Phthalocyanines substituted with dendritic wedges: glass-forming columnar mesogens

Matthew Brewis, Guy J. Clarkson, Andrea M. Holder and Neil B. McKeown*†

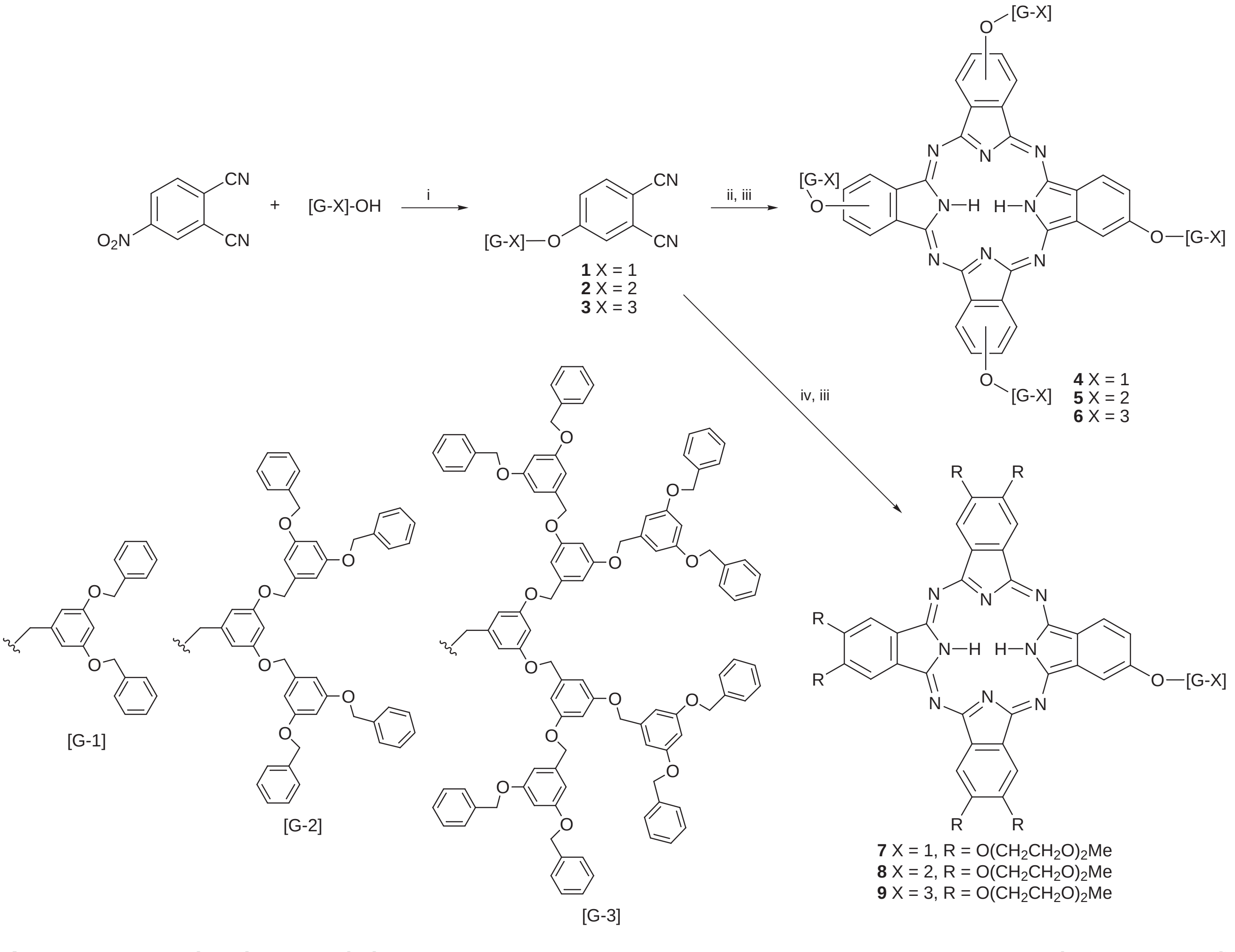
Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

Peripheral substitution of the phthalocyanine macrocycle with poly(aryl ether) dendritic wedges produces materials whose properties are dominated both by the columnar self-association of the phthalocyanine core and by the glass-forming character of the dendritic substituents.

