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Liquid Crystals

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S. Kumar; M. Manickam; H. Schonherr

Online publication date: 06 August 2010

To cite this Article Kumar, S. , Manickam, M. and Schonherr, H.(1999) 'First examples of functionalized triphenylene discotic dimers: molecular engineering of advanced materials', *Liquid Crystals*, 26: 10, 1567 – 1571

To link to this Article: DOI: 10.1080/026782999203913

URL: <http://dx.doi.org/10.1080/026782999203913>

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Preliminary communication

First examples of functionalized triphenylene discotic dimers: molecular engineering of advanced materials

S. KUMAR*, M. MANICKAM

Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore-560 013, India

and H. SCHÖNHERR

University of Twente, Faculty of Chemical Technology,
 Department of Polymer Materials Science and Technology, P.O. Box 217,
 NL-7500 AE Enschede, The Netherlands

(Received 20 March 1999; accepted 19 May 1999)

A series of novel functionalized triphenylene discotic dimers was synthesized starting from 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylene. Nitration of monohydroxypentaalkoxytriphenylene gave the mononitromonohydroxypentaalkoxytriphenylene which was alkylated with 2-bromoethanol. The resulting alcohol was coupled with various diacids. These compounds are unique in that they possess an electron withdrawing group (and consequently a large dipole moment) connected directly to the aromatic core. It is well known that connecting two discotic molecules together via a spacer (discotic dimers) stabilizes the columnar mesophase significantly and often leads to the formation of glassy materials. The introduction of functionality into LCs allows the variation of their properties on a wide scale and opens the route to new synthetic supramolecular systems for various device applications.

Molecular architecture and functionalization are two important aspects in the molecular engineering of liquid crystalline (LC) materials [1]. In general, all optoelectronic LC device configurations need to control a few physical parameters, such as the supramolecular order of the mesophase, the stability of the mesophase, processability and electronic properties of the LC material. A combination of these properties in a compound requires design and synthesis of novel functionalized discotic dimers, oligomers, polymers or networks. Here we report the first examples of functionalized discotic dimers which can be considered as a prepolymer and are well suited for model studies.

Since their discovery [2], there has been an ever increasing interest in the synthesis of new monomeric, oligomeric and polymeric discotic LCs because of their remarkable properties, such as conductivity, photoconductivity, ferroelectrical and optoelectrical switching, electroluminescence, photovoltaic and optical data storage properties [3, 4]. It has been recognized that the supramolecular structure of disc-shaped molecules

is well suited for one dimensional energy transfer and charge migration [3, 4].

Among discotic LCs, triphenylene derivatives play an important role. These thermally and chemically stable materials can easily be prepared and purified. The very high charge carrier mobility in various mesophases of these materials make them suitable for use in one dimensional conductors [4], photoconductors [5] and light emitting diodes [6]. One dimensional energy transfer has also been studied extensively in these materials [7].

The importance of polymeric LCs has been well established [8]. Ringsdorf's group realized the synthesis of polymeric discotic LCs by preparing mono- and di-functionalized triphenylene derivatives and converted them into side chain and main chain polymers [9]. Discotic oligomers in general, or dimers in particular, represent ideal model compounds for discotic polymers or networks, due to their ease of purification and characterization and the possibility of freezing, in their columnar phase, to a glassy state. Discotic twins based on a benzene core were first reported by Lillya and Murthy [10]. Recently, several other dimers based on a benzene core were reported by Zamir *et al.* [11]. Praefcke and co-workers also found a biaxial nematic

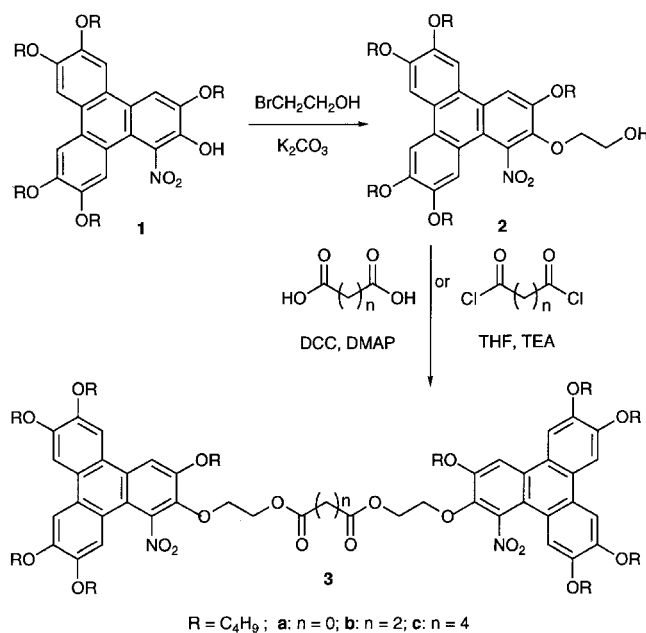
* Author for correspondence; e-mail: uclcr@giasbg01.vsnl.net.in

