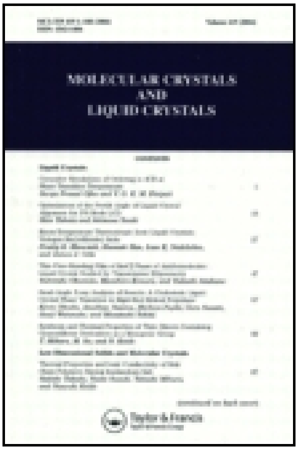

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Discotic Liquid Crystals as Electron Carrier Materials

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DISCOTIC LIQUID CRYSTALS AS ELECTRON CARRIER MATERIALS

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A series of five new hexaalkylthiohexaazatriphenylenes **2a-e** *has been synthesized. Their thermotropic behaviour has been investigated and compared with the corresponding series of hexaalkylthiotriphenylenes* **1a-e** *and hexaalkylthiohexaazatrinaphthylenes* **3a-e**. *Unexpectedly, hexaalkylthiohexaazatriphenylenes* **2a-e**, *hexaalkylthiotriphenylenes* **1d-e** *and hexaalkylthiohexaazatrinaphthylenes* **3e**, *do not form columnar liquid crystalline mesophases.*

Keywords: discotics; thermotropic liquid crystals; columnar mesophases; semiconductors

INTRODUCTION

A wide scientific and technological interest in discotic liquid crystals as one dimensional semiconductors has emerged from the discovery that

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2,3,6,7,10,11-hexahexylthiotriphenylene (**1a**), in a highly ordered helical (H) mesophase, exhibits a charge carrier mobility (μ) on the order of $\mu = 0.1\,\mathrm{cm^2V^{-1}s^{-1}}$ [1,2]. In the last decade, the charge carrier mobilities of several mesogens based on hexabenzocoronene, triphenylene, and phthalocyanine aromatic cores have been studied [3]. Values of μ as high as $0.5\,\mathrm{cm^2V^{-1}s^{-1}}$ have been reported for the columnar mesophase of hexabenzocoronene derivatives [4]. Such mobility approaches the corresponding value for the intersheet mobility in graphite ($\mu \sim 3\,\mathrm{cm^2V^{-1}s^{-1}}$) and matches those of single crystals of aromatic compounds [4]. As many other conjugated organic materials, most discotic mesogens reported so far have in common to be better hole carriers than electron carriers [3]. Only a few examples of electron carrier discotic mesogens exist to date [5,6] creating, therefore, the need for new materials.

Here, we report and discuss the syntheses and mesophase characterisation of discotics **1a-e**, **2a-e**, and **3a-e** (Figure 1), specially designed to carry electrons [6]. The presence of six nitrogen atoms in their aromatic core increases the first reduction potential facilitating electron injection and collection [7]. Moreover, thioalkyl side chains centre the LUMO orbital on the aromatic core leading to large LUMO-LUMO overlap between stacked disks, as recently shown by advanced quantum chemical calculations [8].

RESULTS AND DISCUSSION

Synthesis

The synthesis of mesogens **1a-d** and **3a-d** has previously been reported [6,9]. Compounds **1e** and **3e** are new [10,11]. They have been prepared

