Synthesis and Liquid-Crystal Behavior of a Novel Class of Disklike Metallomesogens: Hexasubstituted Triazolehemiporphyrazines

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The synthesis, characterization and mesomorphic properties of two series of new discotic molecules based on the triazolehemiporphyrazine core is described. This central unit has been attached to six lipophilic chains, two dodecyl groups on the triazole ring and four dodecyloxy or dioctylaminocarbonilmethoxy on the isoindole moiety, and metallic complexes (Cu, Ni) have been prepared. The mesogenic behavior has been studied using optical microscopy, DSC, and X-ray diffraction. The alkoxy-substituted macrocycles melt from the solid to the liquid-crystalline phase at relatively low temperatures (ca. 30 °C), exhibiting hexagonal columnar mesophases (D_{ho}) (despite being elliptical molecules) in a large temperature range, up to 300 °C in the case of metallic complexes. The dialkylamide derivatives are not mesogenic despite the extent of the paraffinic part. This fact is probably due to the steric hindrance between the branched chains, thus difficulting columnar stacking of the cores.

Introduction

Highly delocalized π-conjugated organic systems, such as phthalocyanines[1] (Pcs) and their related analogues hemiporphyrazines[2] (Hps) exhibit unique electrical[3] and nonlinear optical[4] properties that can be modulated taking advantage of their capability to form stable complexes with metal ions. The self-assembling of two or more of these macrocyclic units in one-dimensional arrays[5,6] can lead to molecular materials with improved physicochemical characteristics. Thus, peripheral substitution of the Pc core with long flexible hydrocarbon chains provides these compounds with thermotropic liquid-crystalline behavior,[7,8] showing discotic mesophases in which the macrocycles are stacked up, giving columnar structures surrounded by the hydrocarbon chains. In the mesophase these compounds exhibit one-dimensional conductivity.[6,9]

The preparation of highly soluble triazolehemiporphyrazines[10] able to self-organize in LB films[11] has been recently described. These compounds exhibit third-order nonlinear optical properties in solution[4c,12] and in condensed phase.[13] In the present paper we have focused on the synthesis and characterization of potential discotic liquid crystals based on the triazolehemiporphyrazine core. This is the first time that mesomorphism has been investigated in hemiporphyrazine derivatives. Thus, we have studied the effect of the type of peripheral chains on mesomorphism. We have appended six side chains to the metallomacrocycles, two of which are alkyl groups attached to a triazolic nitrogen atom, and the other four are different alkoxy substituents on the isoindole subunits (**1**−**6**, Figure 1). Alkyl[14] and alkoxy[15] chains are very common as side groups in discotic liquid crystals based on phthalocyanines. The choice of dialkylamide-functionalized alkoxy groups in compounds **4**−**6** is based on their potentiality to promote

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(1) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, 1989, 1993, 1996, Vols. 1−4.

(2) (a) Fernández-Lázaro, F.; de Mendoza, J.; Mó, O.; Rodríguez-Morgade, S.; Torres, T.; Yañez, M.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 797. (b) Haberroth, K.; Rack, M.; Ruff, D.; Hanack, M. *Chem. Ber.* **1995**, *128*, 417. (c) Rack, M.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1646. (d) Hauschel, B.; Ruff, D.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2449. (e) De la Torre, G.; Torres, T. *J. Org. Chem.* **1996**, *61*, 6446.

(3) (a) Simon, J.; Tournilhac, F.; André, J. J. *New J. Chem.* **1987**, *11*, 383. (b) Fernández-Lázaro, F.; Rodríguez-Morgade, S.; Torres, T. *Synth. Met.* **1994**, *62*, 281.

(4) (a) Nalwa H. S.; Shirk J. S. *Phthalocyanines: Properties and Applications*; Leznoff, C. C.; Lever, A. B. P., Eds.; VCH: Weinheim, 1996; Vol. 4, Chapter 3. (b) De la Torre, G.; Torres, T.; Agulló-López, F. *Adv. Mater.* **1997**, 265. (c) Díaz-García, M. A.; Ledoux, I.; Fernández-Lázaro, F.; Sastre, A.; Torres, T.; Agulló-López, F.; Zyss, J. *Nonlinear Opt.* **1995**, *10*, 101.

(5) (a) Schultz, H.; Lehmann, H.; Rein, M.; Hanack, M. *Struct. Bonding* **1991**, *74*, 41. (b) Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819.

(6) Ros, M. B. *Metallomesogens. Synthesis, Properties and Applications*; Serrano, J. L., Ed.; VCH: Weinheim, 1996; Chapter 11.

(7) Simon, J.; André, J. J.; Skoulios, A. *New J. Chem.* **1986**, *10*, 295.

(8) Simon, J.; Bassoul, P. *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, 1993; Vol. 2, Chapter 6.

(9) (a) Belarbi, Z.; Sirlin, C.; Simon, J.; André, J.-J. *J. Phys. Chem.* **1989**, *93*, 8105. (b) Sluyters, J. H.; Baars, J. A.; Van der Pol, J. F.; Drenth, W. *J. Electroanal. Chem.* **1989**, *271*, 41. (c) Van der Pol, J. F.; de Haas, M. P.; Warman, J. M.; Drenth, W. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 411. (d) Schouten, P. G.; Warman, J. M.; de Haas, M. P.; Van Nostrum, C. F.; Gelinck, G. H.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K.; Hanack, M.; Chang, Y. H.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6880.

(10) Fernández-Lázaro, F.; Sastre, A.; Torres, T. *J. Chem. Soc., Chem. Commun.* **1995**, 419.

