

# First examples of monodisperse discotic liquid crystal pentamers: synthesis and mesomorphism

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## Abstract

The synthesis and mesomorphism of the first examples of ‘discotic liquid crystal pentamers’ are reported. Structural characterization of these difunctional pentamers has been achieved by FTIR, NMR, and elemental analysis. The mesophase behavior exhibited by these ‘star-shaped’ molecules has been studied by polarizing optical microscopy and differential scanning calorimetry. The columnar hexagonal structure of the mesophase was established with the help of X-ray diffraction studies.

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Liquid crystals are unique functional self-organized soft-materials which possess order and dynamics. Recently, liquid crystals formed by disc-shaped molecules have attracted growing interest because the supramolecular order of their columnar phases are of fundamental importance, not only as models for the study of energy and charge migration in self-organized systems, but also as functional materials for device applications such as one dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field effect transistors, and gas sensors. The functional capabilities of these materials are due to their ease of processibility, spontaneous alignment between electrodes and self-healing of defects owing to their dynamic nature.<sup>1</sup>

Very recently a great deal of attention has been paid to liquid crystal oligomers.<sup>2</sup> The physical properties of liquid crystal oligomers are significantly different from those of conventional low molar mass liquid crystals. Liquid crystal oligomers serve as ideal models for polymers or networks due to the striking similarity in their transitional behavior and, like polymers, some oligomers form glassy mesopha-

ses. Their purification and characterization are simple, owing to the restricted motion of the components, liquid crystal oligomers provide and stabilize a variety of fluid phases with fascinating functions and the oligomeric approach provides a wide flexibility in molecular design. However, compared to the number of calamitic oligomers, discotic oligomers are rare. In this context, we are interested in the design and synthesis of novel functional discotic oligomeric materials and their mesophase behavior. In this Letter, we report the first examples of monodisperse discotic liquid crystal pentamers. Our aim is threefold: (i) to realize monodisperse discotic liquid crystal pentamers; (ii) the molecular design is such that it contains the well studied electron-rich triphenylene moiety<sup>3</sup> as the periphery and electron-deficient anthraquinone<sup>4</sup> as the central core. These molecular double-cables<sup>5</sup> owing to their disproportionate core sizes may stack one on top of the other in the columns to give columnar double-cables which could eventually provide side-by-side percolation pathways for electrons and holes in solar cells; (iii) since these star-shaped oligomers are difunctional in nature mixed-chain discotic polymers and novel star-shaped heptamers can be realized containing two different kinds of discotic cores possessing opposite electronic properties.

