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Discotic Liquid Crystals from a Bis-Pocketed Porphyrin

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Porphyrin,[1] phthalocyanine,[2] and tetraazaporphyrin[3] liquid crystals[4] are of interest for optoelectronic, NLO, and other device applications due to their synthetic versatility, thermal stability, large π-electron systems, and photochemical properties.[5] With few exceptions,[6] nearly all of the previously reported macrocyclic mesogens share one feature in common; they are flat molecules with alkyl chains coplanar with the macrocycle core. Porphyrins and phthalocyanines with dipole moments perpendicular to the macrocycle plane are very rare;[7] facile dimerization with cancellation of net dipoles presents a serious problem for further applications. We report here the synthesis and characterization of a homologous series of liquid crystalline octa-meta-substituted tetraphenylporphyrins (Figure 1) with protecting pockets on both faces of the macrocycle. Because the phenyl groups of *meso*-tetraarylporphyrins are rotated with respect to the porphin core, the alkyl substituents that provide the mesophase properties of these porphyrins project out and away from the porphin core in three dimensions. This provides pocketed sites which permit axial ligation to the metalloporphyrin without loss of the liquid crystal phase. Five-coordinate metalloporphyrin mesogens of this type will have a permanent dipole moment which may prove useful for control of orientation or of other field responsive properties of the liquid crystal phase. Only a very few metallomesogens have been reported with oriented dipoles.[8]

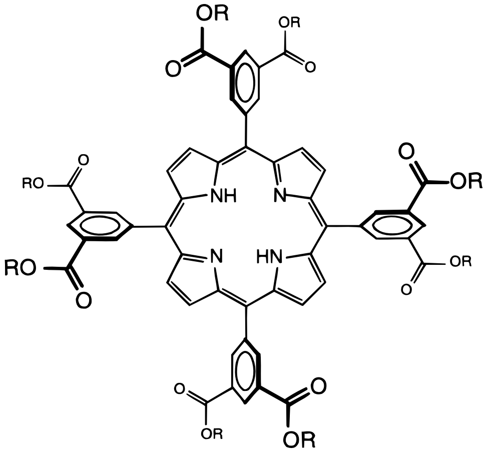

Figure 1. Bis-pocketed columnar hexagonal liquid crystal porphyrins: *n*-alkyl esters of 5,10,15,20-(3,5-dicarboxyphenyl)porphyrin (H_2DCarPP), $R = n\text{-}C_nH_{2n+1}$, $n = 8, 10, 12, 14, 16, 18, 20, 22$.

The parent porphyrin for our mesogenic derivatives is 5,10,15,20-tetrakis(3,5-dicarboxyphenyl)porphyrin (H_2DCarPP), and the liquid crystalline derivatives are its octa-*n*-alkyl esters (Figure 1). We prepared the octa-ethyl ester of H_2DCarPP by the reaction of diethyl 5-formylisophthalate with pyrrole in refluxing acetic acid for 8 h. After the solvent was removed with the use of a rotary evaporator, the porphyrin was washed extensively with methanol and then purified by column chromatography on silica gel. The desired fraction was concentrated, and the porphyrin was precipitated with petroleum ether, isolated by filtration, and then dried in vacuo at 100 °C.[9] The ethyl esters were hydrolyzed in biphasic refluxing THF/KOH (aqueous), and the octacarboxylic acid was precipitated with 50% HCl (aqueous). After the solid was isolated and washed, the porphyrin was recrystallized from pyridine/ethyl acetate, resulting in a red-brown powder which was dried in vacuo at 150 °C.[10]

A homologous series (*n*-alkyl chain: C_nH_{2n+1}, $n = 8, 10, 12, 14, 16, 18, 20$, and 22) of octa-alkyl esters of H_2DCarPP esters were then prepared using the following general method: H_2-DCarPP (20 mg), *p*-toluenesulfonic acid (10 mg), and the appropriate alcohol (1 mL) were stirred and heated at 80 °C for 72 h under argon. The acid was then neutralized with NH_4OH (aqueous), and ethanol was added to the reaction solution to dissolve excess alcohol and precipitate the porphyrin. The product was isolated by filtration, washed with hot ethanol, and then redissolved in chloroform and filtered. The filtrate was concentrated and then chromatographed on silica gel with chloroform.[11]

