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Synthesis and Liquid-Crystal Behavior of Triazolephthalocyanines

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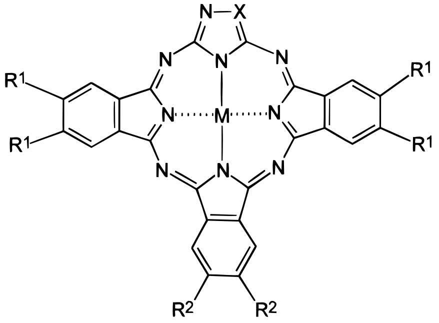
The synthesis, characterization, and mesomorphic properties of new discotic molecules based on the triazolephthalocyanine macrocycle are described. This core has been attached to six lipophilic chains, and metallic complexes (Ni, Cu) have been prepared. The mesogenic behavior has been studied using optical microscopy, DSC, and X-ray diffraction techniques. The hexaalkoxy-substituted triazolephthalocyanines exhibited hexagonal columnar mesophases with a high viscosity from room temperature up to decomposition temperature. Progressive formal replacement of alkoxy chains with alkylamide groups induces the lowering of the clearing point but gradually hinders mesomorphism. Mesomorphism is also suppressed when the compound is ionic.

Introduction

Phthalocyanines (Pcs)[1] and related π-conjugated organic metallomacrocycles, such us triazolehemiporphyrazines[2] and triazolephthalocyanines,[3] can be considered as promising subunits for the construction of molecular materials with unusual electrical[1] and optical properties.[4] However, their potential application in devices not only requires a useful property at a molecular level but also an appropriate supramolecular organization to keep and even to improve their intrinsic characteristics.

The introduction of peripheral lipophilic substituents in the phthalocyanine affords soluble compounds and increases the tendency of the Pc core to stack up, thus giving columnar structures[5] and providing materials with a discotic liquid-crystal behavior.[6] The organization in LB films of peripheral substituted phthalocyanines has also provided in-plane arranged films.[7]



1a X = N , M = Ni , $R^1 = R^2 = OC_8H_{17}$
1b X = N , M = Cu , $R^1 = R^2 = OC_8H_{17}$
2a X = N , M = Ni , $R^1 = R^2 = OC_{12}H_{25}$
2b X = N , M = Cu , $R^1 = R^2 = OC_{12}H_{25}$
3 X = N , M = Ni , $R^1 = R^2 = OCH_2CON(C_8H_{17})_2$
4 X = N , M = Ni , $R^1 = OC_8H_{17}$, $R^2 = OCH_2CON(C_8H_{17})_2$
5 X = $[NC_{12}H_{25}]^+ Br^-$, M = Ni , $R^1 = R^2 = OC_{12}H_{25}$

Figure 1.

The liquid-crystal properties of hexasubstituted triazolehemiporphyrazines have been described recently.[8] These compounds, when substituted with dodecyloxy chains, are self-organized in a hexagonal columnar mesophase that is stable over a broad temperature range. These studies support the idea that the presence of highly coordinating heterocyclic subunits, like triazole, with a higher number of nitrogens in the structure is not an inconvenience to their liquid-crystal properties.

Triazolephthalocyanine (Tpc) (Figure 1) is the trivial name we have assigned to an intrinsically unsymmetric

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phthalocyanine analogue in which one isoindole subunit of the Pc core has been formally replaced by a 1,2,4-triazole moiety. These intrinsically unsymmetric phthalocyanine analogues can be synthesized by two methodologies:[3] (a) the statistical method, which affords compounds with the same kind and degree of substitution in all three isoindole subunits,[9] and (b) the stepwise method, which provides triazolephthalocyanines with a differently substituted isoindole opposite to the triazole moiety.[10] This diversity improves the possibilities of synthetic design, thus allowing a higher control of their properties.

Triazolephthalocyanines display second- and third-order nonlinear optical properties in solution, similar to those showed by unsymmetric Pcs.[11] Soluble triazolephthalocyanines, due to their amphiphilic character, can be self-assembled by the LB technique to afford in-plane organized films,[12] with semiconducting properties, capable of acting as gas sensors.[13]

The synthesis and physical properties of triazolephthalocyanines have been recently reviewed.[3]

In this paper, we describe for the first time the preparation, characterization, and mesomorphic properties of discotic liquid crystals based on the triazolephthalocyanine nucleus. Only compound **2a** has been fully characterized previously,[11] but its liquid-crystal properties were not investigated. We have analyzed the effect on mesomorphism of different side chains in the isoindole and triazole subunits.