(11) Pfeiffer, S.; Mingotaud, C.; Garrigou-Lagrange, C.; Delhaes, P.; Sastre, A.; Torres, T. *Langmuir* **1995**, *11*, 2705.

(12) Díaz-García, M. A.; Ledoux, I.; Fernández-Lázaro, F.; Sastre, A.; Torres, T.; Agulló-López, F.; Zyss, J. *J. Phys. Chem.* **1994**, *98*, 4495.

(13) Fernández-Lázaro, F.; Díaz-García, M. A.; Sastre, A.; Delhaes, P.; Mingotaud, C.; Agulló-López, F.; Torres, T., submitted.

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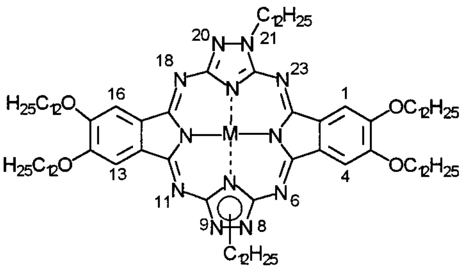
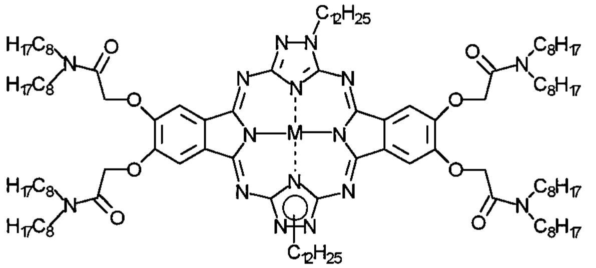


1 M = H_2
2 M = Cu
3 M = Ni



4 M = H_2
5 M = Cu
6 M = Ni

Figure 1.

mesomorphism shown in our previous work on phthalocyanine-based mesogens.[16]

Experimental Section

The compounds were characterized by elemental analysis, IR and UV−visible spectroscopies, fast atom bombardment (FAB) mass spectrometry, and nuclear magnetic resonance. UV−visible and infrared measurements were carried out respectively on Perkin-Elmer Model Lambda 6 and Perkin-Elmer spectrometers. FAB-MS spectra were determined on a MAT 900 (Finnigan MAT, GmbH, Bremen) instrument, using 3-NOBA (3-nitrobenzyl alcohol) as a matrix. NMR spectra were recorded with a Bruker WM-200-SY 200 MHz spectrometer.

The optical textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP8 hot stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C/min on heating. The apparatus was calibrated with indium (156.6 °C; 28.4 J g^{-1}) as standard. X-ray diffraction experiments were carried out on powder samples in a Pinhole camera (Anton-Paar) operating with a Ni-filtered Cu Kα beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated with a variable-temperature attachment. The X-ray patterns were collected on flat photographic film.

General Procedure for the Preparation of Hemiporphyrazines 1 and 4 as Regioisomeric Mixtures. A mixture of **7**[2a] (0.40 g, 1.50 mmol) and the corresponding diiminoisoindoline **8**,[17] **9**[18] (1.50 mmol) in 2-ethoxyethanol (6 mL) was refluxed for 24 h. After cooling at room temperature, the solid was isolated by centrifugation and washed with several portions of 2-ethoxyethanol. The specific purification method is indicated in each case.

*Data for 8,20-Didodecyl-2,3,14,15-tetrakis(dodecyloxy)-5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,20H- and 8,21-Didodecyl-2,3,14,15-tetrakis(dodecyloxy)-5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,21H-dibenz[f,p][1,2,4,9,11,12,14,19]octaazacycloeicosine (**1**).* Recrystallization from pentanol afforded the pure product: yield 38%, orange powder; ^1H NMR (200 MHz, [D]$CHCl_3$, 25 °C, TMS) δ 14.94, 14.79, 14.69 (3 × s, 2H; NH), 7.32, 7.25, 7.23, 7.21 (4 × s, 4H; arom H), 4.31 (t, ^3J(H,H) = 7 Hz, 8H; CH_2O), 4.1 (m, 4H; CH_2N), 2.2, 1.8 (m, 12H; CH_2-CH_2O, CH_2CH_2N), 1.2 (m, 108H; CH_2), 0.86 (m, 18H; CH_3) ppm; ^{13}C NMR (50 MHz, [D]$CHCl_3$, 25 °C) δ 162.8, 160.5 (C-5, C-12, C-17, C-24), 157.6, 153.1, 152.9 (C-2, C-3, C-7, C-10, C-14, C-15, C-19, C-22), 128.4, 127.7, 126.8 (C-1, C-4, C-13, C-16), 105.6, 105.3 (C-4a, C-12a, C-16a, C-24a), 69.1 (CH_2O), 46.4 (CH_2N), 31.9, 29.7, 29.5, 29.4, 29.2, 29.1, 26.4, 26.1, 26.0, 22.7 (CH_2), 14.1 (CH_3) ppm; IR (KBr) ν 3290 (NH), 2910, 2840, 1650 (C=N), 1600, 1490, 1460, 1355, 1280 (C−O−C), 1210, 1050, 760, 720, 660 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 219 (4.67), 226 (4.67), 228 (4.68), 258 (4.80), 357 (4.63), 378 (4.56) nm; FAB-MS (3-NOBA) *m/z* (%) 1494 (100) [$(M + H)^+$]; $C_{92}H_{156}N_{12}O_4$ (1494.33) calcd C, 74.01; H, 10.52; N, 11.04; found C, 73.79; H, 10.25; N, 11.00.

