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Phthalocyanine-containing polymers

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The optical and electronic properties of the phthalocyanine (Pc) macrocycle make it suitable for a wide range of applications. The enormous diversity of Pc-containing polymers, developed over thirty years of research, offers the prospect of readily processed materials in which covalent linkages can be used to control the ordering and arrangement of the Pc units. This article reviews both the synthesis and study of Pc-containing polymers. The types of polymer are classified by the way in which the macrocycle is incorporated within the macromolecular structure as either network, main-chain or side-chain polymers. In addition, recent work on the incorporation of the Pc macrocycle as polymer end-groups or as the core unit in a number of dendrimers is also described.

1 Introduction

Since their accidental discovery over seventy years ago and subsequent structural elucidation,[1] the phthalocyanines have been one of the most studied classes of organic functional materials.[2] The diverse functionality of the phthalocyanine (Pc) macrocycle originates from its 18-π electron aromatic system which is closely related to that of the naturally occurring porphyrin ring. The additional π-orbital conjugation afforded by the benzo moieties and the orbital perturbation caused by the nitrogen atoms at the four *meso*-positions have a profound effect on the UV-VIS spectrum of the porphyrin chromophore resulting in a red-shift of the Q-band and a strong enhancement of its intensity ($\lambda_{\max} \sim 680$ nm, $\varepsilon \sim 2 \times 10^5$ cm^2 mol^{-1}). In addition to their ubiquitous use as highly stable blue and green colorants, Pcs find commercial applications as a photoconductor in Xerography,[3] and in optical data storage as the laser absorption layer within recordable compact discs (R-CDs).[4] In addition, they are of increasing interest for applications in non-linear optics (including optical limitation),[5] molecular electronics,[6] photodynamic cancer therapy,[7] solar energy conversion (most recently as photosensitisers for cheap, amorphous semiconductors),[8] various catalytic processes,[9] electrochromic and electroluminescent displays,[10] chromatography,[11] and as the active component of gas sensors.[12]

The synthesis of Pc is usually acieved by the high temperature cyclotetramerisation of either phthalonitrile or phthalic anhydride (Scheme 1). The former method is generally a cleaner reaction while the latter, which is favoured in industry due to the cheaper precursor, requires a nitrogen donor such as urea as a co-reactant. Both reactions are helped by the template effect afforded by a suitable metal ion. It is known that the Pc macrocycle (formally a Pc^{2-} anion) can hold cations derived from over 70 different elements in its central cavity and some transition metal ions (*e.g.* Cu^{2+} and Ni^{2+}) cannot be removed without the destruction of the macrocycle. However, metal-free Pc can be prepared by removal of labile metal ions such as Li^{+} or Mg^{2+} after cyclotetramerisation.

In order to exploit the interesting properties of Pc, precise control over the molecular packing and ordering in the solid phase is required. Low molar mass derivatives self-assemble into a variety of crystalline polymorphs[2,13] and have been used to prepare ordered thin films by vacuum sublimation,[2,14] the Langmuir–Blodgett (LB) technique[2,15] and spin-coating.[2,16] In addition, many Pc derivatives which are substituted with flexible side-chains form liquid crystals in which the molecules self-assemble into ordered columnar structures.[2,17] However, Pc-containing polymers offer the prospect of robust, processable materials in which the relative orientation of the constituent Pc units can be controlled by strong covalent bonding.[18] The Pc ring provides up to sixteen sites on the benzo groups for covalent attachment to a polymer and two further sites for bonding (covalent or non-covalent) are offered at the axial positions of suitable ions held in the central cavity. For the purposes of this review Pc-containing polymers are defined by the way in which the macrocycle is incorporated within the macromolecular structure as either *network*, *main-chain* or *side-chain* polymers. In addition polymers which incorporate the Pc macrocycle as *end-groups* or as a single *core* are also considered.

2 Network polymers

2.1 Networks formed by Pc formation

In the late 1950s Marvel and co-workers noted that if a bis(phthalonitrile)[19] or a bis(phthalic anhydride)[20] is reacted under conditions which favour Pc formation a dark-blue intractable material is produced (Scheme 2). Since this early work many studies concerning polymer network formation *via* cyclotetramerisation reactions have been described.[18c,21] In each case, the resultant material was insoluble in organic solvents and thus difficult to characterise. However, it is reasonable to assume that the material contains several structural heterogeneities which deviate from an idealised network structure. Firstly, there is likely to be a number of different types of end-group including unreacted phthalonitrile or phthalic anhydride functionality and various hydrolysed groups (*e.g.* imide, carboxylic acid); although post-polymerisation treatment (*e.g.* hydrolysis) can improve end-group uniformity. Secondly, for all of the polymers shown in Scheme 2, each composite Pc unit may be linked to the network by 1, 2, 3 or 4 covalent bonds. Thirdly, each phthalocyanine group in these materials is tetra-substituted and, therefore, there will be a statistical mixture of four structural isomer units of D_{2h}, C_{4h}, C_{2v} and C_s symmetry.[22] Equations for the calculation of the vast number of isomers for this type of polymer have been derived.[23] Finally, even for a highly efficient Pc-forming polymerisation reaction, defects such as triazine and isoindoline groups are likely (Fig. 1). Indeed, simple annealing of bis(phthalonitrile)s at high temperatures (310 °C) without metal, metal salt or reducing agent, is reported to yield brown intractable polyindoline-based networks which contain no Pc units.[24] In addition, during the cyclotetramerisation reaction there may be incomplete metal ion complexation giving metal-free Pc units. With all of these possible causes for heterogeneity, it is statistically unlikely that two defect-free macromolecules of the same

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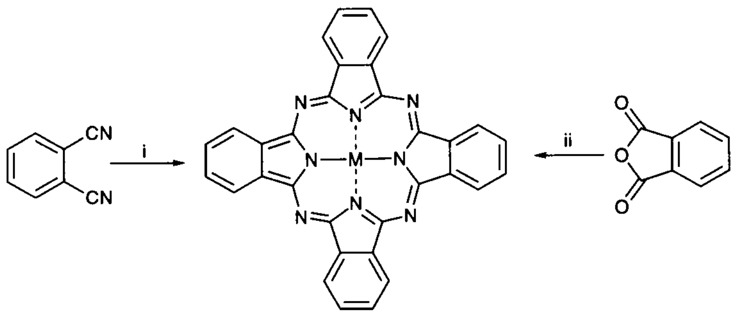
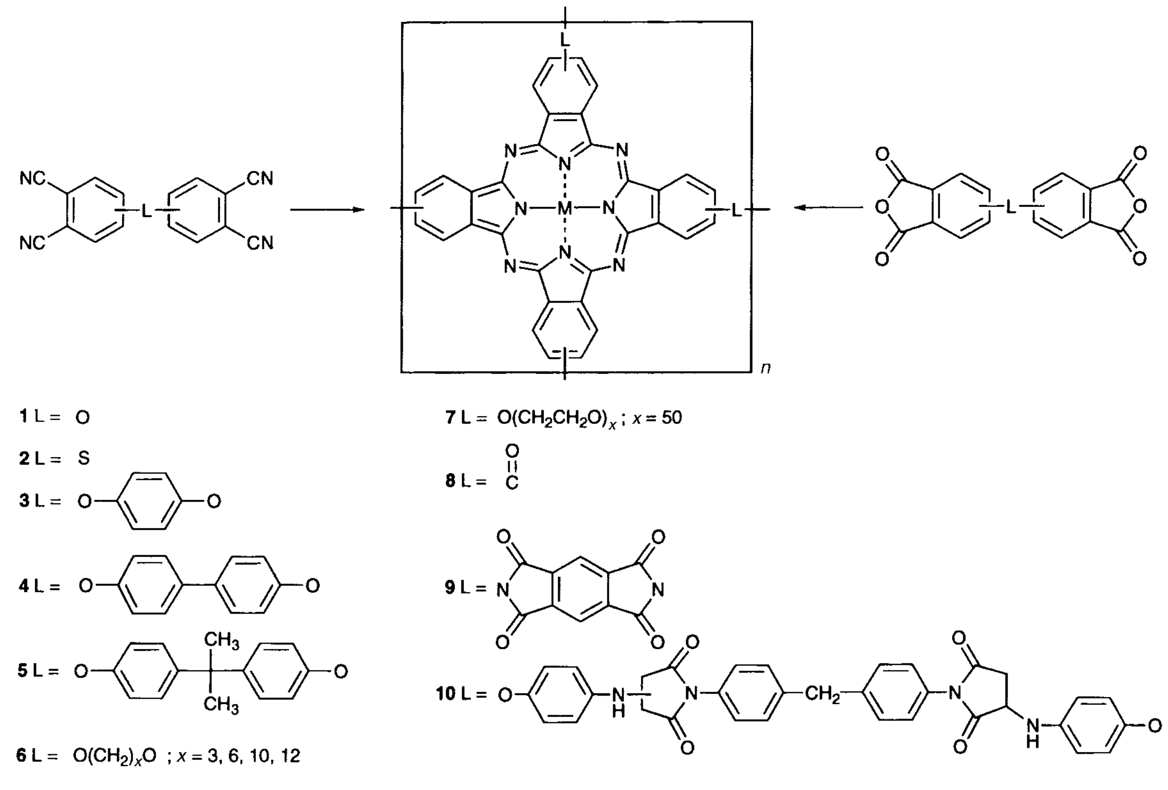


Scheme 1 The synthesis of phthalocyanine (Pc). *Reagents and conditions*: i, metal or metal salt, heat; ii, metal salt and nitrogen donor (*e.g.* urea), heat.

degree of polymerisation, exact structural arrangement and end-group configuration will be produced during network formation.

