The Synthesis of Some Phthalocyanines and Napthalocyanines Derived from Sterically Hindered Phenols

Matthew Brewis, Guy J. Clarkson, Paul Humberstone, Saad Makhseed, and Neil B. McKeown*

Abstract: The synthesis of a number of phthalocyanines (Pcs) and naphthalocyanines (NPcs) bearing bulky substituents is described. Precursors are prepared by using a nucleophilic aromatic substitution reaction between a sterically hindered phenol and 4-nitrophthalonitrile, 3-nitrophthalonitrile or 6-fluoro-2,3-napthalonitrile. Thus, Pcs and NPcs derived from 2,6-diisopropylphenol, 3,5-di-*tert*-butylphenol and 2,6-diphenylphenol possess substituents that are forced by steric constraints to adopt a non-planar conformation which enhances the solubility of the macrocycle. In particular, the Pc derived from 2,6-di-*tert*-butyl-4-methylphenol displays exceptional solubility and a reduced tendency to aggregate in solution. 2,6-Di-*tert*-butylphenol reacts as a carbon nucleophile to produce biphenyl phthalonitrile precursors to Pcs containing redox-active phenolic substituents.

Keywords: atropisomerism · nucleophilic aromatic substitutions · phthalocyanines

Introduction

Phthalocyanine (Pc) and its derivatives are well established as industrial colorants and photoconductors in xerography. In addition, numerous possibilities exist for the exploitation of the fascinating properties of Pcs in such diverse fields as non-linear optics, optical data storage, sensors, photodynamic therapy of cancer, solar energy conversion and electrochromism.[1] Hence, over the past few decades there has been a considerable effort to synthesise novel Pc derivatives which possess enhanced properties relative to the parent macrocycle such as solubility in common organic solvents,[2] absorbency in the near IR (such as shown by 2,3-napthalocyanines (NPcs)),[3] liquid crystallinity,[4] redox behaviour,[5] and the ability to produce well-ordered thin films.[6]

A useful synthetic route to soluble tetrasubstituted Pcs involves the aromatic nucleophilic substitution reaction between commercially available 4-nitrophthalonitrile **1** and a suitable oxygen, nitrogen or sulfur nucleophile followed by the cyclotetramerisation of the resultant phthalonitrile derivative.[7] In particular, 4-(cumylphenoxy)phthalonitrile[8] and 4-(neopentoxy)phthalonitrile[9] have been used as precursors in a number of studies requiring soluble Pc products. Analogous reactions between 3-nitrophthalonitrile **2** and suitable nucleophiles have proved successful in providing precursors to 1,8(11),15(18),22(25)-tetrasubstituted Pcs.[10] The aim of the present work was to extend this synthetic methodology to provide phthalonitrile and naphthalonitrile (2,3-dicyanonaphthalene) precursors derived from sterically hindered phenols. It was anticipated that this would result in Pcs and NPcs containing bulky substituents placed at sites where they can interfere best with cofacial self-association and therefore enhance solubility. In addition, a reduction in the tendency of Pcs to aggregate in solution could be advantageous in a number of applications including photodynamic cancer therapy and non-linear optics.

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Results

The sterically hindered phenols chosen as starting materials for this study were 2,6-diisopropylphenol **3**, 2,6-diphenylphenol **4**, 2,6-di-*tert*-butylphenol **5** and 2,6-di-*tert*-butyl-4-methylphenol **6**. In addition, 3,5-di-*tert*-butylphenol **7**, in which the bulky solubilising groups do not hinder the hydroxyl functionality, was used for comparison. In DMF, at 50–70 °C, the anion of each of these phenols displaces the nitro group of **1** to provide a phthalonitrile derivative (Scheme 1).

Phenols **3**, **4**, **6** and **7** produce the expected 4-phenoxyphthalonitriles **8–11** in good yield**.** However, we found that the anion of **5** reacts efficiently with **1** as a carbon nucleophile to give 4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)phthalonitrile **12**. The biphenyl structure of **12** was confirmed by ^{1}H NMR

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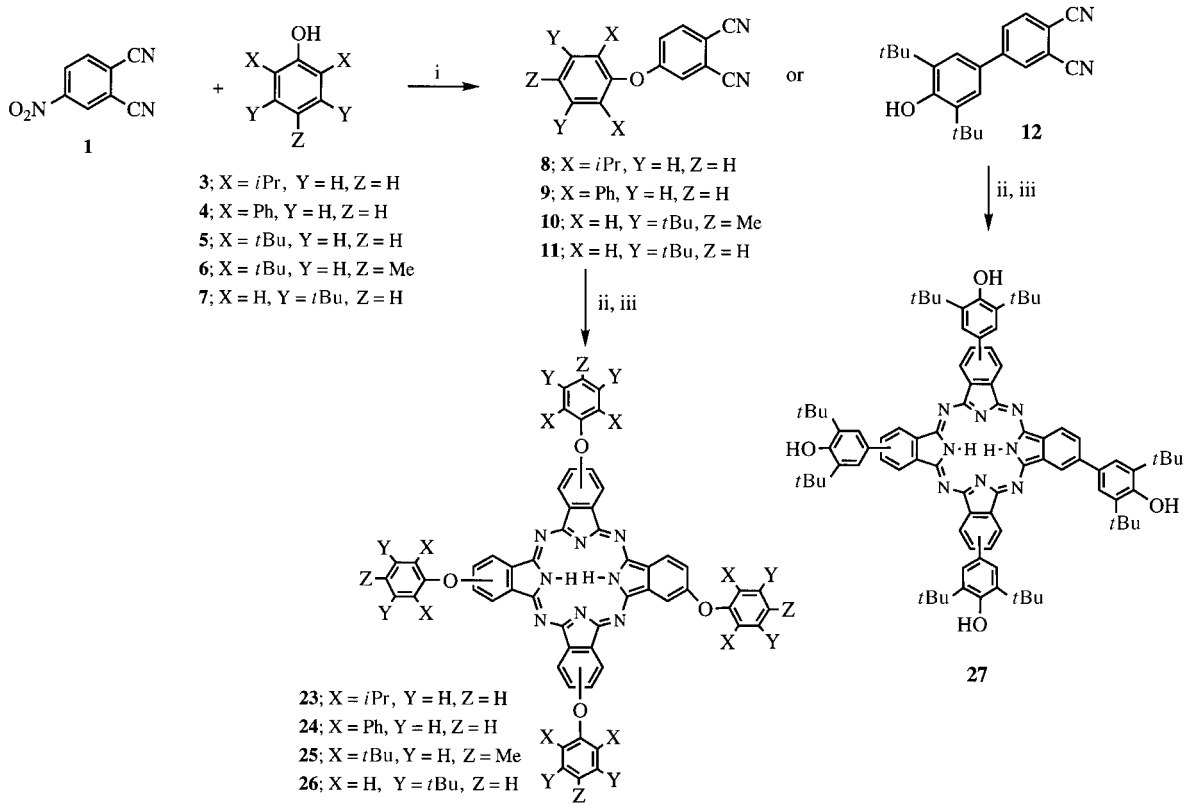
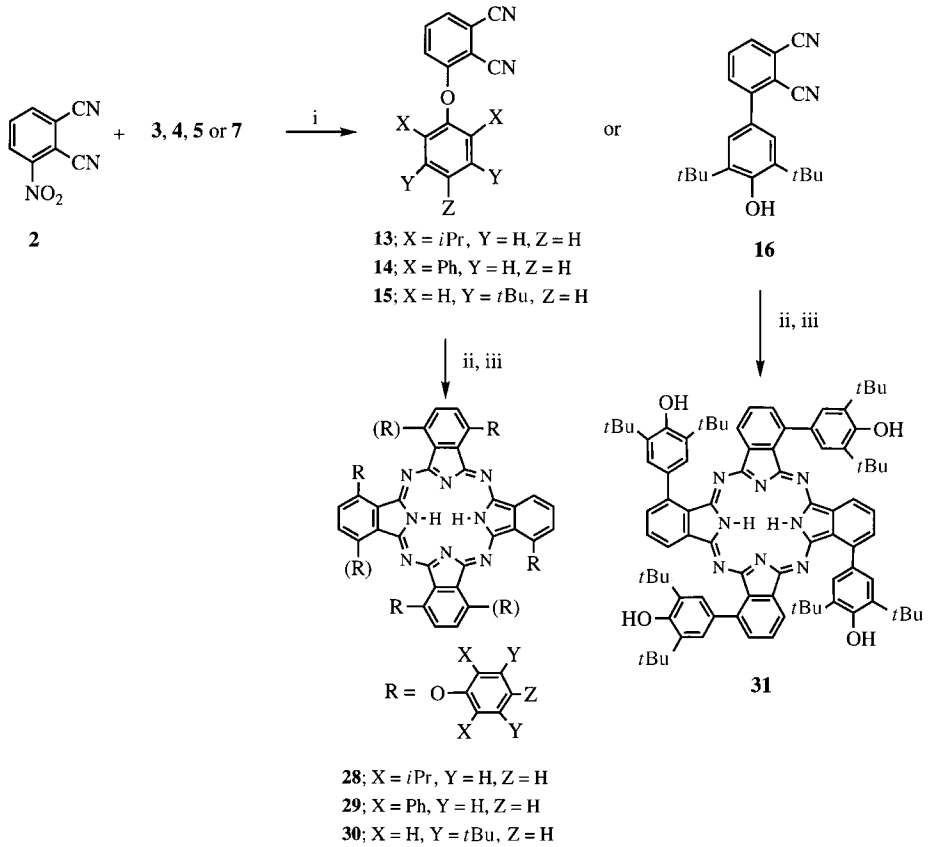