*Data for 8,20-Didodecyl-2,3,14,15-tetrakis[(dioctylaminocarbonyl)methoxy]-5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,-20H- and 8,21-Didodecyl-2,3,14,15-tetrakis[(dioctylaminocarbonyl)methoxy]-5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,21H-dibenz[f,p][1,2,4,9,11,12,14,19]octaazacycloeicosine (**4**).* Column chromatography on silica gel (CH_2Cl_2: MeOH 50:1) and subsequent trituration with methanol afforded the pure product: yield, 45%, reddish powder; mp 156.9 °C; ^1H NMR (200 MHz, [D]$CHCl_3$, 25 °C, TMS) δ 14.99, 14.84, 14.72 (3 × s, 2H; NH), 7.31, 7.23 (2 × s, 4H; arom H), 4.93, 4.90, 4.82 (3 × s, 8H; CH_2O), 4.11 (m, 4H; CH_2N), 3.3 (m, 16H; CH_2NC=O), 1.9, 1.6 (m, 20H; CH_2CH_2N, CH_2CH_2NC=O), 1.2 (m, 116H; CH_2), 0.87 (m, 30H; CH_3) ppm; ^{13}C NMR (50 MHz, [D]$CHCl_3$, 25 °C) δ 166.7, 166.1, 166.0, 165.5 (C=O), 163.2, 162.7 (C-5, C-12, C-17, C-24), 155.8, 155.3, 155.2, 154.2, 153.9, 152.9, 152.6, 152.2, 151.7, 151.5 (C-2, C-3, C-7, C-10, C-14, C-15, C-19, C-22), 128.5, 127.8 (C-1, C-4, C-13, C-16), 109.1, 108.1, 107.2, 106.9 (C-4a, C-12a, C-16a, C-24a), 68.5, 67.8, 67.0, 66.5 (CH_2O), 47.1, 46.7, 46.2, 46.0 (CH_2N), 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 27.6, 27.5, 27.0, 26.9, 26.5, 22.6 (CH_2), 14.0 (CH_3) ppm; IR (KBr) ν 3301 (NH), 2924, 2853, 1666 (C=O), 1640, 1612 (C=N), 1500, 1466, 1375, 1273 (C−O−C), 1218, 1057, 763, 676 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 258 (4.96), 294 (4.78), 340 (4.84), 358 (5.02), 379 (4.94) nm; FAB-MS (3-NOBA) m/z (%) 1969 (100) [$(M + Na)^+$], 1947 (88) [$(M + H)^+$], 1678 (7) [$(M - C_{16}H_{34}NCOH + H)^+$], 1396 (11) [$(M - C_{16}H_{34}NCOH - C_{16}H_{34}NCOCH_2 + H)^+$]; $C_{116}H_{200}N_{16}O_8 \cdot H_2O$ (1964.98) calcd C, 70.91; H, 10.36; N, 11.41; found C, 71.08; H, 10.30; N, 11.48.

In the case of **4**, employing more diluted conditions (25 mL), only one regioisomer was isolated from the crude reaction mixture after centrifugation.

*Data for 8,20-Didodecyl-2,3,14,15-tetrakis[(dioctylaminocarbonyl)methoxy]-5,24:12,17-diimino-7,10:19,22-dinitrilo-8H,20H-dibenz[f,p][1,2,4,9,11,12,14,19]octaazacycloeicosine (**4**).* Yield 10%, orange powder; mp 176.8 °C; ^1H NMR (200 MHz,

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[14] (a) Cook, M. J.; Daniel, M. F.; Harrison, K. J.; Mckeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1086. (b) Ohta, K.; Jacquemin, L.; Sirlin, C.; Simon, J. *New J. Chem.* **1988**, *12*, 751. (c) Engel, K. M.; Bassoul, P.; Bosio, L.; Lehmann, H.; Hanack, M.; Simon, J. *Liq. Cryst.* **1993**, *15*, 709. (d) Komatsu, T.; Ohta, K.; Fujimoto, T.; Yamamoto, I. *J. Mater. Chem.* **1994**, *4*, 533. (e) Cook, M. J. *Adv. Mater.* **1995**, *7*, 877.

[15] (a) Masurel, D.; Sirlin, C.; Simon, J. *New. J. Chem.* **1987**, *11*, 455. (b) Van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988,** *107*, 615. (c) 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. (d) Berlabi, Z.; Sirlin, C.; Simon, J.; André, J. J. *J. Phys. Chem.* **1989**, *93*, 8105. (e) Weber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 369. (f) Vacus, J.; Doppelt, P.; Simon, J.; Memetzidis, G. *J. Mater. Chem.* **1992**, *2*, 1065. (g) 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.

[16] Duro, J. A.; De la Torre, G.; Barberá, J.; Serrano, J. L.; Torres, T. *Chem. Mater.* **1996**, *8*, 1061.

[17] Masurel, D.; Sirlin, C.; Simon, J. *New J. Chem.* **1987**, *11*, 455.

[18] (a) Duro, J. A.; Torres, T. *Chem. Ber.* **1993**, *126*, 269. (b) Díaz-García, M. A.; Ledoux, I.; Duro, J. A.; Torres, T.; Agulló-López, F.; Zyss, J. *J. Phys. Chem.* **1994**, *98*, 8761.

