Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 1319–1328 **1319**
DOI: 10.1021/ma902460c

Synthesis and Optical/Thermal Behavior of New Azo Photoisomerizable Discotic Liquid Crystals

Eduard Westphal,[†] Ivan H. Bechtold,[‡] and Hugo Gallardo*,[†]

[†]*Departamento de Química and* [‡]*Departamento de Física, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil*

Received November 6, 2009; Revised Manuscript Received December 21, 2009

ABSTRACT: In this study, discotic azo compounds were prepared by a reductive coupling of 5-nitroisophthalic acid followed by a convergent synthesis, resulting in five new examples of azo photoisomerizable discotic molecules, which differ from each other by the linking groups (ester, amide or 1,3,4-oxadiazole) and number of aliphatic chain (4 or 8). The thermal and liquid crystalline properties of the compounds were completely characterized by differential scanning calorimetry, polarized optical microscopy and X-ray diffraction analysis. Two products presented a stable columnar hexagonal mesophase with 95 and 134 °C of range. The results obtained show that the choice of the linking group and number of aliphatic chains has a significative influence in the materials properties. The photoisomerization capacity was evaluated in solution by spectroscopic methods and also by ^{1}H NMR, indicating that these molecules are promising candidates for controlling the conductivity in electro-optical devices.

1. Introduction

In the past few years, considerable attention has been directed toward creating new types of materials whose microscopic and macroscopic properties can be controlled by means of an external stimuli[1] such as an electric field, magnetic field, temperature, and even light.[2] The possibility for control at multiple length scales makes liquid crystals ideal candidates for their use as active components or scaffolds in self-assembly processes. Discotic liquid crystal (DLC) molecules consisting of a disk-shaped aromatic core substituted at its peripheral positions with flexible alkyl or alkoxy chains exhibit mesomorphism, including columnar, discotic nematic, and chiral discotic phases. These types of materials have been attracting increasing interest from the industrial and technological point of view because of their unique self-assembled structures and their particular anisotropic physical properties, including electronic conductivity, photoconductivity and photovoltaic properties,[3−5] and also photoluminescence and electroluminescence,[6] which are promising for applications in electrical and optical molecular devices. Furthermore, this approach offers an easy means to achieving fine control of the material properties, possibly increasing the range of applications.

These features are all possible due to an easy and varied form of functionalization, in which other properties (like luminescence, ionic charges, photoisomerization, gelification and others)[7] can be incorporated into a material that has a natural and fascinating self-assembly allied with fluidity.[8] Recently, discotic liquid crystals have gained considerable attention as organic semiconductors, due to their excellent charge carrier mobility.[9] As a result of containing an aromatic and rigid center (conducting core) surrounded by peripheral aliphatic chains (isolating layer), these compounds are known as molecular nano wires, being capable of preferential one-dimensional charge migration.[10]

But the questions of how to obtain control of the intensity of the conductivity and how to connect and disconnect the nanowire remain unanswered. In the case of discotic liquid crystals, this is possible by breaking the columnar organization of the mesophases by melting the compound to its liquid state through a heating process.[3,11] Another way would be to reduce the molecular disk anisometry, a factor that is fundamental to obtaining this kind of organization. To do this, we can use an azo (N═N) linkage which is well-known by the reversible *trans*−*cis*−*trans* photoisomerization,[12] resulting in a material with the behavior schematically presented in Figure 1.

As can be seen, when the molecule is in the *trans* configuration, the high discotic anisometry promotes a columnar organization, in this case, a columnar hexagonal mesophase. After the photoisomerization to the *cis* configuration and consequent lost of the anisometry, this material becomes an isotropic liquid, the organization of which can be restored after the reverse isomerization.[13]

To this aim, we set out to synthesize five new molecules with discotic anisometry and containing an azo linkage in their centers. Besides these requirements, we used different kinds of functional groups and numbers of aliphatic chains (Figure 2). It is important to note that, in this study, we aimed to obtain an unusual type of discotic liquid crystal, where the center of the structure is not really rigid, being able to rotate through the binding axis. There are not many examples of this type of discotic liquid crystals in the literature.[14] Also, there are no reports of discotic liquid crystals containing an azo linkage in the core of the molecule, only at the periphery.[15]

2. Experimental Section

2.1. Materials and Characterizations. 5-Nitroisophthalic acid (98%, Acros Organics), hydroquinone (≥99%, Merck), 1-bromododecane (98%, Acros Organics), catechol (99+%, Acros Organics), 4-hydroxyacetanilide (98%, Aldrich) and 3,4-dihydroxybenzonitrile (97%, Aldrich). All other inorganic, organic and solvents were of the highest purity and purchased from commercial sources (Merck, Aldrich, Fluka and Acros) and used as received. Dry pyridine and CH_2Cl_2 were used when specified. Pyridine was dried by distillation over KOH while CH_2Cl_2 was dried using calcium hydride. TLC was carried out

*Corresponding author. Telephone: + 55 48 37219544. Fax: + 55 48 37216850. E-mail: hugo@qmc.ufsc.br.

Published on Web 01/14/2010

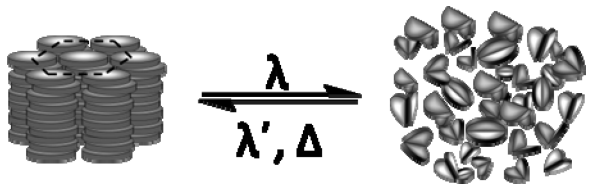


Figure 1. Breaking discotic mesophase by photoisomerization.

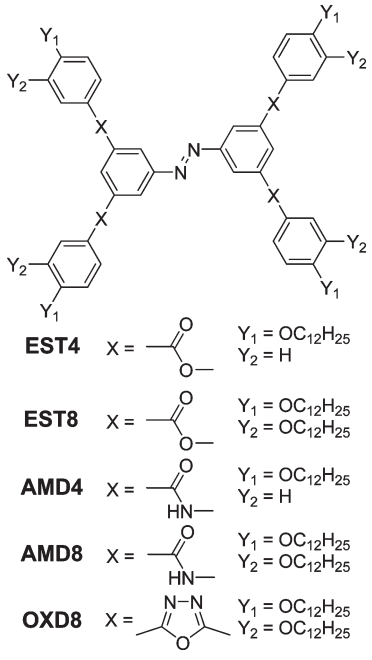


Figure 2. Discotic molecules synthesized. The compounds nomenclature following norm: EST for molecules containing ester groups; AMD for amide groups; OXD for 1,3,4-oxadiazole units; 4 or 8 for the number of alkoxy chains.

using silica-gel Si 60-F254 (Merck). Purifications were carried out by recrystallization using commercial grade solvents and by column chromatography on silica-gel 60−200 mesh 60A (Acros). Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer using KBr discs. ^{1}H and ^{13}C NMR were recorded with a Varian Mercury Plus spectrometer operating at 400 and 100.6 MHz, respectively. Melting points were determined with an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 Hot Stage. Elemental Analysis was carried out using a Carlo Erba model E-1110 instrument. A low resolution mass spectrum was recorded on a Shimadzu model GCMS-QP5050A triple quadrupole mass spectrometer.

(*E*)-*5,5′-(Diazene-1,2-diyl)diisophthalic Acid* (***1***). In a beaker, 8.96 g (49.7 mmol) of dextrose and 30 mL of water were added and heated to 60 °C in a water bath. This solution was added dropwise to a beaker containing 5.00 g (23.7 mmol) of 5-nitroisophthalic acid, 5.69 g (142 mmol) of NaOH, and 100 mL of water under a strong magnetic stirring and also heated to 60 °C in a water bath. After the addition, the water bath was kept under strong stirring for 8 h at 60 °C and 10 h at room temperature. The suspension then was filtered and the resultant yellow solid dissolved in water. The solution was acidified with acetic acid and the precipitate formed was filtered and washed with a lot of water. The solid obtained was stirred in boiling water until the color of the suspension turned to a strong orange. Finally, the solution was filtered while still hot and dried in air to afford 2.59 g (61%) of an orange solid. Mp: > 350 °C. IR (KBr): 3419 (COO-H), 3077, 2993, 2854, 2664, 2590, 1706 (C═O), 1683, 1650, 1605, 1460, 1420, 1403, 1301, 1261, 1219, 1109, 930, 759, 741, 685. ^{1}H NMR (DMSO-d_6) δ ppm: 8.57 (d, J = 1.6 Hz, 4H, 4,6-H isoph.), 8.59 (t, J = 1.6 Hz, 2H, 2-H isoph.), 13.59 (broad, 4H, −COOH). ^{13}C NMR (DMSO-d_6) δ ppm: 127.64, 133.18, 133.47, 152.37, 166.52. Elemental analysis for $C_{16}H_{10}N_2O_8$: Calcd: C, 53.64; H, 2.81; N, 7.82. Found: C, 53.78; H, 2.56; N, 7.73. MS (EI, 70 eV) m/z (%): [M$^+$] 358.4 (5.9%).

4-Dodecyloxyphenol (***2***). This was prepared through a modified procedure given in the literature.[16] First, 44.0 g (400 mmol) of hydroquinone, 32.0 mL (133 mmol) of 1-bromododecane, 5.92 g (148 mmol) of NaOH, 500 mL of methanol, and 40 mL of water were mixed and refluxed for 10 h, after which the solvent was evaporated. The dark gray solid was transferred to a beaker containing 700 mL of water and the solution was acidified to pH 3 using concentrated hydrochloric acid. The resulting solid was then macerated in hot water (60 °C) 3 times. A final recrystallization in hexane gave 37.0 g of the desired material (55%). Mp: 73.7−75.2 °C (lit. 76−77 °C).[17] IR (KBr): 3376 (O−H), 2920, 2851, 1515, 1458, 1373, 1240, 1109, 1028, 826. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.25−1.36 (m, 16H, $-CH_2-$), 1.43 (m, 2H, $-CH_2-$), 1.75 (qui, J = 6.6 Hz, 2H, $-CH_2CH_2O-$), 3.89 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 6.77 (m, 4H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.11, 22.68, 26.04, 29.34, 29.36, 29.41, 29.57, 29.59, 29.62, 29.65, 31.91, 68.71, 115.57, 115.94, 149.26, 153.32.Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 78.15; H, 10.06.