The liquid crystalline phase was characterized by differential scanning calorimetry (DSC) and the characterization was confirmed by viewing the birefringence of the samples between

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[1] (a) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1134−1135. (b) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 3024−3029. (c) Kugimiya, S.; Takemura, M. *Tetrahedron. Lett.* **1990**, *31*, 3157−3160. (d) Ramasseul, R.; Maldivi, P.; Marchon, J.-C.; Taylor, M.; Guillon, D. *Liq. Cryst.* **1993**, *13*, 729−733. (e) Shimizu, Y.; Miya, M.; Nagata, A.; Ohta, K.; Yamamoto, I.; Kusabayashi, S. *Liq. Cryst.* **1993**, *14*, 795−805.

[2] (a) Guillon, D.; Weber, P.; Skoulios, A.; Piechocki, C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1985**; *130*, 223−229. (b) van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6*, 577−592. (c) Cook, M. J.; Cracknell, S. J.; Harrison, K. J. *J. Mater. Chem.* **1991**, *1*, 703−704. (d) van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Picken, S. J.; Schouten, P. G.; Warman, J. M.; Schouten, A.-J.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1120−1122. (e) Ford, W. T.; Sumner, L.; Zhu, W.; Chang, Y. H.; Um, P.-J.; Choi, K. H.; Heiney, P. A.; Maliszewskyj, N. C. *New. J. Chem.* **1994**, *18*, 495−505. (f) Mohr, B.; Wegner, G.; Ohta, K. *J. Chem. Soc., Chem. Commun.* **1995**, 995−996.

[3] (a) Doppelt, P.; Huille, S. *New J. Chem.* **1990**, *14*, 607−609. (b) Lelj, F.; Morelli, G.; Ricciardi, G.; Roviello, A.; Sirigu, A. *Liq. Cryst.* **1992**, *12*, 941−960.

[4] (a) Chandrasekhar, S. *Liq. Cryst.* **1993**, *14*, 3−14. (b) Destrade, C.; Foucher, P.; Gasparoux, H.; Tinh, N. H.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121−146. (c) Destrade, C.; Tinh, N. H.; Gasparoux, H.; Malthete, J.; Levelut, A. M. *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 111−135.

[5] Liu, C.-Y.; Pan, H.-L.; Fox, M. A.; Bard, A. J. *Science* **1993**, *261*, 897−899.

[6] (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 5011−12. (b) Milgrom, L. R.; Yahioglu, G.; Bruce, D. W.; Morrone, S.; Henari, F. Z.; Blau, W. J. *Adv. Mater.* **1997**, *9*, 313−316. (c) Wang, Q. M.; Bruce, D. W. *Angew Chem. Intl. Ed. Engl.* **1997**, *36*, 150−152.

[7] (a) Shimizu, Y.; Matsuno, J.-Y.; Miya, M.; Nagata, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2411−2412. (b) Weber, P.; Guillon, D.; Skoulios, A. *J. Phys. Chem.* **1987**, *91*, 2242−2243. (c) Piechocki, C.; Boulou, J.-C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 115−120.

[8] (a) Weber, P.; Guillon, D.; Skoulios, A. *J. Phys. Chem.* **1987**, *91*, 2242−2243. (b) Hanack, M.; Beck, A.; Lehmann, H. *Synthesis* **1987**, 703−705. (c) Hanack, M. Lang, M. *Adv. Mater*. **1994**, *6*, 819−833. (d) Zheng, H. X.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067−2077.