Scheme 1. Reagents and conditions: i. anhydrous K_2CO_3; DMF, 50–70 °C, (25–82% yield); ii. lithium, pentanol, 135 °C, (12–72% yield); iii. acetic acid.

and IR spectroscopy, and a single-crystal X-ray diffraction study. This structure was also consistent with the observation of a large bathochromic shift of the band of longest wavelength in the UV/Vis absorption spectrum, from 345 to 505 nm, on the addition of base, which is characteristic of the formation of a conjugated phenolic anion. Several previous studies have illustrated the ability of the anion of **5** to behave as a carbon nucleophile in the preparation of biphenyl derivatives through aromatic nucleophilic substitution.[11] Indeed, a precedent for the formation of **12** is the reaction between the anion of **5** with 3,4,5,6-tetrachlorophthalonitrile to give 3,5,6-trichloro-4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)phthalonitrile, a useful precursor to dodecachloro-tetra-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalocyanine.[12]

As expected, under similar conditions the phenols **3**–**5** and **7** react with 3-nitrophthalonitrile **2** to produce the analogous 3-substituted phthalonitriles **13**–**16** (Scheme 2), although in much poorer yield. In



Scheme 2. Reagents and conditions: i. anhydrous K_2CO_3, DMF, 50–70 °C, (4–59% yield). ii. lithium, pentanol, 135 °C, (1–30%); iii. acetic acid.

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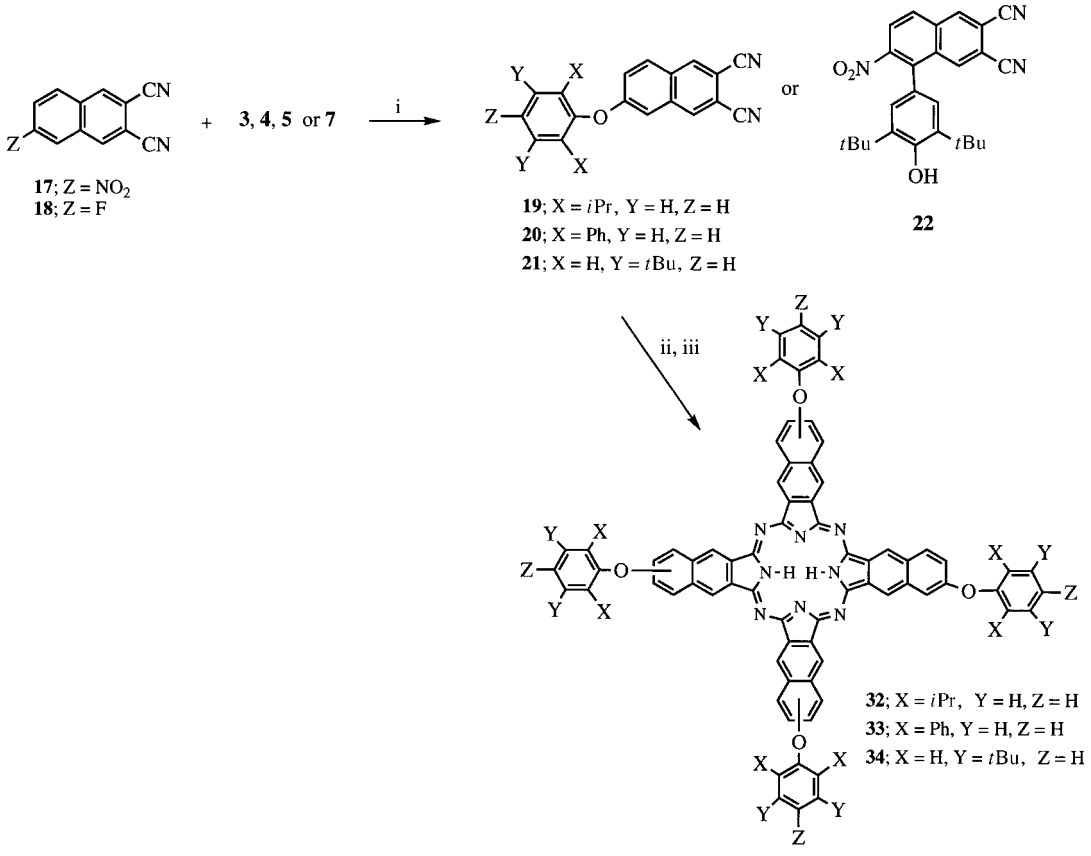
particular, 4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)phthalonitrile **16** was isolated in only 4% yield from the highly complex, tarry, product mixture. The attempted reaction between the anion of **6** and **2** failed.