The structural uniformity of a Pc network can be assessed using IR and UV-VIS spectroscopic comparisons between the network polymer and suitable low molar mass model Pc derivatives.[21] The presence of any triazine within the network is indicated by characteristic IR bands at 1520 and 1360 cm^{-1}. In addition, triazine and isoindoline defects cause more intense absorption in the UV region relative to the intensity of the Q-band, as compared to the UV-VIS spectrum of the model Pc derivative. Similarly, the degree of metal ion incorporation can be measured by comparing the intensity of the metal-free Pc N–H stretching frequency at 3290 cm^{-1} with that of a metal-free Pc model compound. Attempts to determine the average degree of polymerisation (DP) using end-group analysis from IR spectra, elemental analysis or by titration (in the case of carboxylic acid end groups) are hindered by the complex relationship between the number of end-groups and the DP.[18c,25] For example, more highly branched networks (*i.e.* the Pc units possess a greater number of covalent links to the network, on average) have a smaller number of end-groups than a more open network of the same DP. However, a vanishingly small intensity for the distinctive nitrile peak (2220 cm^{-1}) or imide functionality (1770 and 1710 cm^{-1}) does imply a large DP.[26,27]

In order to achieve *relative* structural uniformity it is necessary to prepare network polymers with great care. Bis(phthalonitrile)s appear to give more uniform polymers than bis(phthalic anhydride)s but the precursor must be pure and dry—water is known to encourage triazine formation from phthalonitriles. Snow and co-workers conclude that optimised metal-free Pc network formation for polymers **1** and **2** ($M = 2H^+$) occurs by heating the bis(phthalonitrile) in contact with 1,2,3,6-tetrahydropyridine as reducing agent at 250 °C in a sealed tube.[21] Similarly, Wöhrle and co-workers have demonstrated that relatively uniform metal-containing networks **3–6** (*e.g.* $M = Cu^{2+}$) are formed from the bulk polymerisation of a 2 : 1 mixture of bis(phthalonitrile) and metal salt ($CuCl_2$ is particularly efficient) at elevated temperatures (200–250 °C).[18c,26,27] Purification of the resulting material is achieved by vigorous Soxhlet extraction with various polar solvents (*e.g.* THF, DMF). Networks **1–6** have been prepared with high DP and good structural uniformity as indicated by spectroscopic analysis.[21,26,27] In addition many other networks formed by cyclotetramerisation have been reported including poly(ethyleneoxy) **7**, polyketone **8** and polyimides **9** and **10** for use as heat-resistant materials.[28]



Scheme 2 Network formation using cyclotetramerisation reactions of bis(phthalonitrile)s or bis(phthalic anhydride).

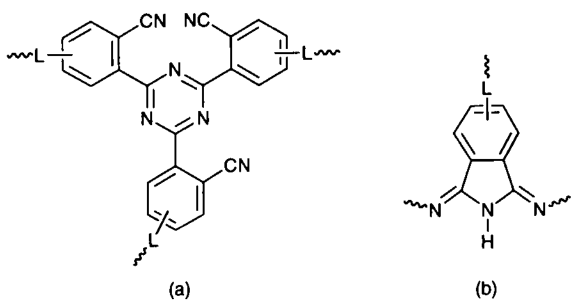


Fig. 1 Potential defects from the idealised structure of a Pc network polymer: (a) triazine and (b) polyindoline.

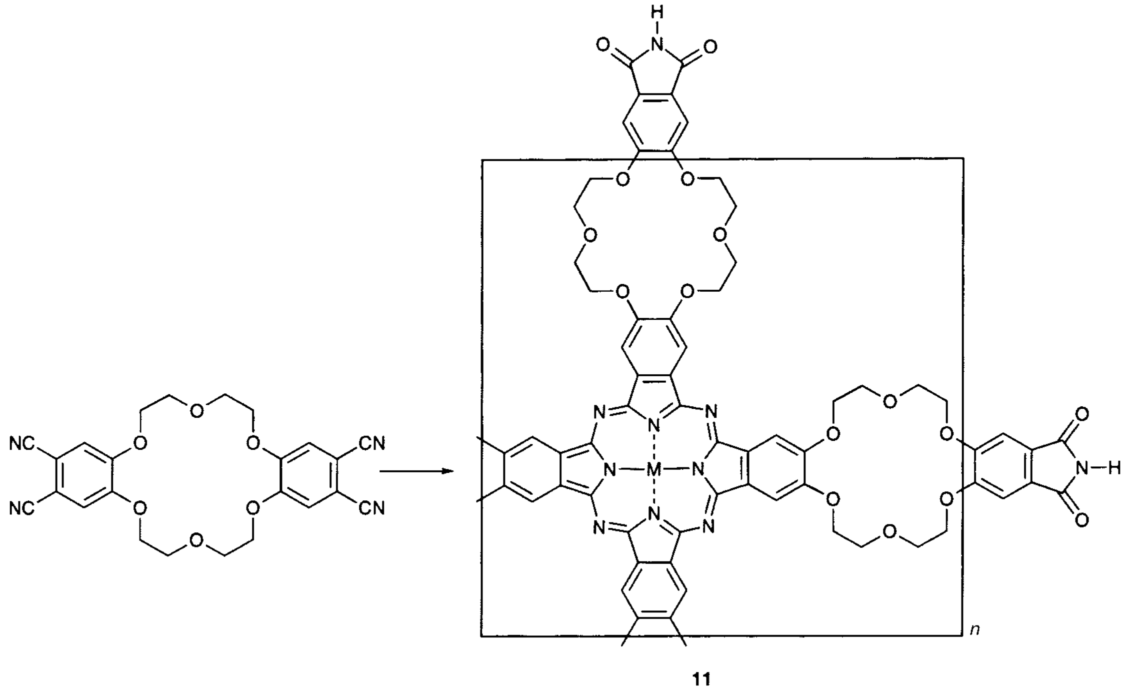
A relatively uniform and well-characterised network polymer **11** is derived from the cyclotetramerisation reaction of a bis(phthalonitrile) linked *via* a crown ether with various metal salts in quinoline at 200 °C.[29] For **11** each of the Pc units is octa-substituted and therefore, the heterogeneity arising from isomerisation due to tetra-substitution need not be considered. In addition, treatment of the polymer with sulfuric acid results in uniform imide end-groups. This allows a meaningful comparison of the intensity of the carbonyl region of the IR spectrum with that of the relevant tetra-imide model Pc obtained from the same bis(phthalonitrile) *via* cyclotetramerisation at high dilution. These network polymers prove suitable for the heterogeneous removal of various metal ions (Na^+, K^+, Rb^+, Cs^+, Ag^+) from solution.

2.2 Poly(phthalocyanine)

The cyclotetramerisation of 1,2,4,5-tetracyanobenzene or pyromellitic anhydride is predicted to form a conjugated 2-dimensional network polymer **12**, often referred to as *polyphthalocyanine* (PPc), in which neighbouring 18-π electron aromatic systems are linked *via* a benzenoid ring. Theoretical calculations suggest that PPc may possess very high intrinsic (*i.e.* undoped) conductivity due to a low band gap.[30] An early study by Epstein and Wildi on PPc prepared from pyromellitic anhydride indicates a reasonably high carrier mobility (1×10^{-3} m^2 V^{-1} s^{-1}) and a band gap of only 0.26 eV.[31] Detailed synthetic work by Wöhrle and co-workers on the optimisation of the formation of PPc from 1,2,4,5-tetracyanobenzene indicates relatively uniform macromolecules (*i.e.* networks with only nitrile end-groups and no triazine formation) are prepared from the bulk polymerisation with $CuCl_2$ at elevated temperatures (350–400 °C).[32] IR spectroscopic comparisons with model Pc **12a**[33] gave an average of less than 3 unreacted nitrile groups on each Pc unit in the PPc network—this suggests that a DP of greater than 8 was obtained. Workers from the same group reported that PPcs containing imide end-groups were obtained, but in lower yield and with incomplete metallisation, from the bulk reaction of pyromellitic anhydride with urea, metal salt and a molybdenum catalyst.[34] IR comparisons of the carbonyl peak intensity of the resulting PPc with that of the model Pc **12b**[33c] indicates that a DP of greater than 9 was achieved.