Experimental Section

All compounds were characterized by elemental analysis and IR, UV−vis, and mass spectroscopies,as well as NMR techniques in the case of diamagnetic nickel complexes. Solvents were either employed as purchased or dried according to procedures described in the literature. UV−vis and IR spectra were recorded on Perkin-Elmer model Lambda 6 and PU 9716 Philips spectrometers, respectively. Melting points were determined on an Büchi melting-point apparatus and are uncorrected. NMR spectra were recorded on a Bruker WM-200-SY spectrometer with either the solvent as reference or TMS as the internal standard. All chemical shifts are quoted on the δ scale. All coupling constants are expressed in hertz (Hz). Fast-atom bombardment mass spectra (FABMS) were obtained from a MAT 900 (Finnigan-MAT GmbH, Bremen Instruments) spectrometer. Samples of the molecules were dissolved in a small volume of *m*-nitrobenzyl alcohol and loaded onto a stainless steel probe tip. Maldi Toff mass spectra were performed employing α-cyano-4-hydroxycinnamic acid as matrix by the Universidad Autónoma de Madrid University Mass-Spectrometry Service. Microanalyses were performed by the Universidad Autónoma de Madrid University Microanalytical Service. The optical textures of the mesophases were investigated with a Nikon polarizing microscope equipped with a Linkam THMS600 hot stage. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments DSC-2910 operated at a scanning rate of 10° min^{-1} in a nitrogen atmosphere. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}) as a standard. Thermogravimetric analysis (TGA) was performed using a TA Instruments STD-2960 with simultaneous DTA−TGA at a heating rate of 10° min^{-1} in a nitrogen atmosphere. X-ray diffraction patterns were obtained using a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction pattern was collected on flat photographic film.

2,3,9,10,16,17-Hexaoctyloxy-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosanate (2-)-*N*^{27},*N*^{28},*N*^{29},*N*^{30} Nickel(II) (1a). *(a) Statistical Process.*[9] 5,6-Dioctyloxy-1,3-diiminoisoindoline (0.65 g, 1.62 mmol), 3,5-diamino-1,2,4-triazole (0.053 g, 0.54 mmol), $Ni(AcO)_2 \cdot 4H_2O$ (0.13 g, 0.54 mmol), and 2-ethoxyethanol (50 mL) were stirred to reflux for 24 h. After filtration, the crude material was triturated with methanol and further purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 20:1) to yield 0.046 g of **1a** (14%). *(b) Stepwise Synthesis.*[10] Equimolar amounts of 1,3-bis[5′,6′-dioctyloxy-(3′-imine-1′-isoindolinylidene)amine]-1,2,4-triazole (**6**) (0.2 g, 0.24 mmol), $Ni(AcO)_2 \cdot 4H_2O$ (0.058 g, 0.24 mmol), and 5,6-dioctyloxy-1,3-diiminoisoindoline (0.094 g, 0.24 mmol) were suspended in 2-ethoxyethanol (15 mL), and the mixture was stirred at 50 °C for 10 days. After filtration and trituration with methanol of the raw material, compound **1a** was fully purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 20:1). Yield: 15%. ^{1}H NMR ($CDCl_3$): δ 7.6−6.5 (broad s, 6H, H arom.), 4.1 (m, 12H, OCH_2), 1.6 (s, 90H, CH_2), 0.9 ppm (m, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 47.8, 31.8, 29.3, 27.5, 27.0, 26.2, 22.6 (CH_2), 14.0 ppm (CH_3). MS-MALDI (CH_2Cl_2): *m/z* 1292 [$(M + H)^+$]. IR (KBr): ν 3600−3200, 2924, 2854, 1600, 1518, 1464 (C═N), 1361, 1288, 1216, 1059, 856, 760 cm^{-1} (C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 284 (4.74), 363 (4.32), 440 (sh), 627 (3.65), 671 nm (3.63). Anal. Calcd for $C_{74}H_{108}N_{10}O_6Ni \cdot 2H_2O$: C 66.91, H 8.50, N 10.54%. Found: C 66.43, H 8.44, N 11.10%.

2,3,9,10,16,17-Hexaoctyloxy-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosanate (2-)-*N*^{27},*N*^{28},*N*^{29},*N*^{30} Copper(II) (1b). 5,6-Dioctyloxy-1,3-diiminoisoindoline (1.40 g, 3.49 mmol), 3,5-diamino-1,2,4-triazole (0.115 g, 1.16 mmol), and methanol (25 mL) were stirred to reflux for 5 d. After removing the solvent under reduced pressure, $Cu(AcO)_2 \cdot 1H_2O$ (0.232 g, 1.16 mmol) and 2-ethoxyethanol (25 mL) were added, and the mixture was stirred to 80 °C for 2 d. After being cooled, the crude was filtrated, and the solid was washed with diethyl ether. Further purification was carried out by column chromatography (silica gel, CH_2Cl_2, CH_2Cl_2:MeOH, 10:1) to afford 0.106 g of **1b** (14%). MS-MALDI (CH_2Cl_2): *m/z* 1296/1298 [$(M + H)^+$]. IR (KBr): ν 3600−3200, 2924, 2854, 1594, 1500, 1457 (C═N), 1348, 1308, 1216, 1073, 865, 721 cm^{-1} (C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 262 (4.73), 380 (4.19), 444 (sh), 581 (sh), 642 (3.34), 676 nm (3.23). Anal. Calcd for $C_{74}H_{108}N_{10}O_6Cu \cdot 2H_2O$: C 66.66, H 8.47, N 10.51%. Found: C 65.91, H 8.27, N 11.22%.

