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Synthesis of Crown Ether-Linked Discotic Triphenylenes

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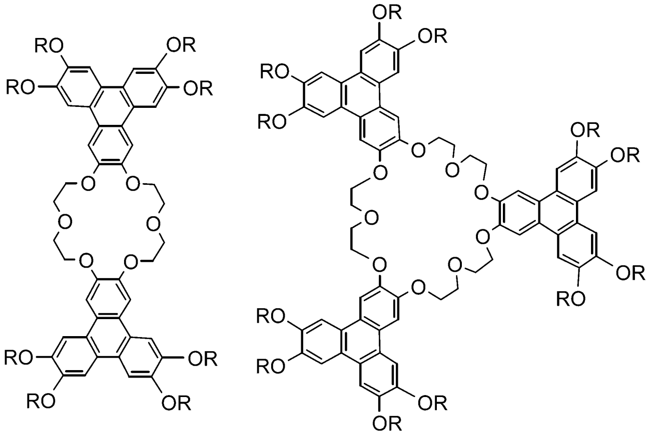
ABSTRACT



Novel triphenylene dimers linked by a central crown ether core have been synthesized and characterized. The crown ether is most conveniently formed as a final step to permit purification and isolation of ion-free material, and extension of the protocol permits synthesis of triad structures linked though a 27-crown-9 macrocycle. The latter compounds present a new discotic motif that supports mesophase formation.

Discotic and columnar liquid crystals have been extensively studied due to their potential application in organic electronic devices since their discovery in 1977.[1,2] Their supramolecular architecture combined with the π-electron rich molecular cores make discotic systems an attractive emerging class of prospective organic optoelectronic materials that could find use in light emitting[3] and photovoltaic[4] devices and field effect transistors.[5]

To use discotic materials in inexpensive organic optoelectronic device applications, two challenging issues must be addressed. Reproducible thin films must be prepared from solution-based processes, and the molecular alignment within the films must be controlled. Low molecular weight organics often show poor film processability while polymers can be too viscous, leading to weakened control of molecular orientation.

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Triphenylene has become the most widely studied scaffold for discotic liquid crystals.[6] Its core, like most discotic liquid crystals, is generally flat, rigid and aromatic and is surrounded by flexible peripheral side chains. Synthetic advances over recent years have permitted investigation of a wide range of symmetrical (hexasubstituted) and unsymmetrically substituted derivatives.[6−9] These structures often form columnar mesophases with beneficial macroscopic molecular orientation. To improve their processability and functionality, twinned and oligomeric structures have received particular attention. It is found that columnar mesophase formation is favored if the individual discotic units are joined by a flexible spacer of appropriate length and composition.[10] Rigid spacers can lead to formation of nematic phases.[11]

In this paper we report the synthesis and properties of discotic triphenylenes linked through a crown ether. Our first targets were ditriphenyleno-18-crown-6 derivatives **2** (Figure 1).[12] The supramolecular properties of crown ethers are well-known and we envisaged that incorporation of the crown structure could conceivably contribute to enhanced columnar order.[13−15] The crown ether linked structure itself presents an unusual motif for interrogation of structural features controlling mesophase formation in triphenylene discotics. In addition, the crown ether linking group can potentially offer the new twinned materials a further functionality or property via a combination of electron and ionic conductivity within one framework if an extended columnar alignment can be achieved. The corresponding "open" bisterphenyl-18-crown-6 derivatives **1** are known[16] and present a non-planar (with respect to the cores) molecular structure. These materials are reported to show columnar phases and are more accurately described as polycatenar materials[17] rather than discotics. As such, although interesting in their own right, they are unlikely to offer favorable properties for optoelectronic applications because they lack extended π-systems.

