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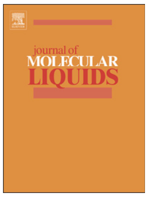

Novel electron-deficient phenanthridine based discotic liquid crystals

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ABSTRACT

Nitrogen-containing polycyclic core 5-phenylnaphtho[1,2,3,4-lmn] phenanthridine and its nitro-functionalized positional isomers were synthesized using Pictet-Spengler reaction between hexaalkoxytriphenylene-1-amine and various aryl aldehydes. The hexagonal columnar phase was observed in all the synthesized novel compounds. Mesomorphic characterization was carried out using conventional thermal analysis and X-ray diffraction techniques. These compounds showed room temperature liquid crystal phase and there is no crystalline phase observed even at −20 °C upon cooling from the isotropic temperature. Further, the long range of mesophase was confirmed by polarizing optical microscopy. Subsequently, charge transfer complexes were prepared by mixing the synthesized polycyclic hetero-aromatic compounds with 2,3,6,7,10,11-hexakis(octyloxy)-triphenylene. In UV–Vis absorption spectra, a redshift was found for the charge transfer complexes; which confirmed the interaction between donor-acceptor counterparts. The electrical conductivity of the charge transfer complexes and their pure target compounds was measured.

1. Introduction

Heterocyclic and polycyclic aromatic hydrocarbons play an important role in the photophysical, electronic and supramolecular properties [1,2]. The stable nitrogen-containing polycyclic aromatic compounds exhibit excellent electronic properties at the molecular level and hence they can be useful in various organic electronic technologies [2]. In the recent era, nitrogen-containing heterocyclic compounds were used as a building block to obtain nitrogen-doped graphene; which are employed in the application of catalysis as well as electronics [3]. Actually, direct incorporation of heteroatoms in a polycyclic aromatic compound is a challenge. There are many synthetic strategies and structure-property relationships available in the literature to understand the significance of heterocyclic aromatic hydrocarbons [4]. The synthetic methodologies have a profound impact on the design of novel polycyclic hetero-aromatic functional materials with tailor made properties. The tuning of the structure and hence the property of these class of compounds usually helps to improve the efficiency of light-emitting-diodes, photo-voltaic cells and field effect transistors [5,6]. The heterocyclic aromatic supramolecular compounds provide good carrier transport and physical properties [7]. In particular, the electron transport and electron injection properties of the compounds are enhanced by replacement of CH group with nitrogen heteroatoms [7a–f]. Wei et al. [8] reported the synthesis of polycyclic heteroaromatic compounds 1,5,9-triazacoronenes. Coronene is graphitic fragment with a zigzag periphery [9–11]. Nevertheless, there are only a few synthetic routes available in the literature to prepare nitrogenated polycyclic compounds [12]; such as 1,2-diazacoronene [12a] and 1,2,7,8-tetraazacoronene [12b]. The synthetic methods of such compounds require vigorous conditions; Diels-Alder reaction of diethyl azodicarboxylate with perylene and maleic anhydride refluxed at 350 °C. Since, these compounds are disc-shaped planar heteroaromatic systems, our aim is to evaluate the liquid crystal (LC) properties of them.

Discotic liquid crystals (DLCs) are composed of planar disc-shaped molecules, which have strong ability to form columnar or nematic phases with long-range order. They exhibit excellent charge carrier mobility because of their well-ordered arrangement at the molecular level. So, most of the DLCs are considered as efficient organic semiconductors and these are promising candidates for the photovoltaic technology [13,14].

The formation of CT complexes is important for the enhancement of stability and mesomorphic range of the LCs. In 1989, Ringsdorf et al. introduced the concept and mechanism of CT in DLCs [15]. They have shown that mesomorphism can be induced in amorphous polymers on doping with electron acceptors. Due to the presence of low molecular weight electron acceptors, the disc-shaped counterparts arranges in a columnar fashion.

In this work, our plan is to synthesize some new polycyclic heteroaromatic DLC compounds. We have synthesized a new series of disk-shaped 5-phenylnaphtho[1,2,3,4-lmn] phenanthridine derivatives. Interestingly, these compounds are LC at room temperature and they are not producing crystalline state even at −20 °C. Using these target compounds, the CT complexes are prepared by mixing them with

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equimolar amount of 2,3,6,7,10,11-hexakis(octyloxy)-triphenylene. The electrical conductivity of the CT complexes and pure target compounds is measured.