Thin films of PPc can be prepared by the polymerisation of 1,2,4,5-tetracyanobenzene deposited on the surface of a metal by chemical vapour deposition (CVD). Simply heating, at 400 °C, an evacuated sealed tube containing the metal foil and a small quantity of the precursor affords a thin highly coloured coating on the metal.[35] For titanium metal, metal-free PPc is obtained whereas deposition onto a copper surface gives Cu^{2+} containing PPc. This technique is convenient for the preparation of PPc modified electrodes and the electrochemistry of such systems has been examined.[36] It appears that the surface polymerisation proceeds *via* **12a** which forms at moderately high temperatures (~200 °C).[37] The selective formation of this low molar mass intermediate on copper has allowed the coating of microelectrodes of 10 μm width whilst leaving the surrounding glass uncoated.[38] After annealing at 500 °C a large decrease in the resistivity of the coating was noted, consistent with the formation of PPc. Electrode modification using non-conjugated networks **1**, **3** and **4** (Scheme 2) by the CVD of the appropriate bis(phthalonitrile) precursors has also been achieved.[39] Simultaneous vacuum deposition of 1,2,4,5-tetracyanobenzene and copper metal using a double source followed by thermal treatment at 420 °C allows the fabrication of uniform films of PPc on any chosen substrate.[40]

Despite three decades of research, PPc remains an enigmatic material. There is little convincing *proof* of an extended two-dimensional structure or of the expected electronic properties due to extensive conjugation. The quoted electronic parameters of PPc are highly dependent on the method of fabrication.[36,38,40–42] Room temperature electronic conductivity appears to range from 10^{-6} to 10^{-1} S cm^{-1}. However, the conductivity measurement of organic semiconductors is



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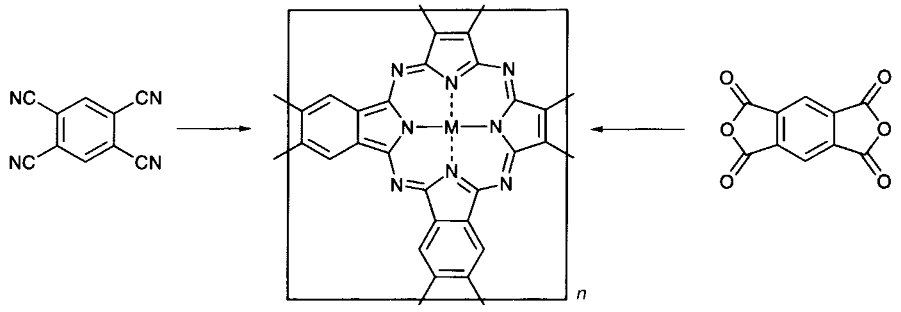

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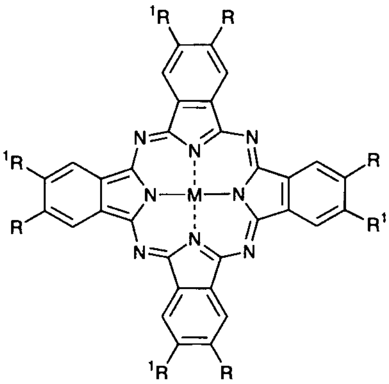
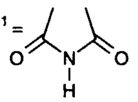


12a R = R^1 = CN

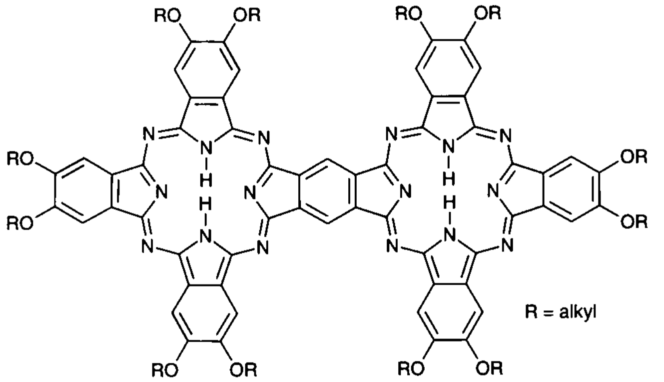
12b R, R^1 =



notoriously complex[2a,6] and experimental values certainly reflect both the heterogeneities present in PPc and environmental factors rather than the properties of the idealised structure considered in the theoretical band gap calculations.[30] It should be noted that some of the better conductivities are obtained from material prepared using very high temperatures (>500 °C)[41] at which point the PPc is known to degrade; therefore, graphitisation of the material is likely to account for the enhanced conductivity.[43] More problematic for the demonstration of a highly conjugated structure is the unperturbed position of the Q-band (~720 nm) in the visible absorption spectrum relative to **12a** (or **12b**). The absence of the expected bathochromic (red) shift is apparent even in well characterised samples of PPc.[32,34] This is particularly curious as the Pc chromophore is very sensitive to benzoannulation, for example, the additional benzo moieties of naphthalocyanines result in a Q-band shift of 100 nm into the near-IR portion of the spectrum.[44] It is possible that the usual method of measuring the UV-VIS spectrum of PPc, by dissolving it in sulfuric acid, may disturb the conjugation by protonation of the linking group,[42k] although spectra obtained directly from thin films of PPc also show no apparent red-shift.[36b] Alternatively, analysis of model dimeric compounds such as **13**, designed to incorporate the same benzenoid linking group as PPc, may provide an explanation.[45] A theoretical study predicts that the Q-band of such dimers should be split and significantly red-shifted. However, accompanying synthetic work, involving a mixed cyclotetramerisation reaction, reports only a modest red-shift of 20 nm for the dimer.[46] A subsequent report states that two dimeric products can be obtained from a similar synthetic procedure; the expected conjugated dimer **13** which does show a large bathochromic shift of the Q-band (~100 nm) relative to a monomeric Pc, and **14** which does not.[47] The lack of any Q-band shift in one of the dimers was attributed to hydrogenation of the benzenoid linking group which destroys any conjugation between the two aromatic systems. It is possible that this dihydrobenzenoid group is a common defect in PPc. Finally, it should be noted that if the band gap of PPc resembles that predicted by calculation then the Q-band should lie in the rarely examined far IR region. One study of PPc derived from pyromellitic anhydride reported a broad absorption band was observed in this region, centred at 2224 nm, in addition to the usual band at around 720 nm.[48] A panchromatic photoconductive response (300–2500 nm) has been observed from PPc which also indicates an extensively conjugated π-system.[49] These observations suggest that the band at 720 nm which is commonly associated with PPc may arise from the presence of low molar mass Pc intermediates such as **12a** and **12b**. Similarly, no convincing evidence exists for the presumed extended two-dimensional structure of PPc. High resolution electron microscopy of PPc films reveals either a featureless amorphous structure or a ribbon like morphology with prominent lattice fringes corresponding to a repeat distance of 1.5 nm depending upon the temperature of preparation.[50] The apparent lack of long range order contrasts with that displayed by the polymer derived from tetracyanoethylene which may possess a structure similar to that of PPc.[51] Re-examination by modern techniques such as scanning tunnelling microscopy[52] and atomic force microscopy[53] may help to confirm the planar structure of PPc.

2.3 Polymer networks derived from preformed Pc derivatives

The use of suitably substituted Pc derivatives as a monomer for the formation of network polymers allows conventional step-growth polymerisation reactions (*e.g.* amide bond formation) to be employed. This gives far greater control over the amount of Pc present in the final material than is achieved using network assembly *via* cyclotetramerisation, for which the



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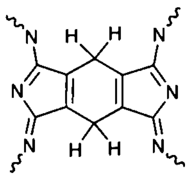

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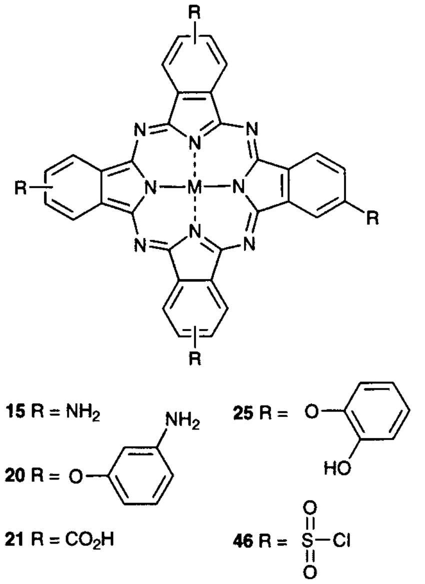
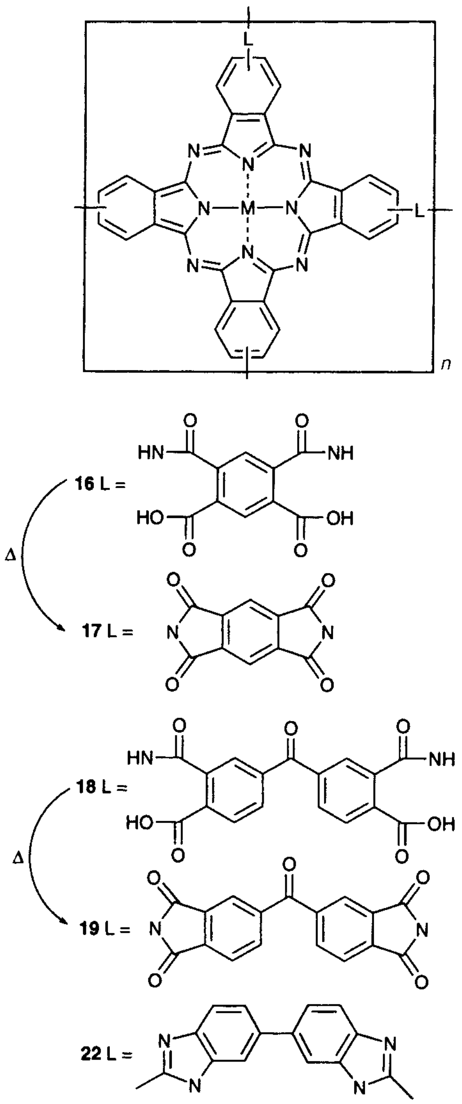
efficiency of Pc formation is uncertain. Tetra-substituted Pcs are relatively easy to prepare and promote rapid network formation.