phase in the discotic twins formed by alkynylarene ethers [12]. They also reported discotic dimers based on scyllo-inositol [13]. Examples of other discotic dimers include derivatives of phthalocyanine [14], cyclotetraveratrylene [15] and a combination of rod- and disk-like mesogenic units [16]. Three types of triphenylene-based discotic dimers are known: (1) where two triphenylene molecules are connected via an alkyl chain spacer [17, 18]; (2) where two triphenylene molecules are connected via two alkyl chains [18]; and (3) a special type of dimer, 'The Wheel of Mainz,' in which the spacer is a rod-like molecule [19].

As mono- and di-functionalized triphenylenes are the precursor molecules for the preparation of discotic dimers, oligomers and polymers, several research groups are currently working on their synthesis [20]. The functionalization, however, is restricted to hydroxy groups, and the desirable possibility to change or tune the electronic properties of the molecule cannot be accomplished in this way. Most triphenylene discotic LCs are colourless, low fluorescent materials and thus their use in many applications is limited. In an effort to enhance the fluorescence as well as the mesogenicity of triphenylene discotic LCs, we have synthesized a number of new monofunctionalized triphenylene and mixed tail triphenylene discotics bearing conjugative electron withdrawing substituents attached directly to the triphenylene core [21]. In order to induce molecular dipoles, colour etc., Boden's group has recently nitrated the triphenylene discotics at the 1-position [22, 23]. We have recently reported that not only the single ring but all the three rings of hexaalkoxytriphenylene can be nitrated easily [24]. Hitherto, only these two types of functionalized discotic materials have been known. We anticipated that hybridization of these two varieties of functionalized discotics would lead to extremely important novel double functionalized derivatives; one type of functional group could be used to tune the electronic nature of the molecule, and at the same time the other may be utilized to convert them into a processable dimer, oligomer or polymer. Here, we present a first step towards this goal by describing the synthesis of functionalized discotic dimers based on a triphenylene core.

The synthesis of the (nitro) functionalized triphenylene dimers is shown in the scheme. The precursor monomer, 1-nitro-2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene **1** was prepared and characterized as previously reported [24]. Compound **1** is not very stable and has to be functionalized rapidly after isolation. Therefore, we alkylated it with 2-bromoethanol to obtain the alcohol **2**. Compound **2** was easily converted to various functionalized dimers by condensing with different diacids or diacid dichlorides. All the compounds appear homogeneous on TLC. Mass, $^1\text{H NMR}$, $^{13}\text{C NMR}$, IR and UV spectra of the products were found to be in good agreement with the structure.

The thermal behaviour of all the compounds was investigated by polarizing optical microscopy and differential scanning calorimetry (Perkin-Elmer DSC7) with heating and cooling rates of $10^\circ\text{C min}^{-1}$. Data from heating and cooling cycles are collected in the table. The peak temperatures are given in $^\circ\text{C}$ and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1} .



Scheme. Synthesis of functionalized triphenylene dimers.

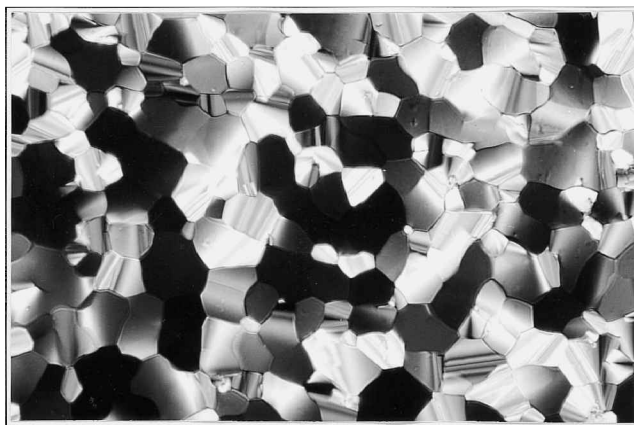
Table. Phase transition temperatures ($^\circ\text{C}$) and enthalpies (kJ mol^{-1} , in parentheses) of nitrotriphenylenes. Cr = crystal, Col_h = hexagonal columnar liquid crystalline phase, I = isotropic.