[9] Yield: 25%. Characterization: Anal. Calcd ($C_{68}H_{62}N_4O_{16}$) C, 68.56; H, 5.26; N, 4.70. Found C, 68.51; H, 5.51; N, 4.82. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17 (4H, *p*-phenyl *H*), 9.08 (8H, *o*-phenyl *H*), 8.80 (8H, β-pyrrole *H*), 4.53 (16H, ArCOOCH_2CH$_3$), 1.44 (24H, ArCOOCH$_2$CH_3), −2.80 (s, 2H, inner pyrrole *H*). ES$^+$MS (chloroform/formic acid, *m/z*) Theory 1191.4 (MH$^+$), 959.4 (MH$^+$ − 8CH$_2$CH$_3$). Found 1191.4 (MH$^+$), 959.4 (MH$^+$ − 8CH$_2$CH$_3$). Found parent peak isotope distribution matched theoretical isotope distribution. Electronic absorption λ_{max} (dichloromethane, 25 °C): 421 Soret, 515, 550, 590, 646 nm.

[10] Yield: quantitative. Characterization: Anal. Calcd ($C_{52}H_{30}N_4O_{16}$) C, 64.60; H, 3.13; N, 5.80. Found C, 64.23; H, 3.36; N, 5.65. ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.55 (s, 8H, −COO*H*), 8.92 (8H, β-pyrrole *H*), 8.90 (4H, *p*-phenyl *H*), 8.85 (8H, *o*-phenyl *H*), −2.96 (s, 2H, inner pyrrole *H*). ES$^+$MS (DMSO/formic acid, *m/z*) Theory 967 (MH$^+$), Found 967 (MH$^+$). Found parent peak isotope distribution matched theoretical isotope distribution. Electronic absorption λ_{max} ($\epsilon \times 10^3$ M^{-1} cm^{-1}, pyridine, 25 °C) 423 Soret (441), 516 (20.0), 561 (7.6), 591 (6.1), 647 (3.5) nm. IR (KBr) 3432, 3107, 2872, 2612, 2555, 2367, 1701 (C═O), 1602, 1443, 1402, 1385, 1279, 1243, 1209, 1114, 979, 916, 801, 761, 720, 670, 603, 532 cm^{-1}.

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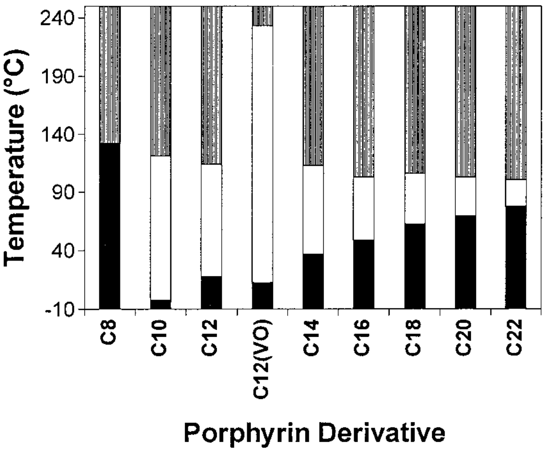

Figure 2. Differential scanning calorimetry of the octa-*n*-alkyl esters of H_2DCarPP; black = solid phase, white = mesophase, gray = isotropic. The DSC peak maxima for the heating cycle (3 °C/s) are as follows: [temperature (ΔH), *M* = melting transition (solid to mesophase), *C* = clearing transition (mesophase to isotropic)]. C_8 [132 °C (143 kJ/mol) *M*]; C_{10} [−3 °C (17 kJ/mol) *M*, 121 °C (35 kJ/mol) *C*]; C_{12} [17 °C (38 kJ/mol) *M*, 114 °C (28 kJ/mol) *C*]; C_{12}VO [13 °C *M*, 233 °C *C*]; C_{14} [36 °C (66 kJ/mol) *M*, 113 °C (23 kJ/mol) *C*]; C_{16} [49 °C (119 kJ/mol) *M*, 103 °C (21 kJ/mol) *C*]; C_{18} [63 °C (188 kJ/mol) *M*, 106 °C (25 kJ/mol) *C*]; C_{20} [70 °C (214 kJ/mol) *M*, 103 °C (22 kJ/mol) *C*]; C_{22} [78 °C (266 kJ/mol) *M*, 101 °C (21 kJ/mol) *C*].

