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Preliminary communication

First example of a functionalized triphenylene discotic trimer: molecular engineering of advanced materials

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A new type of functionalized discotic oligomer system has been realized whose molecular architecture consists of a trisubstituted benzene as central core and three nitro-functionalized triphenylenes as regional cores. These regional cores are linked to the central core via ether linkages through an alkyl chain spacer. Polarizing microscopy and calorimetric measurements reveal the existence of a monotropic columnar mesophase in this novel functionalized oligomer. The product does not crystallize at room temperature over a long period (*c.* five months) or on cooling to − 50°C. The corresponding unfunctionalized trimer is not liquid crystalline. The dipolar interaction of nitro groups is probably responsible for the induction of mesogenicity. The introduction of functionality into liquid crystal oligomers permits the variation of their properties on a wide scale and opens the route to new synthetic supramolecular systems for various device applications.

The work of Chandrasekhar on the hexa-esters of benzene resulted in the discovery of discotic liquid crystals (LCs) [1]. Since then, a number of hexasubstituted benzene derivatives have been reported to show columnar mesophases. These include various hexa-alkanoyloxybenzene derivatives, hexakis(alkoxyphenoxymethyl) derivatives, hexakis(alkylsulfone) derivatives, various multiynes, and a combination of ester and amide groups [2]. Some partially acylated and tetrasubstituted benzene derivatives are also known to show columnar mesophases [2]. A few 1,3,5-trisubstituted benzene derivatives were also reported to form columnar mesophases but their structures have not been confirmed unambiguously [2]. It was anticipated that three elongated chains are not sufficient to fill the space around the core and therefore, could not allow the existence of columnar mesophases [3]. In order to fill the space around the trisubstituted cores, branched substituents have been designed, to create 'super-disk' cores [4] with either six or nine elongated side chains [3, 5]. Only a few compounds having only three side chains, e.g. decacyclene derivatives [6], and triphenylene derivatives [7] are known to show columnar mesophases.

Triphenylene derivatives play an important role in the field of discotic LCs. These thermally and chemically stable materials can easily be prepared and purified. The very high charge carrier mobility in various mesophases of these materials makes them suitable for use in one-dimensional conductors [8, 9], photoconductors [9, 10] and light-emitting diodes [11]. One-dimensional energy transfer has also been studied extensively in these materials [12].

In general, there are four main physical parameters to control in all opto-electronic LC device configurations: (1) supramolecular order of the mesophase, (2) stability of the mesophase, (3) processability, and (4) photophysical 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, networks or polymers. Functionalization of the core is necessary for tailoring the mesophase properties, photophysical properties and processability; several research groups are therefore currently working on the synthesis of functionalized triphenylene derivatives [13]. Previously, we have shown that various hydroxyalkoxytriphenylenes are accessible by simple strategies, often on a large scale [13, 14]. In an effort to enhance 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

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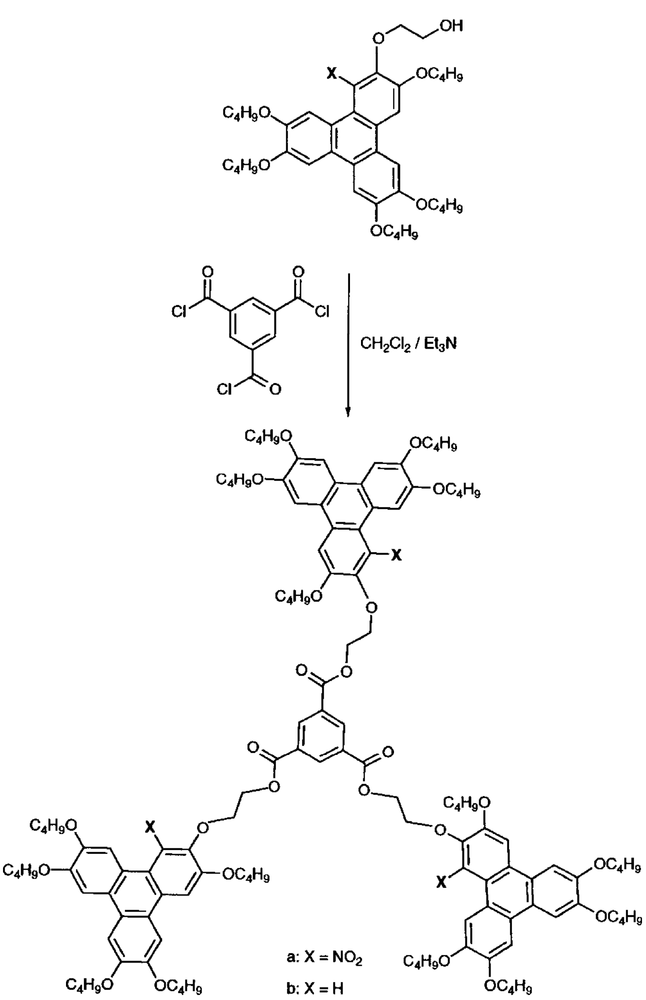
[15]. In order to induce a molecular dipole, colour, etc., Boden and Praefcke and their co-workers have recently nitrated and halogenated the triphenylene core [16, 17]. We have recently observed that not only the one ring as reported [16, 17] but all the three rings of hexa-alkoxytriphenylene can be nitrated easily [18]. Hitherto, only these two types of functionalized discotic materials were known. We realized that hybridization of these two varieties of functionalized discotics would lead to extremely important novel double functionalized derivatives, where one type of functional group can be used to tune the electronic nature of the molecule and, at the same time, the other may be utilized to convert the molecules to a processable dimer, oligomer or polymer. Very recently we have reported the first examples of functionalized discotic dimers [19]. In this preliminary communication we wish to report the first example of a functionalized discotic oligomer.