Compound	Heating scan	Cooling scan
3a	Cr 198.8 (75.0) I	I 169.1 ^a (17.6) Col_h 146.7 (28.5) Cr
3b	Col_h 163.0 (17.1) I	I 160.9 (17.0) Col_h
3c	Col_h 144.9 (11.8) I	I 142.5 (4.0) Col_h 135.2 (2.7) Col_h

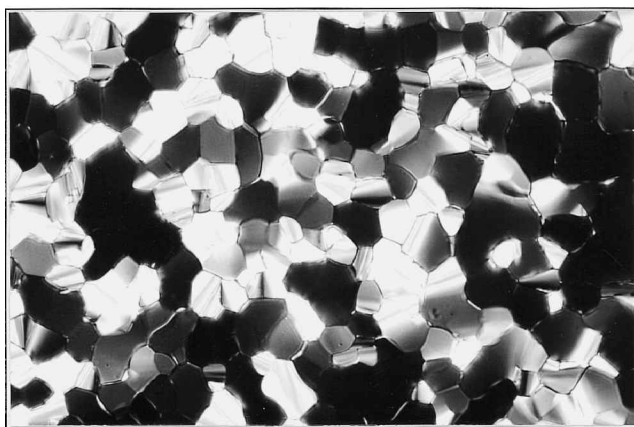
^a Metastable.

All the liquid crystalline materials mentioned above show the classical textures of columnar mesophases upon cooling from the isotropic liquid. These textures are very similar to known textures for Col_h phases and miscible with those of the well characterized Col_h phase of mononitro-hexaalkoxytriphenylenes [22, 24]. On first heating, the functionalized dimer **3a** with the shortest connecting chain, gives only one peak in the DSC at 198.8°C with a large ΔH , corresponding to a transition from the crystalline solid state to the isotropic liquid state. Upon cooling from isotropic liquid it comes to a metastable Col_h phase at about 169.1°C. This monotropic mesophase has a high crystallization tendency, which starts in the mesophase and is complete at 146.7°C. On subsequent heating, this material starts to decompose, as evident from its colour change and the appearance of two broad melting peaks in the DSC run. On the other hand its higher homologues were found to be very stable on several heating and cooling cycles. Compound **3b** on heating shows a sharp transition to the isotropic liquid at 163°C. The transition reappears on the cooling cycle with very limited supercooling. The optical texture at 140°C (obtained upon cooling) is shown in the figure, (a). The room temperature texture shown in the figure, (b), was retained for several days. The material is highly viscous and it is possible that it has formed a glass but we did not observe any clear glass transition in the DSC run. The mesophase also shows no sign of crystallization on keeping at room temperature for more than four months or cooling to -50°C . Similar behaviour has also been reported in the phthalocyanine- and triphenylene-based discotic dimers [14, 17]. It should be noted that Kranig *et al.* have reported glass formation in triphenylene-based discotic dimers and trimers but they were unable to detect it by DSC [17]. Compound **3c**, on cooling from isotropic liquid, forms the columnar mesophase at 142.5°C and does not show any textural change down to room temperature. However its DSC on cooling shows two peaks at 142.5 and 135.5°C. In optical microscopy no change is observed at the transition at 135.5°C. X-ray investigations have yet to be done to assign the nature of these mesophases. On heating, **3c** shows two unresolved broad peaks at the peak temperature 144.9°C. In both **3b** and **3c** we saw no crystal melting transition, but this type of abnormal behaviour has also been reported for many other discotic LCs [14, 25].

In conclusion, we report for the first time the synthesis and mesophase characterization of three functionalized triphenylene-based discotic dimeric liquid crystals by connecting two (nitro) functionalized triphenylene derivatives via ester linkages. These yellow coloured materials with polar nitro group have a broad mesophase range. The nitro group is a valuable precursor to a variety of



(a)



(b)

Figure. Optical texture of the dimer **3b** at (a) 140°C, (b) 30°C (crossed polarizers, magnification $\times 300$).

substituents in aromatic systems. Its effects on monomeric triphenylene discotic LCs have previously been discussed [22, 23]. The present work represents a novel step towards the preparation of potentially useful functionalized triphenylene-based discotic polymeric mesogens. The synthesis of various functionalized discotic oligomers and polymers continues in this laboratory.

