.1, 800.1, 801.1 ([M-pyrene-CH_2CO_2]$^+$). HRMS found 1058.2785, calcd. for $C_{68}H_{38}N_8O_4Si$ 1058.2785.

Silicon phthalocyanine bis(1-pyrenebutanoate) (208).

1-Pyrenebutyric acid (950 mg, 3.29 mmol) and **1** (500 mg, 0.82 mmol) were stirred together in 2-methoxyethyl ether (3.0 cm^3) under argon at 160 °C for 3 h. The solvent was then removed *in vacuo* and the residue was filtered through a short silica gel column (eluent DCM). The solvent was removed *in vacuo* and the residue was purified by chromatography on a preparative silica gel TLC plate (2 mm thickness, eluent DCM) to give **208** as a dark blue solid (30 mg, 3%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ -0.5 (4H, t, ^3J = 6.8 Hz, $CH_2CH_2C\mathbf{H_2}CO_2$), -0.30 (4H, m, $CH_2C\mathbf{H_2}CH_2CO_2$), 0.88 (4H, m, $C\mathbf{H_2}CH_2CH_2CO_2$), 6.57 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 7.12 (2H, d, ^3J = 9.2 Hz, pyrene-**H**), 7.62 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 7.68 (2H, d, ^3J = 9.2 Hz, pyrene-**H**), 7.97 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 7.99-8.18 (6H, m, pyrene-**H**), 8.24 (8H, m, Pc**H**), 8.31 (2H, d, ^3J = 7.8 Hz, pyrene-**H**), 9.56 (8H, m, Pc**H**); MS (ES$^+$): *m/z* 1114.3, 1115.3, 1116.3 ([M]$^+$). HRMS found 1114.3412, calcd. for $C_{72}H_{46}N_8O_4Si$ 1114.3411.

4,5-Dibromophthalimide (210)

Compound **210** was synthesised as described in the literature.[559] Analytical data given is that of impure product.

Phthalimide (14.7 g, 0.10 mmol), bromine (10.26 g, 0.20 mmol) and a catalytic amount of iodine (0.10 g, 0.394 mmol) were stirred together in 30% fuming sulphuric acid (oleum) (60 cm^3) at 75 °C for 24 h. Work-up as described[559] gave a crude white solid (11.3 g). Recrystallisation from acetone gave an inseparable mixture of 4,5-dibromophthalimide and 4-bromophthalimide (7.9 g), which could not be purified further. ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.64-7.66 [1H, d, ^3J = 7.5 Hz, C(Br)C**H**CH], 7.68-7.71 [1H, d, ^3J = 8.7 Hz, C(Br)CHC**H**], 7.95 [1H, s, C**H**C(Br)], 8.11 [2H, s, C(Br)C**H**C**H**C(Br)], 11.49 (2H, b, N**H**); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 123.94, 125.96, 126.47, 128.36, 131.62, 132.21, 133.92, 135.87, 137.98, 168.06, 168.35, 168.52.

4,5-Dibromophthalamide (211)

Compound **211** was synthesised as described in the literature.[559]

The impure 4,5-dibromophthalimide **210** (7.9 g, 25.7 mmol) was stirred in 28% aq. ammonium hydroxide at 60 °C for 1 h. The mixture was allowed to cool to room temperature, filtered and the resultant solid washed with ice-cold water and methanol to remove traces of ammonia and starting material. The solid was dried for 20 h at room temperature to give **211** as a white powder (2.83 g, 34%): mp 239-243 °C (lit mp 240-243 °C). ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.53 (2H, bs, N$\mathbf{H}_2$), 7.84 (2H, s, C**H**), 7.92 (2H, bs, N$\mathbf{H}_2$); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 125.54 (**C**Br), 133.13 (**C**H), 138.02 (**C**CONH$_2$), 168.21 (**C**ONH$_2$); MS (EI): *m/z* 241, 243 ([M-Br]$^+$), 320, 322, 324 ([M]$^+$)

4,5-Dibromophthalonitrile (212)

Compound **212** was synthesised as describe in the literature.[559]

Pyridine (3.5 cm^3, 43.3 mmol) and trifluoroacetic anhydride (3.0 cm^3, 21.2 mmol) were sequentially added dropwise to a stirred solution of **211** (2.83 g, 8.79 mmol) in 1,4-dioxane (90 cm^3) at 0 °C. The solution was then allowed to warm to room temperature and stirred for 20 h, before being poured onto ice (100 g). The resultant suspension was extracted with ethyl acetate (3 x 75 cm^3) and the combined organic layers were then washed with water, 1M aqueous HCl, dilute sodium carbonate solution, water and then dried over anhydrous magnesium sulphate. The solvent was removed *in vacuo* and recrystallisation of the crude solid from ethanol gave **212** as a white solid (1.57 g, 63%): mp 200-203 °C (lit mp 214-216 °C). (Found: C, 33.90, H, 0.71, N, 9.75%; $C_8H_2N_2Br_2$ requires C, 33.61, H, 0.71, N, 9.80%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.05 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 114.03 (**C**N), 115.87 (**C**CN), 131.98 (**C**Br), 138.69 (**C**H); IR (Nujol): 2925, 2854, 2715, 2655, 2225, 1551, 1462, 1377, 1295, 1250, 1197, 1151, 1100, 914, 886, 722, 627, 531, 472; GC-MS (EI): *m/z* 126, 127 ($[M-2Br]^+$), 205, 207 ($[M-Br]^+$), 284, 286, 288 ($[M]^+$).

4,5-Bis(9,9-dihexyl-9H-fluoren-2-yl)benzene-1,2-dicarbonitrile (213).

Compound **212** (0.38 g, 1.33 mmol), compound **202** (1.00 g, 2.64 mmol), tetrakis(triphenylphosphine)palladium(0) (0.06 g, 51.9 μmol) and sodium carbonate (0.46 g, 4.34 mmol) were stirred together in a degassed solution of THF (70 cm^3), toluene (85 cm^3) and water (10 cm^3) at 110 °C for 96 h. The reaction mixture was then allowed to cool to room temperature and the solvents removed *in vacuo*. The residue was redissolved in dichloromethane and water and the layers separated. The aqueous layer was extracted with dichloromethane (2 x 50 cm^3) and the combined organic layers were then washed with water (1 x 50 cm^3) before being dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and subsequent purification by column chromatography (eluent 50% DCM in hexane) gave **213** as a yellow powder (916 mg, 87%): mp 128-130 °C. (Found: C, 87.54, H, 8.65, N, 3.26%; $C_{58}H_{68}N_2$ requires C, 87.83, H, 8.64, N, 3.53%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.58 (8H, m, C**H**$_2$), 0.74 (12H, t, ^3J = 6.75 Hz, C**H**$_3$), 0.99 (24H, m, C**H**$_2$), 1.82 (8H, m, C**H**$_2$), 7.15-7.20 (10H, m, Ar**H**), 7.56-7.62 (4H, m, Ar**H**), 7.93 (2H, s, Ph**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.43 (**C**H$_3$), 22.86 (**C**H$_2$), 23.99 (**C**H$_2$), 29.97 (**C**H$_2$), 32.01 (**C**H$_2$), 40.05 (**C**H$_2$), 55.78 (CH$_2$**C**CH$_2$), 114.03, 116.02, 120.03, 120.09, 123.78, 124.23, 127.83, 128.02, 128.82, 136.22, 136.88, 140.49, 142.04, 146.67, 151.85, 151.99; IR (Nujol): 2925, 2855, 2715, 2660, 1734, 1459, 1376, 1296, 1210, 1201, 1142, 1070, 951, 909, 873, 837, 765, 721, 516; MS (ES$^+$): *m/z* 794, 795, 796 ([M]$^+$), 815.5, 816.5, 817.5 ([M+Na]$^+$, 824.5, 825.5, 826.5 ([M+MeOH]$^+$.

2,3,9,10,16,17,23,24-Octa(9,9-dihexyl-9H-fluoren-2-yl)-29H,31H-phthalocyanine (214).

To a stirred solution of **213** (400 mg, 0.504 mmol) in degassed 1-pentanol (2 cm^3) was added lithium (20 mg, 2.88 mmol). The mixture was heated at 125 °C for 2 h and then allowed to cool to room temperature. The dark solution was acidified with 37% aq. HCl (1 cm^3) and poured into methanol (100 cm^3) forming a bright green precipitate, which was then filtered to give a crude green solid (0.094 g). Purification by column chromatography (eluent 40% DCM in hexane) gave **214** as a green solid (42 mg, 11%): mp 325-327 °C. (Found: C, 87.30, H, 8.56, N, 2.91%; $C_{232}H_{274}N_8.H_2O$ requires C, 87.28, H, 8.71, N, 3.51%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.58 (32H, m, C**H**$_2$), 0.68 (48H, t, ^3J = 6.6 Hz, C**H**$_3$), 0.97 (96H, m, C**H**$_2$), 1.82 (32H, m, C**H**$_2$) 7.30 (24H, m, Ar**H**), 7.52 (8H, m, Ar**H**), 7.64-7.77 (24H, m, Ar**H**) 9.64 (8H, b, Pc**H**) [NH protons not observed down to -5ppm]; ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.05 (**C**H$_3$), 22.32 (**C**H$_2$), 24.01 (**C**H$_2$), 29.97 (**C**H$_2$), 31.89 (**C**H$_2$), 40.33 (**C**H$_2$), 55.57 (CH$_2$**C**CH$_2$), 120.01, 120.03, 123.57, 125.93, 126.04, 127.21, 127.85, 129.98, 136.11, 140.56, 141.23, 144.76, 151.85, 151.97; IR (Nujol): 3175, 2933, 2911, 2853, 2714, 2656, 2595, 1735, 1459, 1376, 1298, 1219, 1201, 1144, 1070, 946, 909, 873, 837, 759, 720, 511; MS (MALDI-ToF): *m/z* 3173, 3174, 3175, 3176 ([M]$^+$); HRMS found 3172.1631, calcd. for $C_{232}H_{274}N_8$ 3172.1686.

5,10,15,20-Tetra-*p*-tolyl-porphyrin (215)

Compound **215** was synthesised according to the literature route[247] which in turn is based on previous literature routes[208,214].

Pyrrole (5.78 cm^3, 83.3 mmol) and p-tolualdehyde (9.82 cm^3, 83.3 mmol) were stirred together in propionic acid (200 cm^3) at 141 °C for 1 h, after which the solution was allowed to cool to room temperature and left to stand or 6 h. Filtration of the solution gave a crude purple crystalline product (2.94 g) after washing with methanol. The crude material was dissolved in degassed anhydrous chloroform (350 cm^3) and heated to 62 °C before addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (0.75 g, 3.30 mmol) in degassed anhydrous THF (25 cm^3). The mixture was stirred at 62 °C for a further 3 h before being allowed to cool to room temperature and filtered under suction through a sintered glass funnel containing alumina (45 g, Brockmann grade I). The alumina was washed thoroughly with dichloromethane and the filtrates were combined and the solvent reduced *in vacuo* to ca. 40 cm^3. Addition of methanol (75 cm^3) and filtration of the resulting precipitate gave **215** as a purple solid (2.67 g, 19%): mp >400 °C. (Found: C, 85.43, H, 5.64, N, 8.18%; $C_{48}H_{38}N_4$ requires C, 85.93, H, 5.71, N, 8.35%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -2.80 (2H, s, NH), 2.71 (12H, s, C**H**$_3$), 7.56 (8H, d, ^3J = 7.5 Hz, Ph**H**), 8.10 (8H, d, ^3J = 7.8 Hz, Ph**H**), 8.86 (8H, s, pyrrole *β*); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.75 (**C**H$_3$), 119.99 (pyrrole *β*), 127.87 (CH$_3$**C**CH), 128.01, 129.54, 134.46 (CH$_3$CCH**C**H), 137.76 (CH$_3$**C**), 139.21, 139.41 (CH$_3$CCHCH**C**), 146.03; IR (Nujol): 3317, 3293, 3013, 2952, 2922, 2853, 2728, 2693, 2369, 1899, 1796, 1689, 1548, 1499, 1463, 1387, 1378, 1337, 1274, 1247, 1213, 1179, 1148, 1105, 1067, 1037, 1020, 992, 980, 966, 944, 877, 846, 797, 777, 735, 706, 632, 586, 557, 531; MS (MALDI-ToF): *m/z* 670.4 ([M]$^+$), 671.4, 672.4, 673.4 ([M+H]$^+$).