2,3,9,10,16,17-Hexadodecyloxy-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[*f*,*k*,*p*][1,2,4,9,14,19]hexaazacycloeicosanate (2-)-*N*^{27},*N*^{28},*N*^{29},*N*^{30} Copper(II) (2b). 5,6-Didodecyloxy-1,3-diiminoisoindoline[14] (0.943 g, 1.84 mmol), 3,5-diamino-1,2,4-triazole (0.061 g, 0.61 mmol), and methanol (50 mL) were stirred to reflux for 3 d. After the solvent was removed under reduced pressure, $Cu(AcO)_2 \cdot 1H_2O$ (0.122 g, 0.61 mmol) and 2-ethoxyethanol (55 mL) were added, and the mixture was stirred to 80 °C for 4 d. After being cooled, the crude was filtrated, and the solid was washed with diethyl ether. Further purification was carried out by column chromatography (silica gel, CH_2Cl_2, CH_2Cl_2:MeOH, 10:1) to afford 0.101 g of **2b** (10%). MS-MALDI (CH_2Cl_2): *m/z* 1633/1635 [$(M + H)^+$]. IR (KBr): ν 3600−3200, 2924, 2853, 1590, 1500, 1460 (C═N), 1375, 1290, 1217, 1058, 805, 758, 723 cm^{-1} (C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 268 (4.61), 348

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(4.32), 444 (sh), 569 (sh), 642 (3.22), 676 nm (3.00). Anal. Calcd for $C_{98}H_{156}N_{10}O_6Cu{\cdot}2H_2O$: C 70.49, H 9.66, N 8.39%. Found: C 69.81, H 9.52, N 9.75%.

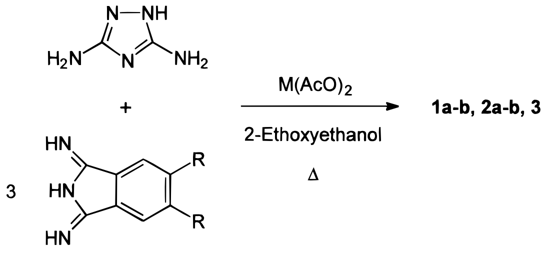
2,3,9,10,16,17-Hexakis[(dioctylaminocarbonyl)methoxy]-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[*f,k,p*]-[1,2,4,9,14,19]hexaazacycloeicosanate (2-)-N^{27},N^{28},N^{29},N^{30} Nickel(II) (3). A mixture of 5,6-bis[(dioctylaminocarbonyl) methoxy]-1,3-diiminoisoindoline[15] (0.44 g, 0.59 mmol), 3,5-diamine-1,2,4-triazole (0.020 g, 0.19 mmol), $Ni(AcO)_2{\cdot}4H_2O$ (0.049 g, 0.19 mmol), and 2-ethoxyethanol (15 mL) were stirred to reflux for 24 h. After filtration, the raw material was triturated with methanol and fully purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 20:1), to yield 0.023 g (5%) of **3** as a black powder. Mp: 100 °C. ^{1}H NMR ($CDCl_3$): δ 7.7−6.7 (broad s, 6H, H arom.), 4.9 (m, 12H, OCH_2), 3.3 (24H, NCH_2), 1.3 (s, 148H, CH_2), 0.9 ppm (m, 36H, CH_3). MS−FAB (*m*-NBA, CH_2Cl_2): *m/z* 2306, 2308 [$(M + H)^+$, 100]. IR (KBr): ν 3500−3200, 2925, 2853, 1659 (C=O), 1466 (C=N), 1369, 1285, 1211, 1078, 801 cm^{-1}(C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 287 (4.57), 368 (4.35), 420 (sh), 534 (3.94), 576 (3.89), 633 nm (4.04).