2. Experimental

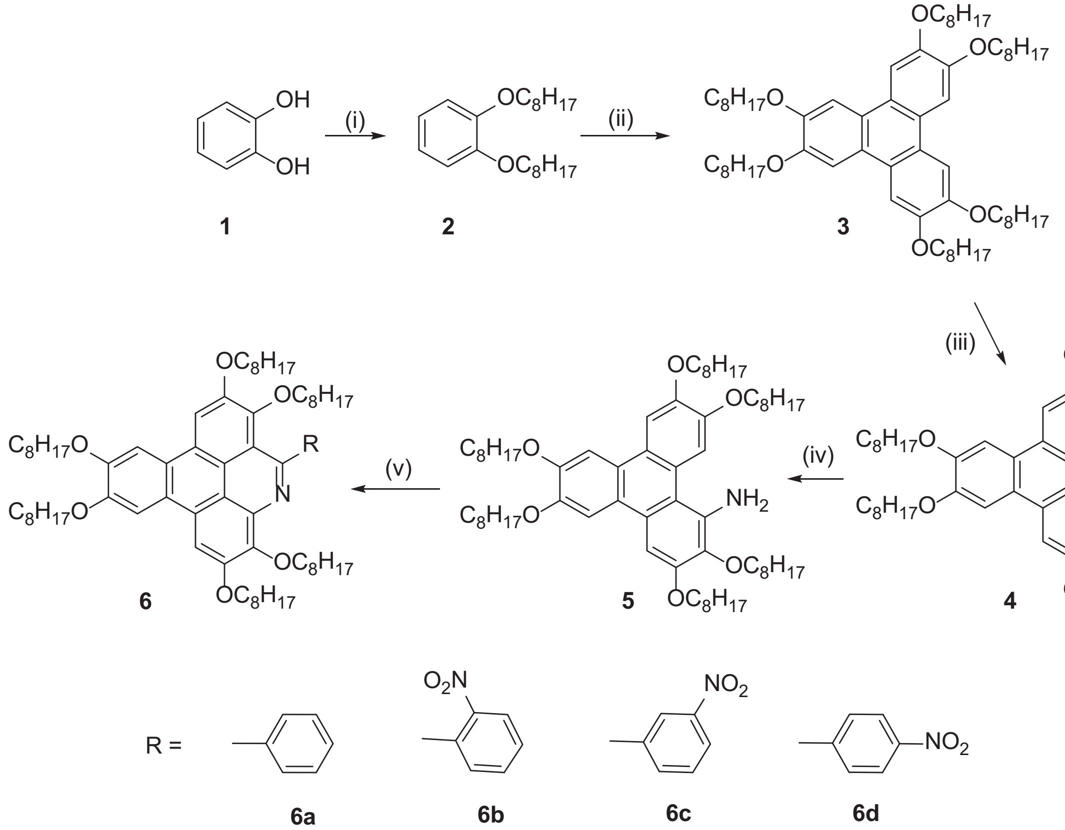
The disk-shaped 5-phenylnaphtho[1,2,3,4-lmn] phenanthridine derivatives **6a**–**6d** are synthesized in five steps (Scheme 1). Firstly, Catechol **1** was alkylated using the calculated amount of 1-bromooctane in presence of a mild base potassium carbonate. Alkylated catechol **2** was stirred with three equivalence of iron(III) chloride for an hour in order to get 2,3,6,7,10,11-hexakis(octyloxy)-triphenylene (**HAT8**) **3** [14a]. Then, mono-nitro triphenylene derivative **4** was synthesized by nitration using concentrated nitric acid [8]. Further, **4** was reduced using H_2/Raney Ni to obtain **5** [8]. The target compounds **6a**–**6d** were synthesized using Pictet-Spengler reaction [8]. In this reaction, hexaalkoxytriphenylene-1-amine **5** reacts with aldehydes such as benzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde; which undergoes condensation followed by cyclization. Here, acetic acid is used to create acidic media and to promote the 'insitu' cyclization.

General procedure for Pictet-Spengler reaction (**6a**): The intermediate compound **5** (1 g, 0.98 mmol) and benzaldehyde (0.116 g, 1.08 mmol) were refluxed in glacial acetic acid (10 mL) media for 10 h. Then, the reaction mixture was quenched with distilled water and extracted the target compound using dichloromethane. Further, the target compound was purified by column chromatography (silica gel: 100–200 mesh; mobile phase: 20% ethyl acetate/petroleum ether). The obtained dark yellow semisolid liquid crystal compound was dried over high vacuum for 10 min. The same procedure was used to synthesize nitro functionalized positional isomers **6b–d**.

