

# Study of mesogenic properties and molecular conformation from a heterogeneous tetramer with a triphenylene centre core and three cyanobiphenyl tails

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## Abstract

A novel liquid crystalline material which consists of both discotic and calamitic units to form a star structure bearing a triphenylene as centre core and three cyanobiphenyl tails has been synthesized. Phase behaviour of the material was investigated using polarised optical microscopy, thermal analysis and X-ray diffraction. The heterogeneous tetramer showed multi-mesophases that can be kinetically controlled. When the pure tetramer was heated up and cooled down at  $10\text{ }^{\circ}\text{C min}^{-1}$  directly, it showed only a crystalline phase and no mesophase. The annealing sample showed smectic mesophase and the quenched sample showed nematic phase, columnar phase can be induced by TNF in the binary system containing the tetramer and TNF.

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## 1. Introduction

The molecular self-organization and self-assembly at a nanometer or micrometer scale are useful strategies in the development of novel function materials and are currently exciting areas of intense research [1]. Liquid crystalline materials are self-assembling by nature and can offer a very elegant and effective way of controlling and tuning the physical properties that ultimately define the self-organizing and self-assembly process. Investigation of the structures and properties of liquid crystalline materials may lead to further understanding the self-organizing and self-assembling processes and the control through the mesophase [2]. Molecule having different types of

mesogenic units bonded within one entity may have interesting phase behaviour and property and will always be used as self-assembly materials. Such structure has been synthesized with two or more of the different mesogenic units tied together to give “heterogeneous” dimer, “heterogeneous” trimer, or even oligomer and dendrimer via covalent or non-covalent bond [3–11]. It has been reported that multiple mesophases may be observed if the molecular entity contain two types of mesogenic units. The shorter the linking group, the more likely the material behaves as one supermolecular entity; whereas the longer the spacer, the more likely it is that the properties of the individual mesogenic unit will dominate the overall properties of the material [12–14].

When two types of mesogens are linked together, three factors may affect the formation of mesophase: (1) The degree of the two which the mesogenic units are decoupled from the central structure is important, the shorter the linking unit, the more likely the material will act as a single supermolecular entity, where the longer the spacer the more likely it is that the properties of the individual mesogenic groups will dominate the

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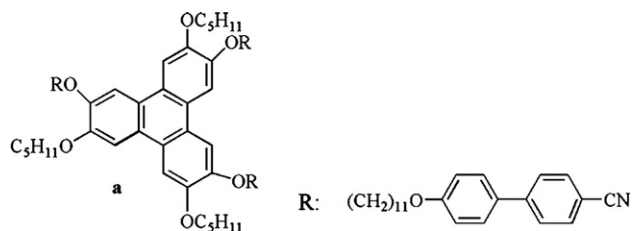


Fig. 1. The molecular structure of the investigated heterogeneous tetramer.

overall properties of the materials. (2) Number density—the number of mesogens groups attached to the periphery, which can effectively change the overall gross shape of the structure of the supermolecule. (3) Orientation of the attachment—the effect that the type (rod-like, disc-like or spherulitic) of mesogenic group attached together has not been researched extensively, each type of molecular shape will support different types of self-organized mesophase structure, thus for supermolecular materials, rod-like systems tend to support nematic mesophases (including the various possibilities of smectic polymorphism), disk-like system tend to support columnar mesophases [15].

In this work, a novel tetramer bearing a triphenylene and three cyanobiphenyl units linked by  $C_{11}$  alkyl chain spacers has been synthesized, the molecular structure was shown in Fig. 1. The symmetric tri-hydroxyl triphenylene core was prepared by the common trimerization of *o*-dialkoxybenzene route with iron chloride [16] and selective ether cleavage with *B*-bromocatecholborane [17]. The linkage of the triphenylene core and the three cyanobiphenyl using esterification to give the tetramer has been described everywhere.

