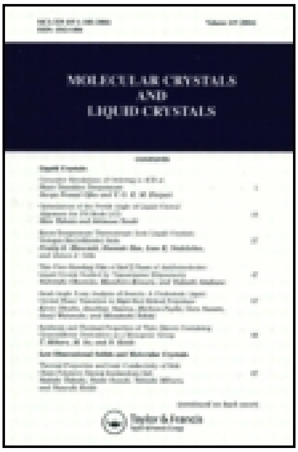

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Functionalisation of Triphenylene Based Discotic Liquid Crystals

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FUNCTIONALISATION OF TRIPHENYLENE BASED DISCOTIC LIQUID CRYSTALS

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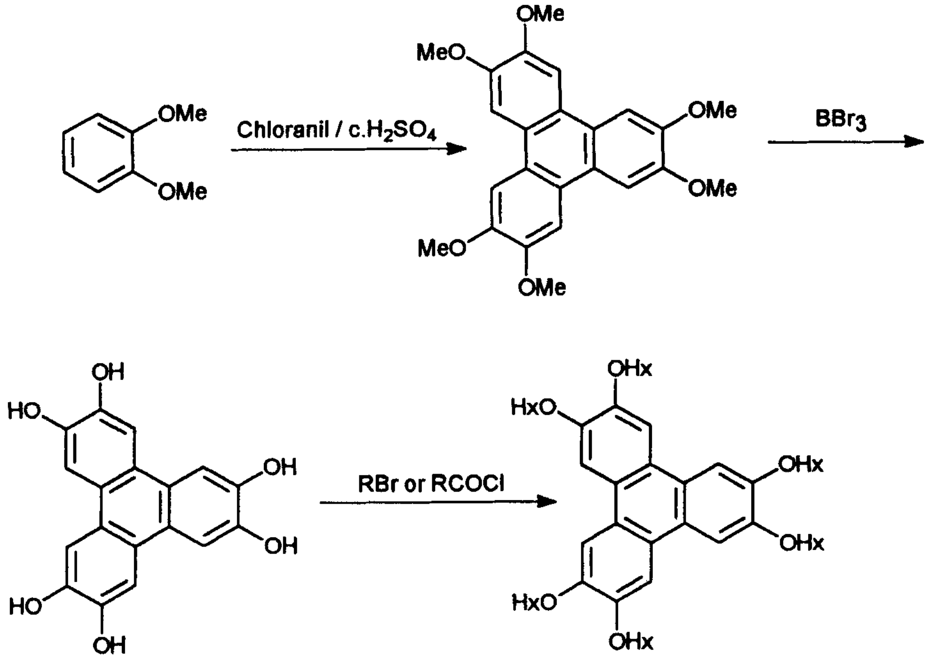
Abstract Nitration of hexahexyloxytriphenylene results in a dramatic enhancement of the mesophase range and offers wide potential for the further functionalisation of triphenylene discotics for device applications.

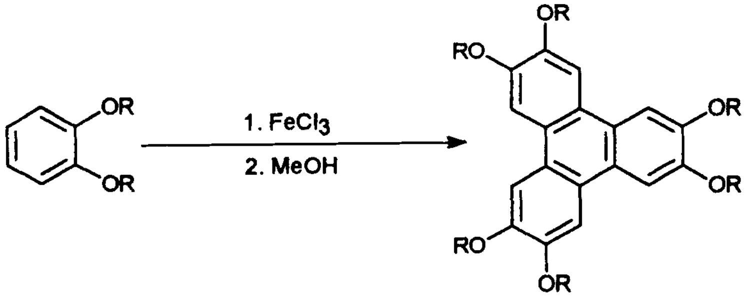
INTRODUCTION

Triphenylene derivatives are among the most extensively studied discotic liquid crystals, not least because they are known to form an ordered hexagonal (Dho) mesophase which is ideal for one-dimensional energy[1] and electron transport.[2] For a long time the development of the science associated with these materials has been hindered by the difficulties encountered in their synthesis. Traditionally, triphenylene hexaethers and hexaesters were synthesised *via* the route outlined in scheme 1.[3, 4] Veratrole (1,2-dimethoxybenzene) is oxidatively trimerised to hexamethoxytriphenylene **1** using chloranil in 70% sulphuric acid. The reaction takes many days and the hexamethoxytriphenylene produced requires extensive chromatographic separation to remove the excess chloranil and for purification. Hexamethoxytriphenylene is demethylated, typically with boron tribromide, and alkylated/acylated to give the discogen.