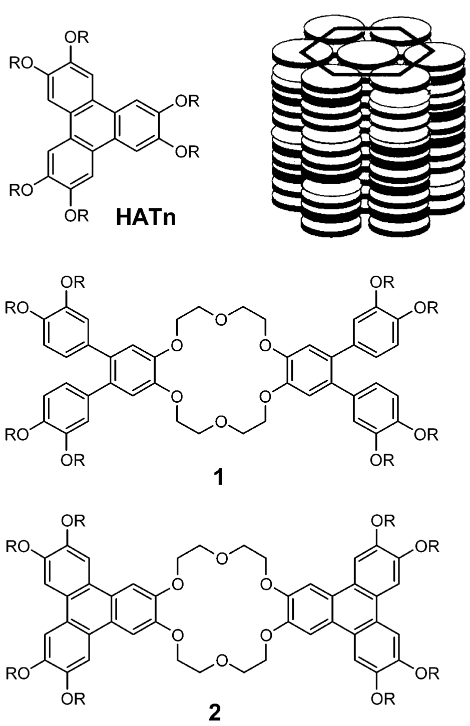
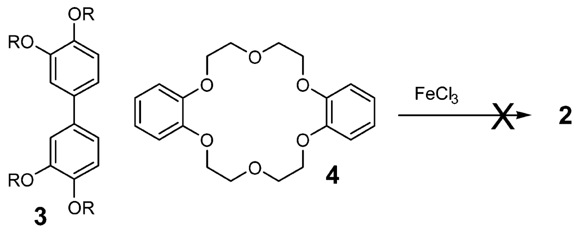


Figure 1. Typical hexaalkoxytriphenylenes (HATn), the hexagonal columnar mesophase, polycatenar bisterphenyl-18-crown-6 (**1**) and target ditriphenyleno-18-crown-6 (**2**).

The synthesis of unsymmetrically substituted triphenylenes can be readily achieved through direct oxidative coupling between suitably substituted biphenyl and benzene derivatives.[7] This protocol was developed, and is most suitable, for synthesis of differentially substituted hexaalkoxytriphenylenes, which is the key structural motif present in target ditriphenyleno-18-crown-6 **2**. Tetraalkoxybiphenyl **3** (R = *n*-hexyl) (Scheme 1) was most conveniently prepared using Suzuki−Miyaura cross-coupling.[18] Oxidative coupling was attempted using iron(III) chloride under the usual conditions (dichloromethane, room temperature followed by reductive methanol workup).

Scheme 1. Attempted Synthesis using Oxidative Biphenyl−Benzene Coupling



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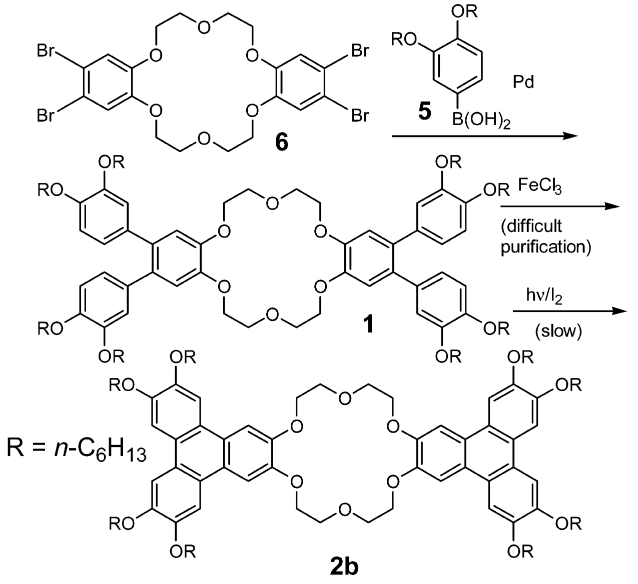
Analysis of the crude product revealed it to comprise a complex mixture of components with no evidence for **2b**. Ether hydrolysis is a known side reaction[19] in such oxidative couplings employing $FeCl_3$, and it seems likely that this pathway accounts for the majority of side products. The reaction stoichiometry and conditions were varied but in all cases resulted in the same disappointing outcome.