9,9-Dihexyl-9H-fluorene-2-carbaldehyde (217)

Compound **217** was synthesised by a modification of the literature method[514] based on[416].

A 2.5 M solution of n-butyllithium in hexane (5.32 cm^3, 13.3 mmol) was added dropwise to a stirred solution of **189** (5.0 g, 12.09 mmol) in degassed anhydrous diethyl ether (150 cm^3) at –78 °C, maintaining a temperature of <-70 °C. The solution was stirred at this temperature for 30 min before being allowed to warm to room temperature and stirred for a further 30 min. The solution was then recooled to –78 °C and degassed anhydrous dimethylformamide (2.5 cm^3, 32.29 mmol) was added dropwise. The solution was allowed to warm to room temperature once more and stirred for 20 h before the addition of 2 M aq. HCl (200 cm^3). After a further 2 h stirring, the layers were separated and the aqueous layer extracted with diethyl ether (3 x 100 cm^3). The combined organic layers were washed with water (50 cm^3), dried over anhydrous magnesium sulphate and the solvent removed *in vacuo* to give a crude colourless oil. Purification by column chromatography (eluent 50% DCM in hexane) gave **217** as a colourless oil (3.21 g, 73%). (Found: C, 85.77, H, 9.43%; $C_{26}H_{34}O$ requires C, 86.13, H, 9.45%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.56-0.58 (4H, m, C**H**$_2$), 0.74 (6H, t, ^3J = 6.9 Hz, C**H**$_3$), 1.01-1.15 (12H, m, C**H**$_2$), 1.95-2.02 (4H, m, C**H**$_2$), 7.38-7.39 (3H, m, Ar**H**), 7.77-7.80 (2H, m, Ar**H**), 7.85-7.87 (2H, d, ^3J = 6.6 Hz, Ar**H**), 10.06 (1H, s, C**H**O); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.01 (**C**H$_3$), 22.34 (**C**H$_2$), 23.98 (**C**H$_2$), 29.97 (**C**H$_2$), 31.98 (**C**H$_2$), 40.05 (**C**H$_2$), 55.96 (CH$_2$**C**CH$_2$), 120.02, 121.01, 123.87, 123.97, 127.89, 129.45, 130.88, 135.98, 139.99, 148.23, 151.92, 152.37, 192.28 (**C**HO); IR (Nujol): 3047, 2954, 2925, 2854, 2726, 1700, 1607, 1574, 1466, 1425, 1378, 1344, 1304, 1242, 1227, 1178, 1157, 1100, 1004, 933, 906, 886, 827, 780, 739, 641, 574, 498; MS (ES$^+$): *m/z* 363.3, 364.3 ([M+H]$^+$, 385.5, 386.5, 387.5 ([M+Na]$^+$), 417.3 ([M+Na+CH$_3$OH]$^+$), 747.6, 748.6 ([2M+Na]$^+$).

5,10,15,20-Tetra(9,9-dihexyl-9H-fluoren-2-yl)-porphyrin (218).

The synthesis is based on the literature route to the dioctyl analogue.[416] Trifluoroacetic acid (0.31 cm^3, 4.02 mmol) was added dropwise to a stirred solution of pyrrole (0.19 cm^3, 2.73 mmol) and **217** (0.13 g, 2.73 mmol) in degassed anhydrous chloroform and the solution was stirred at 61 °C for 3 h. After allowing the solution to cool to room temperature, DDQ (0.62 g, 2.73 mmol) was added and stirring was then continued for a further 10 h. Triethylamine (0.56 cm^3, 4.02 mmol) was added dropwise and the reaction mixture was filtered through a short column (initial eluent DCM followed by ethyl acetate) giving a crude product after the removal of solvents *in vacuo*. Purification via column chromatography (eluent 33% DCM in hexane) gave **218** as a purple solid (145 mg, 13%): mp 276-278 °C. (Found C, 86.93, H, 8.74, N, 3.09%; $C_{120}H_{142}N_4.H_2O$ requires C, 86.91, H, 8.75, N, 3.38%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ -1.50 (2H, s, NH), 0.742 (24H, t, ^3J = 3.6 Hz, C**H**$_3$), 0.87-0.89 (16H, m, C**H**$_2$), 1.13-1.15 (48H, m, C**H**$_2$), 2.12-2.14 (16H, m, C**H**$_2$), 7.43-7.50 (12H, m, Ar**H**), 7.97 (4H, d, ^3J = 7.2 Hz, Ar**H**), 8.08 (4H, d, ^3J = 7.8 Hz, Ar**H**), 8.22 (8H, d, ^3J = 6.6 Hz, Ar**H**), 8.92 (8H, d, ^3J = 13.8 Hz, py**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.06 (**C**H$_3$), 22.76 (**C**H$_2$), 24.02 (**C**H$_2$), 29.99 (**C**H$_2$), 31.99 (**C**H$_2$), 40.07 (**C**H$_2$), 55.95 (CH$_2$**C**CH$_2$), 118.01, 120.03, 120.09, 123.76, 127.74, 127.88, 129.54, 141.43, 141.95, 149.26, 151.97; IR (Nujol): 3304, 3176, 2949, 2918, 2852, 2719, 2663, 1463, 1377, 1299, 1257, 1146, 1054, 1018, 965, 874, 799, 720; MS (MALDI-ToF): *m/z* 1639.7 ([M]$^+$); HRMS found 1639.1236, calcd. for $C_{120}H_{142}N_4$ 1639.1234.

5,10,15,20-Tetrathien-2-yl-porphyrin (219)

Compound **219** was synthesised as described in the literature.[222]
37% aq. HCl (1.0 cm^3, 10 mmol) was added dropwise to a stirred solution of pyrrole (0.07 cm^3, 1.0 mmol) and 2-thienyl-carbaldehyde (0.093 cm^3, 1.0 mmol) in aq. sodium dodecyl sulphate (100 cm^3, 0.5 M) and the solution was then stirred for 0.5 h. A solution of TCQ (220 mg, 0.89 mmol) in THF (5 cm^3, warmed briefly to ensure complete dissolution of TCQ) was then added dropwise to the reaction mixture, which was then stirred, open to air, for a further 20 h. A solution of aq. potassium hydroxide (5 cm^3, 2 M), potassium phosphate pH 7 buffer (10 cm^3, 1 M) and aq. potassium chloride (10 cm^3, 3 M) in ethyl acetate (150 cm^3) was added and the layers were then separated (NB: Addition of a small amount of brine was necessary to ensure facile layer separation). The aqueous phase was washed with a second portion of ethyl acetate (100 cm^3) and the combined organic layers were then washed with water (100 cm^3) and dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* gave a crude purple solid, which after purification via column chromatography (eluent 0.01% pyridine in DCM) and washing of the solid obtained with methanol, gave **219** as a purple solid (28 mg, 18%): mp >400 °C (no lit. mp). (Found C, 63.42, H, 3.89, N, 7.62%; $C_{36}H_{22}N_4S_4.2H_2O$ requires C, 64.07, H, 3.88, N, 8.30%) ^{1}H-NMR (300 MHz, $CDCl_3$) δ -2.74 (2H, s, NH), 7.50-7.51 (4H, m, thiophene-5H), 7.85-7.86 (4H, m, thiophene-4H), 7.91-7.92 (4H, m, thiophene-3H), 9.04 (8H, s, porp-**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 98.87, 112.56, 126.55, 128.38, 134.28, 143.05; IR (Nujol): 3155, 2909, 2852, 2725, 2675, 2033, 1462, 1377, 1298, 1258, 1157, 1154, 1069, 1013, 946, 944, 884, 838, 782, 722, 663, 618, 551; MS (MALDI-ToF): *m/z* 639, 640, 641, 642 ($[M]^+$).

[2,2']Bithienyl-5-carbaldehyde (220)

Method 1: this synthesis is identical to the literature route.[647]

Phosphorus oxychloride (1.17 cm^3, 12.8 mmol) was added dropwise to a stirred solution of 2,2'-bithiophene (2.0 g, 12.0 mmol) and anhydrous dimethylformamide (0.98 cm^3, 12.7 mmol) in anhydrous 1,2-dichloroethane (30 cm^3) at 0 °C. The solution was allowed to warm gradually to room temperature and then heated at 85 °C for 2 h, before being allowed to cool back to room temperature. The reaction mixture was poured into an aqueous solution of sodium acetate (200 cm^3, 1 M) and stirred for 2 h to ensure complete hydrolysis. The majority of the organic phase was separated by decantation and the aqueous phase was then extracted with dichloromethane (3 x 75 cm^3). The organic layers were combined, dried over anhydrous magnesium sulphate and the solvent was removed *in vacuo*. Purification via column chromatography (eluent 50% DCM in petroleum ether) gave **220** as a yellow solid (1.61 g, 69%): mp 56-57 °C (lit mp 57-58 °C)[647]. (Found: C, 55.58, H, 3.06%; $C_9H_6S_2O$ requires C, 55.64, H, 3.11%); ^{1}H-NMR (200 MHz, DMSO-d_6) δ 7.21 (1H, dd, ^3J = 4.3, 4.0 Hz thiophene-4`H), 7.57 (1H, d, $^3J$ = 4.2 Hz, thiophene-5`H), 7.64 (1H, dd, ^3J = 4.0 Hz, ^4J = 1.2 Hz, thiophene-3`H), 7.76 (1H, dd, ^3J = 4.4 Hz, ^4J = 1.1 Hz, thiophene-3H), 8.03 (1H, d, 4.2, thiophene-4H), 9.92 (1H, s, C**H**O); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 125.96, 127.88, 129.34, 129.92, 136.02, 140.05, 142.11, 146.54, 184.73 (**C**HO); MS (ES^+): *m/z* 194 ($[M]^+$, 195,196,197 ($[M+H]^+$), 217, 218, 219 ($[M+Na]^+$), 249, 250 ($[M+Na+MeOH]^+$).

Method 2

Thiophene-2-boronic acid (0.66 g, 5.16 mmol), 5-bromothiophene-2-carbaldehyde (0.62 cm^3, 5.23 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.37 g, 0.52 mmol) and sodium carbonate (1.1 g, 10.38 mmol) was stirred together in a degassed solution of THF (150 cm^3) and water (40 cm^3) at 105 °C for 120 h. The reaction mixture was then allowed to cool to room temperature and the solvents removed *in vacuo*. The residue was then redissolved in diethyl ether (150 cm^3) and water (100 cm^3) and the layers were separated. The aqueous phase was extracted with diethyl ether (100 cm^3) and the combined organic layers were washed with water (50 cm^3) before being dried over magnesium sulphate. Removal of the solvent *in vacuo* and

purification by column chromatography (eluent 50% DCM in petroleum ether) gave **220** as a yellow solid (295 mg, 29%).

Analysis of this compound was identical to that produced by method 1.

Crystals were grown by a slow diffusion of petroleum ether into a solution of **220** in DCM.

5,10,15,20-Tetra(5-bromothien-2-yl)-porphyrin (221).

