

Synthesis of novel mixed tail triphenylene discotic liquid crystals—the search for higher order

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Tribromo-trialkoxytriphenylenes and trialkoxytriphenylenes are derivatized directly on a polyaromatic core to give novel discotic liquid crystals radially substituted symmetrically and asymmetrically with two different functionalities.

Although discotic liquid crystals (LCs) were discovered 18 years ago,¹ only recently has their potential use in optoelectronic devices been investigated. Electrical conductivity in both p-doped and n-doped discotic LCs has been studied extensively.² In addition, photoconductive discotic LCs have been used in photovoltaic cells³ and optical data storage.⁴ Recently, triphenylene based discotics have emerged as a new class of fast photoconductive materials.⁵ A charge carrier mobility (hole mobility) of $0.8 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported for the hexagonal columnar (D_h) phase of hexapentyloxytriphenylene **1**.

An even higher charge carrier mobility of $1 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported⁶ for the unique helical columnar phase of hexahexylsulfanyltriphenylene.⁷ The high charge carrier mobility in this material has been attributed to increased long range positional order that occurs due to a helical arrangement of molecules within the columns.

In light of the dramatically enhanced charge carrier mobility in the helical columnar phase, we became interested in the design and synthesis of triphenylene discotics possessing highly ordered phases. Thus, we propose that limiting or biasing the molecular rotation within the columns will lead to fewer degrees of rotational freedom within the column and result in higher overall order in the mesophase. In principle, hindrance to rotation could be achieved *via* unfavourable steric interactions, and/or intermolecular dipole–dipole interactions.

In order to test and refine this approach we required a synthetic methodology with which we could specifically modify the triphenylene core by adding bulky or polar groups without sacrificing mesogenicity. Here we report our recent efforts in this area and new discotic LC materials thus obtained. Two derivatives do indeed exhibit higher ordered phases.

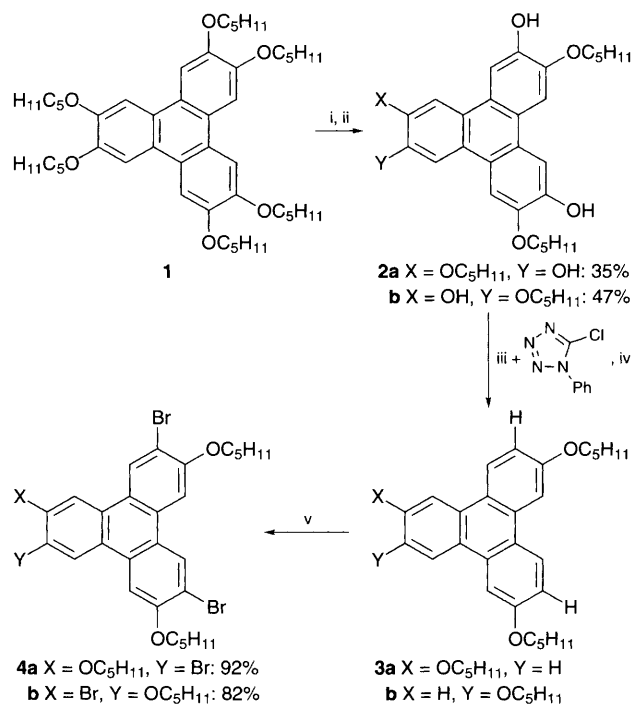
Previously, a selective ether cleavage giving the two isomeric trihydroxytriphenylene derivatives **2a** and **2b** from pentapentyloxytriphenylene was reported⁸ (Scheme 1). Additionally, we showed that **2a** could be derivatized and subsequently hydrogenated to yield the trialkoxytriphenylene **3a**.⁹ **3a** was then brominated to give **4a**, the first triphenylene discotic LC having only three aliphatic tails. We now report that this same two step procedure can be applied to the asymmetric isomer **2b**, albeit in slightly lower yields. While the asymmetric tribromotriphenylene **4b** is also mesogenic, it is interesting to point out that **2a**, **2b**, **3a** and **3b** are all nonmesogenic. We believe that the steric bulk of the bromine atoms plays an important role in inducing mesogenicity by effectively extending the triphenylene core. Efforts are currently underway to synthesize the complete trihalogenated series of trialkoxytriphenylenes in order to further explore this proposal.

As shown in Scheme 2, **3a** and **4a** have proven to be versatile precursors for direct functionalization of the triphenylene core. Friedel–Crafts acylation of **3a** with acetyl chloride and