[D]CHCl$_3$, 25 °C, TMS) δ 14.84 (s, 2H; NH), 7.32 (s, 4H; arom H), 4.93, 4.81 (2 × s, 8H; CH$_2$O), 4.12 (m, 4H; CH$_2$N), 3.3 (m, 16H; CH$_2$NC=O), 1.9, 1.6 (m, 20H; C*H*$_2$CH$_2$N, C*H*$_2$CH$_2$NC=O), 1.2 (m, 116H; CH$_2$), 0.88 (m, 30H; CH$_3$) ppm; ^{13}C NMR (50 MHz, [D]CHCl$_3$, 25 °C) δ 166.7, 165.5 (C=O), 162.8 (C-5, C-12, C-17, C-24), 155.9, 155.3, 152.9, 152.6, 151.5 (C-2, C-3, C-7, C-10, C-14, C-15, C-19, C-22), 129.6, 127.8 (C-1, C-4, C-13, C-16), 109.1, 106.9 (C-4a, C-12a, C-16a, C-24a), 68.6, 66.5 (CH$_2$O), 47.1, 46.7, 46.2, 46.0 (CH$_2$N), 31.9, 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 27.6, 27.5, 27.0, 26.9, 26.5, 22.6 (CH$_2$), 14.0 (CH$_3$) ppm.

*General Procedure for the Preparation of Nickel(II) and Copper(II) Complexes **2**, **3**, **5**, and **6**.* A mixture of **1** or **4** (0.10 mmol) and the corresponding metallic salt ($Cu(OAc)_2 \cdot H_2O$ or $Ni(OAc)_2 \cdot 4H_2O$) (0.10 mmol) in 2-ethoxyethanol (2 mL) was refluxed for 36 h. After cooling, the solid was centrifuged and washed with several portions of 2-ethoxyethanol and methanol. In the case of **5** and **6**, column chromatography on silica gel (CH_2Cl_2:MeOH 25:1) was required to yield the pure product.

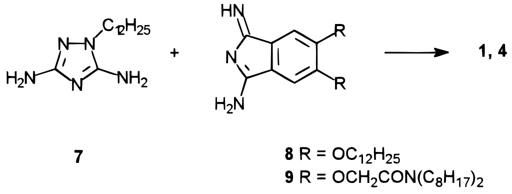
*Data for Copper Complex **2**.* Yield 52%, brown powder; IR (KBr) ν 2900, 2840, 1565 (C=N), 1500, 1490, 1460, 1345, 1280 (C−O−C), 1210, 1140, 1070, 1065, 865, 755, 720 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 266 (4.67), 297 sh, 364 (4.50), 373 (4.60), 394 (4.40) nm; FAB-MS (3-NOBA) *m/z* (%) 1555, 1557 (100) [(M + H)$^+$]; $C_{92}CuH_{154}N_{12}O_4$ (1555.86) calcd C, 71.03; H, 9.98; N, 10.80; found C, 69.90; H, 9.90; N, 10.76.

*Data for Nickel Complex **3**.* Yield 71%, greenish powder; ^{1}H NMR (200 MHz, [D]CHCl$_3$, 25 °C, TMS) δ 7.05, 7.02, 6.80 (3 × s, 4H; arom H), 3.9−3.8 (m, 12H; CH$_2$O, CH$_2$N), 1.9 (m, 12H; C*H*$_2$CH$_2$O, C*H*$_2$CH$_2$N), 1.3 (m, 108H; CH$_2$), 0.92 (m, 18H; CH$_3$) ppm; ^{13}C NMR (50 MHz, [D]CHCl$_3$, 25 °C) δ 163.4, 162.6, 161.0, 159.9 (C-5, C-12, C-17, C-24), 154.8, 153.9, 151.8, 151.3, 150.0, 149.2, 137.9 (C-2, C-3, C-7, C-10, C-14, C-15, C-19, C-22), 130.7, 130.0, 129.3 (C-1, C-4, C-13, C-16), 104.7, 104.3 (C-4a, C-12a, C-16a, C-24a), 68.9 (CH$_2$O), 46.3 (CH$_2$N), 31.9, 29.7, 29.4, 29.2, 28.4, 26.4, 26.1, 26.0, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm; IR (KBr) ν 2920, 2845, 1580 (C=N), 1490, 1470, 1350, 1280 (C−O−C), 1070, 1010, 870 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 265 (4.74), 295 (4.68), 358 (4.56), 378 (4.56), 430 (4.13) nm; FAB-MS (3-NOBA) *m/z* (%) 1550, 1552 (100) [(M + H)$^+$]; $C_{92}H_{154}N_{12}NiO_4 \cdot H_2O$ (1569.02) calcd C, 70.43; H, 10.02; N, 10.71; found C, 70.60; H, 9.96; N, 10.89.

*Data for Copper Complex **5**.* Yield 68%, brown powder; mp 169.9 °C; IR (KBr) ν 2924, 2853, 1666 (C=O), 1639, 1606, 1568 (C=N), 1512, 1489, 1467, 1370, 1344, 1276 (C−O−C), 1216, 1082, 762, 722 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 262 (5.00), 296 sh, 357 (4.78), 375 (4.86), 398 (4.64) nm; FAB-MS (3-NOBA) *m/z* (%) 2031, 2033 (100) [(M + Na)$^+$], 2008, 2010 (36) [(M + H)$^+$], 1762, 1764 (6) [(M − $C_{16}H_{34}$NCOH + Na)$^+$], 1480, 1482 (5) [(M − $C_{16}H_{34}$NCOH − $C_{16}H_{34}$NCOCH$_2$ + Na)$^+$]; $C_{116}CuH_{198}N_{16}O_8 \cdot 2H_2O$ (2044.53) calcd C, 68.15; H, 9.96; N, 10.96; found C, 68.26; H, 9.94; N, 10.87.