We have recently reported an improved procedure for the preparation of hexaalkoxytriphenylenes whereby a 1,2-dialkoxybenzene is trimerised quickly and directly using iron III chloride, followed by a reductive workup using methanol (scheme 2).[5] This reaction, which is typically complete in 1 hour gives the hexaalkoxytriphenylene in high yield and virtually pure.



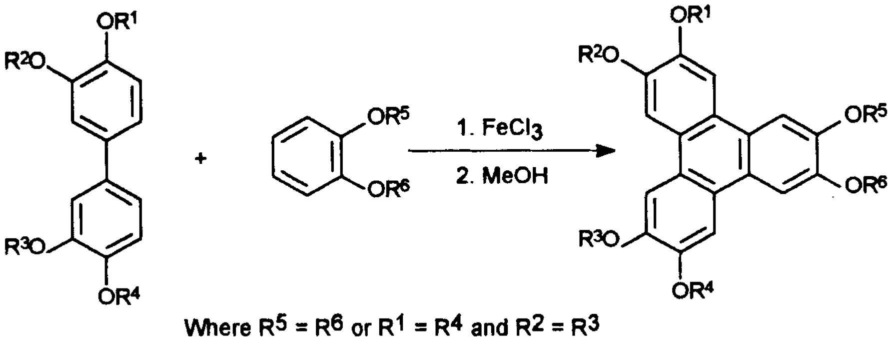
Scheme 1. Traditional synthesis of triphenylene based discotic liquid crystals.



Scheme 2. Improved, one-step synthesis of hexaalkoxytriphenylenes.

In most cases, however, this methodology cannot be applied for the efficient synthesis of unsymmetrically substituted triphenylenes. Such derivatives, which are required for the preparation of discotic polymers, can be synthesised easily and regiospecifically by the coupling of a 3,3',4,4'-

tetraalkoxybiphenyl and a 1,2-dialkoxybenzene, again using iron III chloride followed by a methanol workup (scheme 3).[8]

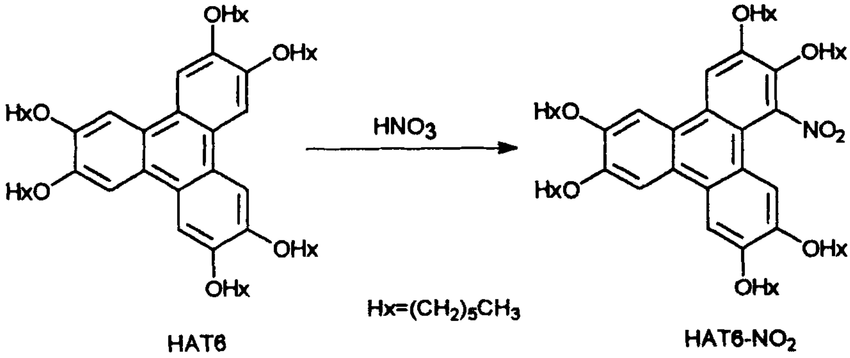


Scheme 3. Regiospecific synthesis of unsymmetrically substituted hexaalkoxytriphenylenes.

The oxidative trimerisation of 1,2-dialkoxybenzenes and the phenyl/biphenyl coupling protocols provide versatile routes to symmetrical and unsymmetrically substituted triphenylene-based discotic monomers and polymers. These materials, however, are predominantly featureless and are colourless insulators in their pure state. It is likely, therefore, that a degree of functionality must be incorporated into these systems before they can achieve their full potential in device applications. Our approach to this goal has been to investigate the functionalisation of triphenylene hexaethers by electrophilic aromatic substitution at the α-sites. In this paper we report our successful attempts to nitrate hexahexyloxytriphenylene (HAT6).

RESULTS AND DISCUSSION

Nitration of HAT6 with concentrated nitric acid in ether/acetic acid was found to proceed smoothly to give the mono-nitrated product (HAT6-NO_2) in >70% yield (scheme 4). The ease of this reaction is, perhaps, surprising when the steric congestion around the α-sites is taken into account (fig. 1a). It would appear that the strongly electron-donating effects of the six oxyalkyl side chains act to compensate for these steric constraints. No evidence of multiple nitration could be detected so it would appear that the steric/electronic factors governing the substitution are finely balanced.



Scheme 4. Nitration of hexahexyloxytriphenylene.