1,2-Didodecyloxybenzene (***3***). Prepared through a modified procedure given in the literature.[18] First, 20.00 g (181.6 mmol) of catechol, 113.0 mL (472 mmol) of 1-bromododecane, 75.0 g (545 mmol) of K_2CO_3, 2.0 g (12 mmol) of KI, and 400 mL of butanone were refluxed under argon atmosphere for 16 h. The suspension was then filtered and washed 2 times with hot butanone. The solvent was removed by rotary evaporation and the solid obtained was dissolved in ethylic ether and washed with water (2 × 100 mL). The organic phase was dried with anhydrous Na_2SO_4 and the solvent removed. After recrystallization from ethanol 42.3 g of a white solid (52%) was obtained. Mp: 45.8−48.1 °C (lit. 47−49 °C).[18] IR (KBr): 2953, 2916, 2848, 1594, 1518, 1509, 1466, 1258, 1222, 1122, 731. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.25−1.37 (m, 32H, $-CH_2-$), 1.46 (m, 4H, $-CH_2-$), 1.81 (qui, J = 6.6 Hz, 4H, $-CH_2CH_2O-$), 3.99 (t, J = 6.6 Hz, 4H, $-CH_2O-$), 6.88 (s, 4H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.36, 22.93, 26.29, 29.58, 29.61, 29.69, 29.88, 29.90, 29.95, 32.16, 69.50, 114.31, 121.20, 149.44.

1-Acetyl-3,4-didodecyloxybenzene (***4***). Under argon atmosphere and vigorous stirring, 10.0 g (22.2 mmol) of 1,2-didocecyloxybenzene (**3**) was dissolved in 50 mL of dry CH_2Cl_2 and the solution was cooled to below −5 °C. In small portions, 3.56 g (26.7 mmol) of $AlCl_3$ were then added, maintaining the solution temperature below −5 °C throughout. After 10 min, 1.90 mL (26.7 mmol) of acetyl chloride was added dropwise taking care not to raise the temperature above 0 °C. After this addition, the solution was stirred at 0 °C for 30 min, refluxed for 2 h, and poured into 100 mL of water. To this mixture was carefully added 20 mL of concentrated hydrochloric acid. The organic solvent was evaporated, and the solid obtained was filtrated and recrystallized in ethanol, yielding 8.98 g (83%) of a white solid. Mp: 63.7−64.9 °C (lit. 65 °C).[19] IR (KBr): 2917, 2848, 1665 (C═O), 1582, 1521, 1468, 1425, 1275, 1216, 1153. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.25−1.38 (m, 32H, $-CH_2-$), 1.47 (m, 4H, $-CH_2-$), 1.85 (m, 4H, $-CH_2CH_2O-$), 2.55 (s, 3H, $-COCH_3$), 4.06 (m, 4H, $-CH_2O-$), 6.86 (d, J = 8.4 Hz, 1H, Ar−H), 7.51 (d, J = 1.9 Hz, 1H, Ar−H), 7.53 (dd, J = 8.4 Hz and 1.9 Hz, 1H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.35, 22.93, 26.19, 26.23, 26.46, 29.26, 29.38, 29.59, 29.64, 29.83, 29.85, 29.89, 29.93, 32.16, 69.25, 69.45, 111.73, 112.54, 123.41, 130.44, 149.03, 153.73, 197.19.

1-Acetoxyl-3,4-didodecyloxybenzene (***5***). Under nitrogen atmosphere, 8.78 g (18.0 mmol) of 1-acetyl-3,4-didodecyloxybenzene (**4**) was dissolved in 30 mL of dry CH_2Cl_2. After complete solubilization, 5.59 g (32.4 mmol) of MCPBA and a further 10 mL of dry CH_2Cl_2 were added, the mixture was cooled to

0 °C, and 1.80 mL (23.4 mmol) of trifluoroacetic acid was then added dropwise. After 30 min the solution was heated to room temperature and vigorously stirred in the dark and under nitrogen atmosphere for 48 h. After this period, 100 mL of a saturated solution of $NaHSO_3$ was slowly added and stirred for a further 30 min. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 40 mL). The combined organic phases were washed with a $NaHCO_3$ saturated solution (3 × 50 mL) and brine (1 × 50 mL) and dried with anhydrous Na_2SO_4. The solvent was removed and the solid obtained was purified by column chromatography using hexane/ethyl acetate (9:1) affording 6.84 g (75%) of a white solid. Mp: 53.4−55.1 °C (lit. 54 °C).[19] IR (KBr): 2955, 2927, 2873, 2849, 1759 (C═O), 1600, 1517, 1468, 1233, 1206, 1019. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.23−1.36 (m, 32H, $-CH_2-$), 1.45 (m, 4H, $-CH_2-$), 1.78 (m, 4H, $-CH_2CH_2O-$), 2.27 (s, 3H, $-OCOCH_3$), 3.95 (m, 4H, $-CH_2O-$), 6.59 (dd, J = 8.6 Hz and 2.7 Hz, 1H, Ar−H), 6.61 (d, J = 2.7 Hz, 1H, Ar−H), 6.84 (d, J = 8.6 Hz, 1H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.36, 22.93, 26.19, 26.23, 26.46, 29.26, 29.39, 29.60, 29.64, 29.84, 29.86, 29.89, 29.93, 32.16, 69.26, 69.46. 111.74, 112.55, 123.42, 130.45, 149.04, 153.75.

3,4-Didodecyloxyphenol (***6***). First, 6.45 g (12.8 mmol) of 1-acetoxyl-3,4-didodecyloxybenzene (**5**) and 100 mL of methanol were heated to reflux, and 5.0 mL of concentrated hydrochloric acid was slowly added. The reflux was maintained until complete conversion of the reagent as verified by TLC (approximately 7 h). The solvent was then removed and the crude solid obtained dissolved in chloroform. The organic phase was washed with distilled water (2 × 100 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated. Recrystallization on hexane afforded 5.49 g (93%) of a light-gray solid. Mp: 81.2−83.5 °C (lit. 78 °C).[19] IR (KBr): 3290 (O−H), 2919, 2849, 1610, 1516, 1464, 1379, 1222, 1167, 1130, 824. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.6 Hz, 6H, CH_3), 1.24−1.35 (m, 32H, $-CH_2-$), 1.44 (m, 4H, $-CH_2-$), 1.77 (m, 4H, $-CH_2CH_2O-$), 3.92 (m, 4H, $-CH_2O-$), 5.30 (br, 1H, Ar−OH), 6.30 (dd, J = 8.6 Hz and 2.3 Hz, 1H, Ar−H), 6.44 (d, J = 2.3 Hz, 1H, Ar−H), 6.75 (d, J = 8.6 Hz, 1H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.36, 22.93, 26.28, 29.43, 29.61, 29.66, 29.72, 29.76, 29.88, 29.95, 32.16, 69.21, 71.04, 102.47, 106.33, 116.60, 153.18, 150.69, 150.77. Anal. Calcd for $C_{30}H_{54}O_3$: C, 77.87; H, 11.76. Found: C, 77.61; H, 11.88.

4-Dodecyloxyacetanilide (*7*). First, 4.00 g (26.5 mmol) of 4-hydroxyacetanilide, 9.6 mL (40 mmol) of 1-bromododecane, 7.31 g (53 mmol) of K_2CO_3 and 80 mL of butanone were mixed and refluxed for 24 h. The suspension was then filtered and washed 2 times with hot butanone. The solvent was removed by rotary evaporation and the solid obtained recrystallized from heptane to afford 8.3 g of a white solid (98%). Mp: 92.1−94.3 °C. IR (KBr): 3312 (CON−H), 2921, 2849, 1661 (C═O), 1608, 1548, 1509, 1466, 1406, 1368, 1307, 1237, 1170, 1030, 826. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.25−1.35 (m, 16H, $-CH_2-$), 1.43 (m, 4H, $-CH_2-$), 1.76 (qui, J = 6.6 Hz, 2H, $-CH_2CH_2O-$), 2.17 (s, 3H, $-COCH_3$), 3.91 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 6.83 (d, J = 9.0 Hz, 2H, Ar−H), 7.37 (d, J = 9.0 Hz, 2H, Ar−H), 7.47 (br, 1H, Ar−NH−). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.36, 22.93, 26.26, 29.50, 29.58, 29.63, 29.81, 29.83, 29.87, 29.89, 32.15, 68.52, 114.99, 121.21, 130.78, 156.36, 168.67, 187.46.