37% aq. HCl (1.0 cm^3, 10 mmol) was added dropwise to a stirred solution of 5-bromothiophene-2-carbaldehyde (0.12 cm^3, 1.0 mmol) and pyrrole (0.07 cm^3, 1.0 mmol) in aq. sodium dodecyl sulphate (100 cm^3, 0.5 M) and the solution was then stirred for 1 h. A solution of TCQ (220 mg, 0.89 mmol) in THF (5 cm^3, warmed briefly to ensure complete dissolution of TCQ) was then added dropwise to the reaction mixture, which was then stirred, open to air, for a further 20 h. A solution of aq. potassium hydroxide (5 cm^3, 2 M), potassium phosphate pH 7 buffer (10 cm^3, 1 M) and aq. potassium chloride (10 cm^3, 3 M) in ethyl acetate (150 cm^3) was added and the layers were then separated. The aqueous phase was washed with a second portion of ethyl acetate (100 cm^3) and the combined organic layers were then washed with water (100 cm^3) and dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* gave a crude black solid, which after purification via column chromatography (eluent DCM) gave **221** as a purple solid (36 mg, 15%); mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ -2.75 (2H, s, N**H**), 7.49 (4H, d, ^3J = 3.9 Hz, thiophene-4H), 7.66 (4H, d, ^3J = 3.6 Hz, thiophene-3H), 9.11 (8H, s, py**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 64.93, 111.92, 115.02, 129.69, 134.21, 144.17; MS (MALDI-ToF): *m/z* 873.8, 874.8, 875.8 ($[M-Br]^+$), 874.8, 875.8, 876.8 ($[M-Br+H]^+$), 951.8, 953.8, 955.8 ($[M]^+$), 952.8, 954.8, 956.8 ($[M+H]^+$).

4-(9,9-Dihexyl-9H-fluoren-2-yl)-benzaldehyde (222).

Compound **202** (0.50 g, 1.32 mmol), 4-bromo-benzaldehyde (0.24 g, 1.29 mmol), tetrakis(triphenylphosphine)palladium(0) (0.03 g, 25.9 μmol) and sodium carbonate (0.17 g, 1.65 mmol) were stirred together in a degassed solution of THF (40 cm^3), toluene (50 cm^3) and water (7 cm^3) at 105 °C for 72 h. The reaction mixture was then allowed to cool to room temperature, the solvents were removed *in vacuo* and the residue was redissolved in DCM (150 cm^3) and water (150 cm^3). After separation of the layers, the aqueous phase was extracted with DCM (2 x 75 cm^3) and the combined organic layers were then washed with water (2 x 50 cm^3) and dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and purification via column chromatography (eluent 50% DCM in hexane) gave **222** as a colourless oil (341 mg, 60%). (Found: C, 87.10, H, 8.80%; $C_{32}H_{38}O$ requires C, 87.62, H, 8.73%); (Found: ($[M]^+$) 438.2920; $C_{32}H_{38}O$ requires 438.2923); ^{1}H-NMR (300MHz, $CDCl_3$) δ 0.66-0.70 (4H, m, C**H**$_2$), 0.77 (6H, t, ^3J = 6.75 Hz, C**H**$_3$), 1.07-1.13 (12H, m, C**H**$_2$), 2.00-2.06 (4H, m, C**H**$_2$), 7.35-7.39 (3H, m, Fl**H**), 7.63 (2H, d, ^3J = 8.7 Hz, Fl**H**), 7.75 (1H, d, ^3J = 4.8 Hz, Fl**H**), 7.80 (1H, d, ^3J = 7.8 Hz, Fl**H**), 7.84 (2H, d, ^3J = 8.1 Hz, Ph**H**), 7.99 (2H, d, ^3J = 8.1 Hz, Ph**H**), 10.08 (s, C**H**O); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.05 (**C**H$_3$), 23.01 (**C**H$_2$), 24.01 (**C**H$_2$), 29.99 (**C**H$_2$), 31.97 (**C**H$_2$), 40.08 (**C**H$_2$), 55.95 (CH$_2$**C**CH$_2$), 120.04, 121.09, 123.54, 126.33, 127.45, 127.85, 127.98 (**Ph**H), 130.86 (**Ph**H), 135.76, 138.52, 140.86, 142.03, 147.94, 151.65, 152.01, 192.02 (**C**HO); MS (MALDI): *m/z* 438.4, 439.4, 440.4 ($[M]^+$).

5,10,15,20-tetrakis(4-bromophenyl)-porphyrin (223)

Compound **223** was synthesised according to the literature route.[501] The product was identified by comparison with the literature melting point and NMR data.
Boron trifluoride diethyl etherate (0.67 cm^3, 5.45 mmol) was added dropwise to a stirred solution of 4-bromobenzaldehyde (3.00 g, 16.21 mmol) and pyrrole (1.09 g, 16.21 mmol) in degassed, anhydrous chloroform (1621 cm^3) and the solution was stirred for 1 h at room temperature. DDQ (2.76 g, 12.16 mmol) was then added and the solution stirred for a further 1 h, after which time the solvent was removed *in vacuo*. The crude solid was placed on a filter and washed with methanol until the washings became colourless, yielding **223** as a purple solid (2.03 g, 58%): mp 169-170 °C (lit mp 170 °C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ -2.86 (1H, s), 7.92 (4H, d, ^3J = 8.0 Hz), 8.08 (4H, d, ^3J = 8.0 Hz), 8.85 (4H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 119.20, 122.86, 130.21, 136.04, 141.04.

5,10,15,20-Tetrakis[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-porphyrin (224).

Compound **223** (93 mg, 0.1 mmol), compound **202** (156 mg, 0.41 mmol), tetrakis(triphenylphosphine)palladium(0) (13.8 mg, 0.012 mmol) and sodium carbonate (53 mg, 0.5 mmol) were stirred together in a degassed solution of THF (12 cm^3), toluene (12 cm^3) and water (0.5 cm^3) at 105 °C for 24 h. The solution was allowed to cool to room temperature and the solvents were removed *in vacuo*. The residue was redissolved in DCM (20 cm^3) and washed with water (30 cm^3) before being dried over anhydrous magnesium sulphate. After removal of the solvent *in vacuo* and purification by column chromatography (eluent 50% DCM in hexane), **224** was obtained as a dark red powder (140 mg, 72%): mp 270-271 °C. (Found: C, 87.89, H, 8.24, N, 2.83%; $C_{144}H_{158}N_4.H_2O$ requires C, 88.11, H, 8.22, N, 2.85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.59 (2H,s), 0.88-0.72 (56H, m), 1.19-1.07 (48H, m), 2.18-2.05 (16H, m), 7.43-7.33 (12H, m), 7.80 (4H, dd, ^3J = 7.2 Hz, ^4J = 0.9 Hz), 7.92-7.90 (12H, m), 8.10 (8H, d, ^3J = 8.4 Hz), 8.36 (8H, d, ^3J = 8.4 Hz), 9.03 (8H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.99, 21.60, 22.85, 28.77, 30.53, 39.53, 54.30, 118.83, 119.01, 119.16, 120.53, 121.95, 124.40, 125.20, 125.84, 126.14, 134.14, 138.51, 139.79,

139.83, 139.86, 140.04, 150.06, 150.69; MS (MALDI-ToF): *m/z* 1945.4 ($[M+H]^+$); HRMS found 1943.2490, calcd. for $C_{144}H_{158}N_4$ 1943.2486.

5,10,15,20-Tetrakis-[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-porphyrin zinc(II) (225).

Compound **224** (38.9 mg, 0.02 mmol) and zinc acetate (20 mg, 0.11 mmol) were stirred together in degassed anhydrous chloroform (10 cm^3) at 62 °C for 4 h. Removal of the solvent *in vacuo* followed by purification via column chromatography (eluent DCM) gave **225** as a dark red powder (38 mg, 95%): mp 302-303 °C. (Found: C, 85.30, H, 7.90, N, 2.74%; $C_{144}H_{156}N_4Zn.H_2O$ requires C, 85.36, H, 7.86, N, 2.77%); ^1H NMR (400 MHz, $CDCl_3$) δ 0.88-0.70 (40H, m), 1.24-1.05 (48H, m), 2.21-2.04 (16H, m), 7.43-7.34 (12H, m, Fl-**H**), 7.79 (4H, dd, ^3J = 7.2 Hz, ^4J = 1.2 Hz, Fl-**H**), 7.93-7.86 (12H, m, Fl-**H**), 8.09 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 8.35 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 9.12 (8H, s, Porp-**H**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.00, 21.60, 22.85, 28.77, 30.53, 39.54, 54.30, 118.82, 119.99, 120.49, 121.94, 124.26, 125.18, 125.83, 126.11, 131.11, 134.00, 138.67, 139.62, 139.77, 139.81, 140.66, 149.31, 150.05, 150.67; MS (MALDI-ToF): *m/z* 2007.1 ($[M]^+$); HRMS found 2005.1618, calcd. for $C_{144}H_{156}N_4Zn$ 2005.1621.

2-Iodo-9,9-bis(6-carbazol-9-yl-hexyl)-9H-fluorene (226).

Aqueous NaOH (50/50, w/w) (20 cm^3) and 18-crown-6-ether (0.2 g, 0.76 mmol) were added to stirred solution of 2-iodofluorene (12.38 g, 42.39 mmol) and 9-(6-bromo-hexyl)-9H-carbazole[694] (28 g, 84.78 mmol) in degassed THF (60 cm^3), and the solution was stirred for 72 h at 100 °C. After cooling to room temperature, the solution was diluted with water (100 cm^3) and extracted with diethyl ether (2 x 100 cm^3). The combined organic layer was washed with water (2 x 50 cm^3) and dried over anhydrous magnesium sulphate. After removal of the solvent *in vacuo*, purification by column chromatography (eluent 40% DCM in pet. ether) gave **226** as a white foam (29.5 g, 88%): mp 74-75 °C. (Found: C, 74.22, H, 5.89, N, 3.47%; $C_{49}H_{47}IN_2$ requires C, 74.42, H, 5.99, N, 3.54%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.47-0.53 (4H, m, C**H**$_2$), 0.95-1.10 (8H, m, C**H**$_2$), 1.62-1.69 (4H, m, C**H**$_2$), 1.76-1.86 (4H, m, C**H**$_2$), 4.15 (4H, t, ^3J = 7.6 Hz, NC**H**$_2$), 7.17 (5H, m, Ar**H**), 7.27 (1H, m, Ar**H**), 7.29 (4H, d, ^3J = 8.4 Hz, Ar**H**), 7.41 (6H, m, Ar**H**), 7.58 (3H, m, Ar**H**), 8.05 (4H, d, ^3J = 7.6 Hz, Ar**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.50, 26.80, 28.76, 29.60, 40.08, 42.91, 55.13, 92.95, 108.64, 118.71, 119.90, 120.33, 121.52, 122.78, 122.82, 125.57, 127.07, 127.76, 131.95, 135.95, 140.05, 140.40, 140.79, 149.74, 152.85; MS (ES): *m/z* 791.4 ($[M+H]^+$).

2-[9,9-Bis(6-carbazol-9-yl-hexyl)-9H-fluoren-2-yl]-[1,3,2]dioxaborolane (227).

A 2.5 M solution of n-butyllithium in hexane (10 cm^3, 25 mmol) was added dropwise to a stirred solution of **226** (14.5 g, 18.3 mmol) in degassed anhydrous THF (400 cm^3) at -78 °C and the solution was stirred for a further 5 h. Trimethylborate (15 cm^3, 134.5 mmol) was added quickly to the solution and stirring was then continued for a further 2 h at -78 °C, before allowing the solution to warm to room temperature and stir for 15 h. After removal of the solvent *in vacuo*, benzene (100 cm^3) and ethylene glycol (15 cm^3) were added to the residue and the resultant solution was stirred for 15 h at 80 °C. After cooling to room temperature, the benzene layer was separated and the solvent removed *in vacuo*. Purification by column chromatography (initial eluent 50% DCM in pet. ether increasing gradually to 10% acetone in DCM) gave **227** as a white foam (9.52 g, 71%): mp 83-84 °C. (Found: C, 83.43, H, 7.12, N, 3.66%; $C_{51}H_{51}BN_2O_2$ requires C, 83.37, H, 7.00, N, 3.81%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.47-0.53 (4H, m, C**H**$_2$), 0.99-1.07 (8H, m, C**H**$_2$), 1.57-1.62 (4H, m, C**H**$_2$), 1.86-1.91 (4H, m, C**H**$_2$), 4.33 (4H, t, ^{3}J = 7.2 Hz, NC**H**$_2$), 7.16 (4H, td, ^{3}J = 7.6 Hz, ^{4}J = 0.8 Hz, Ar**H**), 7.18-7.22 (2H, m, Ar**H**), 7.23 (4H, d, ^{3}J = 8.0 Hz, Ar**H**), 7.27 (1H, td, ^{3}J = 7.2 Hz, ^{4}J = 1.6 Hz, Ar**H**), 7.37 (4H, td, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz, Ar**H**), 7.66-7.69 (2H, m, Ar**H**), 7.72 (1H, s, Ar**H**), 7.78 (1H, dd, ^{3}J = 7.6 Hz, ^{4}J = 0.8 Hz, Ar**H**), 8.03 (4H, d, ^{3}J = 7.6 Hz, Ar**H**); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.54, 26.80, 28.72, 29.64, 40.21, 42.90, 54.89, 66.05, 108.63, 118.66, 119.32, 120.29, 122.78, 122.82, 125.55, 126.91, 127.77, 128.95, 133.86, 140.37, 140.79, 144.40, 149.63, 150.96; MS (ES): *m/z* 737.5 ($[M+2H]^+$).

