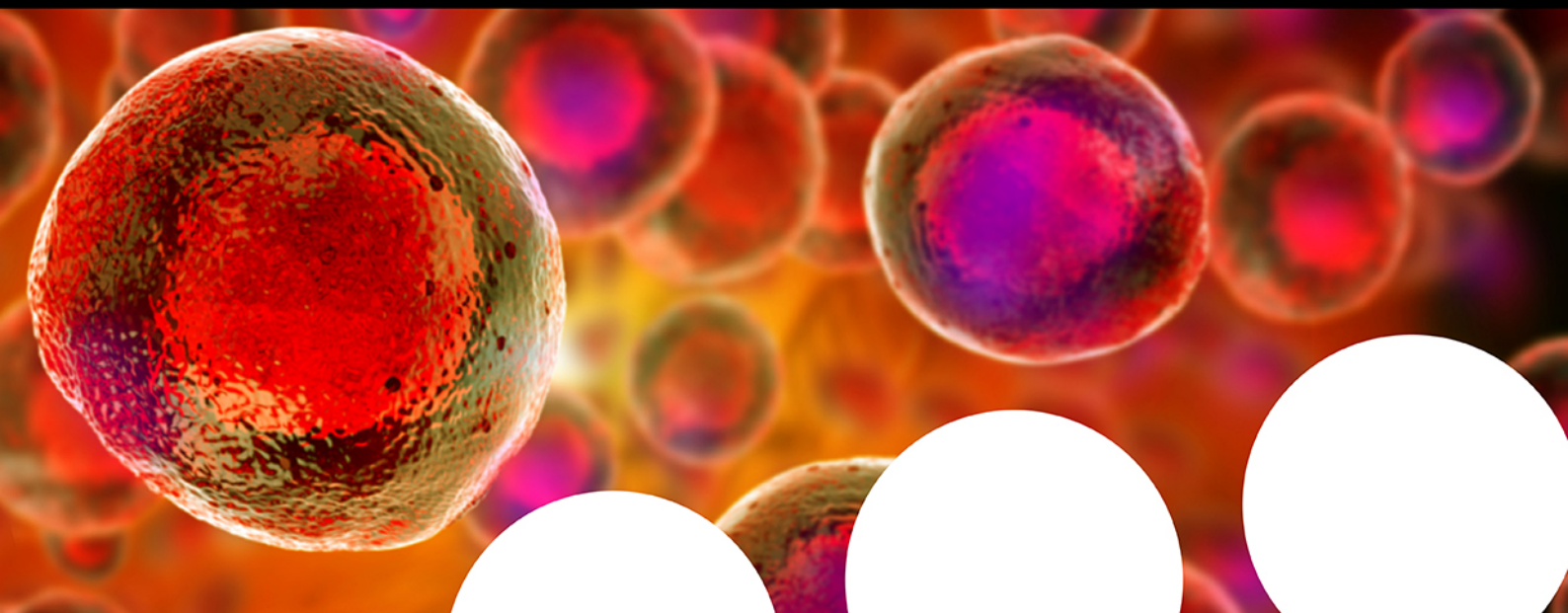


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Synthesis and Mesophase Properties of Triphenylene Dimers Linked through Linear and Bent Alkyne-Aryl-Alkyne Bridges

Ahad O. Alsahli^[a] and Andrew N. Cammidge^{*[a]}

Nematic mesophase formation in disc-like systems remains relatively rare compared to higher-order columnar organisation, but it is observed in some rigid dimeric systems. Mesophase formation in rigid discotic dimers has been sequentially probed and is shown to be predictably controlled through structural choice of the bridge. Moderately bent bridges shorten the

discogen separation and reduce conformational freedom. Severely bent dimers (1,2-phenylene bridge) show no mesophases but, as the angle is widened, columnar and nematic organisation becomes possible and progressively more favoured. The linear arrangement gives the most stable columnar mesophase and a narrow-range nematic mesophase.