4-Dodecyloxyaniline (***8***). A 5.00 g (15.7 mmol) sample of 4-dodecyloxyacetanilide (**7**) and 50 mL of H_2O were heated to reflux and 25.0 mL of concentrated hydrochloric acid was slowly added. The reflux was maintained for 24 h. After this period, the solution was basified with NaOH aqueous solution (1M) and the suspension filtered and washed with plenty of water. The solid obtained was air-dried, affording 4.3 g (99%). Purification was not necessary. Mp: 56.2−58.3 °C. IR (KBr): 3383 and 3312 (N−H prim.), 2918, 2851, 1610, 1516, 1468, 1390, 1248. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.25−1.35 (m, 16H, $-CH_2-$), 1.43 (m, 2H, $-CH_2-$), 1.74 (qui, J = 6.6 Hz, 2H, $-CH_2CH_2O-$), 3.88 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 6.64 (d, J = 8.8 Hz, 2H, Ar−H), 6.74 (d, J = 8.8 Hz, 2H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.37, 22.93, 26.30, 29.59, 29.67, 29.83, 29.85, 29.88, 29.90, 32.16, 68.94, 115.88, 116.67, 139.96, 152.58. Anal. Calcd for $C_{18}H_{31}NO$: C, 77.92; H, 11.26; N, 5.05. Found: C, 77.46; H, 11.24; N, 4.85.

3,4-Didodecyloxynitrobenzene (***9***). This was prepared through a modified procedure given in the literature.[18] First, 4.46 g (10.0 mmol) of 1,2-didodecyloxybenzene (**3**), 0.097 g (1.4 mmol) of $NaNO_2$ and 20 mL of dichloromethane were mixed and cooled to −5 °C, and 2.0 mL of HNO_3 (70%) was added dropwise. The solution was then stirred for 5 min at −5 °C and 1 h at room temperature and was then poured into 100 mL of cold distilled water. The organic phase was extracted with CH_2Cl_2 (4 × 100 mL). The combined organic phases were washed with $NaHCO_3$ saturated solution (1 × 100 mL), H_2O (2 × 100 mL), and brine (1 × 100 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the solid was recrystallized over ethanol, yielding 3.7 g (75%) of an off-white solid. Mp: 72.5−74.8 °C (lit. 73 - 75 °C).[18] IR (KBr): 2955, 2915, 2848, 2363, 1585, 1519, 1497, 1466, 1402, 1350, 1284, 1233, 1140, 1100, 994, 876, 744. ^{1}H NMR ($CDCl_3$) δ ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.23−1.38 (m, 32H, $-CH_2-$), 1.47 (m, 4H, $-CH_2-$), 1.85 (m, 4H, $-CH_2CH_2O-$), 4.07 (m, 4H, $-CH_2O-$), 6.87 (d, J = 8.8 Hz, 1H, Ar−H), 7.73 (d, J = 2.7 Hz, 1H, Ar−H), 7.87 (dd, J = 8.8 Hz and 2.7 Hz, 1H, Ar−H). ^{13}C NMR ($CDCl_3$) δ ppm: 14.37, 22.93, 26.14, 26.18, 29.13, 29.17, 29.57, 29.59, 29.61, 29.84, 29.90, 29.92, 32.16, 69.64, 69.68. 108.21, 111.20, 117.90, 141.37, 148.85, 154.90.

3,4-Didodecyloxyaniline (***10***). In a appropriate hydrogenation flask, 2.3 g (4.7 mmol) of 3,4-didodecyloxynitrobenzene (**9**) was added together with 100 mL of THF and 0.5 g of 10% Pd/C catalyst. The hydrogenation process was maintained for 20 h. After this period the catalyst was removed by filtration, the solvent evaporated and the crude product purified by column chromatography using hexane/ethyl acetate (9:1) as the eluent, obtaining 2.03 g (93%) of a gray solid. Mp: 52.7−53.6 °C (lit. 56 - 58 °C).[18] IR (KBr): 3301 and 3208 (N−H prim.), 2917, 2849, 1594, 1523, 1468, 1389, 1279, 1231, 1185, 1121, 1070, 998, 824, 790, 720, 604. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.24−1.34 (m, 32H, $-CH_2-$), 1.44 (m, 4H, $-CH_2-$), 1.76 (m, 4H, $-CH_2CH_2O-$), 3.91 (m, 4H, $-CH_2O-$), 6.20 (dd, J = 8.4 Hz and 2.7 Hz, 1H, Ar−H), 6.30 (d, J = 2.7 Hz, 1H, Ar−H), 6.73 (d, J = 8.4 Hz, 1H, Ar−H). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.36, 22.93, 26.31, 29.56, 29.61, 29.68, 29.74, 29.85, 29.88, 29.91, 29.95, 32.17, 69.18, 71.19, 102.86, 107.05, 117.53, 141.36, 142.19, 150.82. Anal. Calcd for $C_{30}H_{55}NO_2$: C, 78.03; H, 12.01; N, 3.03. Found: C, 77.72; H, 11.86; N, 2.96.

3,4-Didodecyloxybenzonitrile (***11***). First, 5.07 g (37.0 mmol) of 3,4-dihydroxybenzonitrile, 22.0 mL (92.5 mmol) of 1-bromododecane, 25.19 g (181.2 mmol) of K_2CO_3, 0.49 g (1.55 mmol) of TBAB, and 150 mL of butanone were mixed and refluxed for 31 h. After this period, the suspension was filtered and washed with hot butanone. The solvent was removed and the obtained solid dissolved in dichloromethane. The organic phase was washed with NaOH (5%) (1 × 50 mL), HCl (5%) (1 × 50 mL), and H_2O (1 × 50 mL) and dried over anhydrous N_2SO_4. The solid obtained after removal of the solvent was recrystallized over acetonitrile, affording 15.8 g (91%) of a white solid. Mp: 79.8−82.8 °C (lit. 81−83 °C).[20] IR (KBr): 2954, 2918, 2872, 2849, 2221 (C≡N), 1597, 1581, 1519, 1468, 1422, 1280, 1244, 1139, 992, 812, 722. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (t, J = 6.7 Hz, 6H, CH_3), 1.25−1.36 m, 32H, $-CH_2-$), 1.46 (m, 4H, $-CH_2-$), 1.83 (m, 4H, $-CH_2CH_2O-$), 3.98 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 4.02 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 6.86 (d, J = 8.4 Hz, 1H, Ar−H), 7.07 (d, J = 1.9 Hz, 1H, Ar−H), 7.23 (dd, J = 8.4 Hz and 1.9 Hz, 1H, Ar−H). ^{13}C NMR (DMSO-d_6, −90 °C), δ, ppm: 12.31, 20.59, 24.07, 27.23, 27.27, 27.51, 27.56, 27.61, 29.87, 67.61, 68.05, 107.97, 112.88, 115.84, 117.59, 125.13, 147.72, 151.81.

5-(3,4-Didodecyloxyphenyl)tetrazole (***12***). First, 5.00 g (10.6 mmol) of 3,4-didodecyloxybenzonitrile (**11**), 2.07 g (31.8 mmol) of NaN_3, 1.70 g (31.8 mmol) of NH_4Cl, and 30 mL of DMF were mixed and refluxed for 24 h. After this period, the suspension was cooled to room temperature and poured into 200 mL of ice/water and acidified to pH 3 with an HCl aqueous solution (10%). The solid obtained was filtered, washed with plenty of water and recrystallized over acetone, affording 5.05 g (93%) of an off-white solid. Mp: 157.8−159.0 °C. IR (KBr): 2921, 2848, 2744, 2613, 1607, 1512, 1465, 1272, 1239, 1133, 1039, 812, 746. ^{1}H NMR (pyridine-d_5), δ, ppm: 0.86 (t, J = 6.7 Hz, 6H, CH_3), 1.25 (m, 32H, $-CH_2-$), 1.47 (m, 4H, $-CH_2-$), 1.80 (m, 4H, $-CH_2CH_2O-$), 3.96 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 4.05 (t, J = 6.6 Hz, 2H, $-CH_2O-$), 7.16 (s, 1H partially overlapped with solvent signal, Ar−H), 7.95 (s, 1H, Ar−H), 7.98 (s, 1H, Ar−H). ^{13}C NMR (DMSO-d_6, −90 °C), δ, ppm: 14.35, 22.64, 26.22, 29.29, 29.40, 29.63, 31.92, 69.72, 70.04, 114.02, 115.44, 117.76, 121.28, 150.05, 152.22. Anal. Calcd for $C_{31}H_{54}N_4O_2$: C, 72.33; H, 10.57; N, 10.88. Found: C, 72.61; H, 10.39; N, 10.43.

General Procedure for the Synthesis of the Target Products. In a round-bottomed flask equipped with a condenser and a drying tube was inserted 0.25 g (0.70 mmol) of the (*E*)-5,5′-(diazene-1,2-diyl)diisophthalic acid (**1**), 5 mL of $SOCl_2$ and 1 drop of DMF were placed inside, and the mixture was refluxed for 18 h. After the remaining $SOCl_2$ was removed by vacuum distillation. After this, 4.2 equiv of the desired intermediate (**2**, **6**, **8, 10**, or **12**) were added together with 20 mL of dry pyridine and the mixture refluxed for a further 48 h. The solution was then cooled to room temperature and poured into 300 mL of ice/water. The precipitate was filtered, washed with plenty of water, and purified.

(*E*)-*Tetrakis*(*4-dodecyloxyphenyl*) *5,5′-*(*Diazene-1,2-diyl*)*-diisophthalate* (***EST4***). The product was macerated over hot ethanol and recrystallized over toluene, affording 0.88 g (90%). Mp: 166.9−167.8 °C. IR (KBr): 2953, 2918, 2872, 2850, 1752 and 1740 (C═O), 1509, 1468, 1243, 1156, 830, 744. ^{1}H NMR (C_6D_6, −60 °C), δ, ppm: 0.92 (t, J = 6.7 Hz, 12H, CH_3), 1.23−1.35 (m, 64H, $-CH_2-$), 1.41 (m, 8H, $-CH_2-$), 1.67 (qui, J = 6.6 Hz, 8H, $-CH_2CH_2O-$), 3.69 (t, J = 6.6 Hz, 8H, $-CH_2O-$), 6.83 (d, J = 9.2 Hz, 8H, Ar−H), 7.14 (d, J = 9.2 Hz, 8H, Ar−H), 9.12 (d, J = 1.6 Hz, 4H, 4,6-H isoph.), 9.36 (t, J = 1.6 Hz, 2H, 2-H isoph.). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.37, 22.93, 26.28, 29.50, 29.59, 29.63, 29.62, 29.84, 29.88, 29.90, 32.16, 68.69, 115.42, 122.32, 122.46, 129.21, 132.03, 144.14, 152.71, 157.41, 164.21. Anal. Calcd for $C_{88}H_{122}N_2O_{12}$: C, 75.50; H, 8.78; N, 2.00. Found: C, 75.52; H, 9.05; N, 2.10.