5,10,15,20-Tetrakis-{[9,9-bis(6-carbazol-9-yl-hexyl)-9H-fluoren-2-yl]phenyl}-porphyrin (228).

Compound **223** (139.5 mg, 0.15 mmol), compound **227** (463 mg, 0.63 mmol), tetrakis(triphenylphosphine)palladium (20.7 mg, 0.018 mmol) and sodium carbonate (79 mg, 0.75 mmol) were stirred together in a degassed solution of THF (12 cm^3), toluene (12 cm^3) and water (0.75 cm^3) at 105 °C for 24 h. The residue was redissolved in DCM (20 cm^3) and washed with water (30 cm^3) before being dried over anhydrous magnesium sulphate. After removal of the solvent *in vacuo* and purification by column chromatography (eluent 50% DCM in hexane), **228** was obtained as a dark red powder (252 mg, 52%): mp 140-141 °C. (Found: C, 86.49, H, 6.59, N, 5.04%; $C_{240}H_{214}N_{12}.4H_2O$ requires C, 86.35, H, 6.70, N, 5.03%); ^{1}H NMR (400 MHz, $CDCl_3$) δ -2.55 (2H, s), 0.85-0.71 (16H, m), 1.27-1.11 (32H, m), 1.79-1.67 (16H, m), 2.16-2.01 (16H, m), 4.15 (16H, t, ^3J = 7.2 Hz, C**H**$_2$N), 7.18 (16H, ddd, ^3J = 7.6 Hz, ^3J = 7.4 Hz, ^4J = 0.4 Hz, carbazole-**H**), 7.30 (16H, d, ^3J = 8.0 Hz, carbazole-**H**), 7.44-7.33 (28H, m, carbazole-**H**, Fl-**H**), 7.81 (4H, d, ^3J = 7.2 Hz, Fl-**H**), 7.96-7.90 (12H, m, Fl-**H**), 8.06 (16H, d, ^3J = 7.6 Hz, carbazole-**H**), 8.10 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 8.37 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 9.02 (8H, s, porp-**H**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.78, 26.91, 28.81, 29.81, 40.48, 42.91, 55.20, 108.66, 118.71, 120.03, 120.34, 121.45, 140.90, 141.19, 150.76, 151.40; MS (MALDI-ToF): *m/z* 3266.6 ($[M]^+$); HRMS found 3263.7200, calcd. for $C_{240}H_{214}N_{12}$ 3263.7114.

5,10,15,20-Tetrakis-{[9,9-bis(6-carbazol-9-yl-hexyl)-9H-fluoren-2-yl]phenyl}-porphyrin zinc(II) (229).

Compound **228** (65.3 mg, 0.02 mmol) and zinc acetate (20 mg, 0.11 mmol) were stirred together in degassed anhydrous chloroform (10 cm^3) at 62 °C for 4 h. Removal of the solvent *in vacuo* followed by purification via column chromatography (eluent DCM) gave **229** as a dark red powder (63 mg, 95%): mp 143-144 °C. (Found: C, 83.49, H, 6.51, N, 4.71%; $C_{240}H_{212}N_{12}Zn.7H_2O$ requires C, 83.41, H, 6.59, N, 4.86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.65 (16H, m), 1.21-1.09 (32H, m), 1.73-1.62 (16H, m), 2.12-1.97 (16H, m), 4.13 (16H, t, ^3J = 7.2 Hz, C**H**$_2$N), 7.14 (16H, ddd, ^3J = 7.6 Hz, ^3J = 7.4 Hz, ^4J = 0.8 Hz, carbazole-**H**), 7.27 (16H, d, ^3J = 8.0 Hz, carbazole-**H**), 7.40-7.29 (28H, m, carbazole-**H**, Fl-**H**), 7.78 (4H, d, ^3J = 7.2 Hz, Fl-**H**), 7.94-7.86 (12H, m, Fl-**H**), 8.01 (16H, d, ^3J = 7.6 Hz, carbazole-**H**), 8.07 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 8.33 (8H, d, ^3J = 8.0 Hz, Ph-**H**), 9.07 (8H, s, porp-**H**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.67, 25.81, 27.70, 28.70, 39.38, 41.79, 54.09, 107.54, 117.59, 118.91, 119.21, 119.91, 120.32, 121.69, 121.79, 124.24, 124.45, 125.32, 125.98, 126.22, 131.09, 134.02, 138.62, 139.28, 139.44, 139.74, 140.75, 149.25, 149.64, 150.29; MS (MALDI-ToF): *m/z* 3329.3 ([M]$^+$); HRMS found 3325.6229, calcd. for $C_{240}H_{212}N_{12}Zn$ 3325.6249.

3,5-diphenyl-benzaldehyde (230).

Phenyl boronic acid (1.0 g, 8.20 mmol), 3,5-dibromobenzaldehye (1.03 g, 3.90 mmol), tetrakis(triphenylphosphine)palladium(0) (0.18 g, 0.164 mmol) and sodium carbonate (1.09 g, 10.3 mmol) were stirred together in a degassed solution of THF (60 cm^3), toluene (75 cm^3) and water (9 cm^3) at 105 °C for 120 h. The solution was then allowed to cool to room temperature, the solvents were removed *in vacuo* and the residue was redissolved in DCM (150 cm^3) and water (100 cm^3). The layers were separated, the aqueous phase extracted with DCM (2 x 75 cm^3) and the combined organic layers were then dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and subsequent purification via column chromatography (eluent 50% DCM in hexane) gave **230** as a white solid (994 mg, 98%); mp 96-97.5 °C. (Found: C, 88.15, H, 5.46%; $C_{19}H_{14}O$ requires C, 88.34, H, 5.46%); (Found: $[M]^+$ 258.1046; $C_{19}H_{14}O$ requires 258.1045); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42-7.54 (6H, m, Ar**H**), 7.67 (4H, d, ^3J = 7.95 Hz, Ar**H**), 8.04-8.05 (3H, m, Ar**H**), 10.10 (1H, s, C**H**O); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 127.53, 127.84, 128.65, 129.82, 137.88 (**C**CHO), 140.04 (CH**C**CCH), 143.17 (CHC**C**CH), 192.23 (**C**HO); IR (Nujol): 2944, 2842, 2728, 2665, 1952, 1887, 1806, 1709, 1698, 1591, 1460, 1377, 1335, 1301, 1183, 1165, 1077, 1027, 1002, 972, 941, 910, 883, 851, 758, 722, 697, 642, 613, 551, 539, 499; MS (ES^+): *m/z* 257.2 $([M-H]^+$.

5,10,15,20-tetra(3,5-diphenylbenzyl)-porphyrin (231).

Trifluoroacetic acid (0.11 cm^3, 1.5 mmol) was added dropwise to a stirred solution of pyrrole (0.07 cm^3, 1.0 mmol) and **230** (0.26 g, 1.0 mmol) in degassed anhydrous chloroform and the solution was stirred at 50 °C for 2 h. After allowing the solution to cool to room temperature, DDQ (0.23 g, 1.0 mmol) was added and stirring was then continued for a further 2.5 h. Triethylamine (0.21 cm^3, 1.5 mmol) was added dropwise and the reaction mixture was filtered through a short column (initial eluent DCM followed by ethyl acetate) giving a crude product after the removal of solvents *in vacuo*. Purification via column chromatography (eluent 0.01% methanol in DCM) gave **231** as a purple solid (42 mg, 14%); mp >400 °C. ^{1}H-NMR (300 Mz, $CDCl_3$) δ -2.50 (2H, s, N**H**), 7.41 (8H, t, ^3J = 6.9 Hz, Ar**H**), 7.50 (16H, q, ^3J = 7.2 Hz, Ar**H**),

8.50 (8H, d, ^4J = 1.8 Hz, Ar**H**), 9.07 (8H, s, py**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 127.67, 127.80, 127.86, 129.19, 129.24, 140.30, 141.09; MS (MALDI-ToF): *m/z* 1222.5, 1223.5, 1224.5 ($[M]^+$), 1223.5, 1224.5, 1225,5, 1226.5 ($[M+H]^+$; HRMS found 1222.4979, calcd. for $C_{92}H_{62}N_4$ 1222.4974.

5,6-Di-*p*-tolyl-pyrazine-2,3-dicarbonitrile (232)

Compound **232** was synthesised by a modification of the literature route.[672] 4,4-Dimethylbenzil (1.95 g, 8.18 mmol) and diaminomaleonitrile (0.86 g, 7.96 mmol) were stirred together in a degassed solution of ethanol (25 cm^3), water (15 cm^3) and acetic acid (0.7 cm^3) at 100 °C for 1 h. The solution was allowed to cool to room temperature and then filtered to give a crude yellow solid. Recrystallization from ethanol gave **232** as a pale yellow solid (1.91 g, 77%); mp 165-167 °C (lit mp 160-161 °C). (Found: C, 77.41, H, 4.55, N, 18.31%; $C_{20}H_{14}N_4$ requires C, 77.39, H, 4.55, N, 18.05%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.39 (6H, s, C**H**$_3$), 7.17 (4H, d, ^3J = 8.1 Hz, Ph**H**), 7.55 (4H, d, ^3J = 8.1 Hz, Ph**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 21.99 (**C**H$_3$), 113.99 (**C**N), 129.97 (**C**CN), 130.00 (**Ph**H), 132.96 (**C**CH$_3$), 142.01 (CH$_3$CCHCH**C**), 155.97 (CH$_3$CCHCHC**C**); IR (Nujol): 2924, 2905, 2858, 2714, 2659, 2397, 2225, 1884, 1605, 1502, 1463, 1377, 1299, 1229, 1209, 1182, 1110, 1065, 1017, 946, 937, 885, 822, 790, 723, 690, 677, 665, 640, 612, 563, 531, 506; MS (EI): *m/z* 280 ($[M-2CH_3]^+$), 295 ($[M-CH_3]^+$), 310 ($[M]^+$).

2,3,9,10,16,17,23,24-Octakis(*p*-tolyl)-29H,31H-tetrapyrazinoporphyrazine (233).

A freshly prepared lithium pentoxide solution in 1-pentanol (1.89 M, 125 cm^3) was added to a stirred solution of **232** (5.00 g, 16.11 mmol) in degassed anhydrous 1,4-dioxane (50 cm^3) and the mixture was then stirred at 105 °C for 24 h. The solution was allowed to cool to room temperature, diluted with ethanol (400 cm^3) and left to stand for 20 h. Filtration gave a crude black solid which was dissolved in chloroform to give a dark-green solution. Glacial acetic acid (1 cm^3) was added and the solution stirred for 1 h. Purification by direct filtration of the solution through a Celite column

(eluent DCM) gave **233** as a dark green solid (709 mg, 14%); mp >400 °C. (Found: C, 76.71, 5.01, N, 17.62%; $C_{80}H_{58}N_{16}.H_2O$ requires C, 76.17, H, 4.79, N, 17.77%); IR (Nujol): IR (Nujol): 2930, 2894, 2853, 2725, 2660, 2007, 1592, 1461, 1377, 1306, 1420, 1169, 1153, 1097, 1075, 1057, 1016, 966, 942, 917, 889, 834, 819, 766, 722, 691, 616, 543; MS (MALDI-ToF): *m/z* 1243.4 ($[M]^+$), 2486.8 ($[2M]^+$); HRMS found 1242.5031, calcd. for $C_{80}H_{58}N_{16}$ 1242.5030.