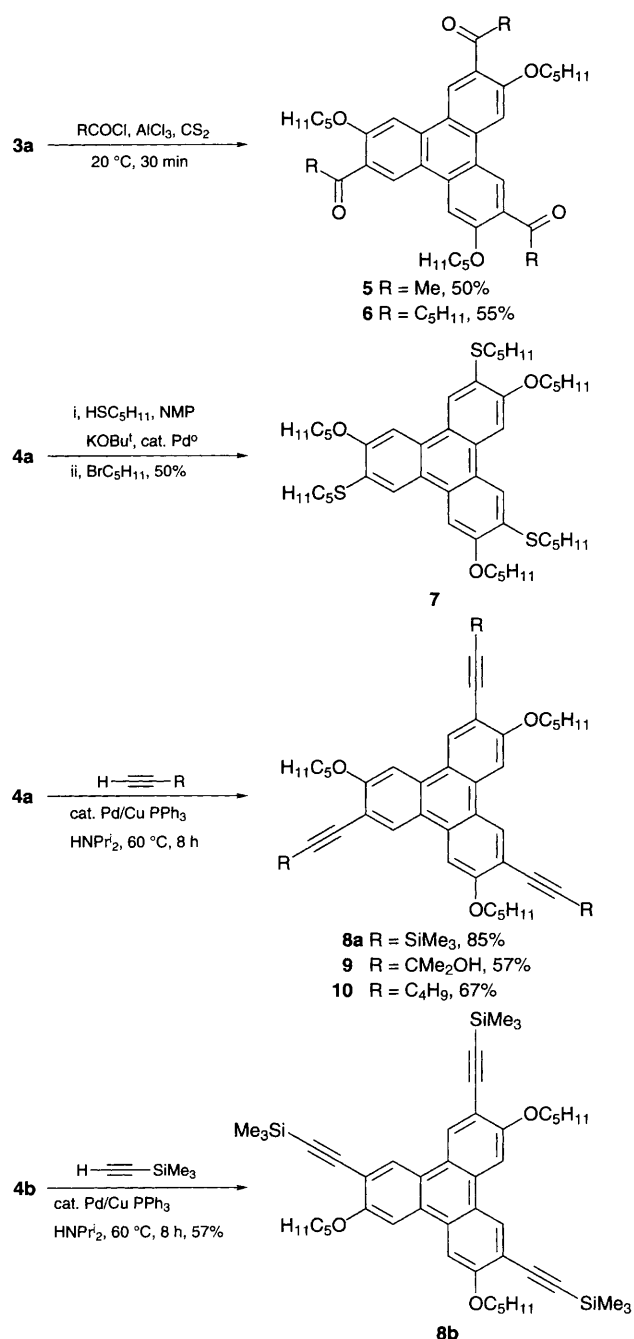
hexanoyl chloride proceeds in moderate yield to give the symmetrically mixed triacyltrialkoxytriphenylene mesogens **5** and **6**. Given the interesting phase behaviour of hexahexylsulfanyltriphenylene, one of our earliest conceived targets was the mixed alkoxy/alkylsulfanyl derivative **7**. It was synthesized in moderate yield by treatment of **4a** with the potassium salt of pentanethiol in *N*-methylpyrrolidone. Quenching the reaction with pentyl bromide assures complete alkylation as ether cleavage can occur in the strongly basic first step. Unfortunately, acylation of **3b** and thiolation of **4b** is much more difficult than the symmetric isomers. This is understandable due to the fact that the third substituent to be attached to the asymmetric core experiences a deactivating moiety in a conjugated position of the triphenylene ring system (a ketone in the case of electrophilic aromatic substitution, and an alkylthio ether in the case of nucleophilic aromatic substitution).

Palladium–copper catalysed trialkynylation¹⁰ of the tribromotriphenylenes **4a** and **4b** proceeds in moderate to good yields with a variety of substituted alkynes. Like the tribromotriphenylenes **4a** and **4b**, the trialkynytriphenylene mesogens **8a** and **8b** allow us to compare the phase behaviour of two isomeric mesogens that differ only in the symmetry of the core substituents.

The phase behaviour of these new mixed tail triphenylene discotics is summarized in Table 1. The parent compound



Scheme 1 Synthesis of tribromo-trialkoxytriphenylenes. *Reagents and conditions:* i, 9-BrBBN, CH₂Cl₂, 20 °C, 24 h; ii, H₂N(CH₂)₂OH; iii, DMF, NaH; iv, EtOH–THF, Pd/C (10%), H₂, 40 °C, 10 atm, 20 h, 25–67%; v, Br₂, CH₂Cl₂, 20 °C, 2 h.



Scheme 2 Synthesis of mixed tail triphenylene discotics

Table 1 Phase behaviour of mixed tail triphenylene discotics

Compound	Phase sequence ^a (T/°C)
1	Cr (69) D _h (122) I
4a	Cr (187) D _h (216) I
4b	Cr (104) D _h (195) I
5	g? (< 10) D _{X1} (194) D _h (250) I
6	g? (< 10) D _h (274) I
7	Cr (27) D _h (127) I
8a	Cr (213) D _{X2} (236) I
8b	Cr (117) D _h (217) I
9	Cr (118) D _h [250 (dec)]
10	Cr (17) D _{X1} (33) D _h (165) I

^a Cr: crystal, D_h: hexagonal columnar phase, D_X: unidentified discotic phase, I: isotropic liquid, g: glass.

hexapentyloxytriphenylene **1** is included for comparison. Transition temperatures were determined with differential scanning calorimetry and polarized optical microscopy. The assignment of phases as D_h was based on the similarity of optical textures to that of **1**.¹¹ Notice that two of the new mesogens exhibit a more ordered phase (denoted D_{X1}) below the D_h phase. Also, the two symmetric triacyl derivatives **5** and **6** show exceptionally broad mesophase ranges and are LCs at room temperature.

Comparison of mesogens **4a** with **4b**, and **8a** with **8b** reveals a general trend in these mixed tail derivatives. Namely, the asymmetric isomers have a lower temperature and broader mesophase range than the symmetric isomers. It seems reasonable that the C₃ symmetric molecules have a much greater chance of optimal packing leading to crystallization. This idea is supported by the fact that although the asymmetric tribromo mesogen **4b** melts at 104 °C when recrystallized from solution, the material does not crystallize from the neat LC phase and remains in a super-cooled discotic phase indefinitely at room temperature. In the trialkynyl mesogens **8a** and **8b**, the difference in symmetry has led to completely different mesophases. The symmetric **8a** displays a phase (D_{X2}) and texture that is yet unidentified, but is distinctly different than the phase of the asymmetric isomer.

The methodology outlined above has given us a great deal of control in the modification of the triphenylene discotic core and has already led to the synthesis of a new class of fluorenes, monofunctionalized triphenylene mesogens.¹² Clearly, a vast array of mono-, di- and tri-functionalized triphenylene discotics can now be designed and created.

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Footnote

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