Recently, a number of elegant routes to soluble octasubstituted NPcs have been described.[13] However the utility of aromatic nucleophilic substitution for the preparation of naphthalonitrile precursors is relatively unexplored.[14] The anion of **7** reacts with 6-nitronaphthalonitrile **17**[15] to produce napthalonitrile **21** in 42% yield. Unfortunately, this compound was contaminated by an unidentified orange byproduct and required purification by column chromatography. By substituting 6-fluoronapthalonitrile **18**[16] for **17** in the appropriate reactions, pure, colourless samples of napthalonitriles **19–21** were obtained after a single recrystallisation and in better yield (Scheme 3). However, no reaction occurs between **18** and the anion of **5** or **6** even after prolonged heating**.** Notably, an oxidative coupling reaction occurs between **17** and the anion of **5** to give **22** in 38% yield. This reaction appears analogous to that, described by Stahly,[17] between the anion of **5** and 1,3-dinitrobenzene which gave (3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-2,4-dinitrobenzene. Compound **22** is yellow both as a solid and in chloroform ($\lambda_{max} = 354$ nm) but turns blue on the addition of base ($\lambda_{max} =$ 610 nm).

The compounds **8–12**, **13–16** and **19–21** all undergo cyclotetramerisation, in refluxing pentanol with lithium pentyloxide catalysis followed by acidic work-up, to afford the expected metal-free Pcs **23–27**, **28–31** and NPcs **32–34**, respectively (Schemes 1–3). Only naphthalonitrile **22** fails to yield a macrocyclic product. Pc **28** can be prepared only in minute quantities (ca. 1% yield) but is isolated easily due to its insolubility in cold solvents. In each case spectroscopic analysis (^{1}H NMR, UV/Vis, IR) and fast atom bombardment mass spectroscopy (FAB-MS) gave spectra consistent with the proposed structures. A well defined (i.e. non-aggregated) ^{1}H NMR spectrum was obtained for each Pc **23–31** under appropriate conditions (60 °C, 1×10^{-3} mol dm^{-3} concentration in C_6D_6). Pc **25** is remarkable in that it displays a sharp ^{1}H NMR spectrum (Figure 1b) under conditions (e. g. 25 °C, concentration $= 1 \times 10^{-2}$ mol dm^{-3} in $CDCl_3$) in which the other Pcs give highly broadened spectra due to aggregation (Figure 1a). The ^{1}H NMR spectra of NPcs **32–34** are each severely broadened due to aggregation even in dilute C_6D_6 solution at elevated temperatures.

Cyclotetramerisation of monosubstituted phthalonitriles usually results in the formation of four regioisomers. These four isomers possess C_{4h}, C_s, C_{2v} and D_{2h} molecular symmetry (ignoring the tautomers formed due to the exchange of the protons between the four inner nitrogen atoms) and, assuming a statistical distribution, are prepared in a relative yield of 1:4:2:1, respectively. It was deduced from their highly complex ^{1}H NMR spectra that all Pcs and NPcs were obtained as mixtures of isomers, with the exception of the sparingly soluble Pc **31** which has a relatively simple spectrum. Previously, Hanack and co-workers separated all four isomers



Scheme 3. Reagents and conditions: i. anhydrous K_2CO_3; DMF, 50–70 °C, (30–51% yield); ii. lithium, pentanol, 135 °C (12–33% yield); iii. acetic acid .

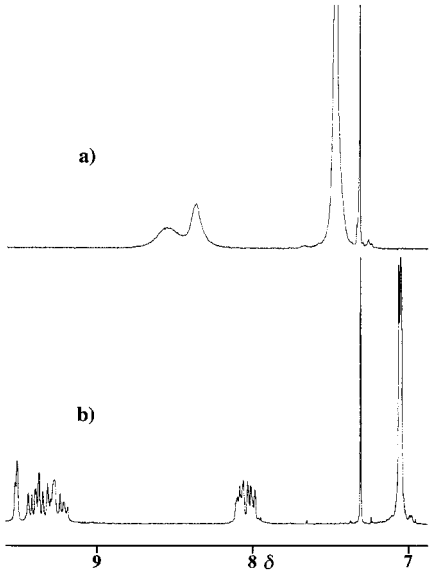


Figure 1. The aromatic region of the ^{1}H NMR spectrum of **23** (a), which is broadened due to aggregation, and **25** (b), which shows no evidence of self-association. Both spectra were obtained under the same conditions (concentration $= 1 \times 10^{-2}$ mol dm^{-3} in $CDCl_3$ at 25 °C).

of two different tetrasubstituted Pcs by HPLC.[18] No attempt was made to separate the isomers by chromatography in this study but the relative insolubility of a portion of Pcs **28** and **30** in cold solvent was investigated by ^{1}H NMR spectroscopy at elevated temperatures (ca. 60 °C). A simple spectrum was obtained from these samples similar to that displayed by Pc **31**. This indicated that these Pcs are composed of a single highly symmetrical isomer (i. e. C_{4h} or D_{2h}); the C_{4h} isomer is the most probable as it was the most insoluble isomer isolated by Hanack et al.[18] In addition, it is likely that steric hindrance would prevent the formation of the C_s, C_{2v} and D_{2h} isomers of Pc **31.** Steric hindrance may also account for the exceptionally low yield of formation for **28** and **29**.

Discussion

The extent to which the sterically hindered phenoxy substituents hinder Pc self-association in solution will be dependent on their conformation relative to the Pc macrocycle. A similar conformation would be expected in the phthalonitrile precursors, information on which can be deduced readily by ^{1}H NMR analysis. It has been suggested that diphenyl ethers, in which one of the phenyl rings contains two large groups *ortho* to the oxygen linkage, preferentially adopt a 'H-inside' conformation (Figure 2).[19–21] This tendency is enhanced if the other phenyl ring contains electron-withdrawing groups which conjugate with a lone pair of electrons of the oxygen link.[20] The H-inside conformation results in the resonances of the *ortho*-hydrogens appearing in unusually shielded positions.

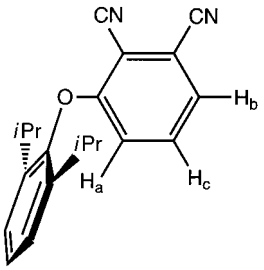
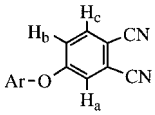
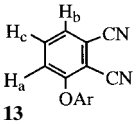
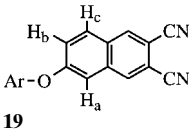
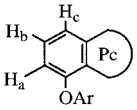


Figure 2. The preferred 'H-inside' conformation of sterically hindered diphenyl ethers illustrated for **13**.