The reactivity of the amine groups of **15**[54] has been used for the formation of epoxy based networks by dissolving the Pc derivative and commercial epoxide in DMSO followed by curing at elevated temperatures.[55] Similarly, Pc-containing polyimides **17** and **19** can be prepared from the condensation of **15** and pyromellitic anhydride or benzophenone tetracarboxylic anhydride. The soluble poly(amic acid) intermediates **16** and **18** are prepared by mixing the monomers at room temperature in polar aprotic solvents. These solutions are used to process the polymer as either films or fibres. Copolymers containing various aromatic diamines (*e.g. p*-phenylenediamine) provide enhanced processability. Subsequent thermal treatment (350 °C) converts the resultant materials into the intractable polyimide.[56] Pc-containing versions of commercial high performance polyimides (*e.g.* Kapton) offer excellent thermal stability with decomposition in air taking place above 500 °C and in nitrogen at 600 °C.[57] Remarkably high char yields (>80%) were obtained at 800 °C. Subsequent studies found the precursor Pc **15** inconvenient due to its lack of solubility and other tetraamine containing Pc derivatives were employed as monomers.[58,59] For example, polyurethane copolymers prepared from **20**, isophorone diisocyanate and butane-1,3-diol proved soluble in γ-butyrolactone and were suitable for the fabrication of films used in nonlinear optical measurements.[59]

Metal derivatives of **21**[60] have been polymerised directly by heating at 350–400 °C *in vacuo*. The gaseous reaction by-products (CO_2, CO and H_2O) together with spectroscopic analysis suggest that the resultant intractable material is composed of Pc units linked by single covalent bonds.[61] The more conventional polymerisation reaction between **21** and 3,3′-diaminobenzidine, in the melt at 400 °C or in polyphosphoric acid at 180 °C, gives a thermally resistant network **22** in which the Pc units are linked by bis(benzimidazole) moieties.[62]



Pcs containing multiple reactive groups are suitable for incorporation into resins for coatings and film fabrication. For example **21**, after reaction with a commercial epoxide (Glydez N-10) produces a highly soluble tetrahydroxylated derivative which enhances adhesion, hardness and impact resistance of a melamine-based coating system.[60] Similarly, polyhydroxylated derivatives such as **23**, prepared by substitution of the axial sites of silicon Pc,[63] are readily incorporated into polyurethane



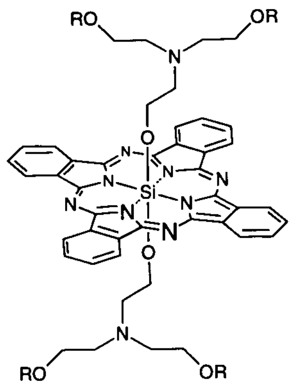
films at high concentrations. Axial substitution ensures that cofacial aggregation of the Pc units is prohibited which prevents broadening of the Q-band absorption by excitonic effects. Therefore, such films are transparent to light of wavelength in the range 400–650 nm and can be used as optical limiters for protection against laser light.[64] Similarly, the reaction of **23** with methacryloyl chloride provides a crosslinkable monomer **24** for incorporation within spin-coated films of poly(methyl methacrylate).[65] Such films have been incorporated into multilayered nonlinear optical devices such as a Bragg mirror[66] and a slab waveguide directional coupler.[67] For both devices pure poly(methyl methacrylate) was used for the passive layers.

2.4 Plasma polymerisation

Plasma polymerisation is a general procedure for obtaining polymer films from low molar mass organic compounds. A sample of the compound in the gas phase is subjected to a low temperature plasma induced by a radio frequency generator. Deposition of the polymerised material occurs on a substrate placed inside the plasma. In the case of Pc, plasma polymerisation gives uniform, amorphous films in which the integrity of the Pc ring is maintained as shown by UV-VIS spectroscopy.[68] The polymeric nature of the material is implied by its insolubility in pyridine or sulfuric acid—both of which are good solvents for low molar mass Pcs. The types of linkages formed from plasma polymerisation are unknown although it is assumed to proceed *via* the formation of radicals. The presence of some oxygen containing species is shown by X-ray photoelectron spectroscopy.[69] Films of plasma polymerised Pcs have been examined for their electrical properties (*e.g.* photovoltaic and electrochromism) and as the active layer within electronic sensors for nitrogen dioxide.[70] Deposition onto a piezoelectric crystal allows the fabrication of sensors for the detection of a range of organic compounds in which the plasma polymerised Pc film forms a chemically stable and abrasion resistant active layer.[69] In particular, the proven affinity of Pc for polycyclic aromatic compounds allows the sensitive detection of mutagenic compounds using these devices.[71]

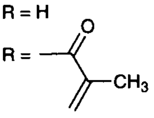
2.5 Electropolymerised Pcs

Pc **15**, like many electron-rich aromatic compounds,[72] can be electropolymerised at the surface of an electrode to obtain an intractable coating.[73] Such modified glassy carbon electrodes have been used for a number of electrocatalytic processes including the four electron reduction of oxygen to water,[74] and the detection of nitrite ions,[75] organic peroxides,[76] dopamine,[77] and glucose in blood serum. The latter was achieved indirectly by the detection of hydrogen peroxide produced by glucose oxidase immobilised on the surface of the polymer.[78] The phenolic substituents on Pc **25** can be electropolymerised to give films which demonstrate electrochromic behaviour.[79]



23 R = H

24 R =



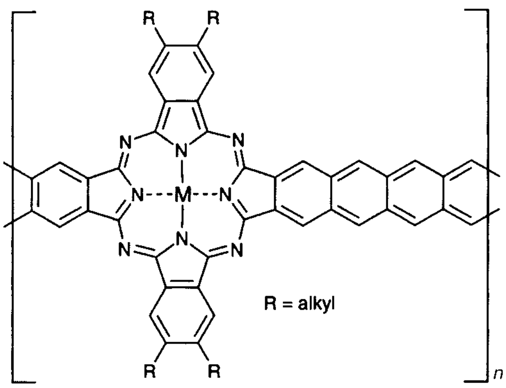
3 Main-chain Pc polymers

3.1 Main-chain polymers linked through the Pc ligand

Main-chain polymers which are linked through the Pc macrocycle require a bifunctional Pc monomer. The synthesis of these compounds represents a difficult challenge which cannot be solved by a simple mixed cyclotetramerisation reaction between two precursors (*e.g.* A and B), only one of which contains the desired functional group for polymer assembly. Such reactions give a complex mixture of products composed of two symmetrical Pcs (AAAA, BBBB), two unsymmetrical Pcs derived from three molecules of one precursor and one of the other type (AAAB, BBBA) in addition to the desired bifunctional derivative (AABB).[80] Simple statistics shows that for a mixed equimolar cyclotetramerisation reaction between two precursors of equal reactivity only 36% of the total Pc product is bifunctional. A further complication arises from structural isomerism in that two thirds of the bifunctional product possesses the reactive groups on *adjacent* benzo moieties (AABB, of C_{2v} symmetry) whereas one third is composed of the *opposite* isomer (ABAB, of D_{2h} symmetry). Should the two precursors contain substituents of different polarity, then chromatographic separation of all six Pc products can be achieved.[81] However, to date, no main chain polymers have been prepared from a *pure* bifunctional Pc monomer of AABB or ABAB structure, although polyesters and polyimides (presumably with a highly branched structure) have been prepared from a Pc mixture with an *average* functionality of two derived from mixed cyclotetramerisation reactions.[82]

Bifunctional monomers of D_{2h} symmetry are desirable because they would provide polymers of linear configuration. Such isomers can be obtained selectively by a mixed cyclotetramerisation reaction between two precursors which cannot self-condense such as diiminoisoindolines and 1,3,3-trichloroisoindolenine, although with only modest yield.[83] A mixed cyclotetramerisation reaction including a sterically hindered precursor (*e.g.* 3,4,5,6-tetraphenylphthalonitrile) can also encourage the formation of the desired D_{2h} isomer.[84] An ambitious synthetic programme by Hanack and co-workers seeks to prepare linear, conjugated ladder polymers (*e.g.* **26**) in which the Pc units are linked by an oligoacene[85] bridge. The polymers are to be assembled using a Diels–Alder reaction between bis(diene) and bis(dienophile) Pc monomers of D_{2h} symmetry followed by aromatisation of the six-membered rings in the linking group. Fully conjugated polymers are predicted to possess intrinsic semiconductivity.[30] Some relevant preparatory work has been achieved including the synthesis of a number of oligomeric structures based on Pc and hemiporphyrazine, a cross-conjugated macrocycle of the required D_{2h} symmetry.[86]

A Pc-containing polyester **27** in which one of the four benzo units of the macrocycle is incorporated within the main chain of the polymer has been described by Cook and co-workers.[87] The non-peripherally substituted Pc monomer, of AAAB configuration, was prepared from a mixed cyclotetramerisation reaction in which one of the phthalonitrile precursors contained two protected alcohol groups. The presence of the polyester backbone failed to disrupt the columnar mesophase formation of the alkyl-substituted Pc components.