2-Hydroxy-1,2-dithien-2-yl-ethanone (234)

Compound **234** was prepared according to the literature method using a different method of purification.[677]

[Th(2)-CH(OH)-CO-Th(2`) with respect to ^{1}H-NMR assignment]

2-Thiophene-carbaldehyde (4.17 cm^3, 44.6 mmol), 3-benzyl-5-(hydroxyethyl)-4-methylthiazolium chloride (0.24 g, 0.892 mmol) and triethylamine (0.62 cm^3, 4.45 mmol) were stirred together in ethanol (40 cm^3) at 90 °C for 5 h. The solution was then allowed to cool to room temperature, diluted with water (20 cm^3) and cooled in an ice bath. Filtration of the chilled solution gave a crude yellow solid (2.64 g) which after purification by column chromatography (eluent 33% hexane in DCM) gave **234** as a pale yellow solid (2.73 g, 55%) and 1,2-dithien-2-yl-ethane-1,2-dione (**235**) as a bright yellow solid (304 mg, 6%). **234**: mp 100-104 °C (lit mp 108-109 °C);[676] (Found: C, 53.15, H, 3.33%; $C_{10}H_8S_2O_2$ requires C, 53.55, H, 3.59%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 6.13 (1H, d, ^{3}J = 5.1 Hz, C**H**OH), 6.58 (1H, d, ^{3}J = 5.1 Hz, CHO**H**), 7.00 (1H, dd, ^{3}J = 4.1, 4.8 Hz, thiophene-4H), 7.14 (1H, d, ^{3}J = 3.9 Hz, thiophene-5H), 7.27 (1H, dd, ^{3}J = 4.2, 4.7 Hz, thiophene-4`H), 7.51 (1H, d, $^3$J = 5.1 Hz, thiophene-3H), 8.07 (1H, d, $^3$J = 4.95 Hz, thiophene-3`H), 8.18 (1H, d, ^{3}J = 3.9 Hz, thiophene-5`H); ^{13}C-NMR (100 MH, DMSO-d_6) δ 73.22, 126.57, 126.98, 127.53, 129.35, 135.34, 136.46, 140.86, 143.73, 191.83 (**C**O); MS (ES^+): *m/z* 207.0 ($[M-OH]^+$), 247.0 ($[M+Na]^+$). **235**: mp 82-83 °C (lit mp 81-82 °C);[676] (Found: C, 54.16, H, 2.71%; $C_{10}H_6S_2O_2$ requires C, 54.04, H, 2.72%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.38 (2H, dd, ^{3}J = 4.0, 4.6 Hz, thiophene-4H), 8.07 (2H, d, ^{3}J = 3.9 Hz, thiophene-5H), 8.34 (2H, d, ^{3}J = 4.8 Hz, thiophene-3H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 130.01, 138.42, 138.87, 140.02, 183.89 (**C**O); MS (ES^+): *m/z* 245.0 ($[M+Na]^+$).

1,2-Dithien-2-yl-ethane-1,2-dione (235)

Compound **235** was prepared according to the literature route.[676]

Compound **234** (2.73 g, 12.16 mmol), bismuth(III) oxide (2.83 g, 6.07 mmol) and acetic acid (5 cm^3) were stirred together in 2-ethoxyethanol (25 cm^3) at 110 °C for 8 h. The boiling mixture was filtered and upon cooling precipitated a yellow solid which after filtration gave **235** as a bright yellow solid (2.57 g, 95%); mp 82-83 °C (lit mp 81-82 °C).[676] Analysis showed product was identical to that formed by previous reaction.

5,6-Di-thien-2-yl-pyrazine-2,3-dicarbonitrile (236)

Compound **236** was prepared by a modification of the literature route.[177]

Compound **235** (0.90 g, 4.05 mmol), diaminomaleonitrile (0.53 g, 4.86 mmol) and acetic acid (1 cm^3) were stirred together in a degassed solution of ethanol (25 cm^3) and water (15 cm^3) at 100 °C for 18 h. The solution was then allowed to cool to room temperature and filtered to give **236** as a yellow solid (979 mg, 82%); mp 186-187 °C (lit mp 179-180 °C). (Found: C, 56.90, H, 2.01, N, 18.98%; $C_{14}H_6N_4S_2$ requires C, 57.13, H, 2.05, N, 19.03%); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.27 (2H, dd, ^3J = 4.0, 4.4 Hz, thiophene-4H), 7.59 (2H, d, ^3J = 3.8 Hz, thiophene-5H), 8.03 (2H, d, ^3J = 4.5 Hz, thiophene-3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 113.43 (**C**N), 128.23, 128.35, 131.99, 133.54, 138.22 (**C**CN), 148.21; MS (ES^+): *m/z* 294.1 ($[M]^+$), 317.0 ($[M+Na]^+$), 620 ($[2M+MeOH]^+$).

2,3,9,10,16,17,23,24-Octakis(thien-2-yl)-29H,31H-tetrapyrazinoporphyrazine (237).

Compound **236** (0.29 g, 0.985 mmol) was stirred in degassed anhydrous 1-pentanol (5 cm^3) at 50 °C until dissolved. An excess of lithium metal (20 mg, 2.88 mmol) was added and the solution stirred at 105 °C for 2 h. The solution was allowed to cool to room temperature, 37% aq. HCl (2 cm^3) was added dropwise and the solution was then poured into methanol (50 cm^3). Filtration gave a crude black solid which was washed with copious amounts of DCM to give **237** as a highly insoluble dark blue solid (36 mg, 12%); mp >400 °C. (Found: C, 54.36, H, 2.40, N, 17.63%; $C_{56}H_{26}N_{16}S_8.3H_2O$ requires C, 54.53, H, 2.61, N, 18.17%); MS (MALDI-ToF): *m/z* 1180.0 ($[M+2H]^+$), 1209.9 ($[M+MeOH]^+$).

5,6-bis(4-bromo-phenyl)-pyrazine-2,3-dicarbonitrile (238)

Compound **238** was synthesised by a modification of the literature route.[685]

Dibromobenzil (2.5 g, 6.79 mmol) and diaminomaleonitrile (0.88 g, 8.15 mmol) were stirred together in a solution of acetic acid (30 cm^3) at 120 °C for 4 h. The solution was allowed to cool to room temperature and the solvents were removed *in vacuo*. The residue was dissolved in methanol (15 cm^3) and placed in an ice bath for 2 h. Precipitation gave a crude brown solid (2.96 g) which after purification by column chromatography (eluent DCM) gave **238** as a pale yellow solid (2.30 g, 77%); mp 209-211 °C (lit mp 208 °C).[685] (Found: C, 49.15, H, 1.80, N, 12.79%; $C_{18}H_8N_4Br_2$ requires C, 49.13, H, 1.83, N, 12.73%); (Found: $[M-2H]^+$ 437.9142; $[C_{18}H_8N_4Br_2-2H]$ requires 437.8939); ^{1}H-NMR (200 MHz, DMSO-d_6) δ 7.48 (4H, d, ^3J = 8.4 Hz, BrCCHC**H**), 7.71 (4H, d, ^3J = 8.2 Hz, BrC**CH**); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 115.23 (**C**N), 125.72, (**C**Br), 131.01 (**C**CN), 132.84 (**Ph**H), 135.79 (BrCCHCH**C**), 154.31 (BrCCHCHC**C**); IR (Nujol): 2934, 2909, 2854, 2715, 2655, 2227, 1897, 1583, 1508, 1463, 1377, 1298, 1272, 1216, 1186, 1125, 1106, 1068, 1065, 1005, 931, 825, 722, 672, 629, 570, 547, 528, 499; MS (MALDI-ToF): *m/z* 305.0 ($[M-2Br+Na]^+$), 438.1, 440.2, 442.2 ($[M]^+$).

Crystals were grown by a slow diffusion of hexane into a solution of **238** in DCM.

5,6-bis[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]pyrazine-2,3-dicarbonitrile (239).

Compound **202** (0.25 g, 0.66 mmol), compound **238** (0.15 g, 0.33 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg, 13.2 μmol) and sodium carbonate (87 mg, 0.825 mmol) were stirred together in a degassed solution of THF (20 cm^3), toluene (25 cm^3) and water (3 cm^3) at 105 °C for 72 h. The solution was then allowed to cool to room temperature, the solvents were removed *in vacuo* and the residue was then redissolved in DCM (100 cm^3) and water (100 cm^3). The layers were separated, the aqueous phase was extracted with DCM (75 cm^3) and the combined organic layers were then washed with water (50 cm^3) and dried over anhydrous magnesium sulphate. Removal of the solvent *in vacuo* and purification via column chromatography (eluent 50% DCM in hexane) gave a crude yellow solid which after a second purification by column chromatography (eluent 33% hexane in chloroform) gave **239** as a bright yellow solid (191 mg, 59%); mp 96-98 °C. (Found: C, 85.80, H, 7.89, N, 5.69%; $C_{68}H_{74}N_4$. requires C, 86.21, H, 7.87, N, 5.91%); (Found: $[M]^+$ 946.5915; $C_{68}H_{74}N_4$ requires 946.5913); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.64.070 (8H, m, C**H**$_2$), 0.75 (12H, t, ^3J = 6.9 Hz, C**H**$_3$), 1.05-1.12 (24H, m, C**H**$_2$), 1.99-2.04 (8H, m, C**H**$_2$), 7.34-7.37 (6H, m, Ar**H**), 7.62 (4H, d, ^3J = 9.75 Hz, Ar**H**), 7.76 (12H, dd, ^3J = 8.1 Hz, ^4J = 4.8 Hz, Ar**H**); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.05 (**C**H$_3$), 22.76 (**C**H$_2$), 24.01 (**C**H$_2$), 29.65 (**C**H$_2$), 31.89 (**C**H$_2$), 40.84 (**C**H$_2$) , 55.93 (CH$_2$**C**CH$_2$), 113.75, 120.02, 120.04, 121.72, 123.64, 126.05, 127.12, 127.95 (**Ph**H), 129.86, 130.84 (**Ph**H), 134.44, 138.45, 140.56, 141.94, 144.89, 151.67, 151.68, 151.99, 155.43, IR (Nujol): 2905, 2857, 2725, 2658, 2022, 1603, 1492, 1463, 1377, 1300, 1219, 1187, 1153, 1067, 1013, 962, 937, 889, 847, 824, 762, 727, 722, 677, 653, 628, 574, 529 MS (MALDI-ToF): *m/z* 946.5, 947.5, 948.5 ($[M]^+$).

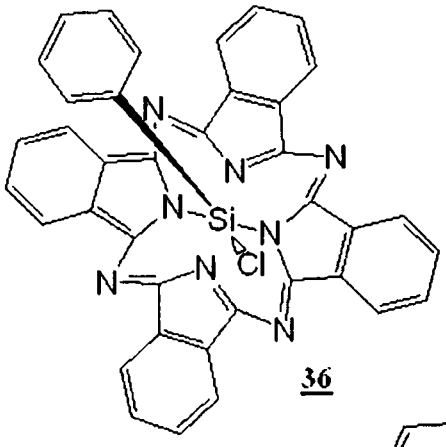
2,3,9,10,16,17,23,24-Octakis[4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl]-29H,31H-tetrapyrazinoporphyrazine (240).