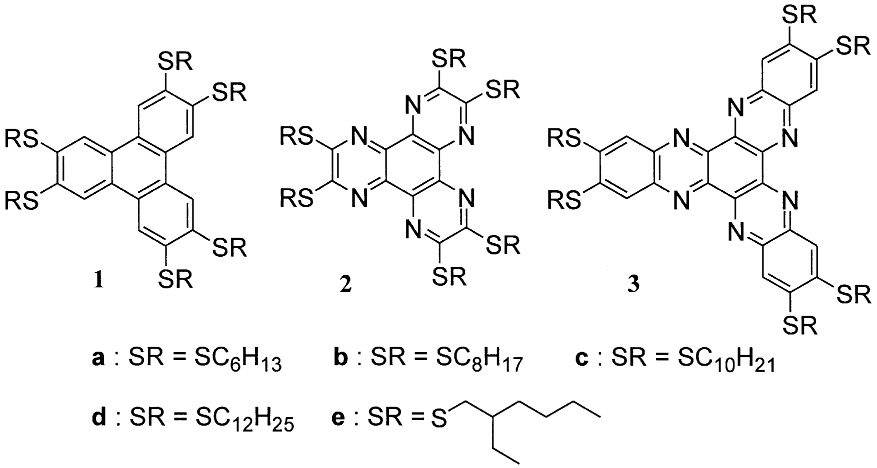


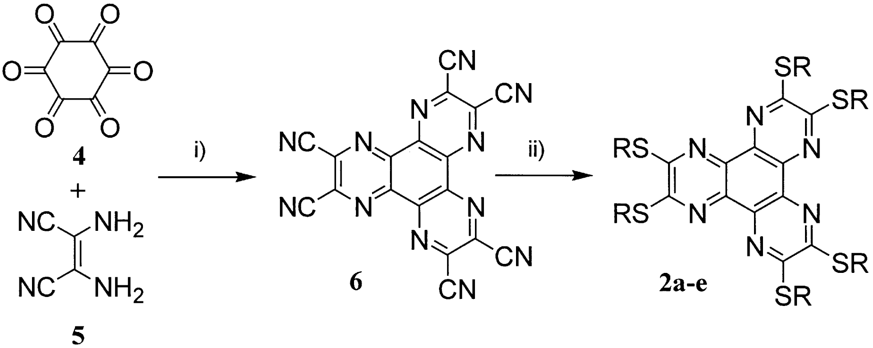
FIGURE 1 Chemical structure of discotics **1a-e**, **2a-e**, and **3a-e**.

following a similar procedure to that used in the syntheses of **1a-d** and **3a-d**. The synthesis of compounds **2a-d** is based on a two step synthetic pathway (Scheme 1). The first step is a condensation of hexaketone **4** with an excess of diaminomaleonitrile (**5**) in refluxing glacial acetic acid [12]. The second step consists in a six-fold substitution of the cyano leaving groups by alkylthiolate in rather mild conditions, i.e. in dimethylformamide in presence potassium carbonate at 85°C. The yield of this second step after column chromatography purification is rather low. Attempts to increase the substitution yield by varying the reaction conditions have not afforded better results. However, one calculates a yield per substitution of cyano function of 67%.

Thermotropic Properties

The thermotropic properties of compounds **1e**, **2a-e**, and **3e** were studied by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). Results are collected in Table 1.

The series of compounds **1a-d** and **2a-d** share very comparable shape, diameter, volume, number of atoms and the absence of permanent dipole. The only difference between these two series of compounds arises from the distribution of partial charges on the conjugated core. Surprisingly enough, hexaazatriphenylenes **2a-c** do not form liquid crystalline phases contrary to the corresponding well-known triphenylene compounds **1a-c**. Moreover compounds **2a-c** melt at higher temperature than the clearing temperature of mesogens **1a-c**, indicating a higher lattice energy. In contrast to hexaazatriphenylenes **2a-d**, all the larger hexaazatrinaphtalenes **3a,d** exhibit at least one liquid crystalline mesophase before decomposition around 250°C. One also notices the extreme dependence of the phase transitions of **3a,d**



SCHEME 1 Synthetic pathway to molecules **2a-e**, i) glacial acetic acid, reflux for 2 hours, ii) DMF/K_2CO_3, 85°C for 24 hours.

TABLE 1 Thermotropic Properties of **1a-e**, **2a-e**, and **3a-e**. Results of DSC and POM Investigations.