(*E*)-*Tetrakis*(*3,4-didodecyloxyphenyl*) *5,5′-*(*Diazene-1,2-diyl*)*-diisophthalate* (***EST8***). The product was recrystallized twice over 2-propanol, affording 1.10 g (73%). Mp: 153.8−154.9 °C. IR (KBr): 2955, 2923, 2870, 2850, 1739 (C═O), 1605, 1509, 1468, 1427, 1391, 1261, 1215, 1183, 1125. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.87 (t, J = 6.7 Hz, 24H, CH_3), 1.20−1.35 (m, 128H, $-CH_2-$), 1.47 (m, 16H, $-CH_2-$), 1.83 (m, 16H, $-CH_2CH_2O-$), 4.00 (m, 16H, $-CH_2O-$), 6.80 (d, J = 8.4 Hz, 4H, Ar−H), 6.82 (s, 4H, Ar−H), 6.93 (d, J = 8.4 Hz, 4H, Ar−H), 9.01 (s, 4H, 4,6-H isoph.), 9.13 (s, 2H, 2-H isoph.). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.35, 22.92, 22.93, 26.26, 26.29, 29.40, 29.59, 29.62, 29.65, 29.69, 29.87, 29.89, 29.94, 29.95, 32.16, 32.27, 69.54, 70.07, 107.73, 113.10, 114.38, 129.19, 132.03, 134.16, 144.57, 147.45, 150.09, 152.73, 164.14. Anal. Calcd for $C_{136}H_{218}N_2O_{16}$: C, 76.43; H, 10.28; N, 1.31. Found: C, 76.12; H, 10.35; N, 1.26.

(*E*)-*Tetrakis*(*4-dodecyloxyphenyl*) *5,5′-*(*Diazene-1,2-diyl*)*-diisophthalamide* (***AMD4***). The product was recrystallized once over butanone and once over methylisobutilketone, affording 0.76 g (78%). Mp: 241.0 °C. IR (KBr): 3288 (CON−H), 2953, 2922, 2871, 2853, 1650 (C═O), 1611, 1535, 1513, 1468, 1413, 1242, 1171, 825. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.88 (s, 12H, CH_3), 1.19−1.49 (br, 64H, $-CH_2-$), 1.75 (br, 8H, $-CH_2CH_2O-$), 3.98 (br, 8H, $-CH_2O-$), 7.12 (br, 8H, Ar−H), 7.39 (br, 4H, $-CONH-$Ar), 7.70 (br, 8H, Ar−H), 8.23−8.54 (br, 6H, 2,4,6-H isoph.). Anal. Calcd for $C_{88}H_{126}N_6O_8$: C, 75.71; H, 9.10; N, 6.02. Found: C, 75.14; H, 9.75; N, 6.08.

(*E*)-*Tetrakis*(*3,4-didodecyloxyphenyl*) *5,5′-*(*Diazene-1,2-diyl*)*-diisophthalamide* (***AMD8***). The product was recrystallized three times over butanone and cold filtrated, affording 1.01 g (68%). Mp: (liquid crystal) Cr−126.5 °C−Col_h−221.5 °C−I. IR (KBr): 3275 (CON−H), 2956, 2923, 2870, 2853, 1652 (C═O), 1607, 1539, 1514, 1467, 1427, 1407, 1389, 1289, 1258, 1230, 1134, 1021, 803, 720. ^{1}H NMR ($CDCl_3$, −50 °C), δ, ppm: 0.89 (m, 24H, CH_3), 1.19−1.46 (br, 144H, $-CH_2-$), 1.75 (br, 16H, $-CH_2CH_2O-$), 3.89 (br, 16H, $-CH_2O-$), 6.72 (br, 4H, Ar−H), 7.19 (br, 4H, Ar−H), 7.52 (br, 4H, Ar−H), 8.29 (br, 4H, 4,6-H isoph.), 8.54 (br, 2H, 2-H isoph.), 9.25 (br, 4H, $-CONH-$Ar). Anal. Calcd for $C_{136}H_{222}N_6O_{12}$: C, 76.57; H, 10.49; N, 3.94. Found: C, 76.40; H, 10.21; N, 4.05.

(*E*)-*1,2-Bis*{*3,5-bis*[*5-*(*3,4-didodecyloxyphenyl*)*-1,3,4-oxadiazol-2-yl*]*phenyl*}*diazene* (***OXD8***). The product was macerated over hot ethanol and recrystallized twice over toluene/acetonitrile, affording 1.31 g (84%). Mp: (liquid crystal) Cr−102.0 °C−Col_h−236.6 °C−I. IR (KBr): 2956, 2921, 2871, 2851, 1604, 1554, 1497, 1466, 1424, 1391, 1271, 1219, 1139, 735. ^{1}H NMR ($CDCl_3$), δ, ppm: 0.87 (t, J = 6.7 Hz, 24H, CH_3), 1.23−1.44 (m, 128H, $-CH_2-$), 1.52 (m, 16H, $-CH_2-$), 1.88 (m, 16H, $-CH_2CH_2O-$), 4.12 (m, 16H, $-CH_2O-$), 7.02 (d, J = 8.6 Hz, 4H, Ar−H), 7.73 (s, 4H, Ar−H), 7.78 (d, J = 8.6 Hz, 4H, Ar−H), 8.89 (s, 4H, 4,6-H isoph.), 9.00 (s, 2H, 2-H isoph.). ^{13}C NMR ($CDCl_3$), δ, ppm: 14.40, 22.98, 26.33, 29.41, 29.53, 29.67, 29.75, 29.96, 32.22, 69.41, 69.77, 111.86, 113.06, 115.90, 121.12, 123.98, 126.76, 149.71, 152.95, 162.95, 165,84. Anal. Calcd for $C_{140}H_{218}N_{10}O_{12}$: C, 75.29; H, 9.84; N, 6.27. Found: C, 75.53; H, 9.58; N, 6.13.

2.2. Thermal Analysis. Thermal transitions and enthalpies were determined by DSC measurements carried out using Shimadzu equipment with a DSC-50 module using a heating/cooling rate of 10 °C min^{-1} and a nitrogen flow of 50 mL min^{-1}. TGA measurements were carried out using Shimadzu equipment with a TGA-50 module using a heating rate of 10 °C min^{-1} and nitrogen flow of 50 mL min^{-1}. Mesomorphic textures were determined using an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage and a PM-30 exposure control unit.

2.3. XRD Analysis. X-ray diffraction experiments were carried out with the X'PERT−PRO (PANalytical) diffractometer using Cu Kα radiation (λ = 1.5418 Å) with an applied power of 1.2 kVA. The scans were performed in continuous mode from 2° to 30° (2θ angle) and the diffracted radiation collected with an X'Celerator detector. The samples were prepared by heating a certain amount of the desired compound on a glass plate until the compound melted to the liquid state, followed by cooling to room temperature, resulting in a film approximately 1 mm thick. The films were then placed in the diffractometer chamber on the TCU2000 temperature control unit (Anton Paar), which allows a precise control of the sample temperature during the measurement. The films were first heated until the isotropic phase and the diffraction patterns collected after cooling back to the mesophase.

2.4. UV−Vis Spectroscopic Measurements and Photoisomerization. The UV−vis absorption spectra were recorded using an HP UV−vis model 8453 spectrophotometer. The samples were dissolved in spectroscopic chloroform and maintained in the dark for 48 h before the spectra were recorded. For the photoisomerization analysis a UVP 4W lamp model UVGL-25 was used. The excitation band used has a maximum at 356 nm and a width at half-maximum of 32 nm. All the optical analyses were performed at room temperature (25 °C).

3. Results and Discussion

3.1. Synthesis. As can be seen in Figure 2, all the desired discotic compounds have a common center, which is a

diphenyldiazene unit. To take advantage of this structural similarity, we opted for a convergent type of synthesis. Initially, all the intermediates were prepared and fully characterized, and in the final step, they were reacted to obtain the target molecules. The diphenyldiazene-derived compound (**1**) was prepared by a reductive coupling of 5-nitroisophthalic acid (Scheme 1). For this purpose, we used a mild reductive agent, such as dextrose in a strongly alkaline water solution.

The synthesis of the 5-arm types used for the preparation of the different target compounds is outlined in Scheme 2. The first type (**2**) was prepared by a simple monoalkylation of hydroquinone. The second, 3,4-didodecyloxyphenol (**6**), was synthesized by a more elaborated route, starting with an alkylation of catechol followed by a Friedel−Crafts acylation using aluminum trichloride. In the next step, **4** was converted to compound **5** by a Baeyer−Villiger oxidation using 3-chloroperbenzoic acid (MCPBA). A final acid hydrolysis afforded the desired phenol **6**.