*Data for Nickel Complex **6**.* Yield 67%, greenish powder; mp 158.4 °C; ^{1}H NMR (200 MHz, [D]CHCl$_3$, 25 °C, TMS) δ 7.15, 7.08, 7.02 (3 × bs, 4H; arom H), 4.87, 4.77 (2 × s, 8H; CH$_2$O), 3.96 (m, 4H; CH$_2$N), 3.3 (m, 16H; CH$_2$NC=O), 1.8, 1.6 (m, 20H; C*H*$_2$CH$_2$N, C*H*$_2$CH$_2$NC=O), 1.2 (m, 116H; CH$_2$), 0.88 (m, 30H; CH$_3$) ppm; ^{13}C NMR (50 MHz, [D]CHCl$_3$, 25 °C) δ 166.9, 166.6, 166.4, 166.0 (C=O), 163.1, 162.1, 160.8, 159.7 (C-5, C-12, C-17, C-24), 154.7, 153.9, 151.6, 151.5, 150.8, 150.0, 149.3 (C-2, C-3, C-7, C-10, C-14, C-15, C-19, C-22), 131.7, 130.9, 130.8, 130.2 (C-1, C-4, C-13, C-16), 108.0, 107.5, 106.4 (C-4a, C-12a, C-16a, C-24a), 68.2, 67.8, 67.1, 66.7 (CH$_2$O), 47.0, 46.6, 46.2, 45.9 (CH$_2$N), 31.8, 29.6, 29.5, 29.4, 29.3, 29.0, 28.6, 27.7, 27.5, 27.1, 26.9, 26.6, 22.6 (CH$_2$), 14.0 (CH$_3$) ppm; IR (KBr) ν 2924, 2853, 1666 (C=O), 1638, 1588 (C=N), 1522, 1490, 1467, 1376, 1349, 1275 (C−O−C), 1215, 1087, 762 cm^{-1}; UV/vis (CHCl$_3$) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}) 264 (4.97), 294 (4.89), 362 (4.68), 373 sh, 425 (4.37) nm; FAB-MS (3-NOBA) *m/z* (%) 2026, 2028 (100) [(M + Na)$^+$], 2004, 2006 (36) [(M + H)$^+$], 1757, 1759 (5) [(M − $C_{16}H_{34}$NCOH + Na)$^+$], 1475, 1477 (4) [(M − $C_{16}H_{34}$NCOH − $C_{16}H_{34}$NCOCH$_2$ + Na)$^+$]; $C_{116}H_{198}N_{16}NiO_8 \cdot 2H_2O$ (2039.67) calcd C, 68.31; H, 9.98; N, 10.99; found C, 68.58; H, 10.11; N, 10.95.

Scheme 1



Results and Discussion

Synthesis. Substituted metal-free triazolehemiporphyrazines **1** and **4** were synthesized in moderate yields by condensation reaction of 1-dodecyl-3,5-diamino-1,2,4-triazole (**7**)[2a] and the corresponding 1,3-diiminoisoindoline **8**,[17] **9**[18] in equimolar amounts (Scheme 1). Compounds **1** and **4** are isolated as mixtures of two regioisomers (*cis* and *trans* isomers), due to the relative orientation of the dodecyl chains on the triazole moiety. However, when the synthesis of **4** is carried out in more diluted conditions, only the *trans* isomer (C_{2h} symmetry) was isolated from the crude mixture in lower yield (10%). The isolation of the *trans* isomer of **4** in these conditions is probably due to a selective crystallization of the compound from the reaction mixture and not to a regioselective operating process.

Copper and nickel hemiporphyrazines **2**, **3**, **5**, and **6** were prepared by treatment of the metal-free derivatives with the corresponding metallic salt. The presence of long chains surrounding the central core affords the solubility of all the compounds in chlorinated and aromatic solvents.

The compounds were characterized by elemental analysis, IR and UV−visible spectroscopies, fast atom bombardment mass spectrometry, and ^{1}H and ^{13}C NMR in the case of diamagnetic complexes.

Metal-free hemiporphyrazine **1** shows in the ^{1}H NMR spectrum in CDCl$_3$ four singlets for the aromatic protons, thus indicating the presence of two constitutional isomers. Two singlets are observed in the case of **4**, while only one signal was observed in the spectrum of the C_{2h} isomer of **4**. Nickel complexes **3** and **6** show three singlets for the aromatic protons.

The inner protons of the triazolehemiporphyrazine core appears in a very low field (ca. 15 ppm), as a consequence of the antiaromatic character of these compounds.[2a] Three signals are shown in the spectra of hemiporphyrazines **1** and **4** for this kind of protons, while a single signal was observed in the case of the trans isomer of **4**.

All the compounds could be identified by FAB mass spectrometry. For triazolehemiporphyrazines **4**−**6**, M + Na$^+$ molecular peaks appear in all the cases due to the capability of these amido chains to coordinate cations.[18a]

The UV−visible spectra in CHCl$_3$ of these compounds are similar to those already described by us for related ones.[10] These hemiporphyrazines bearing four alkoxy groups show the highest wavelength band at ca. 380 nm, in the case of the ligands **1** and **4**. In copper complexes **2** and **5** a slight batochromic shift of this band (ca. 390 nm) is observed, this shift being especially remarkable for nickel compounds **3** and **6** (ca. 425 nm). It seems clear that the electronic distribution of the hemiporphyrazine core is influenced to a great extent, when

Table 1. Optical, Thermal and Thermodynamic Data of Compounds 1−6 (C = Crystal, D_{ho} = Ordered Hexagonal Columnar Mesophase, I = Isotropic Liquid)

compound	transition	temp (°C)	ΔH (J g^{-1})
1	C−D_{ho}	39.0	31.45
	D_{ho}−I[a]	165−175	[a]
2	C−D_{ho}	40.5	55.1
	D_{ho}−I	313.3	4.2
3	C−D_{ho}	37.1	35.9
	D_{ho}−I	303.8	5.6
4	C−I	156.9	24.1
4 (*trans* isomer)	C−I	176.8	33.5
5	C−I	169.9	23.5
6	C−I	158.4	24.1

[a] Transition observed only by optical microscopy.

compared to phthalocyanines, by the electronic character of the substituents[2e] and the nature of the central atom.