9,10-Bis[(dioctylaminocarbonyl)methoxy]-2,3,16,17-tetraoctyloxy-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo[*f,k,p*][1,2,4,9,14,19]hexaazacycloeicosanate (2-)-N^{27},N^{28},N^{29},N^{30} Nickel(II) (4). Equimolar amounts of 1,3-bis[5′,6′-dioctyloxy-(3′-imine-1′-isoindolinylidene)amine]-1,2,4-triazole (**6**) (0.25 g, 0.29 mmol), $Ni(AcO)_2{\cdot}4H_2O$ (0.072 g, 0.29 mmol), and 5,6-bis[(dioctylaminocarbonyl)methoxy]-1,3-diiminoisoindoline[15] (0.21 g, 0.29 mmol) were suspended in 2-ethoxyethanol (20 mL), and the mixture was stirred at 50 °C for 6 days. After filtration, the crude material was triturated with methanol, and the compound was purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 15:1) to yield 0.079 g (17%) of **4**. ^{1}H NMR ($CDCl_3$): δ 7.7−6.7 (broad s, 6H, H arom.), 4.9 (m, 4H, OCH_2), 4.07 (m, 8H, OCH_2), 3.3 (8H, NCH_2), 1.3 (s, 96H, CH_2), 0.9 ppm (m, 24H, CH_3). ^{13}C NMR ($CDCl_3$): δ 47.8, 46.0 (NCH_2), 31.8, 29.3, 27.5, 27.0, 26.2, 22.6 (CH_2), 14.0 ppm (CH_3). MS−FAB (*m*-NBA, CH_2Cl_2): *m/z* 1629, 1631 [$(M + H)^+$]. IR (KBr): ν 3500−3200, 2923, 2853, 1652 (C=O), 1598, 1499, 1465 (C=N), 1365, 1288, 1215, 1063, 859, 755 cm^{-1} (C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 287 (4.75), 364 (4.38), 434 (sh), 579 (3.90), 573 (3.83), 637 (3.75), 667 nm (3.70). Anal. Calcd for $C_{94}H_{146}N_{12}O_8Ni{\cdot}2H_2O$: C 67.73, H 9.07, N 10.08%. Found: C 67.01, H 9.15, N 10.65%.

22-Dodecyl-2,3,9,10,16,17-hexadodecyloxy-7,12:21,24-diimine-5,26:14,19-dinitriletribenzo [*f,k,p*][1,2,4,9,14,19]-hexaazacycloeicosanate (2-)-N^{27},N^{28},N^{29},N^{30} Nickel(II) Bromide (5). A mixture of hexadodecyloxytriazolephthalocyaninato nickel(II) (**2a**)[11] (0.05 g, 0.03 mmol), dodecyl bromide (0.015 g, 0.06 mmol), and benzene (3 mL) was stirred at 60 °C for 4 d. After filtration, the crude material was triturated with methanol and further purified by column chromatography (silica gel, CH_2Cl_2:MeOH, 20:1) to yield 0.02 g (35%) of **5**. ^{1}H NMR ($CDCl_3$): δ 7.6−6.5 (broad signal, 6H, H arom.), 4.1 (m, 12H, OCH_2), 1.3 (broad signal, 126H, CH_2), 0.9 ppm (m, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 47.8, 31.7, 29.4, 29.2, 27.5, 27.1, 26.2, 22.5 (CH_2), 14.2 ppm (CH_3). MS-MALDI ($CHCl_3$): *m/z* 1799 [$(M + H)^+$]. IR (KBr): ν 3600−3200, 2922, 2852, 1596, 1517, 1494, 1466 (C=N), 1382, 1358, 1288, 1215, 1077, 863, 802, 753, 720 cm^{-1} (C−H). UV−vis (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): λ 283 (4.85), 363 (4.39), 439 (sh), 591 nm (3.74).

1,3-Bis[5′,6′-dioctyloxy-(3′-imine-1′-isoindolinylidene)-amine]-1,2,4-triazole (6). 5,6-Dioctyloxy-1,3-diiminoisoindoline (1 g, 2.5 mmol), 3,5-diamine-1,2,4-triazole (0.12 g, 1.24 mmol) and methanol (40 mL) were stirred to reflux for 11 days. After filtration and trituration with methanol, 0.27 g of **6** were obtained (yield: 25%). mp: 175 °C (decomposition). ^{1}H NMR (d-TFA): λ 8.0, 7.8 (2·s, 4H, H arom.), 4.4 (m, 8H, OCH_2), 2.1 (m, 8H, OCH_2CH_2), 1.4 (s, 40H, CH_2), 0.9 ppm (m, 12H, CH_3). ^{13}C NMR, δ (*d*-TFA): 167.2, 157.8 (C-3′, C-1′), 156.7, 156.5 (C-6′, C-5′), 155.9 (C-3), 128.8, 122.0 (C-4a′, C-7a′), 110.4, 109.6 (C-4′, C-7′), 71.7 (OCH_2), 32.9, 30.3, 29.6, 26.8, 23.6 (CH_2), 13.9 ppm (CH_3). MS−FAB (*m*-NBA, TFA) (%): *m/z* 869 [$(M + H)^+$, 91], 484 [$(M{-}C_{24}H_{35}N_2O_2)^+$, 100]. IR (KBr): ν 3500−3000 (N−H), 2930, 2870, 1630, 1610, 1500, 1480 (C=N), 1390, 1350, 1290, 1220, 1030, 870, 770 cm^{-1} (C−H).