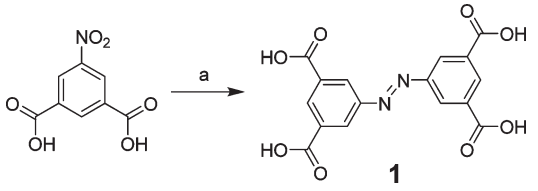
The first intermediate containing the amino group (**8**) was obtained by an O-alkylation of 4-hydroxyacetanilide followed by an acid hydrolysis. The two-chain aniline derivative (**10**) was prepared by a mononitration of **3**, via two-phase nitration, followed by reduction of the nitro group by catalytic hydrogenation using a 10% Pd/C catalyst. Finally, the fifth and final intermediate was obtained by initial alkylation of 3,4-dihydroxybenzonitrile using tetrabutylammonium bromide (TBAB) as the phase-transfer catalyst, followed by a Huisgen 1,3-dipolar cycloaddition over the nitrile group,[21] converting it to the tetrazole heterocycle.

Scheme 3 outlines the method used to obtain the desired discotic molecules. Initially the (*E*)-5,5′-(diazene-1,2-diyl)-diisophthalic acid (**1**) was converted to the respective acid chloride using $SOCl_2$ and a catalytic amount of DMF. The acid chloride obtained was then refluxed in pyridine with the appropriate intermediate (**2**, **6**, **8, 10**, or **12**), resulting in the desired final products with good yields (68 to 90%).

The structures of all the compounds were characterized by IR and ^1H and ^{13}C NMR spectra and elemental analysis, and in the case of compound **1** also the mass spectrum.

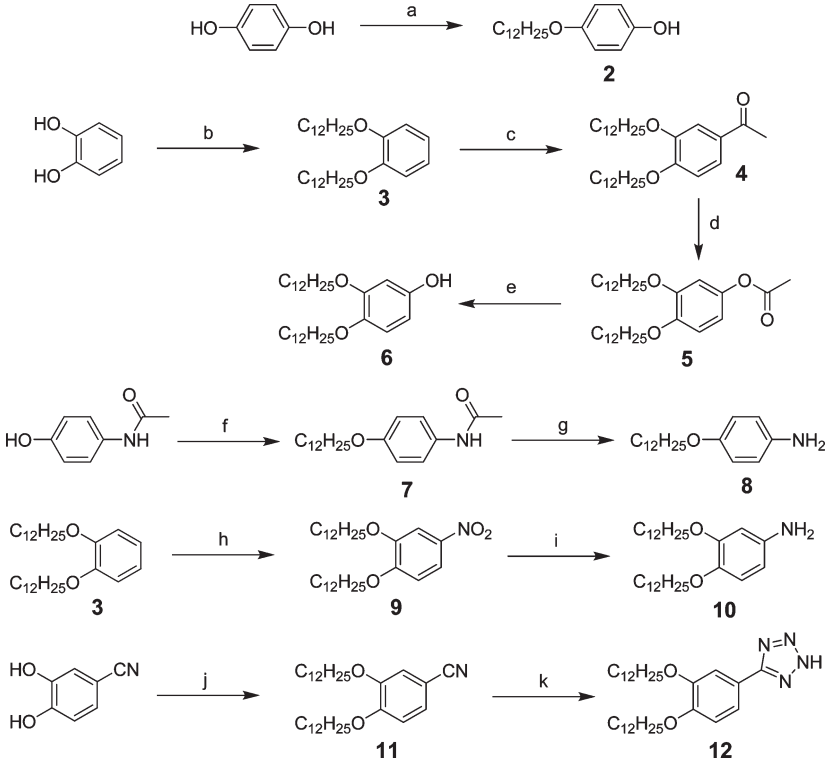
3.2. Thermal and Mesomorphic Behavior. The thermal behavior of the compounds **EST4**, **EST8**, **AMD4**, **AMD8**, and **OXD8** was investigated by DSC, POM and TGA, and the results are summarized in Table 1. Two of the five molecules synthesized showed liquid crystal properties. The DSC analysis showed a typical columnar phase transition, crystal-to-columnar-to-isotropic (Cr → Col → I). Compounds **AMD8** and **OXD8** exhibited an enantiotropic behavior. **AMD8** melts to a mesophase at 126.5 °C and to isotropic liquid at 221.5 °C. In a similar way, **OXD8** also presents a very stable mesophase, ranging from 102.0 to 236.6 °C. In both cases the mesophase was characterized by POM as a discotic hexagonal columnar phase (Col_h). The textures observed after cooling from isotropic liquid can be observed in Figure 3.

Scheme 1. Synthesis of Compound 1[a]



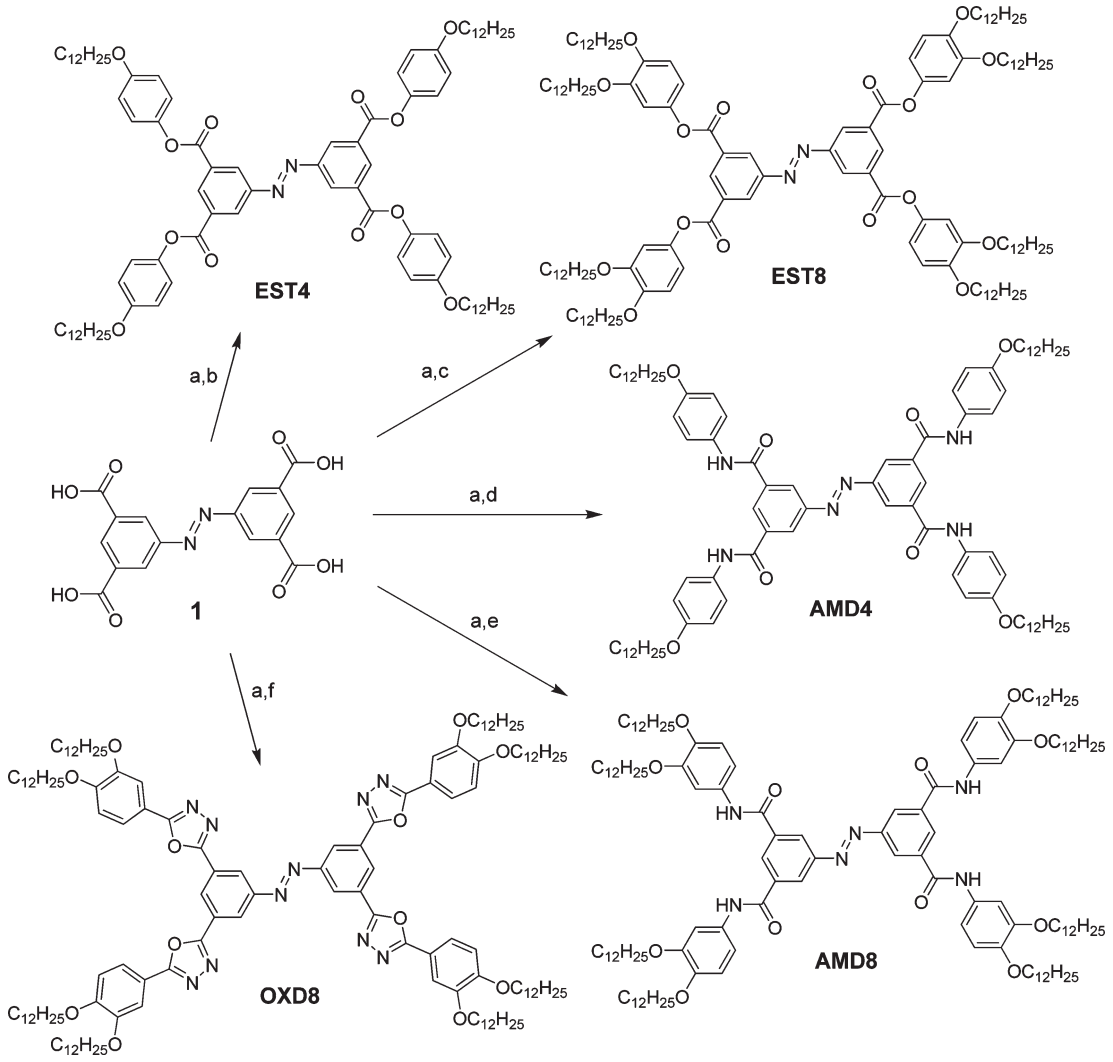
[a] Conditions (yields): (a) (*i*) Dextrose, NaOH, H_2O, 60 °C; (*ii*) H_3O^+ (61%).

Scheme 2. Synthesis of the Intermediates 2, 6, 8, 10, and 12[a]



[a] Conditions (yields): (a) (*i*) 1-bromododecane, NaOH, MeOH/H_2O, reflux; (*ii*) H_3O^+ (55%); (b) 1-bromododecane, K_2CO_3, KI, butanone, reflux (52%); (c) $AlCl_3$, acetyl chloride, dry CH_2Cl_2, −5 °C (83%); (d) MCPBA, CF_3COOH, dry CH_2Cl_2, 0 °C (75%); (e) $HCl_{conc.}$, MeOH, reflux (93%); (f) 1-bromododecane, K_2CO_3, butanone, reflux (98%); (g) (*i*) HCl_{conc}, H_2O, reflux; (*ii*) NaOH (99%); (h) $NaNO_2$, HNO_3 70%, CH_2Cl_2, −5 °C (75%); (i) H_2, Pd/C 10%, THF, rt (93%); (j) 1-bromododecane, K_2CO_3, TBAB, butanone, reflux (91%); (k) NaN_3, NH_4Cl, DMF, reflux (93%).

Scheme 3. Synthesis of Final Products (EST4, EST8, AMD4, AMD8, and OXD8)[a]



[a] Conditions (yields): (a) $SOCl_2$, $DMF_{cat.}$, reflux (not isolated); (b) intermediate **2**, dry pyridine, reflux (90%); (c) intermediate **6**, dry pyridine, reflux (73%); (d) intermediate **8**, dry pyridine, reflux (78%); (e) intermediate **10**, dry pyridine, reflux (68%); (f) intermediate **12**, dry pyridine, reflux (84%).