Optical Microscopy Study. The mesogenic properties of compounds **1**−**6** were investigated using optical microscopy, DSC, and X-ray diffraction. The thermal behavior deduced from these techniques is depicted in Table 1 which collects the types of phase and the transition temperatures and enthalpies determined for each compound.

All the compounds are solid at room temperature. When heated on the stage of the optical microscope under polarized light, compounds **4**−**6** melt directly into the isotropic liquid state. On the other hand, compounds **1**−**3** exhibit mesomorphism. Upon heating, each of these three compounds undergoes a transition from the solid to a birefringent viscous fluid, which exhibits an uncharacteristic texture. Melting was detected by the rounding off of the crystallite edges. In fact, during heating the optical textures are masked by that of the solid phase, and therefore detailed observations had to be undertaken during cooling from the isotropic liquid. No other transitions were observed upon heating before clearing into the isotropic liquid. Clearing was detected by a sudden increase in fluidity and the complete extinction under polarized light.

Slow cooling of the isotropic liquid gave well-developed birefringent domains typical of columnar mesophases. Figure 2 shows a representative example of such microscopic pictures. Optical textures include mosaic regions with rectilinear birefringent defects, fanlike domains and areas with fingerlike contours (digitated stars).

DSC Study. The DSC curves of compounds **1**−**6** are consistent with the microscope observations. Compounds **1**−**3** form a single mesophase with a broad temperature range, whereas compounds **4**−**6** do not exhibit mesomorphism either in the heating or in the cooling processes.

Consistently with their mesomorphic behavior, compounds **2** and **3** exhibit two endothermic peaks in the heating cycles: a large peak at low temperature, assigned to the solid-to-mesophase transition, and a small peak at high temperature, assigned to the mesophase-to-liquid transition (see Table 1). In the free ligand **1** only the low-temperature peak, corresponding to the solid-to-mesophase transition, is observed. The transition from the mesophase to the isotropic liquid is not detected in the DSC thermograms but is clearly observed in the polarizing optical microscope and in the X-ray diffraction patterns to be described below. The absence of the DSC high-temperature peak might due to a very weak enthalpy value or to the slowness of the transition. The melting temperature is relatively low for **1**−**3** (37.1−40.5 °C, see Table 1) and almost constant for the three compounds, regardless of the presence or absence of a metal atom and its nature. On the other hand, the presence of the metal atom in the center of the macrocycle (compounds **2** and **3**) raises to a large extent the clearing temperature relative to the metal-free ligand (compound **1**). As a consequence, the effect of the metal ion is to enhance the temperature range of the mesophase by about 140 °C. The stabilization of the liquid-crystal phase by the presence of the metal atom is a common phenomenon related with intermolecular dative associations that involve the metal.[19]

The DSC curves of compounds **4**−**6** display only the expected single peak assigned to melting from the solid to the isotropic liquid. This transition takes place at relatively high temperatures (156.9−176.8 °C). The regioisomerically pure trans isomer of **4** melts about 20 °C above the mixture of regioisomers (see Table 1).

All the compounds studied (**1**−**6**) exhibit reversible behavior, although some supercooling is detected for the mesophase-to-solid and liquid-to-solid transitions. In some cases, solid-to-solid transitions prior to melting or multiple peaks due to melting of different crystalline phases are observed in the first heating, which in general are not detected in subsequent cycles.

X-ray Diffraction Study. Triazolehemiporphyrazines **1**−**6** were examined in all their phases by X-ray diffraction using a Pinhole camera equipped with a variable-temperature sample holder. For the six compounds the patterns taken at room temperature are characteristic of crystalline phases, as revealed by the presence of sharp diffraction lines in the high-angle region. This is consistent with the lack of mobility of the samples detected in the microscope.

The X-ray patterns of compounds **1**−**3** registered above the melting point yield a set of peaks characteristic of a hexagonal columnar mesophase D_{ho}. Table 2 collects the experimentally measured spacings, the calculated spacings, the proposed indexing, and the mesophase parameters. Three rings are observed near the center of the pattern, the first of which is much stronger than the other two. Their reciprocal spacings follow the ratio $1{:}\sqrt{3}{:}\sqrt{4}$, and they can be indexed as the (1 0), (1 1), and (2 0) Bragg reflections from a two-dimensional hexagonal lattice with a lattice constant a (30.3−30.7 Å) very similar for the three compounds. In addition, two rings are found at high angles. The first of them, centered at 4.6 Å, is broad and diffuse and is usually found in discotic liquid crystals, associated to the liquidlike correlations between the aliphatic chains.[20] The most external ring, found at 3.4 Å, is sharp and is indicative of the periodic stacking of the molecular cores inside a column (c constant of the hexagonal network). The sharpness of this ring means that the correlation length for this linear order is large (D_{ho} mesophase). For each compound the kind of pattern and the measured

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(19) Barberá, J. *Metallomesogens: Synthesis, Properties and Applications*; Serrano, J. L., Ed.; VCH: Weinheim, 1996; Chapter 4 and 8.

(20) (a) Levelut, A. M.; Hardouin, F.; Gasparoux, H.; Destrade, C.; Tinh, N. H. *J. Phys.* **1981**, *42*, 147. (b) Levelut, A. M. *J. Chim. Phys.* **1983**, *80*, 149.