crossed polarizers in a polarizing microscope. The DSC results are summarized in Figure 2. Rate-dependent hysteresis upon cooling the samples is due to supercooling. The peak corresponding to the melting of the solid to the liquid crystal phase was large and sharpened as the alkyl chain length increased. The clearing transition (from liquid crystal to isotropic liquid phase) was somewhat broad in all samples. The enthalpy of melting increased with increasing alkyl chain length (from 38 kJ/mol for R = $C_{12}H_{25}$ to 266 kJ/mol for R = $C_{22}H_{45}$ for the heating cycle) although the clearing enthalpy stayed relatively constant (from 28 kJ/mol for R = $C_{12}H_{25}$ to 21 kJ/mol for R = $C_{22}H_{45}$ for the heating cycle). The C_8 derivative is *not* mesogenic; the C_{10} and C_{12} derivatives are liquid crystals at room temperature.

We grew single liquid crystalline domains on the order of 25−50 μm for all of the mesogenic samples by annealing them at their clearing temperature. Figure 3 shows an example of the birefringence texture for C_{20} H_2DCarPP. Due to alignment of the molecules with the polarizer and the analyzer, a classic Maltese cross extinction pattern[12] was observed in the polarizer direction (vertical in the figure) and analyzer direction (horizontal in the figure).

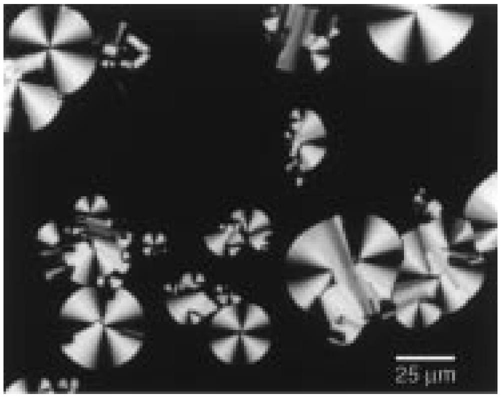

Figure 3. Birefringence texture micrograph of the octa-*n*-alkyl ester, C_{20} H_2DCarPP, viewed between crossed polarizers. The domains were grown from the isotropic phase as the sample was being annealed.

Small-angle X-ray scattering (SAXS) of C_{18} H_2DCarPP at 75 °C shows reflections with *d*-spacing of 32.7 and 19.2 Å, which corresponds to the first two reflections of a hexagonal columnar structure (reciprocal *d*-spacings of $1{:}\sqrt{3}$).[13] The corresponding inter-columnar spacing is 37 Å, which compares well to expected porphyrin dimensions. We conclude that the mesophase structure is probably a hexagonal columnar discotic columnar, Col_h (previously designated D_h).[14] Wide-angle X-ray diffraction[15] gave two broad, overlapping peaks. One of the peaks is centered at ∼4.5 Å and the other at ∼4.2 Å. One of these peaks is due to the commonly seen liquid-like packing of alkyl chains in the mesophase; the other (probably the 4.2 Å peak) is likely due to intra-columnar spacing of the porphyrins. Further studies are required to specifically assign the wide-angle peaks.

We are currently exploiting the unusual pockets of these discotic mesogens to prepare five-coordinate metalloporphyrins that have a perpendicular dipole moment and yet retain their mesogenic behavior. For example, the vanadyl derivatives of the C_{12} bis-pocketed mesogen, C_{12} DCarPP(VO),[16] not only retains its liquid crystallinity (Figure 2) but in fact also has a greatly expanded mesophase temperature range with a span of 246 K! Further work is required to characterize the field-responsive properties of these materials.

In conclusion, a new class of meta-substituted bis-pocket porphyrins and metalloporphyrins have been prepared. We have demonstrated that these materials are mesogenic even in the presence of axial ligation.