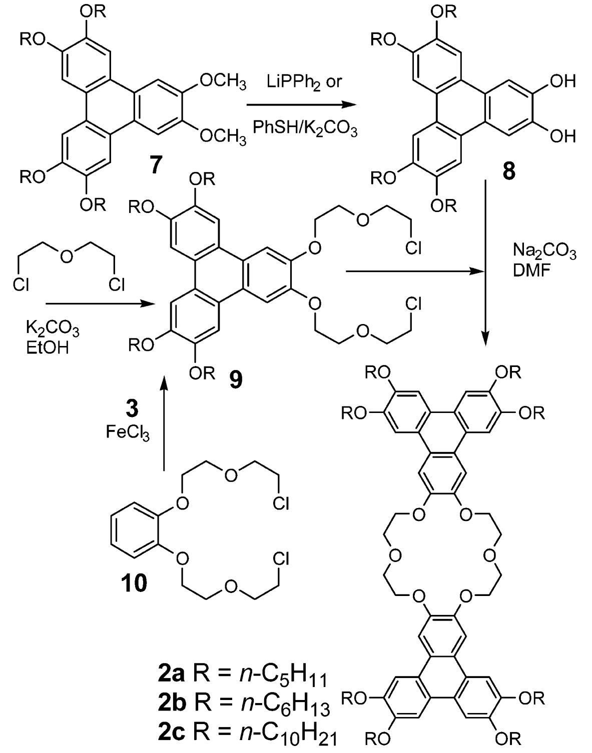
An alternative synthesis was therefore required and we reasoned that intermediate bisterphenyl **1** could be converted to target **2** through oxidative or photoinduced[20] cyclization (Scheme 2). Such oxidative cyclizations of terphenyls are generally smooth and efficient. Bisterphenyl **1** (R = *n*-hexyl) was easily prepared by Suzuki−Miyaura coupling between bishexyloxyphenyl boronic acid **5** (Scheme 3) and tetrabromodibenzo-18-crown-6 **6**. Cyclisation with $FeCl_3$ gave a mixture that appeared to contain significant quantities of the desired product (mass spectral evidence) alongside many other components. Separation proved difficult and, although the compound could be separated and isolated, it was always contaminated with trace impurities. ^{1}HNMR spectra were poorly resolved indicating that the product contaminants included iron salts that could not be easily removed. Clearly the presence of even trace quantities of ionic impurities would be unacceptable for any envisaged optoelectronic applications and characterization so this route, and all others employing metallic oxidants in the final step, were rejected.

Scheme 2. Ring Closure of Bis(terphenyl) Crown Ether **1** to Give the Target Triphenylene Twin **2b**



Photochemical cyclization, employing a UV immersion lamp and iodine, provided a metal-free route to the target ditriphenyleno-crown ether **2b**. The reaction requires two cyclizations per molecule and was expected to be slow. This was indeed the case, and conversion of less than 5% was achieved after 4 weeks irradiation. It appears that the reaction rate slows after the initial conversion, probably because the formed triphenylenes act as better chromophores. The rate was deemed not to be viable for preparation of the target compound in the quantities eventually required for characterization and evaluation.

Scheme 3. Synthesis of Target Triphenylene Twins **2** using Crown Formation as the Final Step



It was decided therefore to construct the crown ether of the molecule in the final step and employ the route outlined in scheme 3. 2,3-Dimethoxy-6,7,10,11-tetrakishexyloxytriphenylene **7** was prepared as previously described[7] and demethylated using lithium diphenylphosphide or thiophenol.[7b,21,22]

Dihydroxytriphenylene **8** could be converted to the second required starting material 2,3-bis(chloroethoxy)ethoxy triphenylene **9** but we favored synthesis of this material via $FeCl_3$ mediated oxidative coupling between biphenyl **3** and 1,2-bis(chloroethoxy)ethoxybenzene **10**. Crown ether formation was then achieved using sodium carbonate as base and the resulting product mixture purified relatively easily by column chromatography. Pure **2b** has a surprisingly high melting point (175 °C) and disappointingly shows no mesophase behavior. Complexation with potassium raised the melting point but did not induce mesophase formation. Further