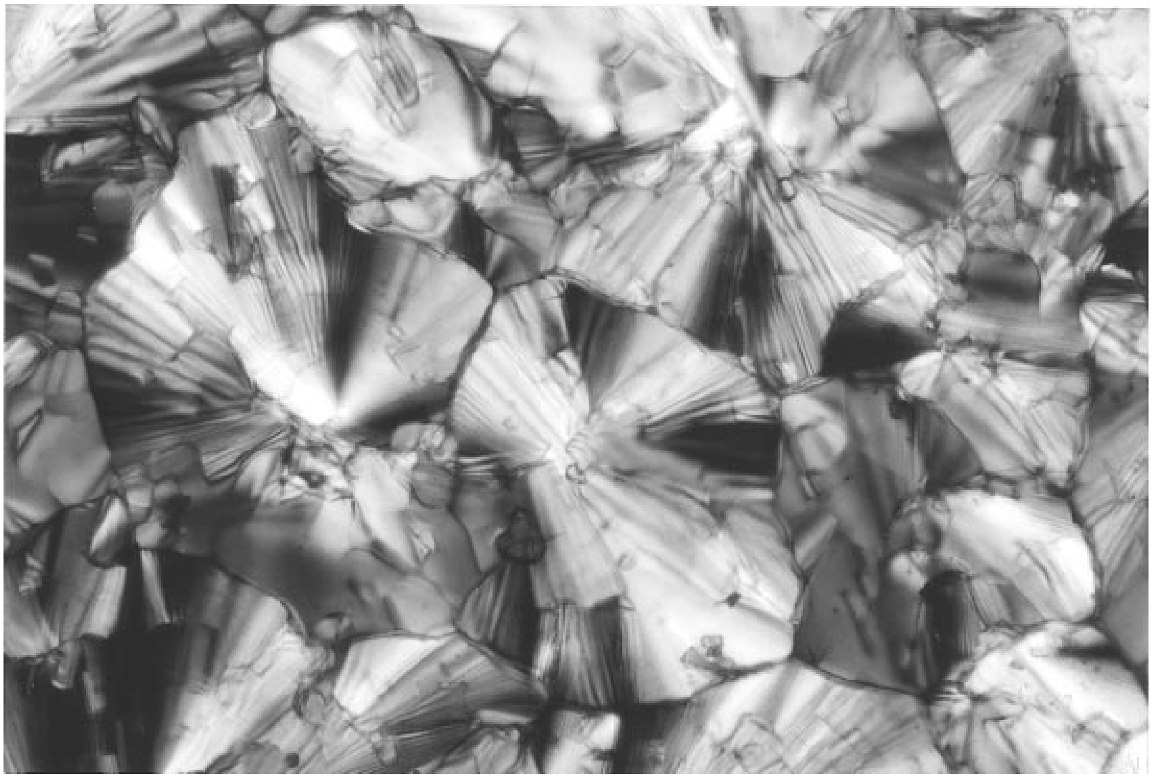

Figure 2. Micrograph of the optical texture of the mesophase of compound **3** at 100 °C observed under polarized light.

Table 2. X-ray Diffraction Data for the Mesophase of Compounds 1−3 at 100 °C

compound	*h k l*	d_{obs} (Å)	d_{calc} (Å)	lattice constants (Å)	calcd density (g cm^{-3})
1	1 0 0	26.5	26.6	$a = 30.7$	0.89
	1 1 0	15.4	15.35		
	2 0 0	13.3	13.3		
		4.6 (broad)			
	0 0 1	3.4		$c = 3.4$	
2	1 0 0	26.3	26.2	$a = 30.3$	0.95
	1 1 0	15.1	15.15		
	2 0 0	13.1	13.1		
		4.6 (broad)			
	0 0 1	3.4		$c = 3.4$	
3	1 0 0	26.4	26.5	$a = 30.6$	0.93
	1 1 0	15.4	15.3		
	2 0 0	13.2	13.25		
		4.6 (broad)			
	0 0 1	3.4		$c = 3.4$	

spacings in the mesophase practically do not change on varying the temperature.

In addition to the peaks characteristic of the hexagonal columnar mesophase, a number of additional sharp peaks of weak intensity are detected in some X-ray patterns, which are the result of the presence of a small amount of crystalline phase. However, the relative amount of the crystalline phase decreases at high temperature and disappears completely at about 150 °C. The presence of this small amount of coexistent crystalline phase could not be observed either by optical microscopy or by DSC. It could be detected only by X-ray diffraction on first heating but not on subsequent cooling or heating, thus indicating that this phase is metastable. Therefore, it is possible to conclude that the thermodinamically stable phase between the melting and the clearing temperatures is the columnar mesophase.

The relationship between the density ρ of the compounds in the mesophase and the number Z of molecules in the unit cell is given by the following equation:

$$\rho = (M/N)/(V/Z)$$

where M is the molar mass (g), N the Avogadro number, and V the unit cell volume (cm^3):

$$V = (\sqrt{3}/2)a^2c \times 10^{-24}$$

Assuming that the density of the compounds is near 1 g cm^{-3}, it is then obvious that there is one molecule per unit cell and the calculated density in the mesophase is 0.89−0.95 g cm^{-3} (see Table 2). For one molecule per unit cell, the hexagonal lattice constant represents the distance between the nearest neighboring columns. This distance ($a = 30.3$−30.7 Å) is intermediate between the length of the long axis of the rigid core (16 Å) and the longest dimension of the molecule with fully extended aliphatic chains (49 Å), estimated from Dreiding stereomodels. This phenomenon is typically found in discotic mesophases and can be attributed to interpenetration between the paraffinic regions of neighboring columns and/or conformational disorder of the alkyl chains. It is interesting to note that the central core of these molecules is not circular but elliptical (see Figure 3). The hexagonal symmetry of the mesophase suggests a rotationally averaged structure inside the column which gives a circular projection along the column axis. This has also been proposed to account for the columnar mesomorphism of other nondiscoid molecules.[21]

A long axis of 16 Å and a short axis of 11 Å are estimated for the elliptical rigid core of these molecules (see Figure 3). This, together with the experimentally found thickness of 3.4 Å, allows to roughly estimate a

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(21) Serrete, A. G.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 2252.