Scheme 1



R = OC_8H_{17}, $OC_{12}H_{25}$, $OCH_2CON(C_8H_{17})_2$

Results and Discussion

Synthesis. The synthesis of compounds **1a, 1b**, **2a**,[11] **2b,** and **3** was carried out by stoichiometrical reaction[9] between the corresponding 1,3-diiminoisoindoline and 3,5-diamino-1,2,4-triazole (guanazole) (3:1 molar ratio) in the presence of the corresponding metal acetate acting as template (Scheme 1). Whereas the preparation of **3** employing the conditions described (1 day reflux in 2-ethoxyethanol) yielded only 5% of **3**, a variation of this methodology was developed to synthesize the copper compounds **1b** and **2b**, because the usual conditions just rendered traces of the corresponding triazolephthalocyanine. **1b** and **2b** were prepared by refluxing a 3:1 mixture of the corresponding 5,6-dialkoxy-1,3-diiminoisoindoline and 3,5-diamino-1,2,4-triazole in methanol for several days; then, after removal of the solvent, the copper(II) salt solved in 2-ethoxyethanol was added, and the mixture was kept at 80 °C for 2−3 days to yield 10−20% of the corresponding triazolephthalocyanine (Scheme 1).

The stepwise synthesis of triazolephthalocyanines is required to achieve **4**.[10] This procedure involves the condensation reaction of equimolar amounts of the three-unit compound **6,** nickel(II) acetate, and 3,5-(dioctylaminocarbonyl)methoxy-1,3-diiminoisoindoline at lower temperature (55 °C) to render 17% of **4** (Scheme 2). The three-unit ligand **6** was prepared in a manner similar to that previously described for related compounds,[16] by heating stoichiometrical amounts of guanazole and 5,6-dioctyloxy-1,3-diiminoisoindoline in methanol for 11 days (Scheme 2).

To prepare **1a,** both methodologies (statistical[9] and stepwise[10] synthesis) were employed in order to compare the yields of both routes. As expected, the statistical strategy is the best one because it requires only a one-step reaction, which gives a yield similar to that of the last reaction in the stepwise process. Nevertheless, purification of **1a** was more tedious with the statistical process due to aggregation phenomena between the desired triazolephthalocyanine (Tpc) **1a** and the octaoctyloxyphthalocyaninato nickel(II) obtained as byproduct in the employed reaction conditions.

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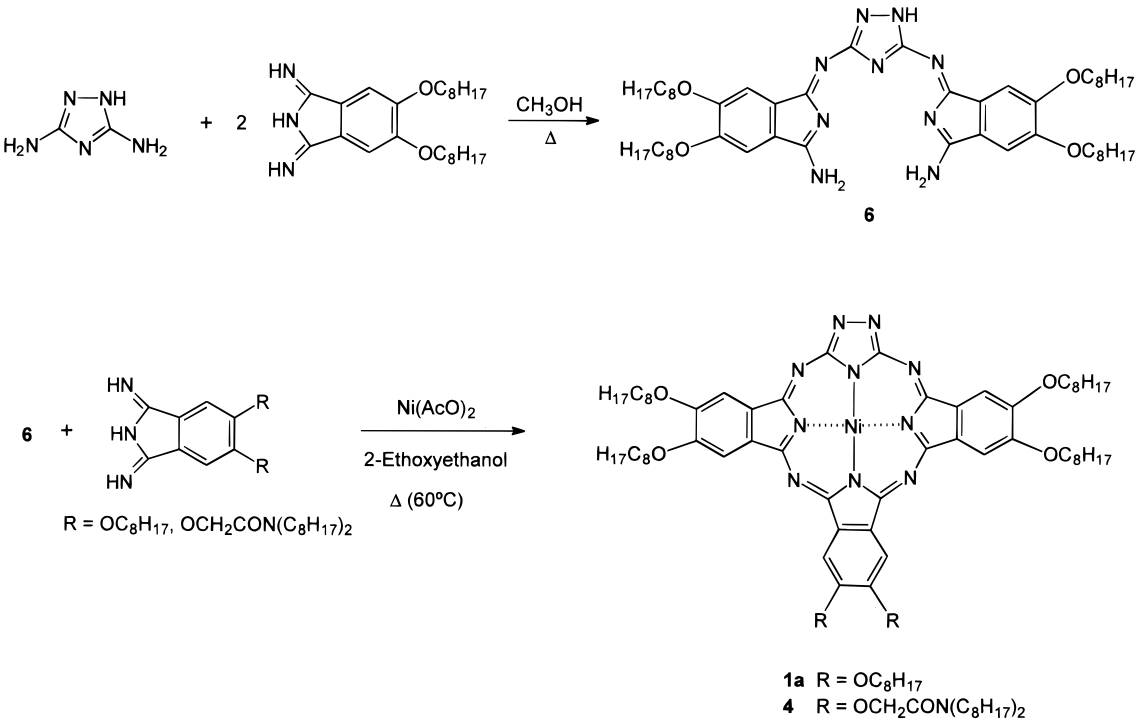
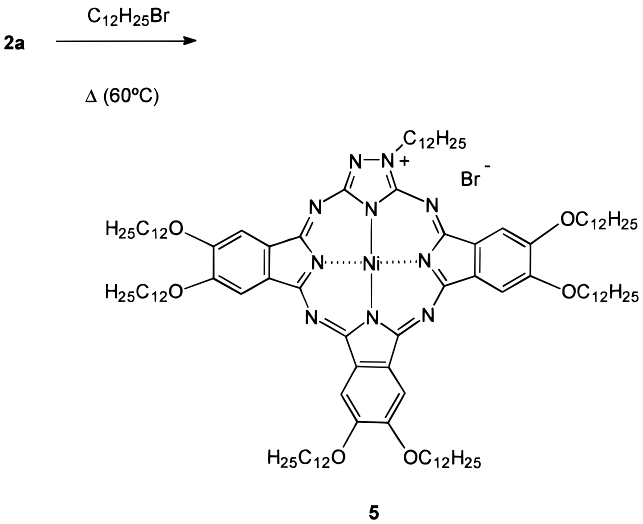
Scheme 2