Introduction of the nitro-group has a dramatic effect on the properties of the mesogen. The symmetry of the hexahexyloxytriphenylene is completely destroyed by the substitution (fig. 1a), and this is clearly seen in the proton NMR spectra of the two compounds (fig. 1b). Introduction of the nitro-group converts colourless HAT6 into a yellow compound in which the optical absorption will be highly anisotropic. The most striking consequence of α-nitration, however, is the greatly enhanced mesophase range of the new product (table 1).

Polarizing optical microscopy (fig.2) and low-angle X-ray diffraction (fig. 3) indicate that, like the parent HAT6, HAT6-NO_2 forms a single (D_h) mesophase. The lowering of the melting point may be due to the packing/ crystallization constraints caused by the breakdown of symmetry. However, arguments based on symmetry alone cannot reasonably account for the magnitude of the mesophase enhancement above and below that of HAT6. The observed enhancement is reasonably rationalised by consideration of the steric and electronic effects of the nitro-group. The polar nitro-group provides additional core-core attraction which is manifested as an increased clearing point. Explanation of the low melting point is, however, less straightforward. The space-filling model (fig. 1a) clearly shows that the nitro-group is forced out of the plane of the ring, which would lead to an increased core-core separation. The net effect of this increased separation would be to increase the entropy ("free volume") of the side chains. When combined with the symmetry constraints to favourable packing, these considerations account for the low melting point observed. Low angle X-ray diffraction measurements (fig. 3) tend to support this argument. The core-core separation of HAT6-NO_2 is larger (3.7A) than that observed for the parent HAT6 (3.5A)[7] and more diffuse indicating that the mesophase is more disordered. As expected the column-column diffraction rings correspond to similar separations (19.0A for HAT6-NO_2 compared to 19.5A for HAT6).