Dendrimers are currently the focus of much attention due to their compact hierarchical structures. Although research into the synthesis of novel dendrimers continues at a rapid pace,[1] there is also considerable interest in the functionalisation of existing systems. For example, the versatile, convergent synthetic route to the poly(aryl ether) dendrimers of Fréchet[2] has allowed the incorporation of functional groups based on fullerene,[3] prophyrin[4] and ferrocene[5] moieties.

Our interests lie in the preparation of novel phthalocyanine (Pc) derivatives in which control over the structure of the bulk material is achieved by the attachment of suitable substituents to the Pc core.[6] This will help exploit the exciting electro-optical properties displayed by Pcs, *e.g.* photoconductivity and third-order harmonic generation. We describe here the synthesis of some phthalocyanine (Pc) derivatives which are substituted by poly(aryl ether) wedges and reveal the interesting properties of these novel materials which are dominated both by the self-association of the Pc subunit and by the glass forming character of the dendritic substituents. The preparation of these phthalocyanine-centred dendrimers involves a novel modification of the convergent route to dendrimer synthesis in which the formation of the core is used for dendrimer assembly, rather than the attachment of the dendritic wedges to a pre-existing core.

Phthalocyanine derivatives are best prepared from substituted phthalonitrile precursors. The aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile and the benzylic alcohol group of the first, second and third generation



Scheme 1 *Reagents and conditions*: i, anhydrous K_2CO_3, DMF, 50 °C; ii, $C_5H_{11}OLi$, $C_5H_{11}OH$, 135 °C; iii, AcOH; iv, 4,5-bis(1,4,7-trioxaoctyl)-phthalonitrile, $C_5H_{11}OLi$, $C_5H_{11}OH$, 135 °C

Table 1 Transition temperatures of dendrimer-substituted Pcs[a]

	Transition/°C			
Compound	Glass → I	Glass → φ_h	φ_h → I	D/Å
4	—	115[b]	270[b]	31.2
5	112	—	—	—
6	71	—	—	
7	—	< -20[b]	> 320[b]	28.9
8	—	115	250–255	30.0
9	—	94	108–112	35.0

[a] I = isotropic liquid, φ_h = hexagonal columnar mesophase, D = intercolumnar distance calculated from 1,0 diffraction ring. [b] Transition not observed by DSC.

poly(aryl ether) wedges ([G-1]-OH, [G-2]-OH, [G-3]-OH)[2] gives the required phthalonitriles **1–3**, respectively, in 75–90% yield (Scheme 1). Cyclotetramerisation of **1–3** using lithium pentanolate in refluxing pentanol gives **4–6** in 10–20% yield, respectively, as a mixture of four inseparable isomers. Alternatively, a mixed cyclotetramerisation between each of the phthalonitriles **1–3** and a ten-fold excess of 4,5-bis(1,4,7-trioxaoctyl)phthalonitrile[7] produces unsymmetrical Pcs **7–9**, respectively. Each of these compounds is readily separated from octakis(1,4,7-trioxaoctyl)phthalocyanine and other Pc by-products by column chromatography. The structures of **1–9** were confirmed by ^{1}H NMR, UV–VIS absorption and IR spectroscopy.‡ All compounds gave satisfactory elemental analyses and all, except Pc **6**, exhibited a parent mass ion using fast atom bombardment (FAB) mass spectrometry.

Despite the steric bulk of the dendritic substituents, there is evidence of self-association of the Pc cores of **4**, **5** and **6** in dilute solution. For example, the ^{1}H NMR resonances corresponding to the twelve protons attached to the Pc core of **4–6** are broadened considerably even at a concentration of 1×10^{-4} mol dm^{-3} in $CDCl_3$. Aggregation is also apparent in the UV–VIS spectra of **4–6** in chloroform solution (1×10^{-5} mol dm^{-3}) by the presence of a broad peak centred at 630 nm. Aggregation is more evident in toluene at similar concentrations. The solution behaviour of these materials is analogous to that of 1,3,4-oxadiazole-based dendrimers which were specifically designed to produce columnar supramolecular structures.[8] There is much less evidence of broadening due to aggregation in the ^{1}H NMR spectra of **7–9**.