Scheme 3



5

5 was prepared by alkylation reaction of the hexadodecyloxytriazolephthalocyanine **2a**[11] in the presence of an excess of dodecyl bromide with moderate yield (Scheme 3).

Although UV–vis spectra in CHCl$_3$ of **1**–**5** are qualitatively similar to those already described by us,[10–12] these spectra show a general batochromic shift of ca. 40 nm in the visible region. Bands also appear broadened. These effects have been associated with both aggregation phenomena and the influence of the six alkoxy-substituents of the isoindole subunits (donating groups) in the π-electronic distribution of the Tpc core.

The broad signals that appeared in the ^{1}H NMR spectra of **1a**, **4**, and **6** also support the presence of aggregates in solution. In the same way, the chemical shifts of the aromatic protons are lower than expected (7.4–6.4 ppm), probably due to the stronger shielding experienced by the protons in a position ortho to the alkoxy substituents. This effect has already been observed for less-substituted alkoxytriazolephthalocyanines.[10]

The IR spectra of the triazolephthalocyanines **1**–**5** are characteristic of a Tpc[10] with a strong absorption band at ca. 1500 cm^{-1} attributed to C=N stretching vibrations. The main difference between cationic Tpc **5** and the related Tpc **2a** is observed in the IR spectra, where the intensity of the bands at 1610 and 1530 cm^{-1}(weak) enlarges for the alkylated compound **5**.

Optical Microscopy and DSC. *Compounds **1a**, **1b**, **2a**, and **2b**.* When observed with a microscope at room temperature, **1a**, **1b**, **2a**, and **2b** offer some resistance to a shear stress applied to the coverslip as if they were solid phases; however, they leave a pasty birefringent trace as expected for a highly viscous phase. No changes occur when the samples are heated between room temperature and about 400 °C. The nonoccurrence of transition to an isotropic liquid precludes the formation of a well-developed microscopic texture when viewed between crossed polarizers.

The DSC thermogram of **1a** shows only a broad exothermic peak between 174 and 220 °C, with the maximum at 199 °C and an enthalpy value of −5.4 J g^{-1}. This peak is only observed in the first heating scan. By thermogravimetry, a mass loss of 1.3% takes place between about 170 and 220 °C with a maximum mass loss rate at about 190 °C. This percentage corresponds to the loss of one molecule of coordinated water per molecule of triazolephthalocyanine complex.

The DSC curve of **1b** exhibits a sharp endothermic peak at 186 °C (onset temperature) with an enthalpy value of 11.0 J g^{-1}. This transition is not observed on cooling and in subsequent scans. Given its endothermic nature, this peak might well correspond to a nonreversible transition from the room temperature state to a more disordered phase.

The DSC thermogram of **2b** contains a very broad endothermic hump between 68 (onset temperature) and 160 °C, with a maximum at 111 °C. This peak is not observed in the cooling process, but it reappears when the sample is heated again after several days. The features of this maximum seem to correspond to some kind of reversible molecule rearrangement.

*Compounds **3** and **4**.* **3** and **4** are solid at room temperature. When heated in the microscope, the melting process is not fast, but it takes an interval of several degrees to occur and is observed as a gradual softening of the sample, which finally melts into a viscous isotropic liquid. When cooled, no optical changes are observed, but at a given temperature, the sample solidifies without developing birefringent texture and remains optically isotropic.