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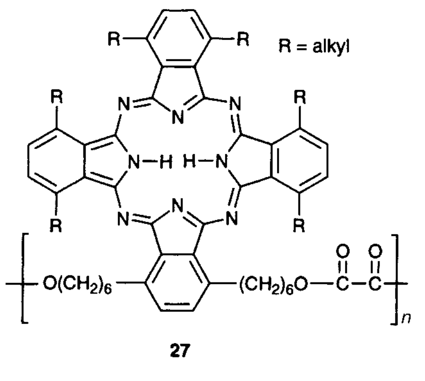
3.2 Main chain polymers linked through the central ion

It is possible to prepare main chain Pc polymers by reactions involving the axial ligands attached to ions resident in the central cavity. On occasion, these systems are termed *shish-kebab* polymers due to the Pc rings appearing to be skewered on a metallic backbone. However, only one example of a purely metallic 'skewer' has been discovered whereby Hg^{2+} cations act both as the central ion and bridging ligand.[88]

3.2.1 Poly(phthalocyanine siloxane). The axially linked polymer which has received by far the most attention, since its initial synthesis by Joyner and Kenney,[89] is the polysiloxane **28** in which the central ion is Si^{4+} and the axial bridging ligand is a simple oxygen atom.[18c,90] The small ligand ensures that neighbouring Pc rings are held together tightly in a cofacial arrangement, at a distance of only 3.32 Å from one another, resulting in an extremely rigid polymer. This polymer, often abbreviated to $[PcSiO]_n$, displays remarkable chemical stability, unlike conventional polysiloxanes, presumably due to the hindrance offered by the Pc macrocycles to the approach of reactants to the siloxane backbone. For example, it can be dissolved in cold concentrated sulfuric acid without decomposition. The synthesis of **28** can be achieved directly from the dihydroxysilicon monomer by dehydration at 400 °C. This process produces **28** with a reported DP in the range 50–100, as measured by end group analysis using the intensity of the Si–OH IR band at 836 cm^{-1} and tritium labelling.[91] The substantial morphological change from the tilted crystal form of the monomer to the cofacial polymer arrangement has been observed using high resolution electron microscopy.[92] A number of variations of the polymerisation step have been reported to increase the degree of polymerisation, including ultrasonication,[93] the use of Lewis acid catalysts (*e.g.* $FeCl_3$ or $CaCl_2$) in high boiling solvents,[94] and more reactive axial leaving groups such as trifluoroacetate.[95] Pc monomers containing peripheral alkoxy[95] or *tert*-butyl[96] substituents lead to polymers which are soluble in organic solvents and can, therefore, be characterised by gel permeation chromatography and X-ray scattering techniques to determine their mass.[95a] For the synthesis of octaalkoxy-substituted polymers a topochemical polymerisation can be carried out in the columnar mesophase of the monomer.[95b,c] However, the DP obtained by this method is small and the use of trifluoroacetate axial leaving groups is preferred for the preparation of substituted polysiloxanes.[95a] In addition to greater solubility, there is evidence that the steric effect of peripheral substituents may cause restricted rotation of the Pc unit about the siloxane backbone and, in the case of chiral substituents, a helical deformation of the structure.[97] Analogous polymers containing Ge^{4+} or Sn^{4+} instead of Si^{4+} have been prepared using similar methods, although these larger ions produce a greater distance (Ge = 3.51 Å, Sn = 3.95 Å) between neighbouring Pc sub-units.[91a,98]



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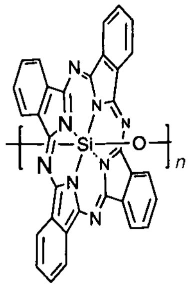


28

Two features of **28** and its substituted derivatives are of interest. Firstly, they are one of the best examples of a rigid-rod polymer and display associated self-ordering properties. Secondly, the π-system of the Pc units forms a linear array in which there is some orbital overlap—thus providing a conduit for efficient electronic conduction. The self-ordering properties of **28** are most evident in the LB film forming characteristics of its alkoxy-substituted derivatives as studied by Wegner and co-workers.[99] These polymers are not typical of the low molar mass amphiphilic molecules normally used to form ordered LB films.[15] The peripheral alkyloxy groups serve only to induce the necessary solubility in volatile organic solvents to facilitate application of the polymer at the air–water interface of the Langmuir trough. The remarkable degree of order results from mechanical deformation during the vertical deposition of the monolayer onto a suitable hydrophobic substrate—this causes alignment of the long axis of the polymer in the direction of the movement of the substrate through the interface (*i.e.* the dipping direction). UV-VIS analysis shows a large dichroic ratio of ~3 : 1 for the intensity of the perturbed Q-band at 560 nm with the larger absorption intensity perpendicular to the dipping direction (*i.e.* parallel to the edge of the macrocycle). This dichroic ratio is increased to ~6 : 1 by thermal annealing at 140 °C. Transmission electron microscopic images confirm the orientation of the rigid polymers within these films.[100] As noted previously, the substitution of **28** with peripheral alkoxy groups encourages thermotropic columnar mesophase formation.[95] In addition, solutions of these polymers form lyotropic liquid crystals, at appropriate concentration. Application of a strong magnetic field (5 T) to a lyotropic solution, and allowing the solvent to evaporate slowly, produces cast films from which a dichroic ratio greater than 7 : 1 for the 560 nm absorption band is obtained.[101] The greater absorbance was in the same direction as the applied magnetic field indicating that the linear polymers align themselves perpendicular to the field.

The extent of the through-space electronic interactions between Pc rings within the enforced linear array of **28** has been analysed indirectly by examination of discrete cofacial oligomers (dimer, trimer and tetramer) using UV-VIS absorption spectrometry, photoelectron spectroscopy and electrochemical measurements.[102] Each method agrees with theoretical calculations[103] that predict a rise in the effective HOMO energy level of the system as the number of electroactive Pc units is increased. For the extended polymeric stack, the HOMO interactions of the Pc units create a semiconductor with a narrow band width ($\sim$0.6 eV) and a relatively large band gap (1.6 eV).[104] This large band gap explains the modest intrinsic (unoxidised) conductivity ($\sigma_{rt} = 3 \times 10^{-8}$ S cm^{-1}) of the polymer. A more efficient semiconductor is obtained from the incorporation of the electron deficient Pc **12a** within the polysiloxane.[105]

Partial oxidation, either chemically with iodine or electrochemically, can result in polycrystalline materials with reasonable conductivity ($\sigma_{rt} = 0.6$ S cm^{-1}, measured as pressed pellets).[90,106] This process, which involves one in three Pc units becoming a radical cation, induces a change in the packing arrangement of the polymeric columns from an orthorhombic (*Ibam*) to a tetragonal (*P*4/*mcc*) crystal structure in order to accommodate the presence of the counter anion (*e.g.* I_3^-). Powder X-ray diffraction studies suggest that the structure of the oxidised polymer (Fig. 2) is almost identical to that of charge-transfer complexes formed from low molar mass Pcs and iodine.[90,107] The precise lattice parameters ($a = b = \sim 14$ Å, $c = 6.6$ Å) are dependent on the size of the incorporated anion. Reversal of the oxidation process does not coincide with a return to orthorhombic packing and the formally unoxidised tetragonal polymorph of **28** shows an enhanced conductivity ($\sigma_{rt} = \sim 2 \times 10^{-6}$ S cm^{-1}) compared to that of the original polymer. This may be related to the replacement of the iodine with oxygen within the intercolumnar voids. Interestingly, the strong oxidising reagent 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) can be used to induce the conducting state of **28**, in contrast to low molar mass Pcs whereby integrated stack formation leads to low conductivity.[90] This cannot occur in **28** due to the enforced cofacial stacking.[108] Maximum conductivity is obtained for the incorporation of 0.4 DDQ molecules per Pc subunit, consistent with the concept of partial oxidation, whereas a 1 : 1 stoichiometric ratio results in an insulating material. Electrochemical measurements (differential pulse voltammetry) on a tetrachloroethane solution of **28**, rendered soluble by peripheral *tert*-butyl groups, indicates that oxidation occurs over a potential range of +0.2 to +1.00 V. A break in the oxidation process at 1.0 V indicates the inherent stability of the partially oxidised system. Similar electrochemical behaviour has been demonstrated for ordered LB films of the alkoxy-substituted polymer deposited on gold electrodes.[109] The anticipated anisotropic conductivity, with greater conductivity in the direction of the aligned polymer, has been confirmed in LB films[110] and in the thermotropic columnar liquid crystal phase.[111]

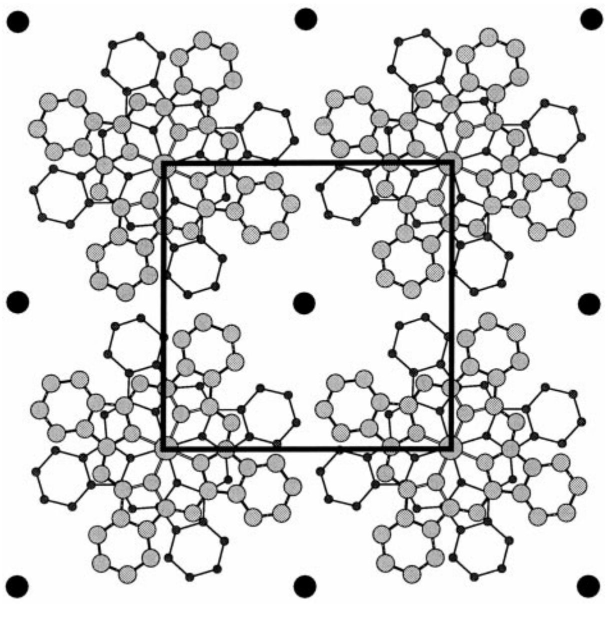
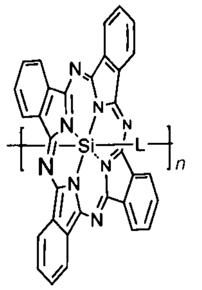


Fig. 2 The tetragonal structure of partially oxidised **28** viewed along the polysiloxane backbone. The precise lattice parameters ($a = b = \sim 14$ Å, $c = 6.6$ Å) are dependent on the size of the counter-on (*e.g.* I_3^-, BF_4^-) represented by the black dot.