Table 1 gives the chemical shifts of the aromatic hydrogen atoms for the phthalonitrile subunit of the diphenyl ethers **8–11** and **13–15**. The degree of importance of the H-inside conformation for the compounds in solution can be estimated by a comparison of the chemical shifts of the *ortho*-hydrogens of the sterically hindered diphenyl ethers **8–10** (H_a and H_b) and **13**, **14** (H_a only) with those of the related, unhindered ethers **11** (H_a and H_b) and **15** (H_a only), respectively. It can be deduced that the H-inside conformation is most important for

Table 1. Selected ^{1}H NMR shifts (δ) in some of the compounds studied.

	H_a	H_b	H_c
			
8	7.13	7.23	7.74
9	6.85	6.89	7.43
10	7.61	7.74	7.82
11	7.27	7.31	7.76
			
13	6.79	7.45	7.54
14	6.60	7.10	7.21
15	7.11	7.47	7.59
			
19	6.96	7.59	7.99
20	6.78	7.20	7.62
21	7.25	7.60	8.00
			
28 (C_{4v})	7.15	7.63	9.33
30 (C_{4v})	7.66	7.74	9.00

13 and **14** which are additionally hindered due to the *ortho*-nitrile substituent. An interesting property of phthalonitrile **13** is that its ^{1}H NMR spectrum shows two environments for the isopropyl methyl groups ($\delta = 1.13$ and 1.27), strongly suggesting that rotation about the aryl–oxygen bonds is slow on the NMR time-scale and that the diphenyl ether is effectively frozen in the H-inside conformation. Similar atropic effects have been observed previously in related diphenyl ethers derived from **3** such as 2,4-dinitro-(2′,6′-diisopropylphenoxy)benzene.[21] That the same conformational arrangements exist in the derived Pc **28** is apparent from the shielded position of the signal for the *ortho*-hydrogen in the spectrum of the single isomer fraction ($\delta(H_a) = 7.15$) relative to that of the analogous hydrogen atoms in **30** ($\delta(H_a) = 7.66$). Atropisomerism is also present in Pc **28** as indicated by two signals ($\delta = 1.26$ and 1.60) for the

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isopropyl methyl groups in the ^{1}H NMR spectrum of the single isomer fraction. No coalescence of these peaks was observed on heating. Similar comparisons of the aromatic resonances of hindered napthalonitriles **19** and **20** (H_a) with unhindered **21** indicate that these two compounds also exist largely in the H-inside conformation in solution.

Compound **10** is anomalous in that despite the two large *ortho tert*-butyl groups there is no evidence of a H-inside conformation from its ^{1}H NMR spectrum. Indeed, the phthalonitrile hydrogens (H_a, H_b and H_c) appear strongly deshielded relative to those of **11** (Table 1). Furthermore, the resonances originating from protons on the other ring ($\delta =$ 6.46 (C*H*), 1.71 (CH_3)) are highly shielded as compared to their position in a previously described alkyl ether of phenol **6** ($\delta = 7.03$ (C*H*) 2.27 (CH_3)).[22] It would appear that **10** adopts a conformation by which the lone pair of electrons of the oxygen link can only conjugate with the phenyl ring which bears the *tert*-butyl groups and not with the phthalonitrile moiety. It is not understood why the ^{1}H NMR spectrum of this compound differs so markedly from the other phthalonitriles in this study, or from similar compounds described previously (e. g. 4-bromo-(2′,4′,6′-tri-*tert*-butylphenoxy)benzene).[21] Nevertheless, this conformation of the phenoxy groups in the derived Pc **25**, as shown by its ^{1}H NMR spectrum, is highly beneficial for the reduction of aggregation (Figure 1b)

Compounds **9**, **14** and **20**, derived from phenol **4**, display relatively shielded aromatic protons associated with the phthalonitrile unit (Table 1); each type of proton (H_a, H_b and H_c) has signals which are shifted upfield by 0.3 – 0.5 ppm compared with the values for the analogous protons on compounds **11**, **15** and **21**, respectively. Molecular models suggest that one of the phenyl substituents must lie in close proximity to the phthalonitrile moiety when the molecule adopts a H-inside conformation. It is proposed that the ring current of the adjacent phenyl ring causes the observed shielding effects. Similar shielding effects are apparent in the highly complex ^{1}H NMR spectra of Pcs **24** and **29** and NPc **33** which all possess signals in the range $\delta = 6.3 - 7.0$. This indicates that the phenyl substituents must be forced by analogous conformational constraints to lie within the shielding portion of the strong ring current of the aromatic macrocycle due to the adoption of a H-inside conformation.

UV/Vis absorption spectra of the blue-green Pcs **22 – 31** in dichloromethane or toluene exhibit the split Q-band which is characteristic of metal-free Pcs (Figure 3a). No cofacial aggregation effects were observed at the concentrations used (5×10^{-5} mol dm^{-3}). The 1,8(11),15(18),22(25)-tetrasubstituted Pcs **28 – 30** (Q-band; $\lambda_{max} = 722$ [$\varepsilon = 110\,000$], 689 nm [$\varepsilon =$ 90 000]) absorb further to the red than the 2,9(10),16(17),23(24)-tetrasubstituted Pcs **23 – 26** (Q-band; $\lambda_{max} = 704$ nm, 669 nm). Pcs **27** (Q-band; $\lambda_{max} = 715$, 683 nm) and **31** (Q-band; $\lambda_{max} = 728$, 694 nm) are red-shifted slightly compared to the phenoxy-substituted Pcs with the same substitution pattern. On addition of an excess of tetrabutylammonium hydroxide (TBAH), the Q-band of Pc **27** exhibits a large bathochromic shift to 796 nm and a reduction in intensity to $\varepsilon = 35\,000$ (Figure 3b). Pc **31** shows a similar shift to 800 nm. This dramatic effect demonstrates that the deprotonated phenolic substituents interact strongly with

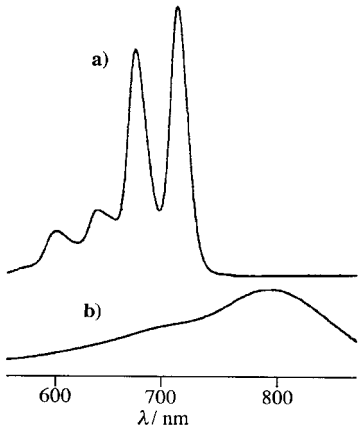

Figure 3. Visible absorption spectra for Pc **27** in CH_2Cl_2: a) under neutral conditions; b) after the addition of base (TBAH).