6a: (911 mg, 91%), m.p. 99.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 8.42 (s, 1H, Ar), 8.2 (s, 1H, Ar), 8.0 (s, 2H, Ar), 7.7 (d, $J = 6.5$ Hz, 2H, Ar), 7.4 (d, $J = 7.5$ Hz, 3H, Ar), 4.4 (t, $J = 6.5$ Hz and 6 Hz, 2H, OCH_2), 4.39 (t, $J = 6.5$ Hz, 2H, OCH_2), 4.33 (q, $J = 6.5$ Hz, 6H, $OCH_2 \times 3$), 3.5 (t, $J = 5.5$ Hz and 6.5 Hz, 2H, OCH_2), 2.2–1.0 (m, 72H, $CH_2 \times 36$), 0.9 (t, 18H, $CH_3 \times 6$); ^{13}C NMR (125 MHz, $CDCl_3$): 158.5, 151.5, 150.9, 150.0, 149.5, 145.2, 144.4, 144.0, 136.2, 129.3, 127.4, 126.9, 124.5, 124.1, 123.3, 123.2, 117.9, 113.8, 110.5, 108.8, 107.7, 107.0, 77.2, 77.0, 76.7, 75.4, 74.8, 71.3, 69.9, 69.5, 31.9, 31.8, 31.6, 30.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 26.2, 25.7, 22.7, 22.6, 14.1, 14.0; Elemental analysis [Found %(Calculated %)]: C 79.77(79.80), H 10.25(10.18), N 1.18(1.27).

6b: (889 mg, 89%). m.p. 121.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 8.4 (s, 1H, Ar), 8.27 (s, 1H, Ar), 8.24 (d, $J = 8$ Hz, 1H, Ar), 8.0 (d, $J = 7$ Hz, 2H, Ar), 7.7 (t, $J = 7$ Hz and 7.5 Hz, 1H, Ar), 7.6 (d, $J = 7$ Hz, 1H, Ar), 7.5 (t, $J = 7.5$ Hz and 8 Hz, 1H, Ar), 4.4–4.2 (m, 10H, $OCH_2 \times 5$), 3.8 (t, $J = 6.5$ Hz and 8.5 Hz, 1H, Ar), 3.6 (t, $J = 6$ Hz and 8 Hz, 1H, OCH_2), 2.0–1.0 (m, 72H, $CH_2 \times 36$), 0.9 (t, 18H, $CH_3 \times 6$); ^{13}C NMR (125 MHz, $CDCl_3$): 155.4, 151.5, 150.4, 150.0, 149.5, 148.2, 144.3, 140.7, 136.1, 132.2, 131.9, 127.7, 124.6, 124.1, 123.8, 123.5, 123.3, 121.9, 118.2, 113.8, 110.7, 109.0, 107.7, 75.7, 73.8, 71.1, 69.9, 69.8, 69.5, 31.93, 31.90, 31.87, 31.84, 30.3, 29.8, 29.7, 29.6, 29.5, 29.48, 29.46, 29.35, 29.32, 29.2, 26.3, 26.2, 26.0, 25.7, 22.7, 22.6, 14.1, 14.0; Elemental analysis [Found %(Calculated %)]: C 76.59(76.66), H 9.72(9.69), N 2.41(2.45).

6c: (903 mg, 90%). m.p. 123.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 8.6 (s, 1H, Ar), 8.4 (s, 1H, Ar), 8.3 (d, $J = 8$ Hz, 1H, Ar), 8.2 (s, 1H, Ar), 8.08 (d, $J = 7.5$ Hz, 1H, Ar), 8.03 (s, 2H, Ar), 7.6 (t, $J = 8$ Hz, 1H, Ar), 4.4 (t, $J = 6$ Hz and 6.5 Hz, 2H, OCH_2), 4.4–4.3 (m, 8H, $OCH_2 \times 4$), 3.6 (t, $J = 5$ Hz and 5.5 Hz, 2H, OCH_2), 2.0–1.0 (m, 72H, $CH_2 \times 36$), 0.9 (t, 18H, $CH_3 \times 6$); ^{13}C NMR (125 MHz, $CDCl_3$): 155.8, 151.6, 150.7, 150.2, 149.7, 147.5, 145.7, 144.5, 136.1, 135.7, 127.7, 124.8, 124.4, 124.0, 123.4, 123.2, 122.4, 122.3, 117.3, 113.7, 111.0, 109.3, 107.6, 77.5, 77.2, 77.0, 76.7, 75.6, 74.5, 71.2, 70.0, 69.9, 69.5, 31.9, 31.8, 30.5, 29.8, 29.7, 29.6, 29.5,



Scheme 1. Synthesis of positional isomers 5-phenylnaphtho[1,2,3,4-lmn] phenanthridine derivatives. (i) Br-C_8H_{17}, K_2CO_3/KI, Me_2CO, 3 h, reflux; (ii) $FeCl_3$, CH_2Cl_2, 1 h, RT; (iii) Conc. HNO_3, CH_3NO_2/CH_2Cl_2, 12 min, RT; (iv) H_2/Raney Ni, dry THF, 2.4 h, RT; (v) RCHO, AcOH, 10 h, reflux.