The synthesis of the (nitro) functionalized triphenylene oligomer is shown in the scheme. The functionalized triphenylene alcohol **1a** was prepared as reported earlier [18]. Condensation of three molecules of this alcohol with one molecule of 1,3,5-benzenetricarboxylic acid chloride easily furnished the desired functionalized trimer **2a**. It was purified by column chromatography over silica gel and well characterized by spectral analysis. The corresponding unfunctionalized trimer **2b** was also prepared similarly, for comparison of the mesophase behaviours.



Scheme: Synthesis of trimers **2a** and **2b**.

The thermal behaviour of both trimers was investigated by polarizing optical microscopy and differential scanning calorimetry (DSC) on 1–2 mg samples using a Perkin-Elmer DSC7 with heating and cooling rates of 10°C min^{-1}. The functionalized trimer shows two peaks on first DSC heating run: a weak transition at 161.1°C (ΔH, 2.0 J g^{-1}) and another broad peak at 181.3°C with a large ΔH (36.3 J g^{-1}), corresponding to a transition from the crystalline solid state to the isotropic liquid state. Upon cooling from isotropic liquid the columnar phase is formed at 158.7°C (ΔH, 10.9 J g^{-1}). The optical texture of this mesophase (figure 1) closely resembles the known textures for $\mathrm{Col_h}$ phases and it is miscible with the well characterized $\mathrm{Col_h}$ phase of mononitro-hexa-alkoxytriphenylene [16, 18]. On second heating it shows a sharp peak at 162.0°C (ΔH, 10.6 J g^{-1}). The mesophase reappears on cooling at 158.8°C and does not show any sign of crystallization on keeping at room temperature for more than five months. Dimers and oligomers often show glass transitions at low temperature but we did not observe any clear glass transition or crystallization on cooling to – 50°C. On the other hand, the corresponding unfunctionalized oligomer **2b** is a non-liquid crystalline material. It melts at 185°C and crystallizes at 166°C on cooling.

In these oligomers, strong interactions of the triphenylene units is rather more important than the core–core interaction of the central benzene core, which

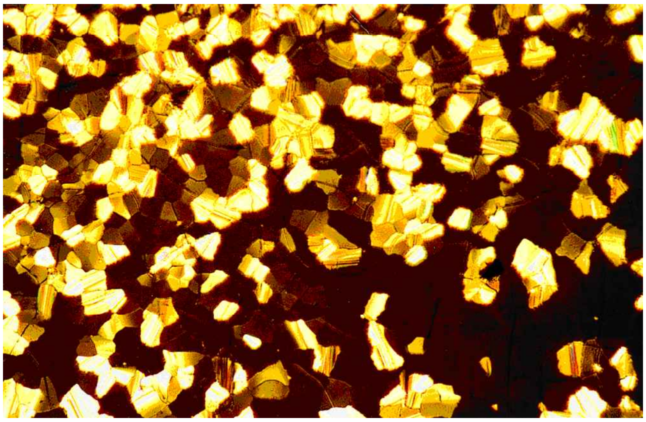


Figure 1. Optical texture of the oligomer **2a** at 30°C.

is negligible as reflected by the long spacing (4.7 Å) between the benzene rings in trisubstituted benzene derivatives [20]. As the unfunctionalized trimer **2b** is non-mesogenic, the dipolar interaction of the nitro group is possibly of importance in the supramolecular structure formation of the functionalized trimer **2a**. However, several other derivatives with different spacers and alkyl chains must be prepared to confirm this conclusion. Work in this direction is in progress in this laboratory.

Selected data for compound **2a**: Mass: m/z (FAB) 2237.4; ^{1}H NMR ($CDCl_3$): δ 9.07 (s, 3H), 7.58 (s, 3H), 7.45 (s, 3H), 7.41 (s, 3H), 7.34 (s, 3H), 7.12 (s, 3H), 4.7 (br s, 6H), 4.5 (br s, 6H), 4.29 (t, 6H), 4.19 (t, 6H), 4.06 (t, 12H), 3.71 (t, 6H), 1.9–1.3 (m, 60H), 1.05 (m, 36H) and 0.77 (t, 9H).

Selected data for compound **2b**: Mass: m/z (FAB) 2102.5; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 3H), 7.76 (m, 18H), 4.7 (m, 6H), 4.5 (m, 6H), 4.2 (m, 30H), 1.9–1.3 (m, 60H) and 1.0 (m, 45H).

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