the Pc macrocycle resulting in a near-IR absorbing chromophore similar to that of the naphthalocyanines. For comparison, the addition of excess TBAH to a solution of the isomeric phenoxy-substituted Pc **26** gives a single, unshifted Q-band at 690 nm consistent with the formation of the more symmetrical Pc^{2-} ion due to the loss of the two protons from the central cavity. In general, hindered phenols are readily oxidised to stable free radical species (e. g. galvinoxyl). They may also undergo further oxidation to form quinones. We are presently investigating the redox properties of Pc **27** and other Pcs derived from phthalonitrile **12**.[23]

As expected, NPcs **32** and **34** are green solids which are soluble in a wide range of organic solvents and display the typical single sharp Q-band absorption ($\lambda_{max} = 784$ nm, $\varepsilon = 160$ 000) of NPcs in the near-IR region of the spectrum (Figure 4a). A less intense absorption ($\lambda = 722$ nm) is

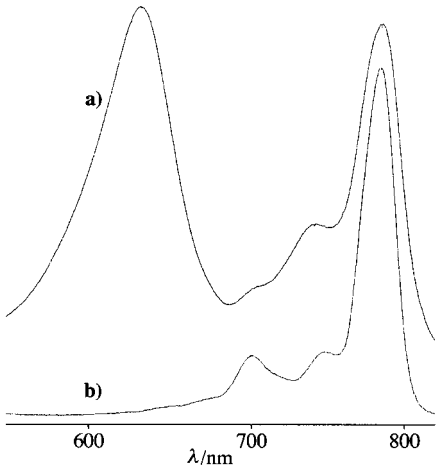

Figure 4. Visible absorption spectra for **33** (a) and **32** (b). Both spectra were obtained under the same conditions (concentration 5×10^{-6} mol dm^{-3} in CH_2CCl_2).

exhibited by solutions at 5×10^{-5} mol dm^{-3} but this band is not evident in the spectrum of more dilute solutions (5×10^{-6} mol dm^{-3}). Therefore, we conclude that the minor band arises from exciton coupling due to cofacial aggregation in solution.

Surprisingly, NPc **33** is a blue compound, not unlike a Pc in appearance, both as a solid and in solution. This unusual colour originates from a strong absorption at 620 nm ($\varepsilon = 41\,000$) which is present in addition to the Q-band ($\lambda_{max} = 782$ nm, $\varepsilon = 46\,000$) and the band due to intermolecular excition coupling at 736 nm (Figure 4b). Variation of the concentration of **33** in toluene confirms the assignment of the band at 736 nm to a dimeric species as it disappears at high dilution. The ratio of the intensity of the Q-band to that of the absorption at 620 nm remains constant over the concentration range from 5×10^{-5} to 5×10^{-6} mol dm^{-3}. In addition, the relative intensity of these bands is not influenced when the UV/Vis spectrum is measured in other solvents (THF, dichloromethane, pyridine). These observations suggest that the anomalous band at 620 nm arises from an intramolecular rather than intermolecular phenomenon. It is possible that the position of the phenyl substituents over the macrocycle, as evident from the shielded position of the relevant hydrogens in the NMR spectrum of **33**, encourages an electron transfer from the relatively easily oxidised NPc ring. It is notable that the visible absorpton spectrum of the one-electron oxidised radical of tetra-*tert*-butylnaphthalocyanine has a major absorption band at 630 nm.[24]

Conclusions

As found in previous studies,[8, 9] the aromatic nucleophilic substitution reaction between phenols and **1** is an extremely useful and high yielding reaction for the preparation of precursors to highly soluble Pcs. Of particular interest are the Pcs derived from highly hindered phenols **5**, which possesses redox-active phenolic substituents, and **6**, which displays an unusual lack of aggregation in solution. The use of analogous reactions employing **2** for the preparation of 1,8(11),15(18),22(25)-tetrasubstituted Pcs is less useful due to the much lower yield for cyclotetramerisation and different solubilities of the resulting isomers. However, it has been demonstrated that the synthetic methodology can be readily extended to the preparation of soluble NPcs by using 6-fluoro-2,3-naphthalonitrile as the starting material.

Experimental Section

Routine ^{1}H NMR spectra were measured at 300 MHz by using a Inova 300 spectrometer. High resolution (500 MHz) ^{1}H NMR spectra were recorded by using a Varian Unity 500 spectrometer. UV/Vis spectra were recorded on a Shimadzu UV-260 spectrophotometer from toluene or dichloromethane solutions using cells of pathlength 10 mm. IR spectra were recorded on a ATI Mattson Genesis Series FTIR (KBr/Germanium beam splitter). Elemental analyses were obtained with a Carlo Erba Instruments CHNS-O EA 108 Elemental Analyser. Routine low-resolution chemical ionisation (CI) and electron ionisation (EI) were obtained by using a Fisons instruments Trio 2000. Pc fast atom bombardment (FAB) spectra were recorded on a Kratos Concept spectrometer. Routine melting point determination was carried out with a Gallenkemp melting point apparatus and melting points are uncorrected. All solvents were dried and purified as described in Perrin and Armarego.[25] Silica gel (60 Merck 9385) was used in the separation and purification of compounds by column chromatography.

Preparation of phthalonitriles: In a typical procedure, anhydrous potassium carbonate (9 g) was added to a solution of 4-nitrophthalonitrile (8 g, 46 mmol) and 2,6-di-*tert*-butylphenol **5** (11.4 g, 55 mmol) in dry DMF (50 mL). Immediately a deep red colour was evolved and the mixture was stirred under a nitrogen atmosphere for 72 h at 60 °C. Water (300 mL) was added and the mixture extracted with ethyl acetate (3×100 mL). The organic layer was washed with NaOH (1×100 mL) and water (3×75 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the crude product. Recrystallisation from ethanol gave 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitrile **12** as colourless, prismatic crystals (12.5 g, 82%), m.p. 209–210 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.55$ (s, 18H, 6 CH_3), 5.58 (s, 1H, OH), 7.42 (s, 2H, CH), 7.80–8.00 (m, 3H, 3 CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 30.1, 34.5, 112.3, 114.5, 115.8, 116.2, 124.1, 128.1, 130.8, 131.5, 133.7, 137.1, 147.3, 162.5; IR(KBr): $\tilde{\nu} = 3416$ (OH), 2232 cm^{-1}(C≡N); MS(CI): *m/z*: 350 [M^++NH_4^+], 332 [M^+]; elemental analysis; C 79.55, H 7.50, N 8.20; calculated for $C_{22}H_{24}N_2O$: C 79.47, H 7.28, N 8.43.