The thermal behaviour of **4–9**, as measured by optical polarising microscopy and differential scanning calorimetry (DSC), is reported in Table 1. On cooling from the isotropic melt, **4**, **7**, **8** and **9** display optical textures characteristic of a hexagonal columnar mesophase, although the initially observed 'sandy texture' exhibited by **9** requires annealing at 105 °C for several hours in order to obtain a recognisable texture. The hexagonal columnar mesophase is commonly encountered in Pc derivatives.[9] It is remarkable that the presence of the large dendritic wedge on Pc **9** does not prohibit columnar mesophase formation but merely limits the thermal range over which the mesophase is stable. A small angle X-ray diffraction analysis (powder) of the mesophase of **4** and **7–9** reveals in each case a single strong, sharp band which we believe originates from the (1, 0) plane of the hexagonal lattice. Based on this assumption, the calculated intercolumnar spacings are given in Table 1.

A potentially useful aspect of the thermal behaviour of these materials is their tendency to form a glassy rather than a crystalline solid phase, as indicated by DSC studies which show distinct second-order glass transitions both on heating and cooling. Thus, the non-mesogenic **5** and **6** produce clear, crack-free solid films by cooling from the melt or by spin-coating onto a glass substrate. UV–VIS absorption spectra of these non-birefringent films (λ_{max} = 620 nm) indicates strong cofacial interactions of the Pc cores. The absence of light scattering from domain boundaries is an attractive feature for optical studies.[10]

DSC analysis of **8** and **9** also shows a distinct reversible glass transition. No change in the optical texture is observed on cooling the mesophase below the glass transition temperature and it is concluded that an anisotropic glassy state is obtained in which the columnar structure is 'frozen'.[11] Small angle X-ray diffraction studies of the resulting brittle solids are also consistent with the retention of the columnar structure. Materials such as **8** and **9** which display both an anisotropic glassy phase and a readily aligned mesophase could be used to fabricate monodomainal films suitable for optical or electronic studies.