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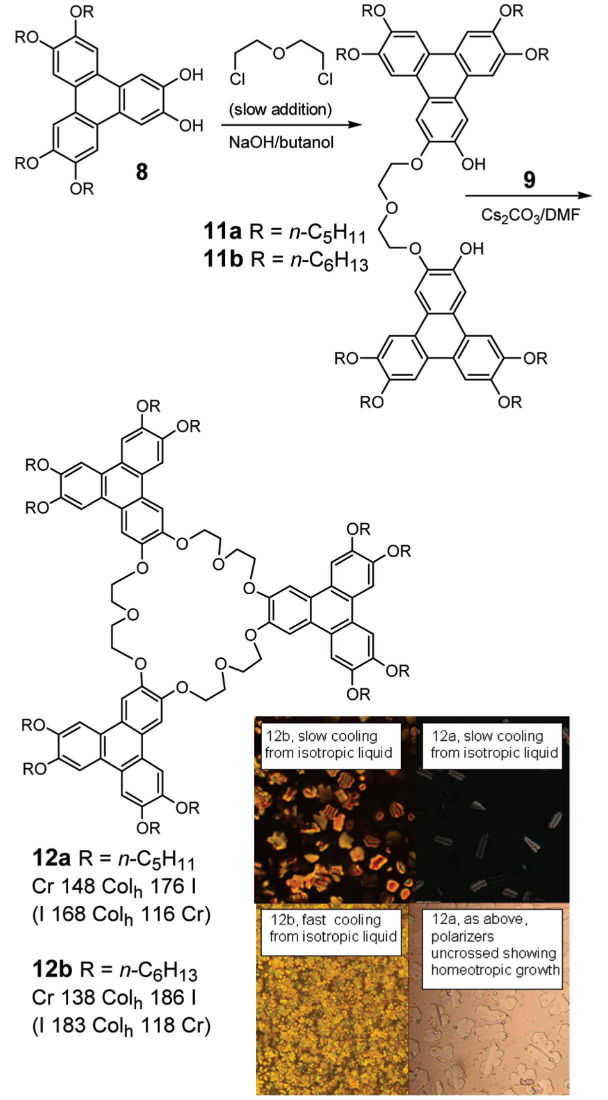
Scheme 4. Synthesis, Mesophase Behavior and Polarized Optical Microscopy Images of Triphenylene Discotic Triads **12**



derivatives were therefore prepared using our optimized synthesis. However, those bearing both pentyl (**2a**) and decyl (**2c**) chains similarly displayed no mesophase behavior. This appeared to contrast with the reported properties of the related polycatenar structures **1** and we reasoned that this most likely arises because of the nonplanar arrangement of appended aryl groups favored by the 18-crown-6 core. Terphenyl units present in **1** are able to twist in order to approach a geometry that can support columnar structure and cyclization to give the triphenylene systems removes this option and disfavors close columnar packing. However, we re-examined **1** (R = hexyl) and found no evidence of the reported mesophase behavior,[16] suggesting that the geometrical constraints are also present in the open system.

We therefore turned our attention to more flexible, triad systems, namely triphenyleno-27-crown-9 derivatives **12**. Their synthesis, shown in scheme 4, was significantly simplified by our findings in the earlier work. The crown ether macrocycle was assembled in a stepwise manner,[23] initially by slow addition of bis(2chloroethyl)ether to dihydroxytriphenylene **8** to give the open twinned triphenylene inermediate **11**. Reaction of dihydroxide **11** with dichloride **9** using cesium carbonate as base afforded the 27-crown-9 macrocycle.

The behavior of these flexible, large macrocyclic triphenylene triads significantly contrasts the smaller twinned crown derivatives **2**. Triads **12** present a structural motif that has no real comparison with any other discotic assembly and show mesophases up to 176 °C (pentyl) and 186 °C (hexyl). The mesophase behavior was characterized by DSC (ESI) and polarized optical microscopy (Scheme 4) where textures characteristic of columnar hexagonal phases are observed. The balance between discotic structure and flexibility therefore clearly supports columnar mesophase formation, and the liquid crystal phases show a strong tendency to align (homeotropically) on the glass surfaces.

In summary, we have reported a convenient synthesis of triphenylene discotics twinned through an 18-crown-6 core. Formation of the crown ether is performed as a final step to permit purification and isolation of ion-free material, and extension of the protocol permits synthesis of triad structures linked though a 27-crown-9 macrocycle. The latter compounds present a new discotic motif that supports mesophase formation. The mesophases align easily on surfaces making them of interest for both fundamental investigation of structural factors controlling mesophase formation in discotics and for optoelectronic device applications.

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Supporting Information Available: Experimental procedures, and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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