Introduction

The first examples of discotic liquid crystals, reported by Chandrasekhar, Sadashiva and Suresh, were hexaesters of benzene (**1**)^[1] and triphenylene based liquid crystals were reported soon after the initial report (Figure 1).^[2,3] Since then the triphenylene nucleus has become the most widely studied and versatile core in discotic systems.^[4,7] The heavily studied hexaesters (**2**) form stable columnar mesophases,^[4,5] and columnar phase formation is retained as the symmetry is broken and one or more alkoxy substituents are replaced by alternative, conjugating groups.^[9–12] The nematic discotic mesophase, though rare, has gained specific relevance due to its ubiquitous commercial application in optical compensating films for displays, where incorporation widens the viewing angle to deliver useful devices. Several design strategies have successfully produced the nematic phase by introducing packing constraints on the molecular self-assembly^[13] such that face-to-face (columnar) organisation is disfavoured. Examples include the hexa(aryl) esters (**3**) where steric interactions between the (twisted) substituents destabilise the columnar system.^[14–17] Alkyne linkages are perhaps the most encountered structural feature in nematic discotics, providing (linear) structural rigidity with essentially barrier-free rotation (in the absence of additional constraints). Multiple aryl-alkynyl substituents have been introduced onto benzene, triphenylene and other aromatic cores, leading to nematic behaviour.^[16,17] Alkyne and particularly diyne linkages have been used to join discotic cores to give nematic materials (e.g., **5**),^[17–19] in contrast to systems linked by flexible

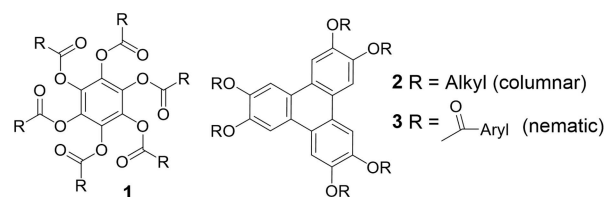


Figure 1. Examples of symmetrically substituted discotic liquid crystals based on benzene and triphenylene cores.

spacers of appropriate length that retain the stable columnar phase (e.g., **4**).^[20–23] We have found that rigid twins (e.g. **6**, **7**, where there are two rigid links resulting in a macrocycle) also tend to only give stable nematic phases (Figure 2).^[24–26] In this case we have reasoned that columnar arrangement of the triphenylene cores would prevent efficient packing due to the void region created in the centre of the macrocycle and is therefore disfavoured.^[24,27]

Results and Discussion

Here we report a systematic investigation to further understand the molecular design parameters that govern the type and stability of discotic mesophase formation in triphenylene systems. Alkynyl (and particularly di-alkynyl) linkages between triphenylenes have successfully produced nematic materials.^[18] The links, by their nature, provide a linear arrangement between discogens, with either an available (when linked) or enforced (when twinned) co-planar arrangement of cores. Furthermore, macrocycle formation in several twinned systems bends and strains the alkyne links and creates a void region at its centre. In this study we have targeted structures where two triphenylene discogen cores are separated, through alkyne units, by a single rigid bridge with free rotation. The overall distance between cores and the angle formed by the bridge are controlled by a central aromatic link point. The general structure (**11**) is shown in Scheme 1.

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejoc.202200990>

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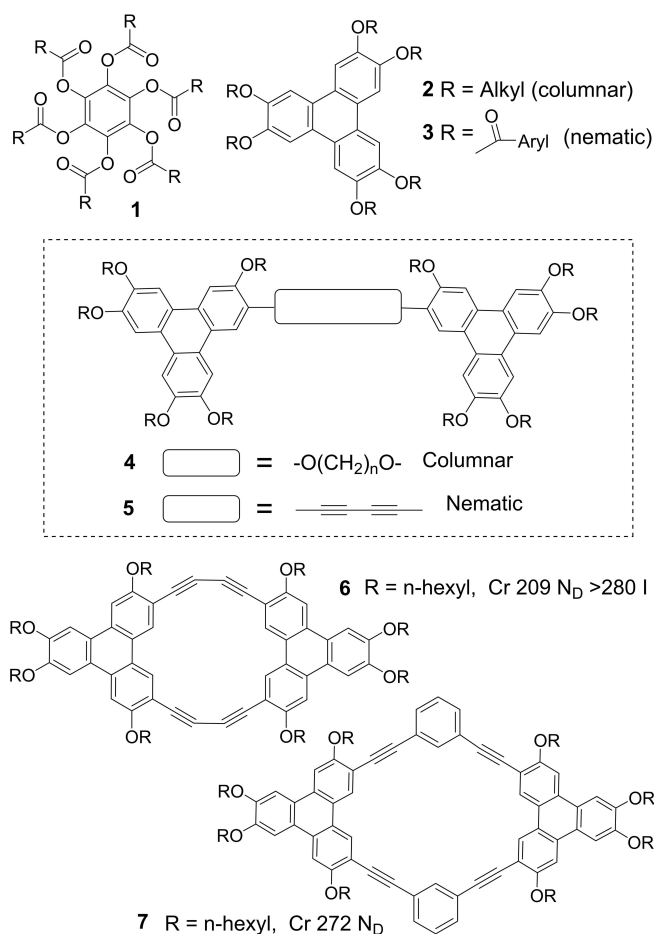