A freshly prepared lithium pentoxide solution in 1-pentanol (1.89 M, 5 cm^3) was added to a stirred solution of **239** (99.5 mg, 0.105 mmol) in degassed anhydrous 1,4-dioxane (2 cm^3) and the solution was stirred at 105 °C for 12 h. The solution was allowed to cool to room temperature and the solvent removed *in vacuo*. The black residue was redissolved in degassed anhydrous chloroform (2 cm^3), a solution of acetic acid (1 cm^3) in ethanol (30 cm^3) was added and the mixture was then stirred at 78 °C for 20 h. After being allowed to cool to room temperature, the mixture was placed in an ice bath for 1 h and then filtered to give a crude blue solid. Purification by flash chromatography (eluent DCM) gave **240** as a dark blue solid (23 mg, 23%); mp >400 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.71 (96H, m, C**H**$_2$), 1.03 (80H, m, C**H**$_2$/C**H**$_3$), 1.88 (32H, m, C**H**$_2$) 7.34 (32H, m, Ph**H**), 7.57-7.74 (56H, m, Ar**H**), [NH protons not observed down to -5ppm]; IR (Nujol): 3162, 2911, 2852, 2710, 2658, 2032, 1610, 1489, 1376, 1299, 1219, 1174, 1070, 986, 919, 873, 837, 759, 720, 511; MS (MALDI-ToF): *m/z* 1924.3, 2862.9, 3793.5 ($[M+2H]^+$); HRMS found 3788.3826, calcd. for $C_{272}H_{298}N_{16}$ 3788.3810.

9-Oxo-9H-indeno[2,1-b]pyrazine-2,3-dicarbonitrile (241)

Compound **242** was synthesised by a modification of the literature route.[688] Ninhydrin (0.25 g, 1.40 mmol) and diaminomaleonitrile (0.15 g, 1.40 mmol) were stirred together in ethanol (25 cm^3) at 78 °C for 20 h. The stirred solution was allowed to cool to room temperature and water (10 cm^3) was added. Filtration of the resultant precipitate gave **241** as a golden-brown solid (212 mg, 65%); mp 266-267 °C (lit mp 262-263 °C). (Found: C, 66.88, H, 1.71, N, 24.56%; $C_{13}H_4N_4O$ requires C, 67.24, H, 1.74, N, 24.13%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77 (1H, t, ^3J = 7.5 Hz), 7.87 (1H, t, ^3J = 7.65 Hz), 7.99 (1H, d, ^3J = 7.5 Hz), 8.07 (1H, d, ^3J = 7.5 Hz); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 115.56 (**C**N), 124.43, 126.02, 132.85, 135.02, 135.96, 136.55, 138.00, 138.99, 151.21, 160.97, 187.02 (**C**O); MS (MALDI-ToF): *m/z* 232.0 ($[M]^+$).

Appendix A – Structures of the compounds synthesised



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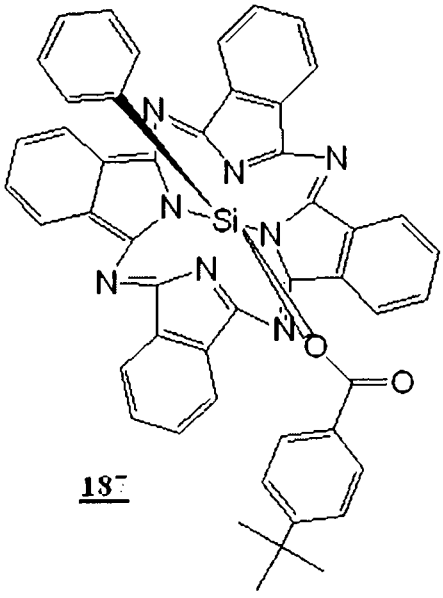

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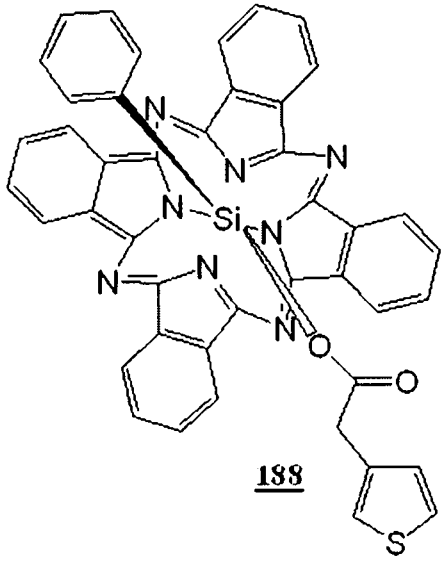

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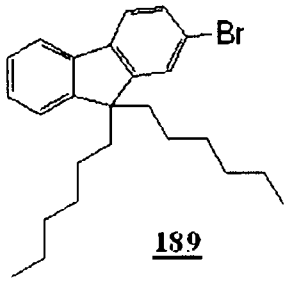

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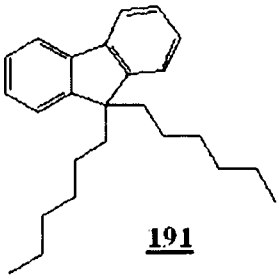

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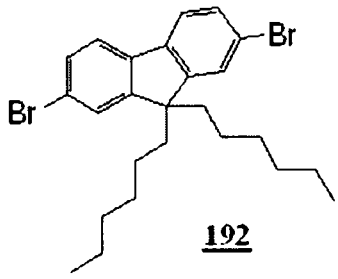

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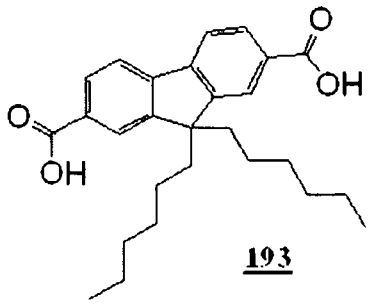

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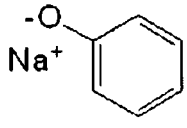

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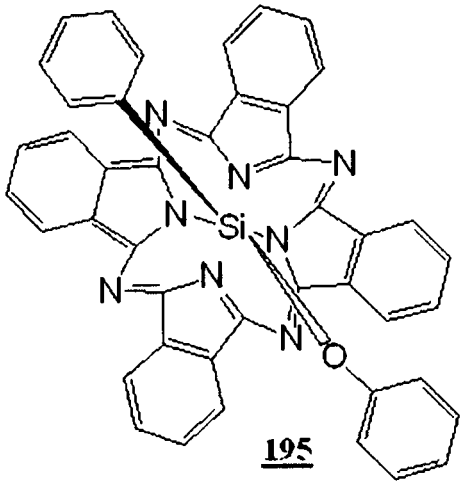

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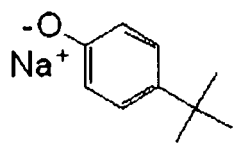

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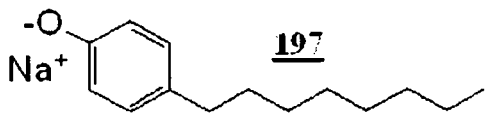

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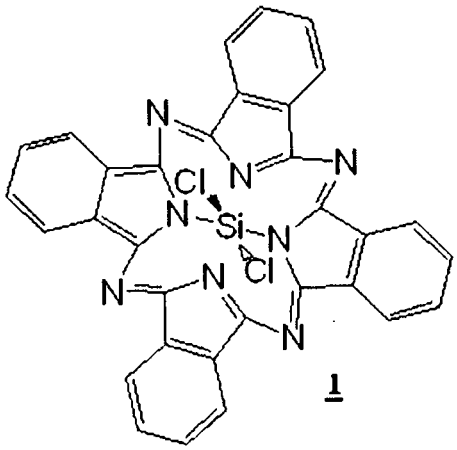

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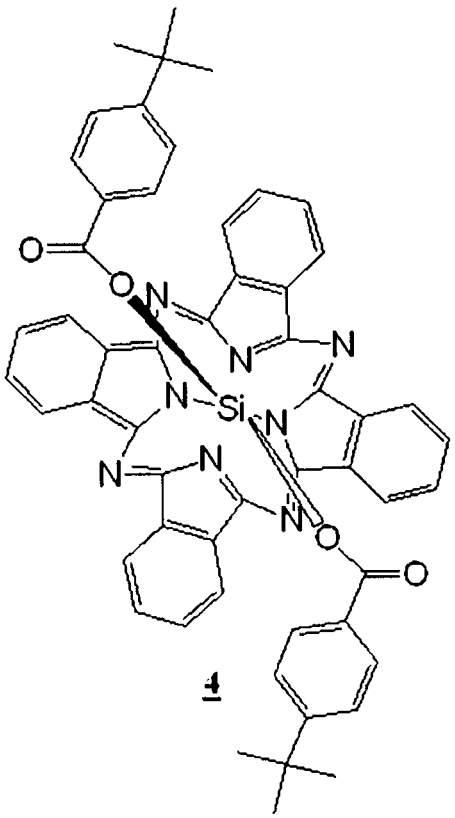

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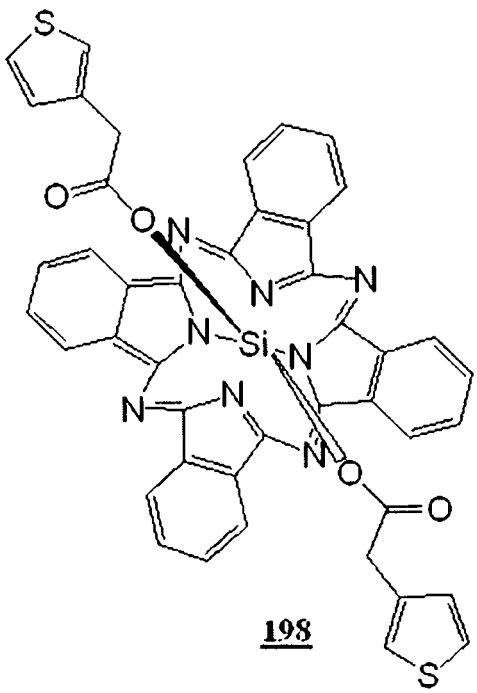

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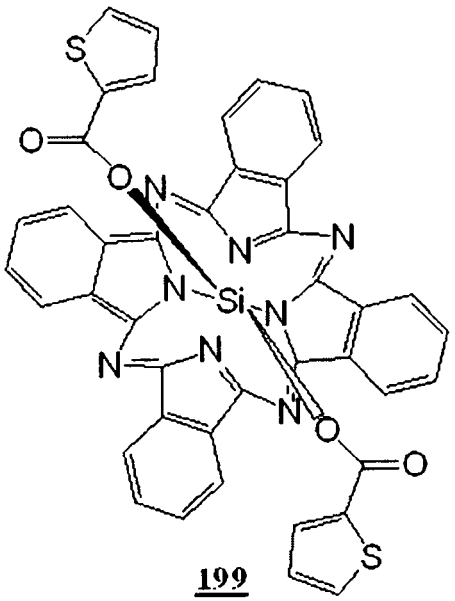

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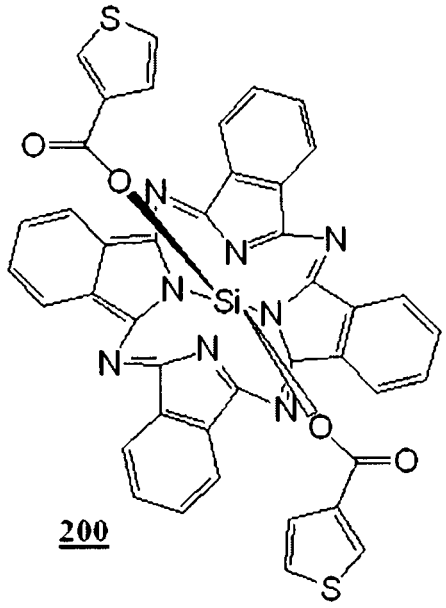