Table 1. Phase Transitions, Enthalpies, and Thermal Stability of Target Compounds (Temperatures Presented in °C and ΔH in kJ mol^{-1})

compound	transitions	T (ΔH)[a] heating	T ($-\Delta H$)[a] cooling	$T_{dec.}$[b]
EST4	Cr−Cr′	132.5 (64.5)	-	353
	Cr′−I	167.2 (69.5)	159.2 (70.8)	
EST8	Cr−Cr′	51.2 (3.2)[c]	-	341
	Cr′−Cr″	67.0 (32.8)[c]	-	
	Cr″−Cr‴	108.4 (4.4)	-	
	Cr‴−I	154.4 (0.9)	-	
AMD4	Cr−Cr′	195.1 (36.8)	171.8 (16.2)	360
	Cr′−I	241.0 (42.8)	230.6 (34.8)	
AMD8	Cr−Col_h	126.5 (11.1)	-	388
	Col_h−I	221.5 (25.0)	196.2 (3.9)	
OXD8	Cr−Cr′	83.9 (39.0)[c]	-	384
	Cr′−Col_h	102.0 (11.9)[c]	-	
	Col_h−I	236.6 (5.4)	223.8 (2.8)	

[a] Determined by DSC using a heating/cooling rate of 10 °C min^{-1}. [b] Determined by TGA using a heating rate of 10 °C min^{-1}. Onset of decomposition under nitrogen. [c] Estimated values by deconvolution of overlapped bands.

Compounds **AMD8** and **OXD8** displayed a pseudo focal-conic optical texture with linear birefringent defects (Figure 3), suggesting hexagonal columnar structures. A large area of homeotropic domains was observed, suggesting a Col_h phase with a preferentially uniaxial character. A variable temperature XRD experiment confirmed the Col_h phase.

EST4 and **AMD4** have a thermal property of an ordinary solid, melting directly to liquid state. This difference of behavior in comparison with **AMD8** and **OXD8** can be explained by the number of aliphatic chains present at the molecule periphery. In this regard, 4 aliphatic chains seems to be a low number in terms of achieving a good packing and stabilization of a columnar mesophase. On the other hand, **EST8** has the same number of aliphatic chains as **AMD8** and **OXD8** but, as in the case of **EST4**, it does not have liquid crystal properties. This could be the result of a lower degree of planarity due to the presence of ester groups. This lack of planarity difficult the molecular packing, preventing the assembling in a columnar mesophase. This is confirmed by comparing the liquid state transition temperatures, where **EST8** has a lower transition temperature than **AMD8** and **OXD8** (in a similar way, **EST4** has a lower melting point than **AMD4**). Also, the lack of planarity hinders the solidification

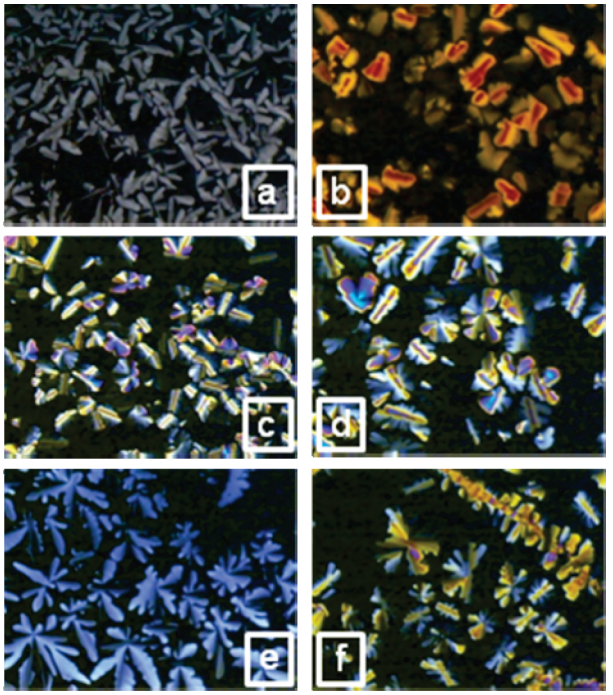


Figure 3. Optical textures observed under crossed polarizers. Photomicrographs showing hexagonal columnar mesophase textures. Parts a and b show compound **AMD8** at 205.3 and 209.5 °C, respectively (200×). Parts c, d, e and f show compound **OXD8** at 221.0, 227.9, 225.2, and 215.3 °C, respectively (100×).

of the material, which is noted by the absence of a defined exothermic peak on cooling in the DSC. Furthermore, **AMD8** contains four amide groups, which enhance the attractive interactions between the discotic mesogens by intermolecular hydrogen bonding. Amide groups have already been used by several research groups to obtain stabilized columnar phases.[22]

XRD experiments were performed to confirm the Col_h mesophases of compounds **AMD8** and **OXD8** observed in the POM and to obtain their structural parameters. In the spectra obtained, as shown in Figure 4, there is a well-defined peak (100) at the low angle region for both compounds. Typical XR diffractograms of well organized Col_h mesophases show the following order peaks related to the Miller Indices (100), (110) and (200), whose ratios obey the relation $1:(3)^{1/2}:2$ according to the first peak.[9,23] Here, compound **OXD8** presented only the (200) reflection, while compound **AMD8** presented neither the (110) nor (200) reflections, indicating a weak correlation order. However, as the disk-like structure of the molecules favors columnar packing resulting in columnar phases due to their long-range stacking order, the existence of only one fundamental Bragg reflection at the low angle region suggests that the only possibility is the hexagonal symmetry. In such case, 2D rectangular and oblique lattices are excluded.[24]

The mesophase conformation parameters obtained from the XRD data are given in Table 2. It can also be noted that the molecular diameter for both mesogens is between the minimum and maximum values estimated for these compounds[25] (23.6 Å/53.7 Å and 21.9 Å/51.3 Å for **OXD8** and **AMD8**, respectively). This indicates that the aliphatic chains are not in the most extended form and/or that there is an interdigitation of the aliphatic chains of the molecules in different columns. In both compounds, even after cooling to ambient temperature, the diffractograms are very similar and also the absence of new peaks supports the lack of

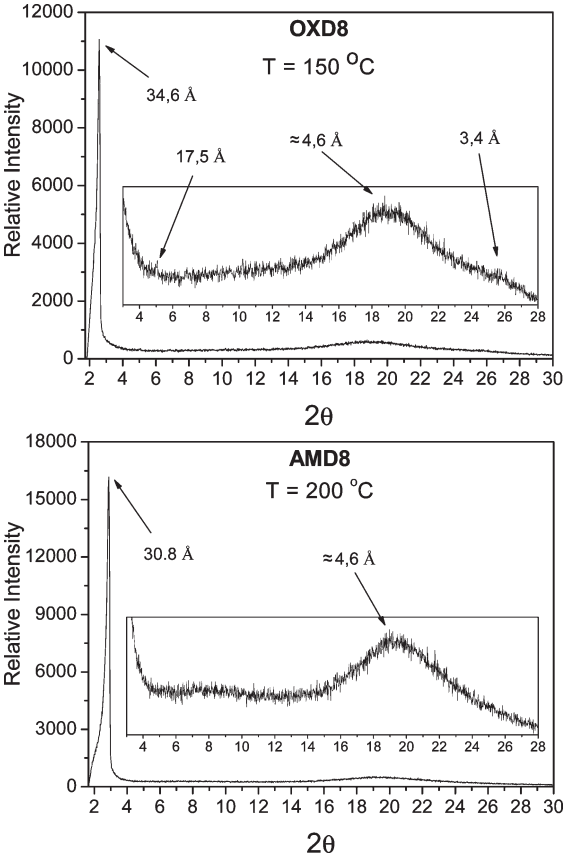


Figure 4. X-ray diffraction patterns of hexagonal columnar mesophase of **OXD8** at 150 °C (upper) and **AMD8** at 200 °C (lower).

Table 2. XRD data for OXD8 and AMD8 at Mesophase Temperature

comp (temp.)	d_{obs}(Å)	(*hkl*)	d_{cal} (Å)	cell const (Å)
OXD8	34.6	(100)	34.8	$\alpha = 40.2^a$
(150 °C)	17.5	(200)	17.4	
	≈4.6	*broad*		
	3.4	(001)		
AMD8	30.8	(100)	30.8	$\alpha = 35.6^b$
(200 °C)	≈4.6	*broad*		

$^a\alpha = (2/n\sqrt{3})(d_{100} + 2d_{200})$, where $n = 2$. ^{b}Calculated without d_{200} and $n = 1$.

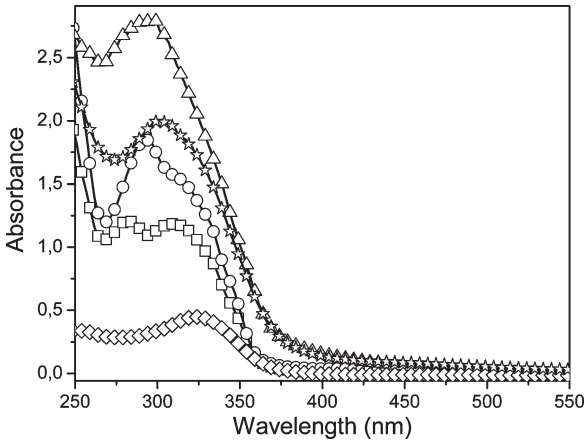


Figure 5. Optical absorption spectra of compounds (□) **EST4**; (○) **EST8**; (☆) **AMD4**; (△) **AMD8 and** (◇) **OXD8**) in $CHCl_3$ at room temperature. The concentrations of the solutions were 5.0×10^{-5} mol L^{-1}, except for **OXD8** (5.0×10^{-6} mol L^{-1}).