In DSC, **3** shows two endothermic peaks in the heating process at 45 (3.5 J g^{-1}) and 72 °C (1.7 J g^{-1}). The latter seems to correspond to the isotropization observed by microscopy. In the cooling scan, an exothermic peak is observed at 51 °C (2.2 J g^{-1}) that could correspond to some crystallization.

4 yields a single DSC peak at 137 °C (18.9 J g^{-1}) that does not correspond to any change observable under the microscope, as the transition to the isotropic liquid is observed by microscopy at higher temperature (near 200 °C). The DSC peak is not observed in either the cooling process nor subsequent cycles.

*Compound **5**.* **5** is a solid at room temperature, and no changes are observed with a microscope up to about 350 °C. In accordance with this, no peaks are detected in the DSC experiments between 0 and 350 °C.

X-ray Diffraction. *Compounds **1a**, **1b**, **2a**, and **2b**.* Patterns of **1a**, **1b**, **2a,** and **2b** were registered at room temperature for both virgin samples and thermally treated samples. The virgin samples of the four compounds yield X-ray patterns characteristic of a hexagonal columnar (Col_h) mesophase (Table 1). This is revealed by the presence of a set of low-angle maxima characteristic of the hexagonal packing of columns. In addition to this, two diffuse haloes are detected in all the patterns, one of them at 4.5−4.6 Å, characteristic of the conformationally disordered hydrocarbon chains, and the other one at 3.35−3.45 Å, characteristic of the mean intracolumnar distance between stacked molecules. The absence of any other maximum excludes the existence of three-dimensional order and thus confirms the mesomorphic nature of these compounds at room temperature. After heating to 200−220 °C and cooling to room temperature, the samples yielded X-ray figures very similar to those taken on the virgin samples, indicating that the structure remained hexagonal columnar. Nevertheless, in compounds **1a** and **1b**, there is a variation in the hexagonal lattice constant *a* (Table 1), which confirms the structural changes suggested by the DSC studies. For **1a**, an X-ray pattern was taken also at 200 °C, that indicates that the mesophase remains at high temperatures. The hexagonal lattice constant determined at high temperature is the same, within the experimental error, as that determined on the thermally treated sample. This is consistent with the nonreversible loss of coordinated water at about 190 °C, that produces a change in the mesophase parameters.

Table 1. X-ray Diffraction Data for the Mesophase of Compounds: Experimental Conditions, Type of Phase, Proposed Indexing, Measured and Calculated Spacings, and Lattice Constant

compd	cond.	phase	*h k l*	d_{obs} (Å)	d_{calcd} (Å)	lattice const. (Å)
1a	virgin	Col_h	1 0 0	26.8	26.76	$a = 30.9$
			1 1 0	15.4	15.45	
				4.5 (broad)		
				3.45 (broad)		
	treated	Col_h	1 0 0	27.6	27.71	$a = 32.0$
			1 1 0	16.1	16.00	
				4.6 (broad)		
				3.45 (broad)		
	200 °C	Col_h	1 0 0	27.5	27.54	$a = 31.8$
			1 1 0	15.9	15.90	
1b	virgin	Col_h	1 0 0	28.9	28.93	$a = 33.4$
				4.5 (broad)		
				3.35 (broad)		
	treated	Col_h	1 0 0	28.2	28.23	$a = 32.6$
				4.5 (broad)		
				3.35 (broad)		
2a	virgin	Col_h	1 0 0	31.4	31.26	$a = 36.1$
			1 1 0	18.1	18.05	
			2 0 0	15.5	15.63	
				4.6 (broad)		
				3.45 (broad)		
	treated	Col_h	1 0 0	31.3	31.26	$a = 36.1$
				4.6 (broad)		
				3.45 (broad)		
2b	virgin	Col_h	1 0 0	32.2	32.22	$a = 37.2$
				4.6 (broad)		
				3.4 (broad)		
	treated	Col_h	1 0 0	32.4	32.48	$a = 37.5$
			1 1 0	18.9	18.75	
			2 0 0	16.1	16.24	
				4.6 (broad)		
				3.4 (broad)		
4	virgin	Col_h (glassy)	1 0 0	27.4	27.37	$a = 31.6$
				4.5 (broad)		
				3.45 (broad)		
	treated	Col_h (glassy)	1 0 0	27.4	27.37	$a = 31.6$
			1 1 0	15.8	15.80	
				4.5 (broad)		
				3.4 (broad)		
	145 °C	Col_h (glassy)	1 0 0	27.6	27.63	$a = 31.9$
			1 1 0	16.0	15.95	