A number of applications for **28** have been realised including the fabrication of sensors, where the increase in conductivity due to partial oxidation by nitrogen dioxide or chlorine allows for sensitive detection,[112] ion-selective field effect transistors[113] or photovoltaic devices.[114] Conducting fibre composites of the high performance polymer Kevlar, poly(*p*-phenylene terephthalamide), are made by dissolving **28** into the concentrated sulfuric acid solution from which the polyaramide fibres are spun. A room temperature conductivity parallel to the fibre direction of 5 S cm^{-1} is obtained, after treatment with iodine vapour, without adversely affecting the tensile strength of the Kevlar.[90,115] An interesting experiment reported by Wegner and collaborators explored the concept of using single molecules of alkoxy-substituted **28** as a wire.[116] A monolayer composed of sparsely dispersed **28** in a suitable cellulose derivative was deposited onto microfabricated electrodes using the LB technique. TEM and AFM images clearly differentiate between the Pc polymer, of larger diameter, and the cellulose matrix. The structure of the single molecule of **28** is not disturbed by the height of the metal electrodes (15 nm) and therefore, this technique could result in two closely spaced electrodes being connected by a single molecular wire. Related derivatives of **28** comprised of crown ether containing Pc units offer the prospect of a 'molecular cable' capable of simultaneous electronic and ionic conductivity.[117]



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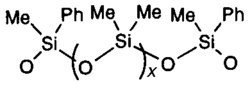

$x = 2, 4, 6$

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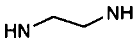

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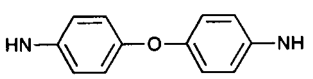

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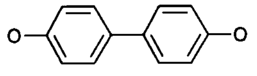

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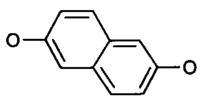
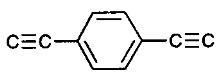


34 L = $C\equiv C$

35 L =

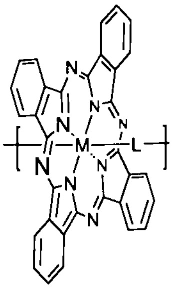


3.2.2 Other axially linked polymer systems.

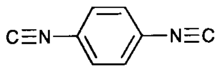
Many other polymers in which Pc units are incorporated through axial ligands have been reported. Much larger axial ligands than a single oxygen atom have been used to link silicon Pc such as oligosiloxanes (*e.g.* **29**),[104,118] aromatic and aliphatic diamines (*e.g.* **30** and **31**),[119] rigid bisphenols and aliphatic alcohols (*e.g.* **32** and **33**),[120] ethynylene **34**,[121] and diethynyl-*p*-phenylene **35**.[122] The Pc units in these polymers show no evidence of electronic interaction.

Non-covalent bonding between a central metal ion and various bridging ligands can also be used to construct axially-linked Pc polymers.[123] Numerous examples of these materials have been described by Hanack and co-workers.[2d,123] The central metal ion must be in an octahedral configuration (thus M = Fe, Co, Mn, Cr, Rh, Os or Ru are suitable) and, in order to maintain electrical neutrality, the ion should possess a formal charge of +2 or +3 depending on the charge associated with the bridging ligand. Successful ligands are 1,4-diisocyanobenzene **36**,[124] cyanide **37**,[125] thiocyanide **38**[126] and various nitrogen containing heterocycles such as pyrazine (py) **39**,[127] tetrazine (tz) **40**,[128] 4,4′-bipyridyl **41**,[129] azobispyridine **42**[130] and diazabicyclooctane (dabco) **43**.[123b,e] The cofacial polymers are prepared directly by heating the metallated Pc with the bridging ligand in a high boiling solvent (*e.g.* chlorobenzene) or by the condensation reaction of the relatively soluble bis-ligated Pc. As for **28**, peripheral substitution of the Pc units provides polymers with good solubility in organic solvents.[124,125e,130]

The interesting aspect of this family of Pc polymers is their remarkable electronic conductivity, even in the undoped state (Table 1). It is clear that the bridging ligand plays an active role in the mechanism of conduction as ligands such as dabco, which does not possess a π-orbital system, produce only insulating polymers. It has been suggested that the degree of interaction between the LUMO of the bridging ligand and the HOMO of the Pc subunit is of primary importance for the efficiency of conductivity.[123] Large HOMO–LUMO interaction encourages charge transfer between the metal Pc and the bridging ligand resulting in a 'self-doped' system. For example, substitution of pyrazine with tetrazine, which possesses a LUMO of lower energy, results in a polymer which is five orders of magnitude more conducting. Similarly, Pc derivatives with a higher energy HOMO such as naphthalocyanine result in bridged polymers with enhanced conductivity whereas electron-withdrawing substituents such as nitrile decrease conductivity. Alternatively, conductivity can be improved by partial oxidation of the Pc units using I_2 or electrochemical doping.[127,131] A number of these polymers have been studied as photoconductors[132] and as nonlinear optical materials.[124]

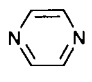


M = Fe, Co, Mn, Cr, Rh, Os or Ru

36 L =


37 L = C≡N

38 L = S–C≡N

39 L =


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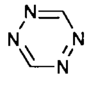

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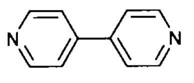

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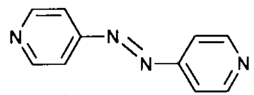

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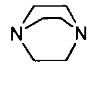
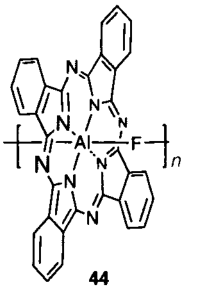




44

Fluoroaluminium Pc **44** assembles in a crystalline structure that is characterised by the Pc units forming a cofacial linear stack within which they are separated by the fluorine atom at a distance of 3.66 Å.[133] The large electric dipole of the bond between the metal ion and fluorine atom results in a strong electrostatic interaction which stabilises the linear array. This non-covalent polymer has the advantage over other bridged Pc polymers in that it can be purified and processed into thin films by vacuum sublimation without decomposition. On electrochemical oxidation or chemical oxidation with iodine **44** becomes an efficient electronic conductor ($\sigma_{rt} = \sim 3 \times 10^{-1}$ S cm^{-1}).[134] A sensor for nitrogen dioxide based on a sublimed film of **44** has been constructed.[135] In addition, this sensor detects the reductive gas carbon monoxide by a decrease in conductivity.

4 Side-chain polymers

There are three general methods for the synthesis of side-chain polymers in which the Pc unit is attached to a polymer backbone *via* a single linking group. These are (i) the grafting of a preformed Pc derivative to a preformed polymer, (ii) a mixed

Table 1 Room temperature conductivities of pressed pellets samples of some bridged polymers (abbreviations: dabco = diazabicyclooctane, py = pyrazine, tz = tetrazine, NPc = napthalocyanine, CN = nitrile, I_2 = iodine doped)

	σ_{rt}/S cm^{-1}	Ref.
$[PcSiO]_n$	3×10^{-8}	106*e*
$[(CN)_8PcSiO]_n$	1×10^{-6}	105
$[PcSiO]_n/(I_2)$	6×10^{-1}	90*b*
$[PcFe(dabco)]_n$	1×10^{-10}	123*a*
$[PcFe(CN)]_n$	6×10^{-3}	129
$[PcCo(CN)]_n$	1×10^{-2}	129
$[PcFe(Py)]_n$	8×10^{-8}	127*e*
$[PcFe(tz)]_n$	2×10^{-2}	123*e*
$[NPcFe(Py)]_n$	5×10^{-5}	123*e*
$[NPcFe(tz)]_n$	3×10^{-1}	123*e*
$[(CN)_4PcFe(Py)]_n$	5×10^{-9}	123*e*
$[(CN)_4PcFe(tz)]_n$	1×10^{-6}	123*e*
$[PcFe(Py)]_n/(I_2)$	1×10^{-1}	127*e*

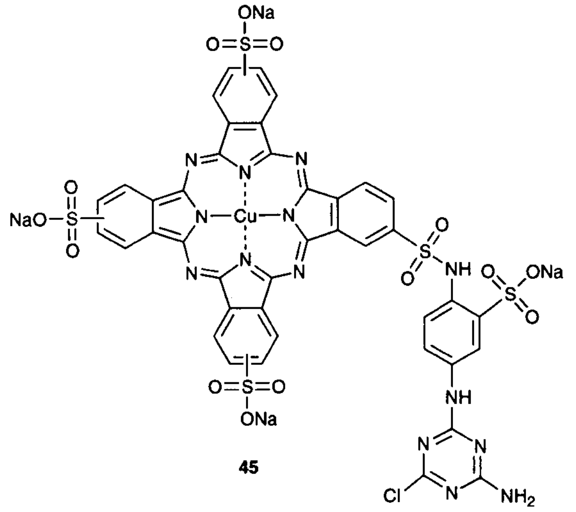
cyclotetramerisation involving a polymer bound precursor and (iii) polymerisation of a phthalocyanine containing monomer. The impetus for the development of polymer-bound Pcs derives from the proven utility of transition metal containing Pcs (*e.g.* FePc, MnPc and CoPc) as catalysts for the industrial-scale aerobic oxidation of thiols in crude petrochemicals (the Merox process)[136] and for numerous other reactions.[2*a*] Cofacial aggregation disrupts the catalytic activity of Pc due to shielding of the metal centre. Polymer supported Pcs offer the possibility of controlling self-association and facile recovery of the catalyst. An extensively used methodology to provide polymer-based catalytic systems with similar advantages is the immobilisation of a Pc derivative onto a polymer using non-covalent bonding based on electrostatic or metal–ligand interactions.[137]