Notes and References

† E-mail: neil.mckeown@man.ac.uk

‡ *Selected data* for **1**: ν(KBr)/cm^{-1} 2229 (CN); δ_H($CDCl_3$, 500 MHz) 5.05 (4 H, s), 5.10 (2 H, s), 6.58 (1 H, t), 6.60 (2 H, d), 7.15 (1 H, dd), 7.25 (1 H, d), 7.29–7.45 (10 H, m), 7.65 (1 H, d); *m/z* (EI) 446 (M^+). For **2**: ν(KBr)/cm^{-1} 2230 (CN); δ_H($CDCl_3$, 500 MHz) 4.97 (4 H, s), 5.02 (8 H, s), 5.08 (2 H, s), 6.52 (1 H, t), 6.57 (2 H, t), 6.59 (2 H, d), 6.67 (4 H, d), 7.14 (1 H, dd), 7.23 (1 H, d), 7.29–7.42 (20 H, m), 7.65 (1 H, d); *m/z* (EI) 871 (M^+. For **3**: ν(KBr)/cm^{-1} 2232 (CN); δ_H($CDCl_3$, 500 MHz) 4.97 (8 H, s), 5.03 (16 H, s), 5.05 (2 H, s), 6.60–6.63 (7 H, m), 6.69–6.74 (14 H, m), 7.10 (1 H, dd), 7.23 (1 H, d), 7.29–7.46 (40 H, m), 7.64 (1 H, d); *m/z* (EI) 871 (M^+). For **4**: λ(CH_2Cl_2)/nm 718, 682, 654, 620, 422, 346; ν(KBr)/cm^{-1} 3275 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C) -3.2 (2 H, br s), 5.06 (16 H, br s), 5.26 (8 H, br s), 6.65 (4 H, br s), 6.80 (8 H, brs), 7.29–7.45 (40 H, m), 7.7–9.1 (12 H, br M); *m/z* (FAB) 1788, (M^+). For **5**: λ(CH_2Cl_2/nm 716, 680, 654, 620, 422, 346; ν(KBr)/cm^{-1} 3276 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C) -3.5 (2 H, br s), 4.75–5.05 (48 H, br m), 5.26 (8 H, br s), 6.40–6.75 (28 H, br m), 6.90 (8 H, br s), 7.29–7.45 (80 H, m), 7.7–9.1 (12 H, br m); *m/z* (FAB) 3488, (M^+). For **6**: λ(CH_2Cl_2)/nm 715, 680, 654, 620, 422, 346; ν(KBr)/cm^{-1} 3277 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C -3.4 (2 H, br s), 4.66–5.05 (96 H, br m), 5.28 (8 H, br s), 6.30–6.70 (76 H, br m), 6.90 (8 H, br s), 7.29–7.45 (160 H, m), 7.7–9.1 (12 H, br m). For **7**: λ(CH_2Cl_2)/nm 700, 664, 646, 398, 342; ν(KBr)/cm^{-1} 3433 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C) -2.14 (2 H, br s), 3.47 (18 H, s), 3.70 (12 H, t), 3.95 (12 H, t), 4.20 (12 H, t), 4.74 (12 H, t), 5.18 (4 H, s), 5.33 (2 H, s), 6.69 (1 H, t), 7.05 (2 H, d), 7.22–7.50 (10 H, br m), 8.55–8.70 (8 H, brm), 9.05 (1 H, d); *m/z* (FAB) 1542 (M^+). For **8**: λ(CH_2Cl_2)/nm 700, 664, 646, 398, 342; ν(KBr)/cm^{-1} 3422 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C) -2.00 (2 H, br s), 3.46 (18 H, s), 3.70 (12 H, t), 3.95 (12 H, t), 4.20 (12 H, t), 4.74 (12 H, t), 4.98 (8 H, s), 5.10 (4 H, s), 5.53 (2 H, s), 6.52 (2 H, t), 6.65 (1 H, t), 6.73 (4 H, d), 7.03 (2 H, d), 7.18–7.32 (20 H, br m), 8.52–8.70 (8 H, br m), 9.02 (1 H, d); *m/z* (FAB) 1989 ($M^+ + Na^+$). For **9**: λ(CH_2Cl_2)/nm 702, 664, 640, 400, 340; ν(KBr)/cm^{-1} 3429 (NH); δ_H($CDCl_3$, 500 MHz, 50 °C) -1.70 (2 H, br s), 3.42 (18 H, s), 3.70 (12 H, t), 3.95 (12 H, t), 4.20 (12 H, t), 4.74 (12 H, t), 4.88 (16 H, s), 4.98 (8 H, s), 5.06 (4 H, s), 5.50 (2 H, s), 6.48 (2 H, t), 6.49 (1 H, t), 6.52 (4 H, t), 6.69 (8 H, d), 6.72 (4 H, d), 7.00 (2 H, d), 7.15–7.35 (40 H, br m), 8.62–8.75 (8 H, br m), 9.10 (1 H, d); *m/z* (FAB) 1989 ($M^+ + Na^+$).

1 For a recent review see: G. R. Newcombe, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Syntheses and Perspectives*, VCH, Weinheim, 1996.

2 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638; K. L. Wooley, C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4252.

3 K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, F. Wudl, G. Srdanov, S. Shi, C. Li and M. Kao, *J. Am. Chem. Soc.*, 1993, **115**, 9836.

4 R.-H. Jin, T. Aida and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1993, 1260.

5 C.-F. Shu and H.-M. Shen, *J. Mater. Chem.*, 1997, **7**, 47.

6 N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.

7 G. J. Clarkson, N. B. McKeown and K. E. Treacher, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1817.

8 A. Kraft *Chem. Commun.*, 1996, 77.

9 J. Simon and C. Piechocki, *J. Am. Chem. Soc.*, 1982, **104**, 5245; K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio and J. Simon, *New J. Chem.*, 1988, **12**, 751.

10 R. D. George and A. W. Snow, *Chem. Mater.*, 1994, **4**, 209; M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder and N. B. McKeown, *Angew. Chem., Int. Ed. Engl.*, in the press.

11 K. E. Treacher, G. J. Clarkson and N. B. McKeown, *Liq. Cryst.*, 1995, **19**, 887.

Received in Liverpool, UK, 4th March 1998; 8/01799I