## 2. Experimental section

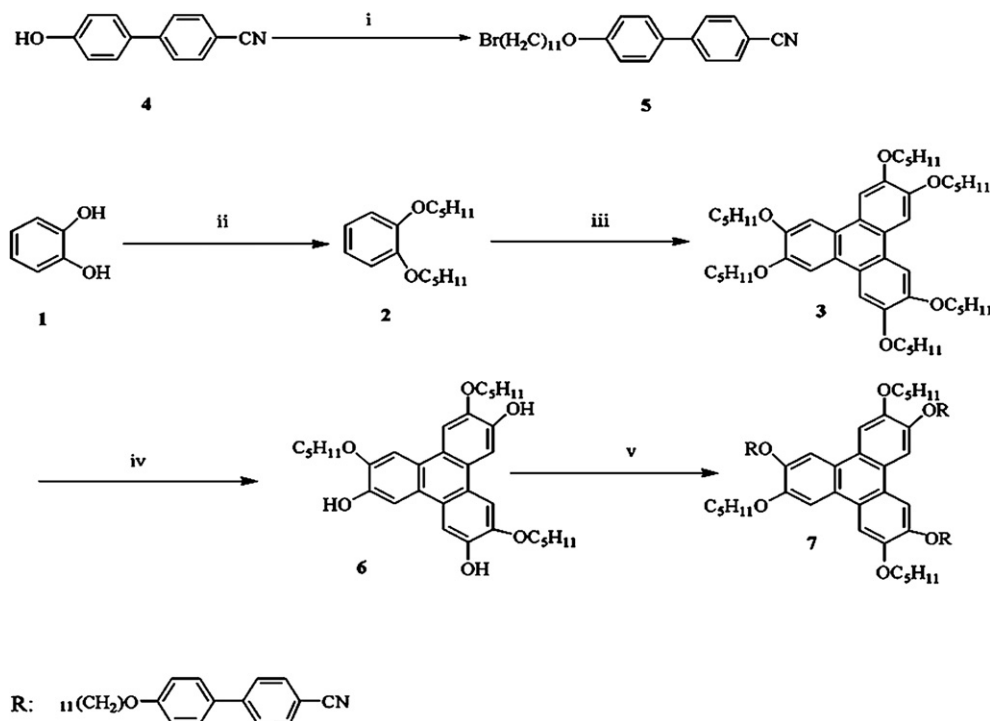
### 2.1. General

The heterotetramer was synthesized following the general synthetic route in Scheme 1. Catechol was alkylated with 1-bromopentane as described in the literature. Hexakis(pentyloxy) triphenylene was prepared by the trimerization of *o*-bis(pentyloxy)benzene using iron chloride as oxidant in the presence of only a catalytic amount of  $H_2SO_4$  (0.3%) in dichloromethane. The hexaki(alkoxy)triphenylene was selective ether cleavage using *B*-bromocatecholborane. The linkage of the triphenylene core and the three cyanobiphenyl was prepared by using esterification to give the heterotetramer.

### 2.2. Synthesis

#### 2.2.1. 2, 6, 10-tri [(11-(4'-cyano-biphenyl-4-loxy) undecyloxy)]-3, 7, 11-tris (pentyloxy) triphenylene

The mixture of 4'-(11-bromoundecyloxy)-4-cyanobiphenyl (0.94 g, 2.2 mmol), 2,6,10-trihydroxy-3,7,11-tris(pentyloxy) triphenylene (0.29 g, 0.55 mmol), potassium carbonate (3 g, 21.7 mmol), and DMF (30 ml) was placed in a 100 ml flask equipped with a condenser,  $N_2$  inlet, and magnetic stirrer. The mixture was heated to 75 °C and stirred overnight. The reaction mixture was removed from heat, filtered, and washed with  $CHCl_3$ . The excess solvent was evaporated under reduced pressure and the remaining liquid was poured in methanol to precipitate the product. The solid was filtered, dissolved in  $CH_2Cl_2$  and the mixture was transferred to a



Scheme 1. Synthetic routes for the preparation of the tetramer. Reagents and conditions: (I)  $Br(CH_2)_{11}Br$ ,  $K_2CO_3$ , acetone, reflux, yield:78%; (II)  $Br(CH_2)_4CH_3$ ,  $K_2CO_3$ /ethanol, reflux, yield: 91%; (III)  $FeCl_3/CH_2Cl_2$ , MeOH, yield: 64%; (IV) *B*-Bromocatecholborane/ $CH_2Cl_2$ , yield: 47%; (V) DMF,  $K_2CO_3$ , 78 °C, 12 h, yield: 11.8%.

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