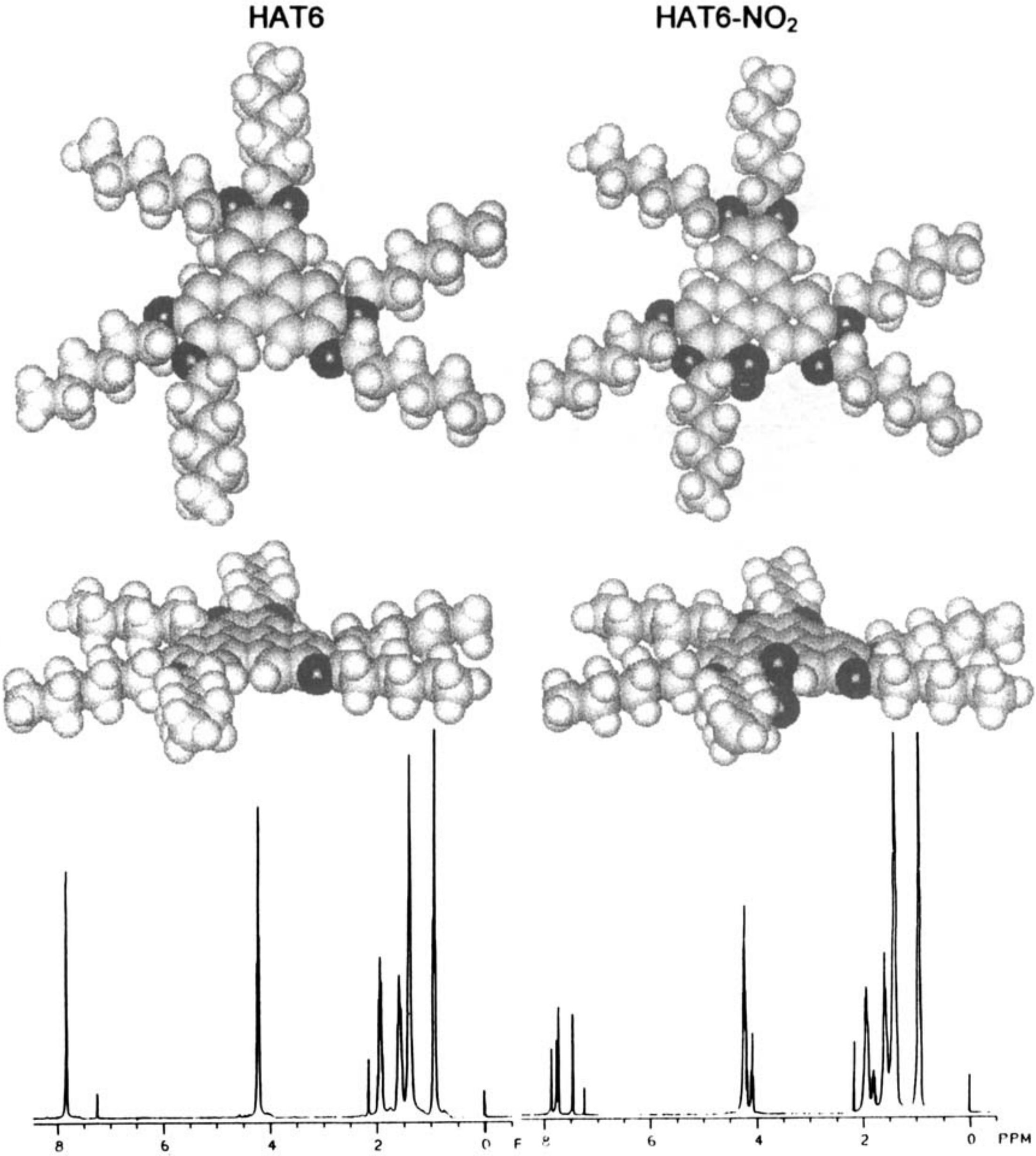


Figure 1. (a) Space-filling model showing the steric congestion α-sites. (b) 1H NMR spectra showing the destruction of molecular symmetry.

See Color Plate XIII.

	K-D (°C)	D-I (°C)
HAT6	70	100
HAT6-NO_2	<RT	136

Table 1. Mesophase behaviour of HAT6 and HAT6-NO_2.

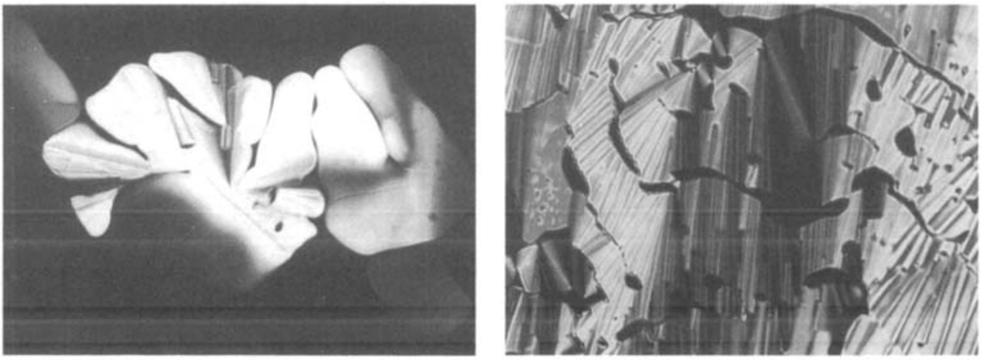

(a) (b)

Figure 2. Texture of the HAT6-NO_2 mesophase. (a) After cooling from the isotropic liquid. (b) After shearing. See Color Plate XIV.

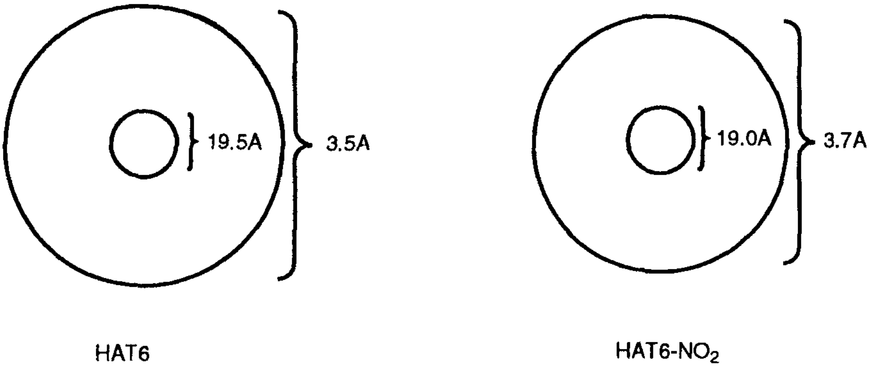


Figure 3. X-ray diffraction pattern of HAT6 and HAT6-NO_2.

CONCLUSIONS

Functionalisation of hexaalkoxytriphenylenes through the nitration reaction described provides the final tool required for the full manipulation of these discotic liquid crystals. Most encouragingly, introduction of the nitro-group is found to improve the liquid crystal properties and by its modification a host of potentially useful new materials can now be synthesised.

ACKNOWLEDGEMENTS

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