Figure 2. Examples of columnar and nematic triphenylene dimers and macrocyclic twins.

The key starting material for all syntheses was the triphenylene unit bearing five hexyloxy-substituents and a single ethyne (**10**).^[19] It was most conveniently prepared following the sequence shown in Scheme 1. The monohydroxytriphenylene (MHT)^[28–30] was prepared by treatment of a 2:1 mixture 1,2-dihexyloxybenzene and 2-hexyloxyphenol with iron chloride in DCM/MeNO₂. After separation and isolation, MHT was converted to its triflate derivative (**8**), and then coupled with 2-methyl-3-butyn-2-ol using Pd(PPh₃)₂Cl₂/CuI. Slow addition of the alkyne (syringe pump) was required to avoid the competing homocoupling reaction. Deprotection (NaH) yielded the triphenylene acetylene **10**.

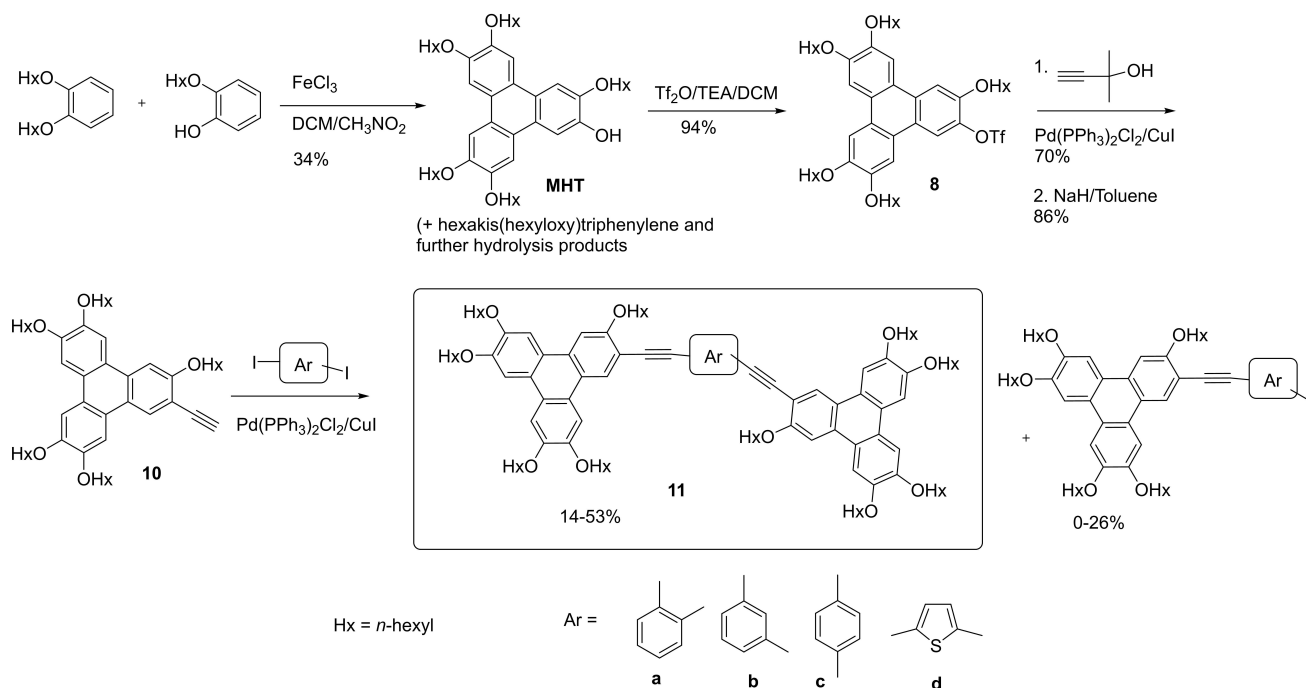
Initial attempts to couple triphenylene acetylene **10** with 1,3-dibromobenzene under Sonogashira conditions failed to give satisfactory results and the dominant product was always the homocoupled triphenylene (**5** R = hexyl), even under slow syringe-pump addition conditions. Copper-free conditions were attempted but coupling was slow and yielded a complex mixture of products. Diiodides were therefore employed in all subsequent syntheses, but very slow addition was still required to avoid excessive homocoupling. Under these conditions the reactions with 1,2-, 1,3-, and 1,4-diiodobenzene afforded the three isomeric bridged triphenylene dimers **11a–c**. In the reactions of 1,2- and 1,3-diiodobenzene the products from a single coupling (**12** and **13**)