We are very grateful to Prof. S. Chandrasekhar for helpful discussions and gratefully acknowledge the technical assistance of Mr. Sanjay K. Varshney. We are indebted to Professor G. J. Vancso for his keen interest in this work.

Appendix

*Synthesis of dimers **3a**, **3b** and **3c***

Chemicals and solvents (AR quality) were obtained from E. Merck and used without further purification. Column chromatographic separations were performed

on silica gel (Merck, Kieselgel 60, 230–400 mesh) and neutral aluminum oxide. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). NMR and mass spectra were recorded on a 200 or 250 MHz Bruker Ac 250 NMR spectrometer and Finnigan Mat 90 spectrometer. All chemical shifts are reported in δ units downfield from Me₄Si. UV spectra were recorded on a Perkin Elmer Lambda 20 spectrometer; IR spectra were recorded on a Perkin Elmer Spectrum 1000 spectrometer. Compounds **1** and **2** were prepared as reported earlier [24].

Procedure (a). A stirred solution of the nitroalcohol **2** (100 mg, 0.144 mmol) in dry THF (1 ml containing 4 drops of triethylamine) was cooled to 0°C. The appropriate diacid dichloride (0.072 mmol) in 0.5 ml CCl₄ was added to this solution. The reaction mixture was stirred at room temperature for 15 h; it was then poured into ice-cold aqueous 0.1 N HCl (10 ml) and extracted with dichloromethane (3 × 10 ml). The combined ether extracts were washed with water and brine and then dried over anhydrous sodium sulphate. The solvent was removed under vacuum and the resultant product purified by column chromatography over silica gel. Elution with hexane–dichloromethane afforded a yellow solid that was recrystallized from ether–ethyl alcohol. Yields, 60–70%.

Procedure (b). A solution of the appropriate diacid (0.072 mmol) in dry DMF and carbon tetrachloride was cooled to 0°C. DCC (0.079 mmol); nitroalcohol **2** (0.144 mmol) and DMAP (5 mg) were added to this mixture. The reaction mixture was stirred at room temperature for 24 h. The crude products were purified as described above. Yields, 50–55%.

3a: MS (FAB): M⁺ 1440.9. ¹H NMR: δ 7.68, s, 2H; 7.59, s, 2H; 7.37, 2s, 4H; 4.65, m, 4H; 4.50, t, 4H; 4.25–4.0, 4 unresolved t, 16H; 3.29, t, 4H; 1.89, m, 20H; 1.55, m, 20H; 1.0, m, 30H.

3b: MS (FAB): M⁺ 1468.8. ¹H NMR: δ 7.82, s, 2H; 7.75, s, 2H; 7.71, s, 2H; 7.65, s, 2H; 7.44, s, 2H; 4.43, s, 8H; 4.3–4.0, 3 unresolved t, 20H; 2.77, s, 4H; 1.89, m, 20H; 1.56, m, 20H; 1.0, m, 30H.

3c: MS (FAB): M⁺ 1496.8. ¹H NMR: δ 7.85, s, 2H; 7.76, s, 2H; 7.72, s, 2H; 7.68, s, 2H; 7.44, s, 2H; 4.41, s, 8H; 4.3–4.0, 3 unresolved t, 20H; 2.42, t, 4H; 1.89, m, 20H; 1.56, m, 22H; 1.0, m, 30H. ¹³C NMR: δ 173.30, 150.27, 150.06, 149.12, 149.04, 148.92, 143.60, 139.64, 127.01, 124.68, 124.45, 121.78, 119.17, 114.30, 107.71, 107.32, 107.01, 106.59, 72.41, 69.53, 69.33, 69.09, 68.56, 63.20, 33.74, 31.39, 31.24, 31.03, 24.29, 19.32 and 13.92. UV: λ_{max} (CHCl₃) 380, 328, 280 nm. IR: ν_{max} (KBr) 2959, 2936, 2872, 1740, 1616, 1529, 1462, 1433, 1392, 1269, 1178, 1082 cm⁻¹.

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