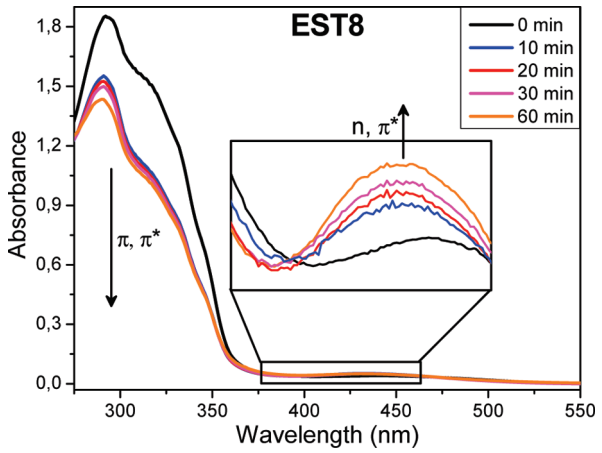


Figure 6. Photoisomerization of compound **EST8** in chloroform solution (5.0×10^{-5} mol L^{-1}) at room temperature. The upper right corner time represents the irradiation time at 356 nm. The inset illustrates the small increase of absorption in 430 nm and also the isosbestic point.

crystallinity of these materials (see Supporting Information). The easy rotation around the ester group, difficult a columnar packing of the mesogens, resulting in the absence of liquid crystalline behavior for **EST8** and **EST4**.

Both diffractograms shown in Figure 4 have a broad diffuse band at 4.6 Å, which is due to a liquid-like order between the aliphatic chains.[24,26] The absence of the (001) Bragg's reflection for **AMD8**, when compared with **OXD8** (around 3.4 Å), indicates a lesser periodicity in the columnar packing of the former, which can also be noted through a small difference in the texture of the mesophase of the two compounds.

3.3. Optical Behavior and Photoisomerization. The optical absorbance of the target compounds in $CHCl_3$ solution are shown in Figure 5 and summarized in Table 3. The concentrations of the solutions are given in the figure and also in the table. The respective solutions utilized were maintained in the dark for 48 h before the analysis. Thus, we can infer that the compounds were exclusively in the *trans* configuration.

According to the data presented, we observe that the addition of alkoxy chains promotes two different effects,

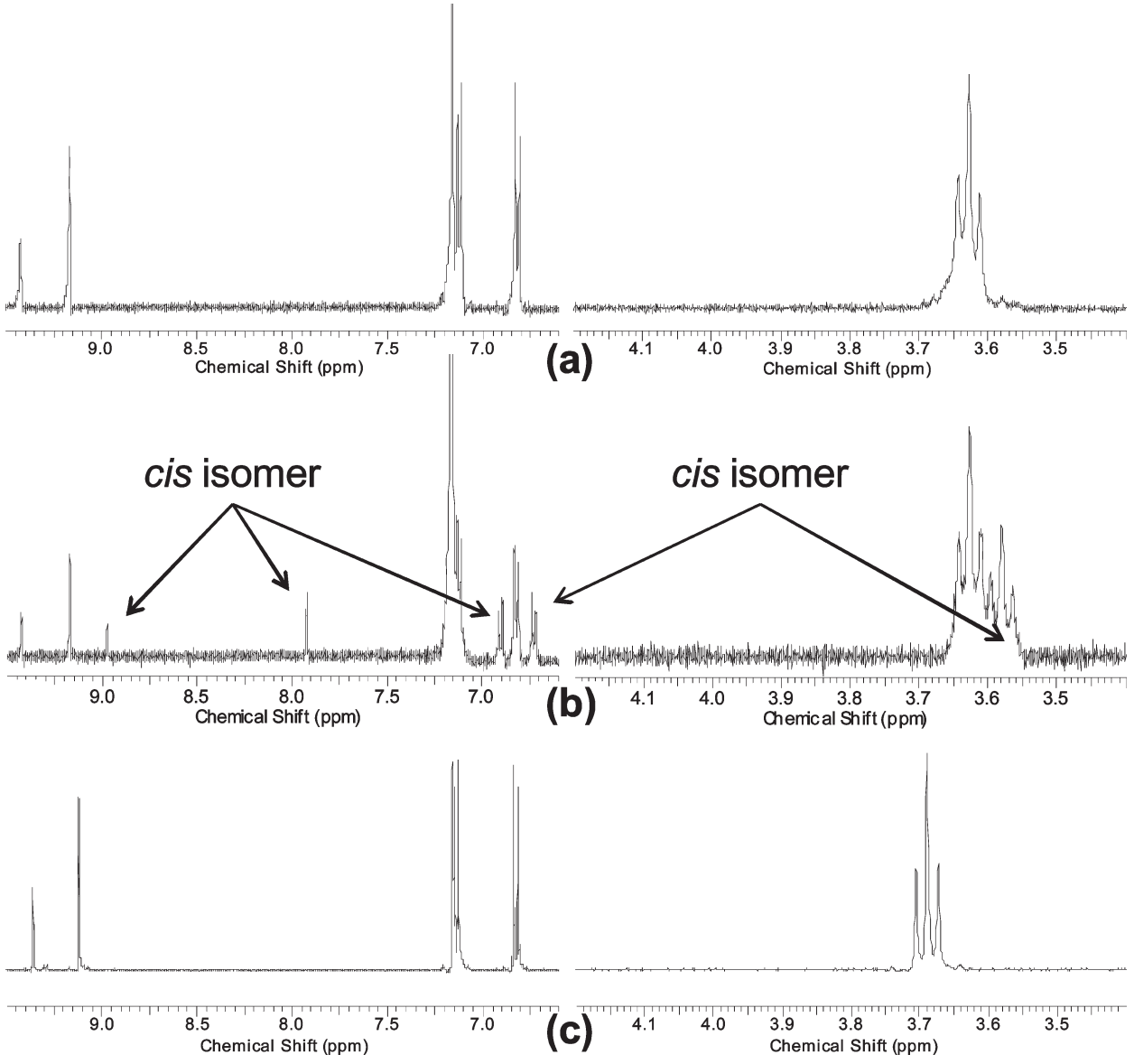


Figure 7. Evidence of photoisomerization (*trans*−*cis*) and thermal isomerization (*cis*−*trans*) of compound **EST4** observed through ^{1}H NMR using C_6D_6 has solvent. (a) NMR obtained at room temperature. (b) Same sample after 10 min of irradiation at 356 nm at room temperature. (c) NMR recorded at 60 °C for the same sample.

Table 3. UV−Vis Absorption Spectroscopic Data at Room Temperature (Solvents Used: $CHCl_3$)

compd	$\lambda_{máx}$ (nm)	ε_{max}[a]	concn[b]
EST4	282	2.4×10^4	5.0×10^{-5}
	309	2.4×10^4	
EST8	292	3.7×10^4	5.0×10^{-5}
	312[c]		
AMD4	301	4.0×10^4	5.0×10^{-5}
AMD8	293	5.6×10^4	5.0×10^{-5}
OXD8	323	8.9×10^4	5.0×10^{-6}
	253	6.8×10^4	

[a] Units = L mol^{-1} cm^{-1}. [b] Units = mol L^{-1}. [c] Shoulder.

but both attributable to the increase of the electronic density in the benzene ring to which they are bonded. The first effect is a shift of the absorption bands, being more pronounced in the aromatic ring than in the azo band. In the **EST** group, the addition of alkoxy chains causes a bathochromic shift, promoting the superposition of these absorption bands in the case of the **EST8** compound, as observed in Figure 5. This superposition, as already mentioned, is derived from the bathochromic shift in the benzene absorption band from the **EST4** (282 nm) to **EST8** (292 nm), while the azo absorption band stays practically unaltered (from 309 to 312 nm). On another hand, the same addition promotes a small hypsochromic shift on the absorption bands of the **AMD** group. The second effect is a hyperchromic one, increasing the ε value. In a similar way, the higher degree of planarity and consequent conjugation effectiveness of the amide functional group and 1,3,4-oxadiazole heterocycle also promote a hyperchromic effect over the benzene absorption band.

Although molecules containing the 1,3,4-oxadiazole heterocycle are known to exhibit strong blue luminescence,[27] **OXD8** does not show luminescence in the visible region. **EST4**, **EST8**, **AMD4**, and **AMD8** also did not show luminescence in visible region.

The photostationary equilibrium capacity of the target compounds was also analyzed. With this purpose, the same solution used to obtain the optical absorbance spectra was used. The solution was irradiated at a wavelength of 356 nm and the absorbance spectra were measured from time to time, during 1 h of irradiation. All the compounds showed *trans* to *cis* photoisomerization under light, which is exemplified in Figure 6 for compound **EST8** (the photoisomerization for the other compounds are listed in the Supporting Information). This isomerization process is confirmed by the reduction of the absorbance band around 300 nm, attributed to the *trans* configuration, and the small increase of the band at around 430 nm relating to the *cis* form. We can also observe that in the first few minutes, the photoisomerization is fast, with the speed decreasing with time. But even after half an hour this process continues, and the photostationary point was not reached after 1 h.