Compound	Reproducible DSC results of the second heating, rate 10 °C/min (Onset [°C]/ΔH [kJ/mol])
1a (I)	**Cr** 62/−25 **H** 70/−15 **Col**$_{\mathbf{h}}$ 93/−8 **I**
2a	**Cr** 105/−35.3 **I**
3a (II)	**X** 206/−26.4 **LC** ~ 250 **decomp.**
1b (I)	**Cr** 55/−45 **Col**$_{\mathbf{h}}$ 87/−10 **I**
2b	**Cr** 49/−7.7 **Cr** 93/−47.2 **I**
3b (II)	**Cr** 77/−5.6 **X**$_{\mathbf{1}}$ 142/ −14 **X**$_{\mathbf{2}}$ 178/−13.5 ~ 250 **decomp.**
1c(I)	**Cr** 40/−28 **Col**$_{\mathbf{h}}$ 71/−6 **I**
2c	**Cr** −7/−12.7 **Cr** 74/−69.4 **I**
3c(II)	**Cr**$_{\mathbf{1}}$ 26/−4.5 **Cr**$_{\mathbf{2}}$ 40/−18.4 **X**$_{\mathbf{1}}$ 50/−24.1 **X**$_{\mathbf{2}}$ 116/−30.6 **LC**$_{\mathbf{1}}$ 134/−1.6 **LC**$_{\mathbf{2}}$ 180/−0.4 **LC**$_{\mathbf{3}}$ ~ 250 **decomp.**
1d(I)	**Cr** 80/(III) **I**
2d	**Cr** 90/−94.3 **I**
3d(II)	**X** 99/−31.7 **LC** ~ 250 **decomp.**
1e	**Amorphous**
2e	**Amorphous**
3e	**Cr** −5/−1.2 **Cr** 231/−12.1 **Cr** ~ 250 **decomp.**

(I)From ref. 13, (II)From ref. 6, (III)Not given ref. 13.

on the chain length. Ethyl-hexylthioether side chains have also been introduced on compounds **1e**, **2e** and **3e** with the hope to depress the transition temperature to the isotropic melt. Again unexpected but reproducible results were obtained. Compounds **1e** and **2e** form amorphous phases whereas **3e** exhibits only crystalline phases until decomposition.

CONCLUSIONS

A series of new disk-like hexaazatriphenylenes **2a-e** have been synthesized. The comparison of the thermal behaviour of **2a-c** with that of structurally related discotic mesogens, i.e. **1a-c** and **3a-c** stresses the subtle dependence of thermotropic properties on minor changes of the chemical structures.

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[10] Spectroscopic data for **1e** : ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.37$ (s, 6H), 3.09 (d, 12H), 1.74 (m, 6H), 1.59 (m, 24H), 1.35 (m, 24H), 0.98 (d, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 137.85$ (arom.), 127.39 (arom.), 123.25 (arom.), 39.04 (aliph.), 38.49 (aliph.), 32.71 (aliph.), 28.97 (aliph.), 25.96 (aliph.), 23.14 (aliph.), 14.23 (aliph.), 11.04 (aliph.). MS (FD) m/z (%) = 1092.7 (calculated) 1093 (found, 100, M^+). Rf = 0.6 (silica gel, toluene/hexane 6/4)

[11] Spectroscopic data for **3e** : ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.28$ (s, 6 H), 3.24 (d, 12 H), 1.92 (q, 6 H), 1.62 (m, 24 H), 1.40 (m, 24 H), 1.00 (m, 36 H), ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.06$ (arom.), 142.36 (arom.), 141.55 (arom.), 123.17 (arom.), 38.16 (aliph.), 37.73 (aliph.), 32.71 (aliph.), 28.68 (aliph.), 25.96 (aliph.), 22.99 (aliph.), 14.10 (aliph.), 10.66 (aliph.). MS (FD) m/z (%) = 1249.6 (calculated) 1250.1 (found, 100, M^+). Rf = 0.55 (silica gel, $CHCl_3$/hexane 1/1)

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