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(11) Yields of isolated octaesters averaged ca. 25%. The octa-alkyl esters of H_2DCarPP were characterized by ES^+MS (chloroform/formic acid) and elemental analysis. Found parent peak isotope distribution matched theoretical isotope distribution for all compounds. For R = *n*-C_8H_{17}: Anal. Calcd ($C_{116}H_{158}N_4O_{16}$) C, 74.72; H, 8.54; N, 3.00. Found C, 74.37; H, 8.34; N, 2.62. ES^+MS (*m/z*) Theory 1865.2 (MH^+). Found 1864.8 (MH^+). For R = *n*-$C_{10}H_{21}$: Anal. Calcd ($C_{132}H_{190}N_4O_{16}$): C, 75.90; H, 9.17; N, 2.68. Found: C, 75.70; H, 8.50; N, 2.78. ES^+MS (*m/z*) Theory 2089.4 (MH^+). Found 2089.4 (MH^+). For R = *n*-$C_{12}H_{25}$: Anal. Calcd ($C_{148}H_{222}N_4O_{16}$) C, 76.83; H, 9.69; N, 2.42. Found C, 76.68; H, 9.73; N, 2.44. ES^+MS (*m/z*) Theory 2313.7 (MH^+). Found 2313.7 (MH^+). For R = *n*-$C_{14}H_{29}$: Anal. Calcd ($C_{164}H_{254}N_4O_{16}$) C, 77.62; H, 10.09; N, 2.21. Found C, 77.55; H, 10.18; N, 2.45. ES^+MS (*m/z*) Theory 2537.9 (MH^+). Found 2537.5 (MH^+). For R = *n*-$C_{16}H_{33}$: Anal. Calcd ($C_{180}H_{286}N_4O_{16}$) C, 78.27; H, 10.44; N, 2.03. Found C, 78.48; H, 10.48; N, 2.12. ES^+MS (*m/z*) Theory 2763.2 (MH^+). Found 2762.6 (MH^+). For R = *n*-$C_{18}H_{37}$: Anal. Calcd ($C_{196}H_{318}N_4O_{16}$) C, 78.82; H, 10.75; N, 1.88. Found C, 79.07; H, 10.78; N, 1.91. ES^+MS (*m/z*) Theory 2987.4 (MH^+). Found 2987.6 (MH^+). For R = *n*-$C_{20}H_{41}$: Anal. Calcd ($C_{212}H_{350}N_4O_{16}$) C, 79.30; H, 10.99; N, 1.74. Found C, 79.98; H, 11.19; N, 1.72. ES^+MS (*m/z*) Theory 3211.7 (MH^+). Found 3211.1 (MH^+). For R = *n*-$C_{22}H_{45}$: Anal. Calcd ($C_{228}H_{382}N_4O_{16}$) C, 79.71; H, 11.21; N, 1.63. Found C, 80.08; H, 11.51; N, 1.76. ES^+MS (*m/z*) Theory 3635.9 (MH^+). Found 3635.4 (MH^+).

(12) Haudin, J. M. In *Optical Properties of Polymers*; Meeten, G. H., Ed.; Elsevier: New York, 1986; pp 167−264.

(13) SAXS data were collected on a Rigaku RU300 diffractometer with rotating anode using Cu Kα radiation (λ = 1.5418 Å).

(14) In some cases, disorder within the columns may produce a discotic lamellar phase instead. The reciprocal *d*-spacings would then be 1:2.

(15) Wide-angle X-ray data were collected using a Rigaku D-Max diffractometer in the 6−26° 2θ range using Cu Kα radiation (λ = 1.5418 Å).

(16) Metalation with $VO(SO_4)$ refluxed in glacial acetic acid 18 h; purification by silica gel chromatography. Yield: 83%. UV/Vis λ_{max} (dichloromethane, 25 °C) 425 Soret, 547 nm; addition of acid confirmed the absence of nonmetalated porphyrin. MALDI *m/z* 2378.2 [M^+].