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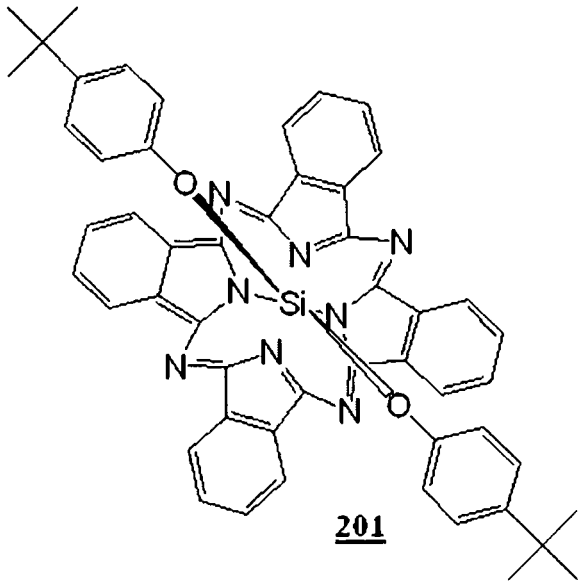

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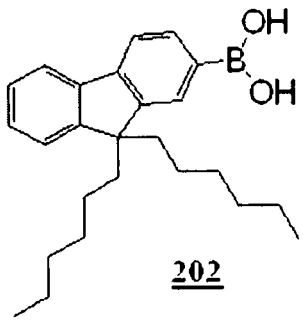

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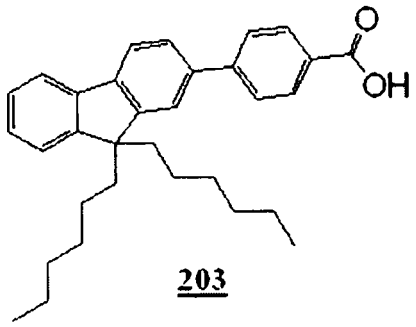

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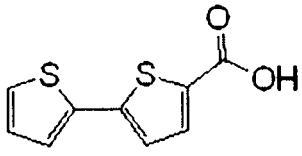

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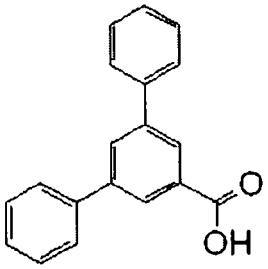

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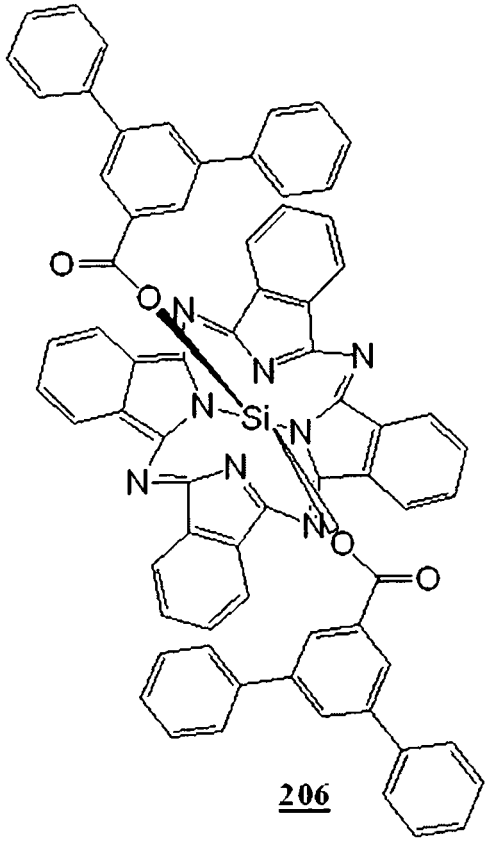

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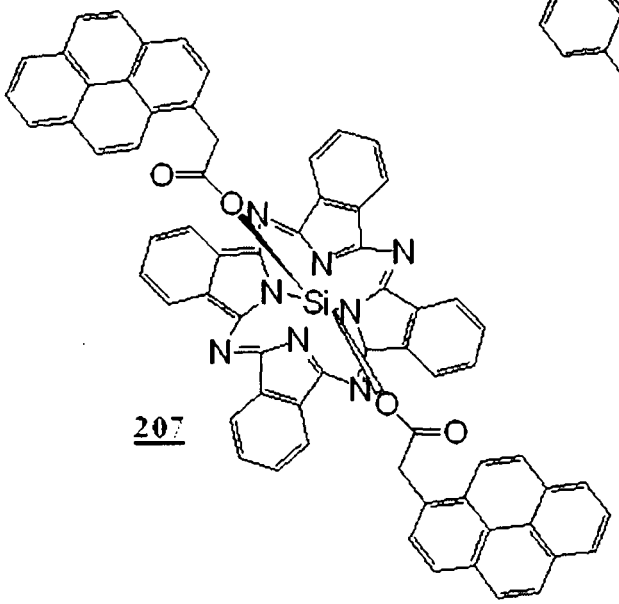

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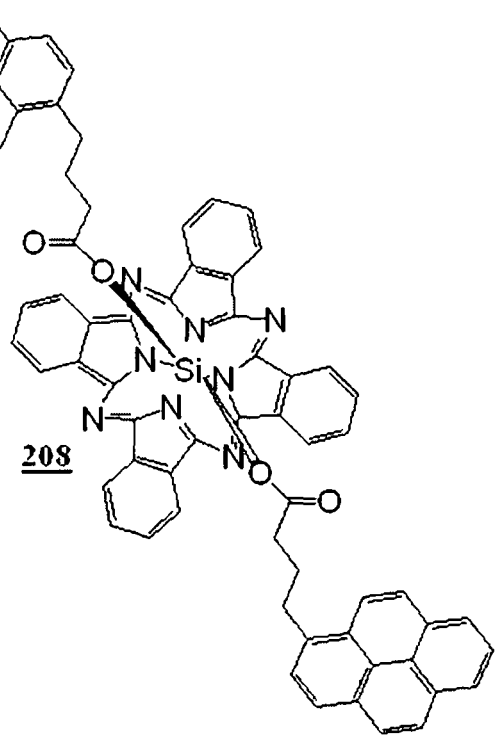

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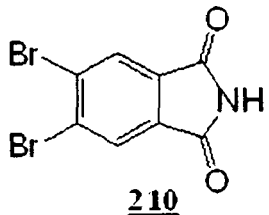

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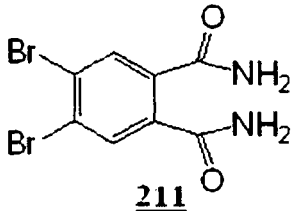

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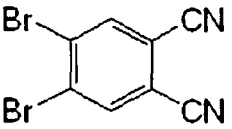

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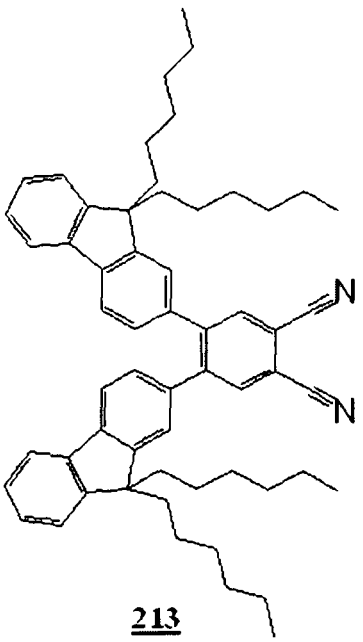

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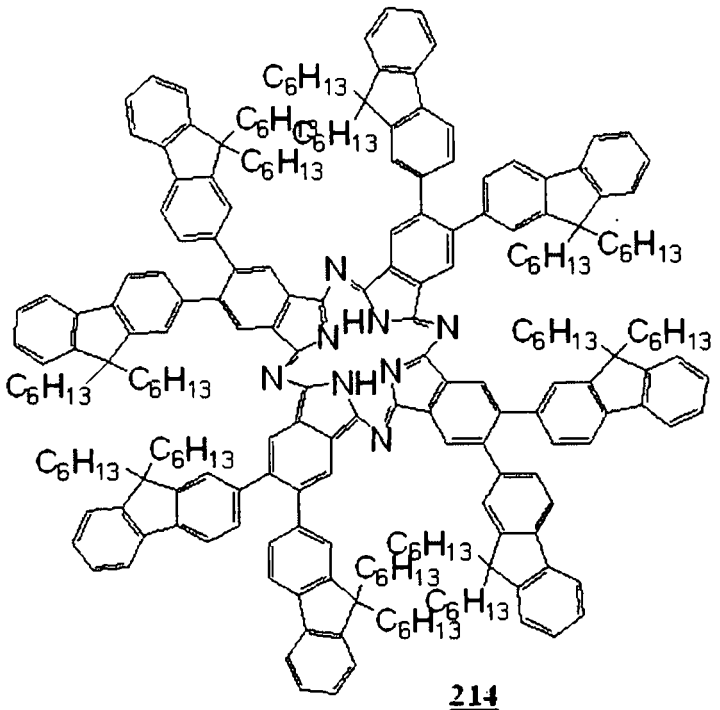

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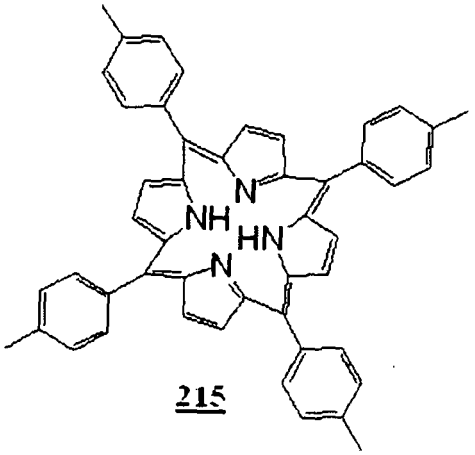

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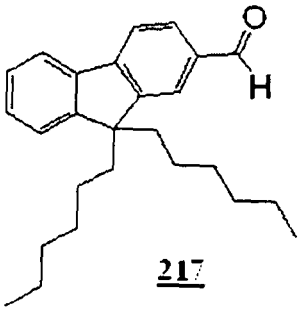

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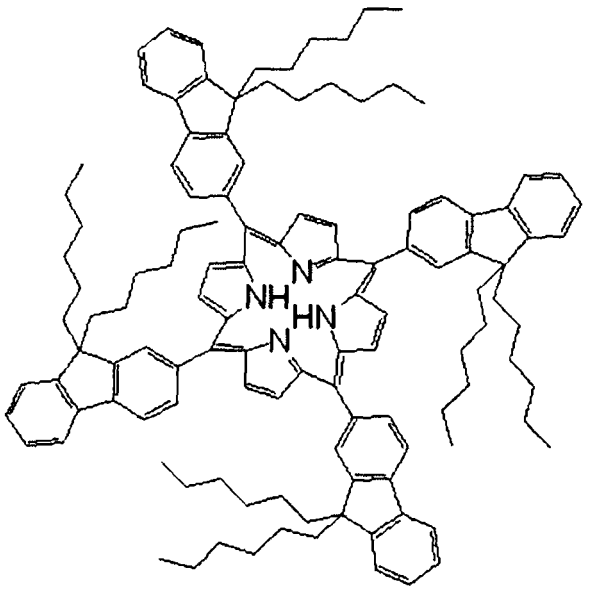

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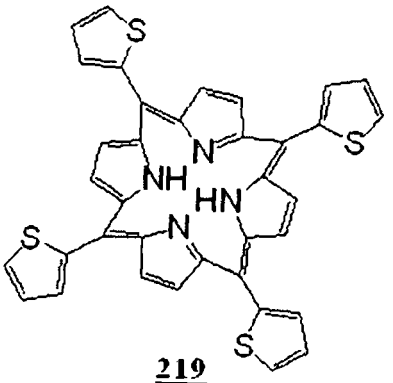

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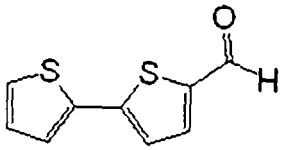