*Compounds **3** and **4**.* The X-ray patterns of **3** taken both in the virgin and in the treated sample (cooled from 125 °C) are characteristic of a crystalline structure and not of a mesophase. **4** (virgin sample) yielded a difficult-to-interpret X-ray pattern containing a low number of weak or diffuse maxima, which indicates a high degree of disorder. On the other hand, the solid obtained by cooling the isotropic liquid yielded a pattern characteristic of a columnar hexagonal mesophase (Table 1). In the microscopic examinations, the compound does not flow under a shear stress; therefore, it is concluded that we are dealing with a glass that possesses the structure of a mesophase, i.e., a frozen hexagonal columnar mesophase. Although the nature of the virgin solid is not as clear as that of the thermally treated sample, its X-ray pattern is also consistent with a columnar structure (Table 1). To know if the DSC peak detected at 137 °C corresponds to a phase transition, an X-ray pattern was taken at 145 °C. The pattern is characteristic of a hexagonal columnar structure with approximately the same lattice constant as at room temperature, and thus it is concluded that the DSC peak does not correspond to a phase transition.

*Compound **5**.* The X-ray patterns taken on **5** indicate the crystalline nature of the pristine compound as well as that of a thermally treated sample. However, there is a high degree of disorder, as revealed by the presence of few, weak maxima and diffuse haloes.

Conclusions

Although the nature of the inner central metal (Ni, Cu) does not influence the liquid-crystal properties (see **1a**, **1b**, **2a**, and **2b**), different behavior is observed for **1**−**5** depending upon the nature of the peripheral chains they possess.

Hexaalkoxy-derivatives **1a**, **1b**, **2a**, and **2b** show room temperature mesophases with a high viscosity. Because of their high clearing points, isotropic liquid phases could not be obtained for either of them in the microscope under our experimental conditions. Therefore, because well-developed pictures are only obtained when an isotropic liquid is cooled into the mesophase, mesophases of **1a**, **1b**, **2a**, and **2b** did not exhibit characteristic textures in the polarizing microscope. However, the X-ray experiments unambiguously reveal that the mesophases are columnar hexagonal ($\mathrm{Col_h}$).

The formal replacement of two alkoxy chains with two branched (dioctylaminocarbonyl)methoxy groups (**4**) has two main effects. First, it decreases the clearing point (up to 200 °C), as has already been observed when introducing branched substituents in phthalocyanines.[6b,17] This must be related to the increase of disorder that branching induces. Second, **4** presents a glassy hexagonal mesophase at room temperature. On cooling, the isotropic liquid transforms directly into a mesomorphic glass and not into a fluid mesophase. This sudden freezing of molecule mobility precludes once more the development of texture in the polarizing microscope. The glassy nature of **4** means that the molecules preserve the arrangement shown by **1a**, **1b**, **2a**, and **2b** although they have lost their mobility.

Interestingly, when the six alkoxy chains of **1a**, **1b**, **2a**, and **2b** are formally replaced with six (dioctylaminocarbonyl)methoxy groups, that is, six branched chains, to yield **3**, no mesomorphism is detected, the molecules adopting a crystalline form. Moreover, the isotropization point is still decreased, and the compound melts at about 72 °C.

The trends observed while going from **1a**, **1b**, **2a**, and **2b** to **4** and then to **3** indicate that replacing alkoxy by dialkylamide groups progressively suppresses mesomorphism in triazolephthalocyanines. This is consistent with our results in a previous work[8] on triazolehemiporphyrazines and is related to the steric hindrance promoted by dialkylamide groups, which disrupts the stacking into columns of the macrocycle cores. Similar results were found by other authors in phthalocyanines substituted with alkyl groups, in which branching of the chains near the core suppresses mesomorphism.[18] Furthermore, it should be pointed out that in our compounds the presence of a very polar amide group must affect the intermolecular forces. In particular, it seems that this effect tends to stabilize a crystalline packing rather than a liquid-crystal arrangement. In contrast, dialkylamidephthalocyanines also studied by us[6b] exhibit hexagonal columnar mesophases at room temperature, thus indicating that such a substitution pattern is not an inconvenience for obtaining liquid-crystalline properties in phthalocyanines. These observations point out some differences in the liquid-crystalline behavior between, on one side, octasubstituted phthalocyanines, which present an appropriate balance between the aromatic central core and the paraffinic surrounding tails, and, on the other side, triazolephthalocyanines and triazolehemiporphyrazines. The central core being smaller in triazole-containing macrocycles, the adequate balance between the tendency of the cores to stack and the tendency of the flexible chains to discorrelate the columns becomes more critical when intending to obtain liquid crystals.

5 is crystalline throughout the temperature range studied (up to 350 °C). The absence of mesomorphism in this compound can be accounted for by its ionic nature, which increases the melting point up to a temperature range incompatible with mesomorphism.

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