The following compounds were prepared by similar procedures:

8: Yield 76% (from **1** and **3**); m.p. 115–116 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.18$ (d, ^3J(H,H) = 7 Hz, 12H, 4 CH_3), 2.87 (sept, ^3J(H,H) = 7 Hz, 2H, 2 CH), 7.13 (br d, ^3J(H,H) = 8 Hz, 1H, CH), 7.23 (br s, 1H, CH), 7.27–7.40 (m, 3H, 3 CH), 7.74 (d, ^3J(H,H) = 8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 23.2$, 27.1, 108.2, 114.9, 115.4, 117.7, 119.4, 119.8, 125.1, 127.3, 135.4, 140.8, 146.8, 162.3; IR(KBr): $\tilde{\nu} =$ 2232 cm^{-1}(C≡N); MS(CI): *m/z*: 322 [M^++NH_4^+], 304 [M^+]; elemental analysis; C 78.78, H 6.69, N 9.25; calculated for $C_{20}H_{20}N_2O$: C 78.91, H 6.63, N 9.20.

9: Yield 70% (from **1** and **4**); m.p. 117–119 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.85$ (dd, ^3J(H,H) = 9, 2 Hz, 1H, CH), 6.89 (d, ^3J(H,H) = 2 Hz, 1H, CH), 7.28–7.60 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 107.8$, 114.9, 115.3, 116.8, 120.1, 120.2, 127.2, 127.8, 128.4, 129.0, 130.1, 134.7, 135.8, 136.5, 146.8, 160.6; IR(KBr): $\tilde{\nu} = 2230$ cm^{-1}(C≡N); MS(CI): *m/z*: 390 [M^++NH_4^+], 372 [M^+]; elemental analysis; C 83.60, H 4.20, N 7.60; calculated for $C_{26}H_{16}N_2O$: C 83.85, H 4.33, N 7.52.

10: Yield 25% (from **1** and **6**); m.p. 176–178 °C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.29$ (s, 18H, 2 $C(CH_3)_3$), 1.71 (s, 3H, CH_3), 6.46 (s, 2H, CH), 7.61 (dd, ^3J(H,H) = 8, 2 Hz,1H, CH), 7.74 (d, ^3J(H,H) = 8 Hz, 1H, CH),7.82 (d, ^3J(H,H) = 8 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 24.7$, 29.3, 34.7, 114.3, 115.0, 115.3, 118.2, 121.3, 131.1, 131.3, 133.8, 143.3, 146.7, 149.4, 162.0; IR(KBr): $\tilde{\nu} = 2232$ cm^{-1}(C≡N); MS(CI): *m/z*: 364 [M^++NH_4^+], 346 [M^+]; elemental analysis; C 80.08, H 7.64, N 8.13; calculated for $C_{23}H_{26}N_2O$: C 79.73, H 7.56, N 8.08.

11: Yield 80% (from **1** and **7**); m.p. 127–128 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.37$ (s, 18H, 6 CH_3), 6.93 (d, ^3J(H,H) = 2 Hz, 2H, CH), 7.27 (dd, ^3J(H,H) = 9, 2 Hz, 1H, CH), 7.31 (d, ^3J(H,H) = 2 Hz, 1H, CH), 7.41 (t, ^3J(H,H) = 2 Hz, 2H, 2 CH), 7.76(d, ^3J(H,H) = 9 Hz, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.3$, 35.1, 108.2, 114.6, 115.4, 115.8, 117.7, 120.2, 121.0, 121.2, 135.3, 153.0, 153.9, 162.3; IR(KBr): $\tilde{\nu} =$ 2233 cm^{-1}(C≡N); MS(CI): *m/z*: 350 [M^++NH_4^+], 332 [M^+]; elemental analysis; C 79.20, H 7.31, N 8.62; calculated for $C_{22}H_{24}N_2O$: C 79.48, H 7.28, N 8.43.

13: Yield 21% (from **2** and **3**); m.p. 136–137 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.13$ (d, ^3J(H,H) = 7 Hz, 6H, 2 CH_3), 1.27 (d, ^3J(H,H) = 7 Hz, 6H, 2 CH_3), 2.91 (sept, ^3J(H,H) = 7 Hz, 2H, 2 CH), 6.79 (dd, ^3J(H,H) = 9, 1 Hz,1H, CH), 7.26–7.40 (m, 3H, 3 CH), 7.45 (dd, ^3J(H,H) = 9, 1 Hz, 1H, CH), 7.54 (t, ^3J(H,H) = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 22.3$, 24.1, 27.3, 104.1, 112.6, 115.2, 117.3, 117.9, 124.9, 126.1, 127.3, 134.2, 140.7, 146.9, 161.5; IR(KBr): $\tilde{\nu} = 2232$ cm^{-1}(C≡N); MS(CI): *m/z*: 322 [M^++NH_4^+], 304 [M^+]; elemental analysis; C 78.98, H 6.54, N 9.25; calculated for $C_{20}H_{20}N_2O$: C 78.91, H 6.63, N 9.20.

14: Yield 45% (from **2** and **4**); m.p. 128–129 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.60$ (dd, ^3J(H,H) = 8, 1 Hz, 1H, CH), 7.10 (dd, ^3J(H,H) = 8, 1 Hz, 1H, CH), 7.21 (t, ^3J(H,H) = 8 Hz, 1H, CH), 7.24–7.42 (m 7H, 7 CH), 7.5–7.6 (m, 6H, 6 CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 104.2$, 112.5, 115.0, 116.4, 118.5, 125.8, 127.3, 127.9, 128.4, 129.0, 130.8, 133.5, 135.8, 136.3, 146.6, 159.6; IR(KBr): $\tilde{\nu} = 2230$ cm^{-1}(C≡N); MS(CI): *m/z*: 390 [M^++NH_4^+], 372 [M^+]; elemental analysis; C 83.73, H 4.28, N 7.82; calculated for $C_{26}H_{16}N_2O$: C 83.85, H 4.33, N 7.52.

15: Yield 59% (from **2** and **7**); m.p. 154–155 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.36$ (s, 18H, 6 CH_3), 6.97 (d, ^3J(H,H) = 1 Hz, 2H, CH), 7.11 (dd, ^3J(H,H) = 9, 1 Hz, 1H, CH), 7.39 (t, ^3J(H,H) = 1 Hz, 2H, 2 CH), 7.47(dd, ^3J(H,H) = 9, 1 Hz, 1H, CH), 7.59 (t, ^3J(H,H) = 9 Hz, 1H,

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CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.3$, 35.1, 102.8, 114.6, 115.4, 117.4, 117.7, 119.8, 120.1, 126.4, 134.2, 153.1, 153.8, 160.2; IR(KBr): $\tilde{\nu} = 2233\ cm^{-1}$(C≡N); MS(CI): *m/z*: 350 [M^++NH_4^+], 332 [M^+]; elemental analysis; C 79.35, H 7.38, N 8.45; calculated for $C_{22}H_{24}N_2O$: C 79.48, H 7.28, N 8.43.

16: Yield 4% (from **2** and **5**); m.p. 201–203 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.50$ (s, 18H, 6 CH_3), 5.51 (s, 1H, OH), 7.39 (s, 2H, CH), 7.70–8.00 (m, 3H, 3 CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 30.3, 34.2, 112.5, 114.6, 115.2, 116.3, 124.1, 128.1, 130.6, 131.8, 133.5, 137.3, 147.5, 162.6; IR(KBr): $\tilde{\nu} = 3493$ (OH), 2234 cm^{-1}(C≡N); MS(CI): *m/z*: 350 [M^++NH_4^+], 332 [M^+]; elemental analysis; C 79.52, H 7.34, N 8.42; calculated for $C_{22}H_{24}N_2O$: C 79.47, H 7.28, N 8.43.