The photoisomerization process was also qualitatively observed during the ^{1}H NMR analysis of compound **EST4**. Initially, a sample of **EST4** was prepared in C_6D_6, heated to certify that all compound was in the *trans* configuration and the spectrum was recorded at room temperature (Figure 7a). We observe two peaks around 9.0−9.5 ppm, attributed to the aromatic hydrogens from the benzene ring that is bonded to the N=N group, and a AA′XX′ system for *p*-phenylene group at 6.8 and 7.2 ppm. Also, we observe a triplet at 3.6 ppm that is attributed to the hydrogens of the alkoxy chain ($-CH_2O-$). After this, the sample (kept inside the NMR tube) was maintained under irradiation for 10 min, at 356 nm, and the spectrum was recorded at room temperature (Figure 7b). Now, we observe a duplication of the aromatic and aliphatic hydrogens. The formation of the *cis* isomer is the result of the photoisomerization reaction provoked by light irradiation at 356 nm. When the same sample was heated and its NMR spectrum recorded at 60 °C, the duplicated peaks disappeared (Figure 7c). The heating reverses the photoisomerization, promoting an equilibrium shift toward the stable *trans* configuration, which is the thermodynamically more stable form. In general, not all peaks were duplicated, only the hydrogens closer to the N = N bond. The closer the azo bond, the bigger the peak shift. Clearly, the hydrogens at the end of the aliphatic chains do not show a significant difference in the chemical shift.[28]

4. Conclusions

We have designed and synthesized new examples of azo photoisomerizable discotic molecules. This opens up ways not only to understand the detailed physical properties of discotic liquid crystals, but also to design novel electro-optical devices. Their structural characterization was achieved by FTIR, NMR, and elemental analysis. All of the compounds had good thermal stability with decomposition temperatures higher than 341 °C. The mesomorphic behavior of these compounds was studied by DSC and POM, indicating that two of the five molecules (**AMD8** and **OXD8**) present liquid crystal mesophases, which were identified through POM and established via XRD studies as columnar hexagonal. All the compounds showed *trans* to *cis* photoisomerization under visible light and *cis* to *trans* thermal isomerization. In the case of those with a columnar mesophase, this property seems to be promising in terms of controlling the conductivity through the columns, as graphically illustrated herein.

Acknowledgment. This work was supported by CAPES, CNPq, FAPESC and INCT-Catalise. The X-ray diffraction experiments were performed at the Laboratório de Difração de Raios-X (LDRX-DF/UFSC).

Supporting Information Available: Figures showing ^{1}H NMR and ^{13}C NMR spectra of the compounds prepared and an MS spectrum of **1**, DSC, TGA, and the photoisomerization process of **EST4**, **EST8**, **AMD4**, **AMD8**, and **OXD8**. XRD at room temperature for **AMD8** and **OXD8**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25–35.
(2) (a) Cacciapaglia, R.; Stefano, S. D.; Mandolini, L. *J. Am. Chem. Soc.* **2003**, *125*, 2224–2227. (b) Sasaki, T.; Tour, J. M. *Org. Lett.* **2008**, *10*, 897–900. (c) Yamada, M.; Kondo, M.; Mamiya, J.; Yu, Y.; Kinoshita, M.; Barrett, C. J.; Ikeda, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 4986–4988.
(3) Adam, D.; Schuhmacher, P.; Simmerer, J.; Haussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143.
(4) (a) An, Z.; Yu, J.; Domercq, B.; Jones, S. C.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 6688–6698. (b) Zhang, Y. −D.; Jespersen, K. G.; Kempe, M.; Kornfield, J. A.; Barlow, S.; Kippelen, B.; Marder, S. R. *Langmuir* **2003**, *19*, 6534–6536. (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1122.
(5) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902–1929.
(6) (a) Varghese, S.; Kumar, N. S. S.; Krishna, A.; Rao, D. S. S.; Prasad, S. K.; Das, S. *Adv. Funct. Mater.* **2009**, *19*, 2064–2073. (b)

Mao, H.; He, Z.; Wang, J.; Zhang, C.; Xie, P.; Zhang, R. *J. Lumin*. **2007**, *122*−*123*, 942–945. (c) Benning, S. A.; Oesterhaus, R.; Kitzerow, H. −S. *Liq. Cryst*. **2004**, *31* (2), 201–205.

(7) (a) Laschat, S.; Giesselmann, F.; et al.et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832–4887. (b) Binnemans, K. *Chem. Rev*. **2005**, *105*, 4148–4204. (c) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed*. **2006**, *45*, 38–68. (d) Kato, T.; Yasuda, T.; Kamikawa, Y.; Yoshio, M. *Chem. Commun*. **2009**, 729–739.

(8) Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H. -W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1998.

(9) Cristiano, R.; Gallardo, H.; Bortoluzzi, A. J.; Bechtold, I. H.; Campos, C. E. M.; Longo, R. L. *Chem. Commun*. **2008**, 5134–5136.

(10) (a) Kumar, S. *Chem. Soc. Rev*. **2006**, *35*, 83–109. (b) Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc*. **2004**, *126*, 994–995. (c) van Nostrum, C. F. *Adv. Mater*. **1996**, *8*, 1027–1030.

(11) (a) Monobe, H.; Mima, S.; Sugino, T.; Shimizu, Y. *J. Mater. Chem*. **2001**, *11*, 1383–1392. (b) Warman, J. M.; Haas, M. P.; Dicker, G.; Grozema, F. C.; Piris, J.; Debije, G. *Chem. Mater*. **2004**, *16*, 4600–4609.

(12) (a) Rau, H. *Photochromism: Molecules and System*; Elsevier: Amsterdam, 1990. (b) Griffiths, J. *Chem. Soc. Rev*. **1972**, *1*, 481–493. (c) Nishihara, H. *Bull. Chem. Soc. Jpn*. **2004**, *77*, 407–428. (d) Sebastião, P. J.; Corsellis, E.; Heinrich, B.; Guillon, D. *Liq. Cryst*. **2002**, *29*, 479–482.

(13) (a) Folcia, C. L.; Alonso, I.; Ortega, J.; Etxebarria, J.; Pintre, I.; Ros, M. B. *Chem. Mater*. **2006**, *18*, 4617–4626. (b) Prasad, V.; Kang, S.; Qi, X.; Kumar, S. *J. Mater. Chem*. **2004**, *14*, 1495–1502.

(14) Tschierske, C. *J. Mater. Chem*. **1998**, *8*, 1485–1508.

(15) Rahman, M. L.; Tschierske, C.; Yusoff, M.; Silong, S. *Tetrahedron Lett*. **2005**, *46*, 2303–2306.

(16) Bialecka-Florjanczyk, E. *Synth. Commun*. **2000**, *30*, 4417–4424.

(17) Montani, R. S.; Hegguilustoy, C. M.; Del Rosso, P. G.; Donnio, B.; Guillon, D.; Garay, R. O. *Tetrahedron Lett*. **2009**, *50*, 5231–5234.

(18) Yelamaggad, C. V.; Achalkumar, A. S.; Rao, D. S. S.; Prasad, S. K. *J. Org. Chem*. **2007**, *72*, 8308–8318.

(19) Gürol, I.; Ahsen, V. *Mol. Cryst. Liq. Cryst*. **2005**, *442*, 103–118.

(20) Lin, Y.; Lai, C. K.; Chang, Y.; Liu, K. *Liq. Cryst*. **2002**, *29*, 237–242.

(21) (a) Gallardo, H.; Magnago, R.; Bortoluzzi, A. J. *Liq. Cryst*. **2001**, *28*, 1343–1352. (b) Gallardo, H.; Meyer, E.; Bortoluzzi, A. J.; Molin, F.; Mangrich, A. S. *Inorg. Chim. Acta* **2004**, *357*, 505–512.

(22) (a) Gearba, R. I.; Lehmann, M.; Levin, J.; Ivanov, D. A.; Koch, M. H. J.; Barbera, J.; Debije, M. G.; Piris, J.; Geerts, Y. *Adv. Mater*. **2003**, *15*, 1614–1628. (b) van Gorp, J. J.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc*. **2002**, *124*, 14759–14769. (c) Paraschiv, I.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhölter, E. J. R. *Chem. Mater*. **2006**, *18*, 968–974.

(23) Wen, C. -R.; Wang, Y. -J.; Wang, H. -C.; Sheu, H. -S.; Lee, G. -H.; Lai, C. K. *Chem. Mater*. **2005**, *17*, 1646–1654.

(24) Attias, A. -J.; Cavalli, C.; Donnio, B.; Guillon, D.; Hapiot, P.; Malthete, J. *Chem. Mater*. **2002**, *14*, 375–384.

(25) The minimum and maximum diameter values for the compounds were estimated using ChemBio3D Ultra Software, version 11.0.1. The optimized structures had their energy minimized using the MM2 energy minimization method.

(26) (a) Barberá, J.; Puig, L.; Serrano, J. L.; Sierra, T. *Chem. Mater*. **2004**, *16*, 3308–3317. (b) Lai, C. K.; Tsai, C. -H.; Pang, Y. -S. *J. Mater. Chem*. **1998**, *8*, 1355–1360.

(27) (a) Wu, F. -I.; Shu, C. -F.; Chien, C. -H.; Tao, Y. -T. *Synth. Met*. **2005**, *148*, 133–139. (b) Srivastava, R. M.; Neves, R. A. W.; Schneider, R.; Vieira, A. A.; Gallardo, H. *Liq. Cryst*. **2008**, *35*, 737–742. (c) Cristiano, R.; Santos, D. M. P. O.; Gallardo, H. *Liq. Cryst*. **2005**, *32* (1), 7–14. (d) Cristiano, R.; Ely, F.; Gallardo, H. *Liq. Cryst*. **2005**, *32* (1), 15–25.

(28) Rudolph-Böhner, S.; Krüger, M.; Oesterhelt, D.; Moroder, L.; Nägele, T.; Wachtveitl, J. *J. Photochem. Photobiol. A: Chem*. **1997**, *105*, 235–248.