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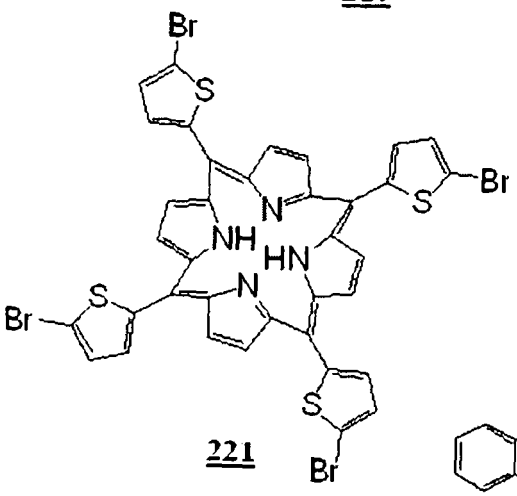

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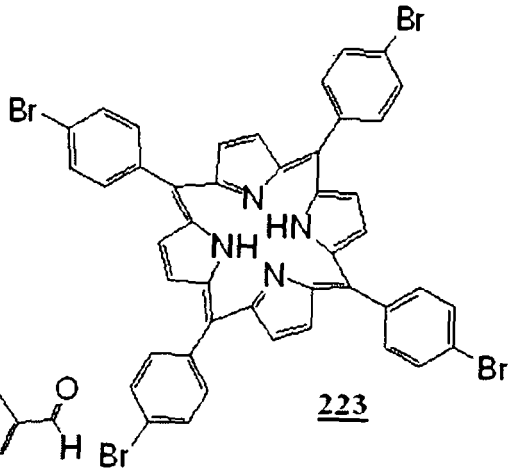

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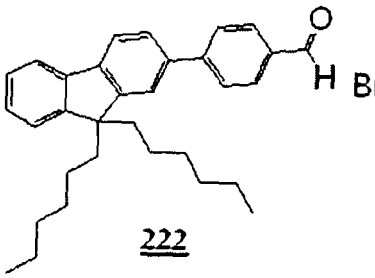

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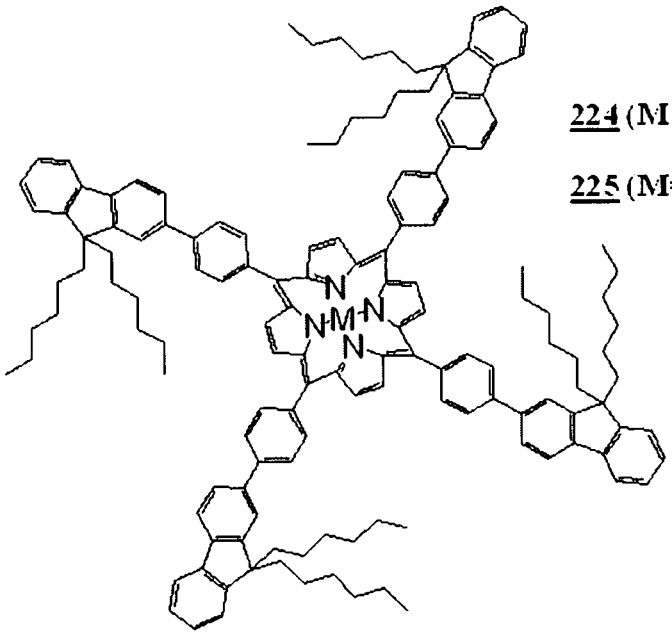

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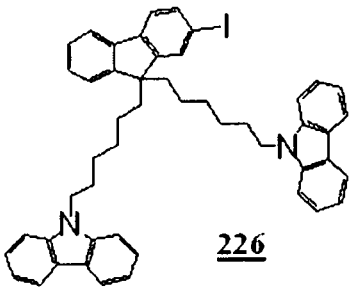
225 (M=Zn)



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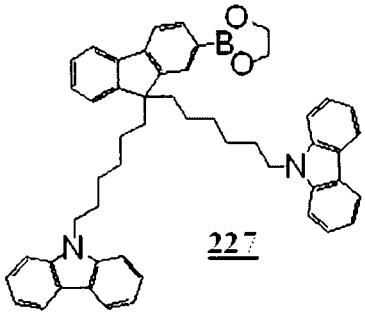

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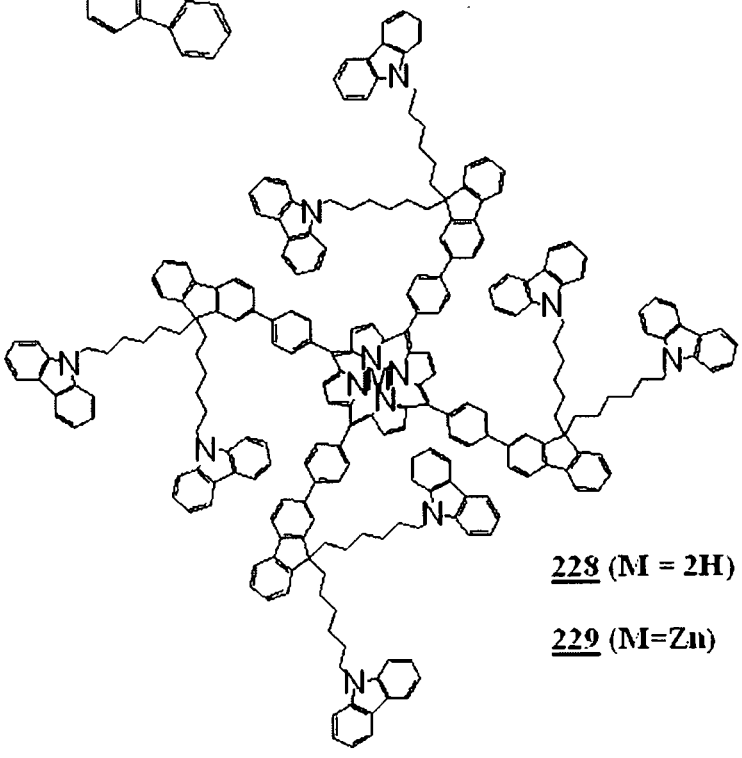

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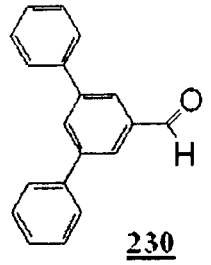

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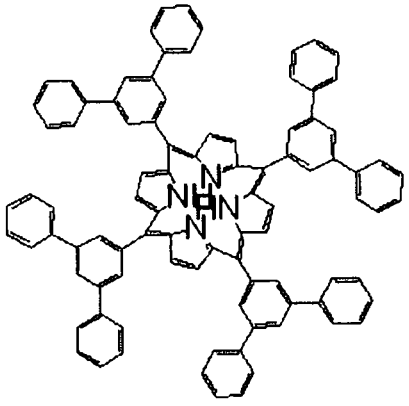

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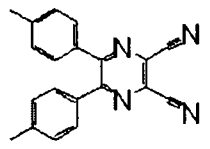

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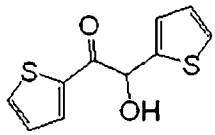

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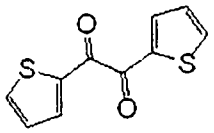

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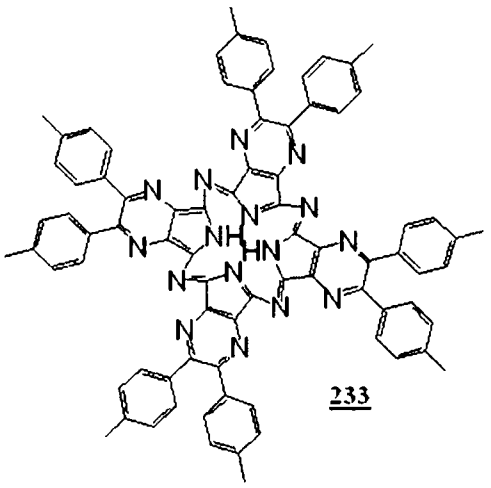
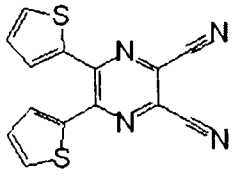
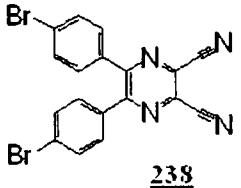


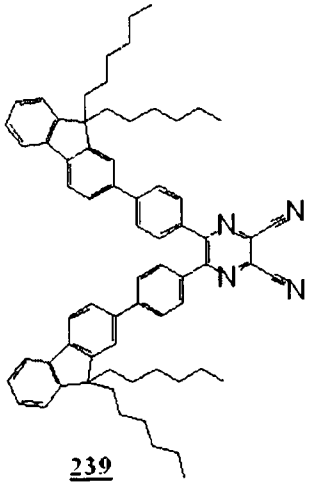
233



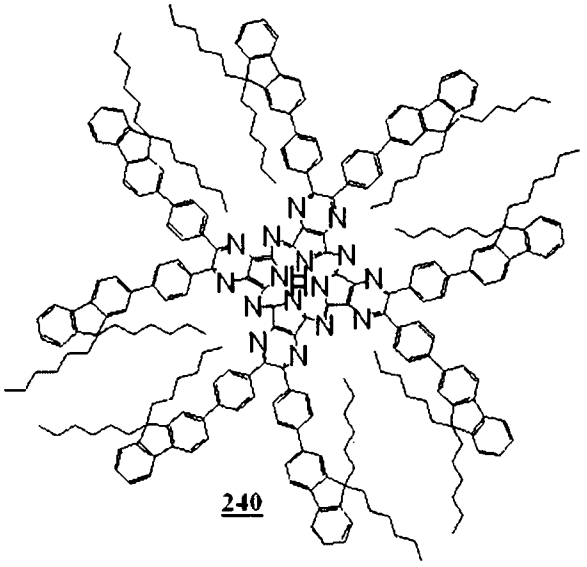
236



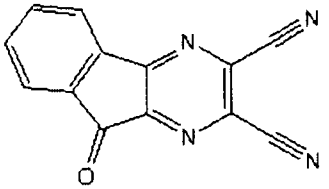
238



239

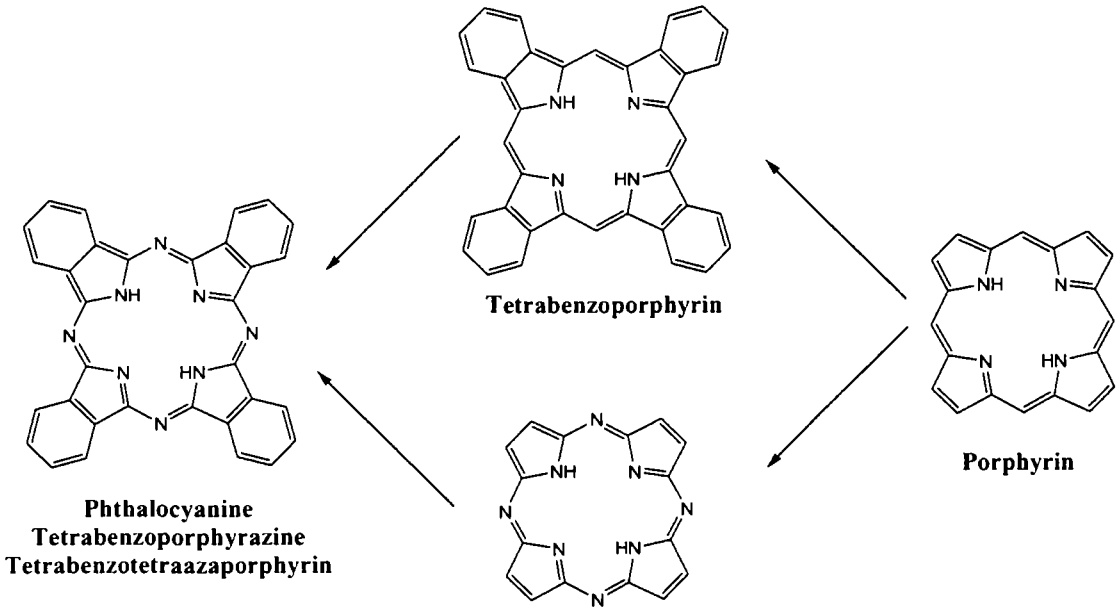


240



241

Appendix B - Macrocycle Nomenclature



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