19: Yield 41% (from **3** and **18**); m.p. 233–234 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.18$ (d, ^3J(H,H) = 7 Hz, 12H, 4 CH_3), 3.00 (sept, ^3J(H,H) = 7 Hz, 2H, 2 CH), 6.96 (d, ^3J(H,H) = 2 Hz, 1H, CH), 7.30–7.44 (m, 3H, 3 CH), 7.59 (dd, ^3J(H,H) = 9,2 Hz,1H, CH), 7.99 (d, ^3J(H,H) = 9 Hz, 1H, CH), 8.12 (s, 1H, CH), 8.34 (s, 1H, CH) ; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 23.3$, 27.1, 107.7, 109.2, 110.8, 115.8, 116.0, 122.4, 124.8, 126.8, 128.8, 130.8, 134.3, 134.8, 135.4, 141.1, 147.1, 160.8; IR(KBr): $\tilde{\nu} =$ 2232 cm^{-1}(C≡N); MS(CI): *m/z*: 372 [M^++NH_4^+], 354 [M^+]; elemental analysis; C 81.01, H 5.97, N 7.50; calculated for $C_{24}H_{22}N_2O$: C 81.33, H 6.26, N 7.90.

20: Yield 30% (from **4** and **18**); m.p. 240–241 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.78$ (d, ^3J(H,H) = 2 Hz, 1H, CH), 7.20 (dd, ^3J(H,H) = 9, 2 Hz, 1H, CH), 7.24–7.34 (m, 6H), 7.49–7.59 (m, 7H), 7.62 (d, ^3J(H,H) = 9 Hz, 1H, CH), 7.82 (s, 1H, CH), 8.18 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 107.8$, 110.2, 110.4, 115.7, 116.0, 122.6, 122.9, 126.7, 127.5, 128.2, 128.3, 128.9, 130.2, 130.9, 134.1, 135.1, 136.1, 137.1, 148.0, 159.3; IR(KBr): $\tilde{\nu} = 2232\ cm^{-1}$(C≡N); MS(CI): *m/z*: 440 [M^++NH_4^+], 422 [M^+]; elemental analysis; C 85.01, H 4.27, N 6.60; calculated for $C_{30}H_{18}N_2O$: C 85.29, H 4.29, N 6.63;

21: Yield 51% (from **7** and **18**; 42% from **17**); m.p. 208–209 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.38$ (s, 18H, 6 CH_3), 7.00 (d, ^3J(H,H) = 2 Hz, 2H, CH), 7.25 (d, ^3J(H,H) = 2 Hz, 1H, CH), 7.38 (t, ^3J(H,H) = 2 Hz, 2H, 2 CH), 7.60 (dd, ^3J(H,H) = 9, 2 Hz, 1H, CH), 8.00 (d, ^3J(H,H) = 9 Hz, 1H, CH), 8.18 (s, 1H, CH), 8.33 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 31.3$, 35.0, 108.3, 110.5, 111.4, 113.0, 114.7, 115.4, 115.8, 119.4, 123.7, 129.4, 130.6, 134.5, 134.9, 135.4, 153.5, 160.5; IR(KBr): $\tilde{\nu} = 2232\ cm^{-1}$(C≡N); MS(CI): *m/z*: 400 [M^++NH_4^+], 382 [M^+]; elemental analysis; C 81.52, H 6.61, N 7.23; calculated for $C_{26}H_{26}N_2O$: C 81.64, H 6.85, N 7.33.

22: Yield 38% (from **5** and **17**); m.p. 276–278 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.52$ (s, 18H, 6 CH_3), 5.58 (s, 1H, OH), 7.12 (s, 2H, 2 CH), 8.08 (d, ^3J(H,H) = 9 Hz, 1H, CH), 8.13 (d, ^3J(H,H) = 9 Hz, 1H, CH), 8.33 (s, 1H, CH), 8.49 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 30.2$, 34.5, 111.9, 112.3, 114.9, 115.8, 116.6, 122.1, 124.3, 126.2, 129.0, 133.6, 134.2, 135.6, 136.2, 136.7, 155.0, 163.5; IR(KBr): $\tilde{\nu} = 3620$ (OH), 2237 (C≡N), 1533, 1355 (NO_2) cm^{-1}; MS(CI): *m/z*: 445 [M^++NH_4^+], 427 [M^+]; elemental analysis; C 73.02, H 5.90, N 9.80; calculated for $C_{26}H_{25}N_3O_3$: C 73.04, H 5.89, N 9.83.

Preparation of phthalocyanines: In a typical procedure, 4-(2′,6′-di-*tert*-butyl-4′-methylphenoxy)phthalonitrile **10** (0.5 g, 0.36 mmol) was dissolved in dry 1-pentanol (2 mL). The solution was heated to reflux under a nitrogen atmosphere and lithium (20 mg) added. After 24 h, the solution was cooled and acetic acid added (0.5 mL). The solvents were removed under reduced pressure and the residue purified by column chromatography (silica gel, toluene:hexane (2:1) eluant). Reprecipitation from toluene into hexane afforded pure metal-free 2,9(10),16(17),23(24)-tetra(2′,6′-di-*tert*-butyl-4′-methylphenoxy)phthalocyanine **25** (350 mg, 70% yield), m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.0$ (br s, 2H, 2 NH), 1.40 (br s, 72H, 8 $C(CH_3)_3$), 2.15 (m, 12H, 4 CH_3), 6.96 (m, 8H, 8CH), 7.99–8.02 (m, 4H, 4CH), 9.30–9.50 (m, 8H, 8CH); IR(KBr): $\tilde{\nu} =$ 3290 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 704, 669, 641, 608, 343 nm; MS(FAB): *m/z*: 1388 [M^++ H^+]; elemental analysis; C 79.82, H 7.75, N 7.95; calculated for $C_{92}H_{106}N_8O_4$: C 79.61, H 7.70, N 8.08.

The following compounds were prepared by similar procedures:

23: Yield 43% (from **8**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.0$ (br s, 2H, 2 NH), 1.40–1.50 (m, 48H, 16 CH_3), 3.65–3.80 (m, 8H, 8 CH), 7.40–7.50 (m, 12H, 12 CH), 7.60–7.80 (m, 4H, 4 CH), 9.10–9.40 (m, 8H, 8 CH); IR(KBr): $\tilde{\nu} = 3290\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 704, 669, 641, 608, 343 nm; MS(FAB): *m/z*: 1219 [M^++H^+]; elemental analysis; C 78.59, H 6.81, N 9.07; calculated for $C_{80}H_{82}N_8O_4$: C 78.78, H 6.78, N 9.19.