4.1 Grafting Pc onto a preformed polymer

This method is exemplified by the industrially important coloration of cotton (cellulose) by a monofunctional Pc dye containing a reactive triazine (*e.g.* Reactive Blue 15, **45**). Pc-doped cotton has been used for the adsorption of polyaromatic hydrocarbons from effluent water.[138] The covalent grafting of **15** (M = Co^{2+}) onto aminated, cross-linked polystyrene using highly reactive cyanuric chloride as a grafting agent produces a material capable of thiol oxidation.[139] Equally effective catalytic systems are achieved by the direct grafting of **21** onto partially chloromethylated polystyrene using an ester bond forming reaction[140] or poly(vinyl amine) *via* dicyclohexylcarbodiimide mediated amide bond formation.[141] The acyl chloride derivative of **21** reacts with polystyrene[142] or poly(γ-benzyl-L-glutamate)[143] *via* a Friedel–Craft reaction. Similarly, **46** can be bound to polystyrene.[144] Friedel–Craft and diazo coupling reactions have been used to prepare Pc containing poly(*N*-vinylcarbazole)s which show high photoconductivities.[145]

4.2 The use of polymer-bound precursors

A mixed cyclotetramerisation between a polymer bound phthalonitrile and a large excess of solvent borne phthalonitrile leads to Pc derivatised polymers such as **47** and **48**. This method was originally developed by Leznoff and co-workers for the synthesis of unsymmetrical (AAAB) substituted Pcs by the use of polymer supported reactions on solvent-swollen, cross-linked polystyrene beads.[146] Although this procedure represent a laborious method of producing unsymmetrical Pcs it appears a viable procedure for producing Pc-based polymer supported catalysts with a high concentration of active sites. Other, rare examples of the use of polymer-bound phthalonitrile precursors for the preparation of Pc-containing side-chains involve poly(phosphazene)[147] and poly(aryl ether)[148] main-chains.



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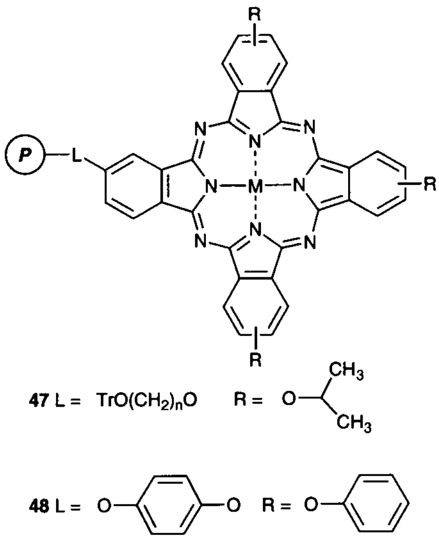
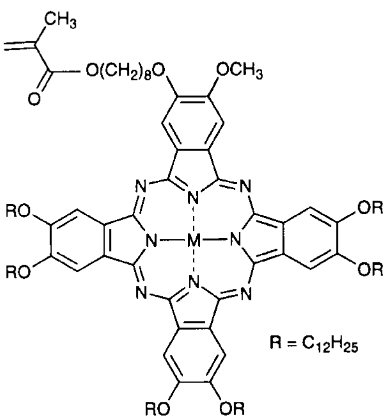


4.3 Polymerisation of Pc containing monomers

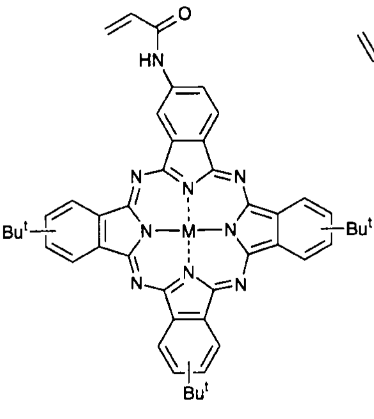
Both of the previously described methods of preparing side-chain Pc polymers suffer from the possibility of severe cross-linking, producing an insoluble polymer, unless the concentration of incorporated Pc units is kept low. Therefore, the method of choice for preparing structurally uniform side-chain Pcs involves the polymerisation of a Pc-containing vinyl monomer. Clearly, only a single vinyl moiety is required, otherwise an insoluble network results,[149,150] and therefore the monomer must be derived from an AAAB-type unsymmetrical Pc (see section 3.1). Suitable Pcs possessing a single reactive hydroxy or amino group, prepared using mixed phthalonitrile cyclotetramerisation reactions, serve as precursors for the subsequent synthesis of acrylate or methyacrylate **49**,[151] acrylamide **50**[152] or styrene **51**[153] monomers. The use of peripheral alkyl substituents is crucial as they provide the necessary solubility for chromatographic purification of the precursors and monomers. In addition the solubilising groups facilitate solution-based free radical polymerisation and molecular mass determination of the resulting polymer using GPC. The styrene-based polymerisation appears particularly well behaved with high values of DP and low polydispersity, especially when Zn^{2+} is incorporated into the Pc monomer.[153] The solution behaviour of all of these polymers is characterised by cofacial aggregation of the Pc units. Despite this, these side-chain polymers do not display columnar liquid crystallinity, however, a powder X-ray diffraction study of the methacrylate-based materials showed that its molecular-scale ordering is very similar to that of the hexagonal columnar mesophase exhibited by low molar mass Pc derivatives.[151] The catalytic behaviour of poly(acrylamide) copolymers, containing various transition metal ions in their Pc side-chains, has been studied in detail.[152]

5 Pc polymer end-groups and dendritic cores

Polymers containing Pc end-groups have been the subject of two recent reports. In each case Pc influenced the properties of the polymer by self-association. For example, the introduction of a phthalonitrile moiety onto poly(ethyleneoxy) monomethyl ether (DP of 50) was achieved using the aromatic nucleophilic substitution reaction of 4-nitrophthalonitrile with the hydroxy end-group. A cyclotetramerisation reaction with an excess of 4,5-bis(dodecyl)phthalonitrile gave **52**.[154] The Pc end-group enforced a columnar mesophase over a large thermal range similar to that displayed by low molar mass Pc derivatives. Differential scanning calorimetry showed that this material


R = $C_{12}H_{25}$

49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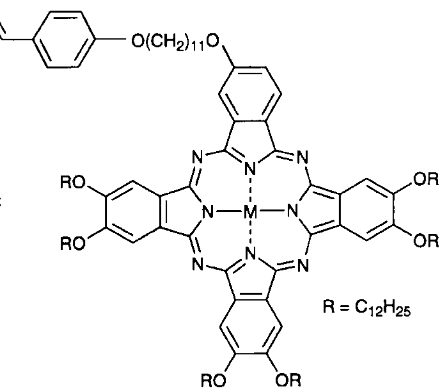
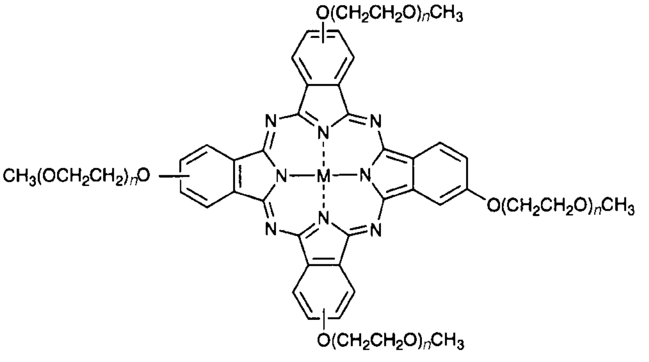

R = $C_{12}H_{25}$

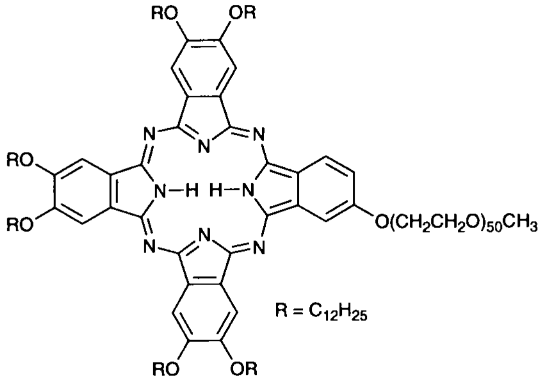
51

undergoes three distinct transitions at 35, 70 and 210 °C. X-Ray diffraction revealed that these transitions were associated with the melting of crystalline domains of poly(ethyleneoxy), the melting of the dodecyoxy side chains, and finally, the transition from columnar mesophase to isotropic liquid. Similarly, Pc units were attached to both ends of a rigid poly(aryl ether sulfone) **53**.[155] The high glass transition temperature of this material was attributed to aggregation of the Pc end-groups.