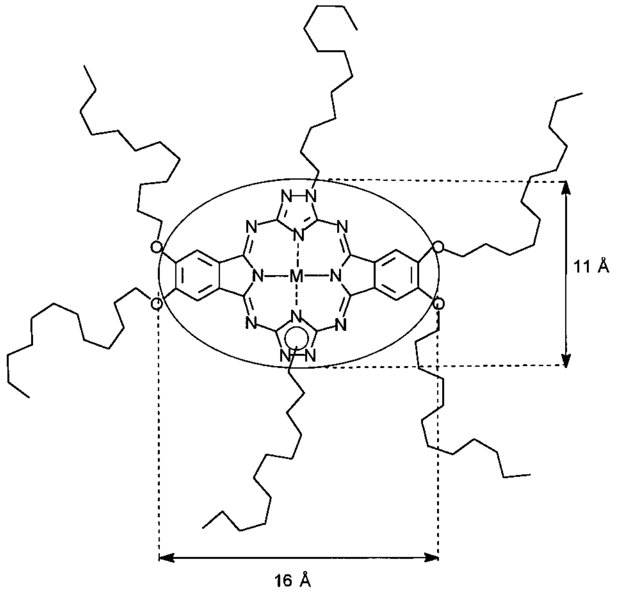

Figure 3. Schematic representation of the molecular shape of compounds **1**−**3** (M = H_2, Cu, Ni).

core volume V_{core}. From this, the volume ocuppied by the alkyl chains can be estimated as

$$V_{\mathrm{chain}} = V - V_{\mathrm{core}} = (\sqrt{3}/2)30.5^2 \cdot 3.4 - (\pi/4 \cdot 16 \cdot 11 \cdot 3.4) = 2739 - 470 = 2269\ \text{Å}^3$$

where V is the cell volume considering an average value of $a = 30.5$ Å. The volume per methylene group is then

$$V_{\mathrm{CH_2}} = 2269/(12 \cdot 6) = 31.5\ \text{Å}^3$$

which corresponds well to typical values found in columnar mesophases.[22]

The X-ray diffraction patterns of compound **1** taken above the clearing temperature only exhibit two broad peaks, one of them in the low-angle region and the other one in the high-angle region. This pattern is characteristic of an isotropic liquid and confirms the existence of the mesophase-to-isotropic liquid transition, despite the absence of the corresponding peak in DSC. We were not able to register the X-ray patterns of compounds **2** and **3** in the isotropic liquid because clearing takes place at temperatures beyond the upper limit of the variable-temperature attachment of our instrument.

The diffraction study of compounds **4**−**6** confirms that they are nonmesomorphic. Indeed, the X-ray patterns taken at temperatures below the solid-to-liquid transition observed in the microscope and in DSC are typical of crystalline phases, whereas the patterns taken above that temperature contain the two broad halos charasteristic of an isotropic phase. The absence of mesomorphism in these compounds is surprising at first sight. In other series of discotic compounds the increase of the flexible paraffinic part of the molecules has been shown to preserve, and even improve, the mesomorphic properties.[16,23] The opposite effect found in this case could be due to an unfavorable balance between the two main factors that determine the tendency of disklike molecules to form liquid-crystal phases: core−core attractive forces and chain−chain hydrophobic forces. The existence of repulsive steric interactions between the branched chains might increase the molecule thickness and thus render columnar stacking difficult. Moreover, we must take into account that the rigid core is smaller for the molecules described here than for phthalocyanines substituted with the same dialkylamide groups that yielded hexagonal columnar mesomorphism.[16] This may hinder the cylindrically symmetrical arrangement of the aliphatic chains around the central core necessary for the appearance of hexagonal columnar mesomorphism.[23]

In summary, we have presented the synthesis of the first metallomesogens derived from a hemiporphyrazine. When the central core is substituted with four dodecyloxy groups on the benzene rings in addition to two dodecyl groups on the triazole rings, a hexagonal columnar mesophase has been identified which is stable over a broad temperature region. The disk stacking is long range, and thus the mesophase can be denoted D_{ho}. The mesophase parameters are practically constant regardless of the presence or absence of metal and the temperature. Melting from the solid to the mesophase takes place at mild temperatures.

On the other hand, if the simple alkoxy groups are replaced by alkoxy chains functionalized with dialkylamide groups no liquid-crystal properties are found. This is probably related to the steric hindrance due to the voluminous, branched dialkylamide groups, which disrupts the stacking of the aromatic cores. Thus, it seems that in this series the presence of linear alkoxy groups is necessary to obtain mesomorphic compounds.

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[22] (a) Seurin, P.; Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 51. (b) Zinsou, A.; Veber, M.; Strzelecka, H.; Jallabert, C.; Levelut, A. M. *Liq. Cryst.* **1994**, *17*, 513.

[23] Barberá, J.; Esteruelas, M. A.; Levelut, A. M.; Oro, L. A.; Serrano, J. L.; Sola, E. *Inorg. Chem.* **1992**, *31*, 732.