24: Yield 59% (from **9**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.2$ (br s, 2H, 2 NH), 6.60–9.50 (m, 64H, 64 CH); IR(KBr): $\tilde{\nu} =$ 3290 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 705, 669, 641, 606, 352 nm; MS(FAB): *m/z*: 1494 [M^++H^+]; elemental analysis; C 83.90, H 4.49, N 7.55; calculated for $C_{104}H_{66}N_8O_4$: C 83.73, H 4.46, N 7.51

26: Yield 72% (from **10**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.3$ (br s, 2H, 2 NH), 1.40–1.50 (br s, 72H, 24 CH_3), 7.40–7.80 (m, 16H, 16 CH), 8.80–9.00 (m, 8H, 8 CH); IR(KBr): $\tilde{\nu} = 3294\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 701, 667, 639, 607, 342 nm; MS(FAB): *m/z*: 1333 [M^++ H^+]; elemental analysis; C 79.50, H 7.70, N 8.20; calculated for $C_{88}H_{98}N_8O_4$: C 79.35, H 7.42, N 8.42.

27: Yield 12% (from **12**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.3$ (br s, 2H, 2 NH), 1.70 (br s, 72H, 24 CH_3), 5.25 (s, 4H, 4 OH), 8.00–8.50 (m, 12H, 12 CH), 9.00–9.90 (m, 12H, 12 CH); IR(KBr): $\tilde{\nu} =$ 3641 (OH), 3289 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 715, 683, 652, 620, 344 nm; MS(FAB): *m/z*: 1334 [M^++ H^+]; elemental analysis; C 79.60, H 7.52, N 8.79; calculated for $C_{88}H_{98}N_8O_4$: C 79.35, H 7.42, N 8.42.

28: Yield 3% (from **13**; 1% single isomer fraction, probably C_{4v} isomer); m.p. >300 °C; ^{1}H NMR (C_{4v} isomer, 500 MHz, C_6D_6, 60 °C): $\delta = -2.0$ (br s, 2H, 2 NH), 1.26 (d, ^3J(H,H) = 7 Hz, 14H, 8 CH_3), 1.60 (d, ^3J(H,H) = 7 Hz, 14H, 8 CH_3), 3.74 (sept, ^3J(H,H) = 7 Hz, 8H, 8 CH), 7.15 (d, ^3J(H,H) = 8 Hz, 4H, 4 CH), 7.36–7.45 (m, 12H, 12 CH), 7.63 (t, ^3J(H,H) = 8 Hz, 4H, 4 CH), 9.33 (d, ^3J(H,H) = 8 Hz, 4H, 4 CH); IR(KBr): $\tilde{\nu} = 3290\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 712, 679, 648, 612, 343 nm; MS(FAB): *m/z*: 1219 [M^++ H^+]; elemental analysis; C 78.65, H 6.73, N 9.41; calculated for $C_{80}H_{82}N_8O_4$: C 78.78, H 6.78, N 9.19.

29: Yield 4% (from **14**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.8$ (br s, 2H, 2 NH), 6.30–9.40 (m, 64H, 64 CH); IR(KBr): $\tilde{\nu} =$ 3290 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 712, 680, 649, 615, 352 nm; MS(FAB): *m/z*: 1494 [M^++ H^+]; elemental analysis; C 83.98, H 4.25, N 7.59; calculated for $C_{104}H_{66}N_8O_4$: C 83.73, H 4.46, N 7.51.

30: Yield 30% (from **15**; 4% single isomer fraction, probably C_{4v} isomer); m.p. >300 °C; ^{1}H NMR (C_{4v} isomer, 500 MHz, C_6D_6, 60 °C): $\delta = -1.7$ (br s, 2H, 2 NH), 1.30 (br s, 72H, 24 CH_3), 7.43 (t, ^3J(H,H) = 1 Hz, 1H CH), 7.63 (d, ^3J(H,H) = 1 Hz, 2H, 2 CH), 7.66 (d, ^3J(H,H) = 8 Hz, 4H, 4 CH), 7.74 (t, ^3J(H,H) = 8 Hz, 4H, 4 CH), 9.00 (d, ^3J(H,H) = 8 Hz, 4H, 4 CH); IR(KBr): $\tilde{\nu} = 3294\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 712, 680, 649, 615, 352 nm; MS(FAB): *m/z*: 1332 [M^++ H^+]; elemental analysis; C 79.23, H 7.35, N 8.40; calculated for $C_{88}H_{98}N_8O_4$: C 79.35, H 7.42, N 8.42.

31: Yield 1% (from **16**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -1.3$ (br s, 2H, 2 NH), 1.70 (s, 72H, 24 CH_3), 5.30 (s, 4H, 4 OH), 8.00–8.50 (m, 12H, 12 CH), 9.00–9.90 (m, 12H, 12 CH); IR(KBr): $\tilde{\nu} = 3641$ (OH), 3289 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 728, 694, 655, 623, 344 nm; MS(FAB): *m/z*: 1334 [M^++H^+].

32: Yield 30% (from **19**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -0.5$ (br s, 2H, 2 NH), 1.40–1.60 (br m, 48H, 16 CH_3), 3.65–3.85 (br m, 8H, 8 CH), 7.40–8.90 (m, 32H, 32 CH); IR(KBr): $\tilde{\nu} = 3290\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 784, 740, 710, 330 nm; MS(FAB): *m/z*: 1420 [M^++ H^+]; elemental analysis; C 81.52, H 6.71, N 7.56; calculated for $C_{96}H_{90}N_8O_4$: C 81.21, H 6.39, N 7.89.

33: Yield 12% (from **20**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -0.4$ (br s, 2H, 2 NH), 6.60–9.50 (br m, 72H, 72 CH); IR(KBr): $\tilde{\nu} =$ 3290 cm^{-1}(NH); UV/Vis (CH_2Cl_2): 784, 736, 620, 338 nm; MS(FAB): *m/z*: 1692 [M^++H^+]; elemental analysis; C 84.79, H 4.66, N 6.39; calculated for $C_{120}H_{74}N_8O_4$: C 85.19, H 4.41, N 6.62.

34: Yield 33% (from **21**); m.p. >300 °C; ^{1}H NMR (500 MHz, C_6D_6, 60 °C): $\delta = -0.5$ (br s, 2H, 2 NH), 1.45–1.65 (br s, 72H, 24 CH_3), 7.40–7.80 (m, 24H, 24 CH), 8.80–9.00 (m, 8H, 8 CH); IR(KBr): $\tilde{\nu} = 3294\ cm^{-1}$(NH); UV/Vis ($CH_2Cl_2$): 782, 720, 330 nm; MS(FAB): *m/z*: 1332 [M^++H^+]; elemental analysis; C 81.56, H 7.11, N 7.52; calculated for $C_{104}H_{106}N_8O_4$: C 81.53, H 6.97, N 7.31.

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