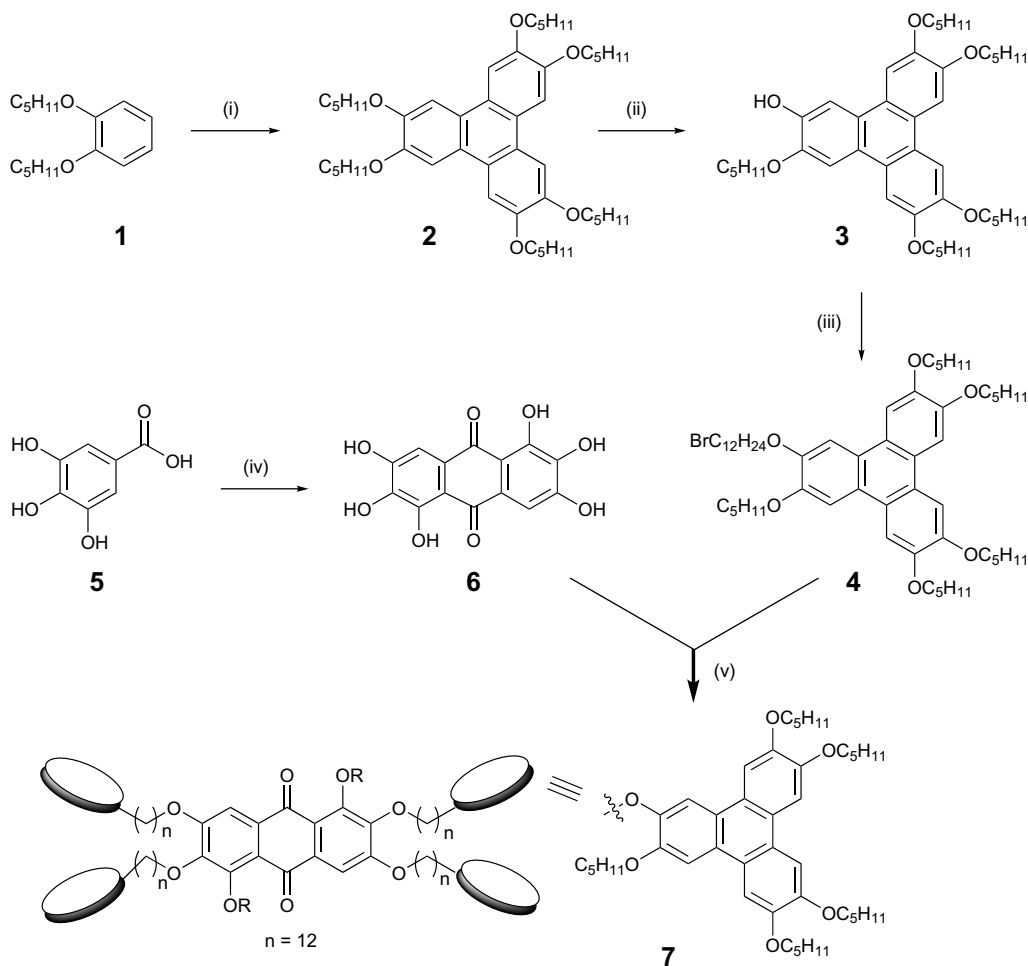
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The synthetic route to the discotic pentamers **7** is shown in Scheme 1. Hexapentyloxytriphenylene **2**, monohydroxy-pentakis(pentyloxy)triphenylene **3**,  $\omega$ -bromo-substituted triphenylene **4**, and rufigallol **6** were prepared as reported earlier.<sup>6,7</sup> Rufigallol **6** was alkylated under mild etherification conditions<sup>8</sup> with  $\omega$ -bromo-substituted triphenylene **4** to furnish the pentamer **7** leaving the less reactive intramolecular hydrogen-bonded hydroxyl groups at the 1- and 5-positions unreacted. The dihydroxyl functionalized pentamer **7** was acetylated to its corresponding diacetate (**7diAc**, not shown in Scheme 1) with acetic anhydride and sulfuric acid under classical conditions. The chemical structure of the pentamer was confirmed by spectral techniques and elemental analysis.<sup>9</sup> The notable spectral features of the pentamer are as follows: in its proton NMR **7** shows a peak at  $\delta$  12.74 corresponding to two intramolecular hydrogen bonded protons along with two aromatic-proton resonances at  $\delta$  7.8 and 7.3 corresponding to triphenylene and anthraquinone in the ratio 12:1, whereas diacetate **7diAc** did not show any signal at  $\delta$  12.74 but instead demonstrated a singlet at  $\delta$  2.47 corresponding to the  $-\text{COCH}_3$  protons. The aromatic peak corresponding to anthraquinone protons shifted from  $\delta$  7.3 to  $\delta$  7.6 upon acetylation. Similarly pentamer **7** shows

a signal at  $\delta$  186.3 in its  $^{13}\text{C}$  NMR spectrum corresponding to intramolecular hydrogen-bonded quinone carbonyl groups. This signal was shifted to  $\delta$  180.1 in pentamer **7diAc**, the acetyl carbonyl group appeared at  $\delta$  169.0. In addition, the FTIR spectrum of **7diAc** shows the acetyl carbonyl absorption at  $1763\text{ cm}^{-1}$ . The elemental analysis data were in very good agreement with the chemical structures of the star-shaped pentamers **7** and **7diAc**.

The mesophase behavior of both the solvent crystallized compounds **7** and **7diAc** was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Both compounds exhibited enantiotropic liquid crystalline phases over broad temperature ranges. Between crossed polarizers, the growth of typical defect textures of columnar phases appeared on cooling from the isotropic phases. The formation of mosaic texture with homeotropic domains like other star-shaped oligomers has been observed (Fig. 1). The textures are mobile down to room temperature without further change in the texture. Even over a period of months, no indication of crystallization could be detected by microscopy.

DSC measurements of both the pentamers revealed only one first order transition for cooling and heating runs,



Scheme 1. Synthesis of discotic liquid crystalline pentamers. Reagents and conditions: (i), (ii), (iii), (iv) as given in Refs. 6 and 7; (v) DMSO, NaOH, 90 °C, 20 h, 10%.

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