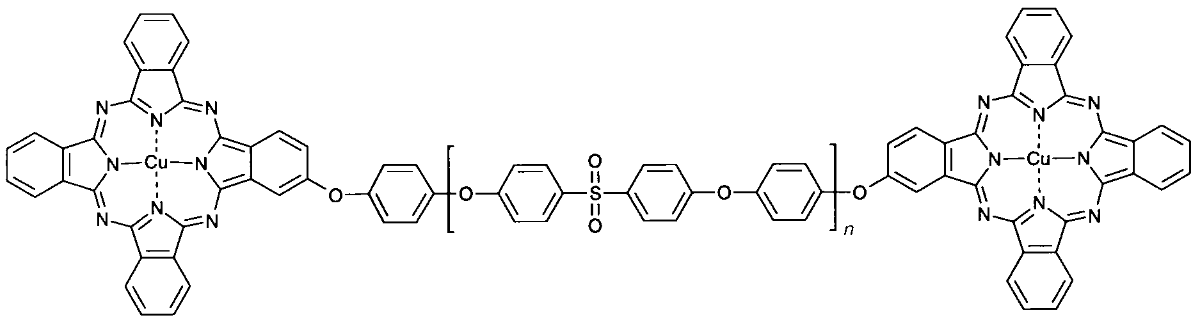
The concept of using Pc as the single core of a star polymer or dendrimer has been explored by McKeown and co-workers. Water-soluble Pc-centred poly(ethyleneoxy) species **54**, prepared by the cyclotetramerisation of phthalonitrile-capped oligo(ethyleneoxy) precursors of modest DP (3, 8, 12 and 16), show interesting behaviour as amphiphiles.[156] In the case of the polymer with longer side-chains (DP = 16) radiating from the Pc core, the pure material forms sperilitic crystallites typical of poly(ethyleneoxy) and showed no thermotropic columnar mesophase. However, in aqueous solution this material exhibited lyotropic liquid crystallinity resulting from the self-association of the hydrophopic Pc cores into columnar aggregates. Cofacial aggregation can be prohibited by placing poly(ethyleneoxy) side-chains at the axial sites of metal-containing Pcs. These water-soluble materials have been examined as photosensitisers for PDT.[157]


54

Dendrimers are well-defined macromolecules of uniform mass which contain a core, successive layers of branched repeat units and terminal groups.[158] It was anticipated that the steric bulk of the dendrimer would prevent aggregation of a Pc unit placed at the core. Pc-centred poly(aryl ether) dendrimers **55**–**59** with either benzyl or tri(ethyleneoxy) terminal groups were


R = $C_{12}H_{25}$

52


53

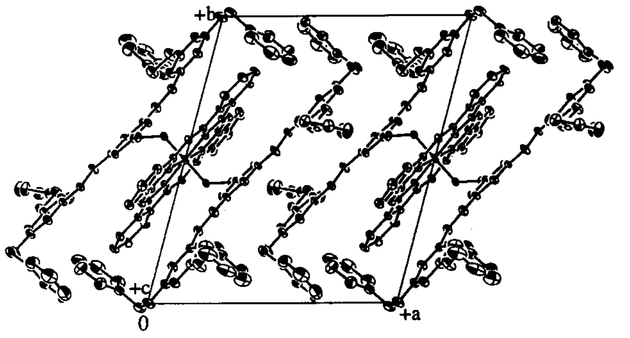
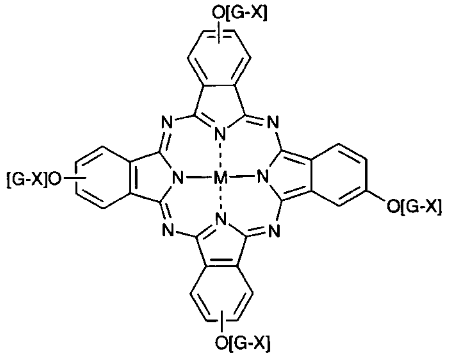


Fig. 3 The X-ray crystal structure of **61** showing the effectiveness of the axial dendritic substituents for the prevention of sef-association. The cofacial distance between Pc units is 14 Å (from reference 161 with permission).

constructed using the well established convergent synthetic route devised by Fréchet.[159] Dendrimer assembly was achieved using the cyclotetramerisation of dendritic wedges with a single phthalonitrile group at the focal point. Remarkably, even the steric bulk of the third generation dendrimer does not interfere with cofacial aggregation of the Pc core as shown by the large blue-shift of the Q-band displayed by the UV-VIS absorption spectrum of a spin-coated film.[160] Self-association was even apparent in the matrix assisted laser desorption ionisation (MALDI) mass spectra of **58** with peaks corresponding to dimeric, trimeric, tetrameric and pentameric cofacial aggregates. In order to suppress cofacial self-association dendritic poly(aryl ether) wedges can be placed in the axial sites of silicon-Pc as in **61**–**64**.[161] The efficiency of this strategy is illustrated by the crystal structure of **61** (Fig. 3). Spin-coated films fabricated from these materials exhibit Q-bands which are relatively unperturbed by exciton effects and approximate to *solid solutions*. They are particularly attractive for optical studies due to their robust, glassy characteristics. In addition, water-soluble polyanionic dendrimers **59** and **60** show enhanced fluorescence in solution, as compared to low molar mass model compounds, due to a reduction in self-quenching of the photo-excited state.[162]

6 Conclusions

This review demonstrates the structural diversity of Pc-containing polymers and hence their potential use in a wide range of applications and devices from photodynamic



55 X = 2; R = benzyl

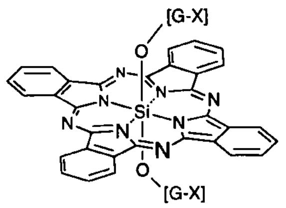
56 X = 3; R = benzyl

57 X = 2; R = $(CH_2CH_2O)_3CH_3$

58 X = 3; R = $(CH_2CH_2O)_3CH_3$

59 X = 3; R = CO_2^-

60 X = 3a

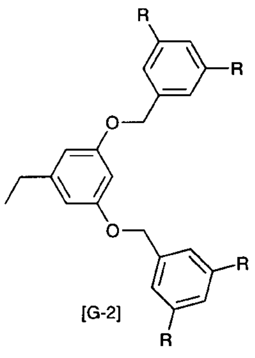


61 X = 2; R = benzyl

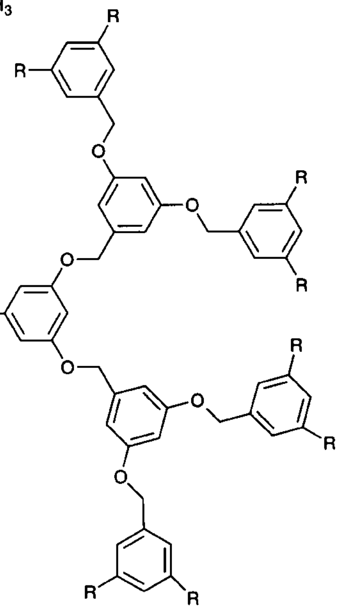
62 X = 3; R = benzyl

63 X = 2; R = $(CH_2CH_2O)_3CH_3$

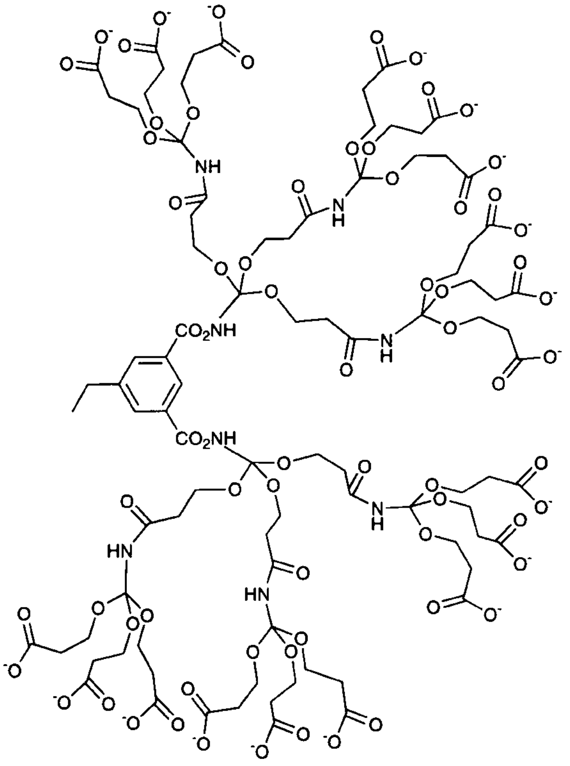
64 X = 3; R = $(CH_2CH_2O)_3CH_3$



[G-2]



[G-3]



[G-3a]

therapy[157,163] to odour removal[82d,164] and from cytotoxic materials[165] to fuel cells.[166] However, there are several areas of research where progress has been disappointing. Conjugated polymers have been the focus of renewed interest in recent years and yet there is still no *bona fide* example of a conjugate polymer which takes advantage of the unique electronic and optical properties of the Pc macrocycle. This is in contrast to the numerous types of porphyrin-containing conjugated systems.[167] Porphyrin chemists have also been highly successful at preparing discrete conjugated oligomers which are useful model compounds for the understanding of related polymers. It is encouraging that reports of similar conjugated Pc-containing oligomers have begun to appear in the literature.[86,168] In addition, the promise of Pc polymers to enforce covalent control over the 3-dimensional arrangement of the Pc unit in the solid phase has yet to be fulfilled. In most Pc polymers cofacial association predominates, as it does in low molar mass derivatives, and only axial substitution of the central ion is successful for its prevention—but at the cost of blocked access to the central ion for catalytic purposes. Clearly, there are still exciting challenges to be met in the design and synthesis of Pc-containing polymers.

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