were also isolated. 2,5-Diiodothiophene was subsequently coupled with triphenylene acetylene **10**. In this case the separation of the target linked system **11d** proved particularly challenging and required careful chromatography and repeated recrystallisation to remove traces of the homocoupled side product.

The mesophase behaviour of new materials **11a–d**, **12** and **13** are shown in Figure 3, alongside related twinned structures, and it is immediately apparent that the mesophase type and stability are strongly influenced by the structural variation imposed by the link (or indeed absence of a link). In accordance with previous observations on simple triphenylene discotics, the monomeric intermediates **12** and **13** show only stable (wide range) columnar hexagonal mesophases (unambiguously identified by the characteristic texture observed by polarising optical microscopy). 1,2-Phenylene linked dimer **11a** shows no mesophase behaviour. It is a fluid isotropic liquid at 77 °C and cools to give an amorphous, viscous wax at room temperature. It does not crystallise from solution, or on prolonged standing (months) following thermal cycling. Here we conclude that the *ortho*-linkage brings the triphenylene discogen cores into close proximity, preventing coplanarity of the system such that efficient self-assembly (packing) is heavily disfavoured.

The 1,4-phenylene link in dimer **11c** presents no such issue and the benzene and triphenylene units are free to rotate while maintaining a linear arrangement. Here the separation^[31] (~1.75 nm) is just marginally shorter than that observed in the columnar mesophase for HAT6 (**2**, R = *n*-hexyl, 1.87 nm)^[32,33] allowing more efficient face-to-face packing of each triphenylene (in neighbouring stacks) and it results in a wide-range, high temperature columnar mesophase. A highly fluid nematic phase is formed before clearing, reflecting the general observation that nematic phases are induced in rigid linked systems. It is notable that, in the nematic mesophase, homeotropic alignment is achieved immediately, and this alignment is transferred when the sample is cooled to the columnar phase.

1,3-Phenylene linked dimer **11b** presents an intriguing intermediate structure. In this bent system a parallel arrangement of the triphenylenes is possible but has a shorter separation (max ~1.6 nm for a coplanar conformation). Entropic rotational freedom of the linking phenylene is also lost. A columnar phase is observed for **11b**, but it is significantly less favoured than for the 1,4-isomer. The linking in **11b** also leads to nematic mesophase formation, again at lower temperature compared to linear **11c**. The observations complement the behaviour of the related rigid twin **7**, which displays nematic behaviour only because of the enforced void region that would be present if each triphenylene formed part of neighbouring columnar stacks. The 2,5-thiophene linked dimer **11d** demonstrates the generality of the design principle and provides an intermediate arrangement, in terms of discogen-discogen angle and separation, between **11b** and **11c**. Here the mesophase behaviour also lies between the two phenylene bridged isomers, with both intermediate-temperature columnar and nematic mesophases observed. The contrast with its analogous rigid twin **14**^[25] (which displays only a high temperature nematic phase) follows the same pattern.



Scheme 1. Synthesis of alkyne-aryl-alkyne bridged triphenylene dimers.

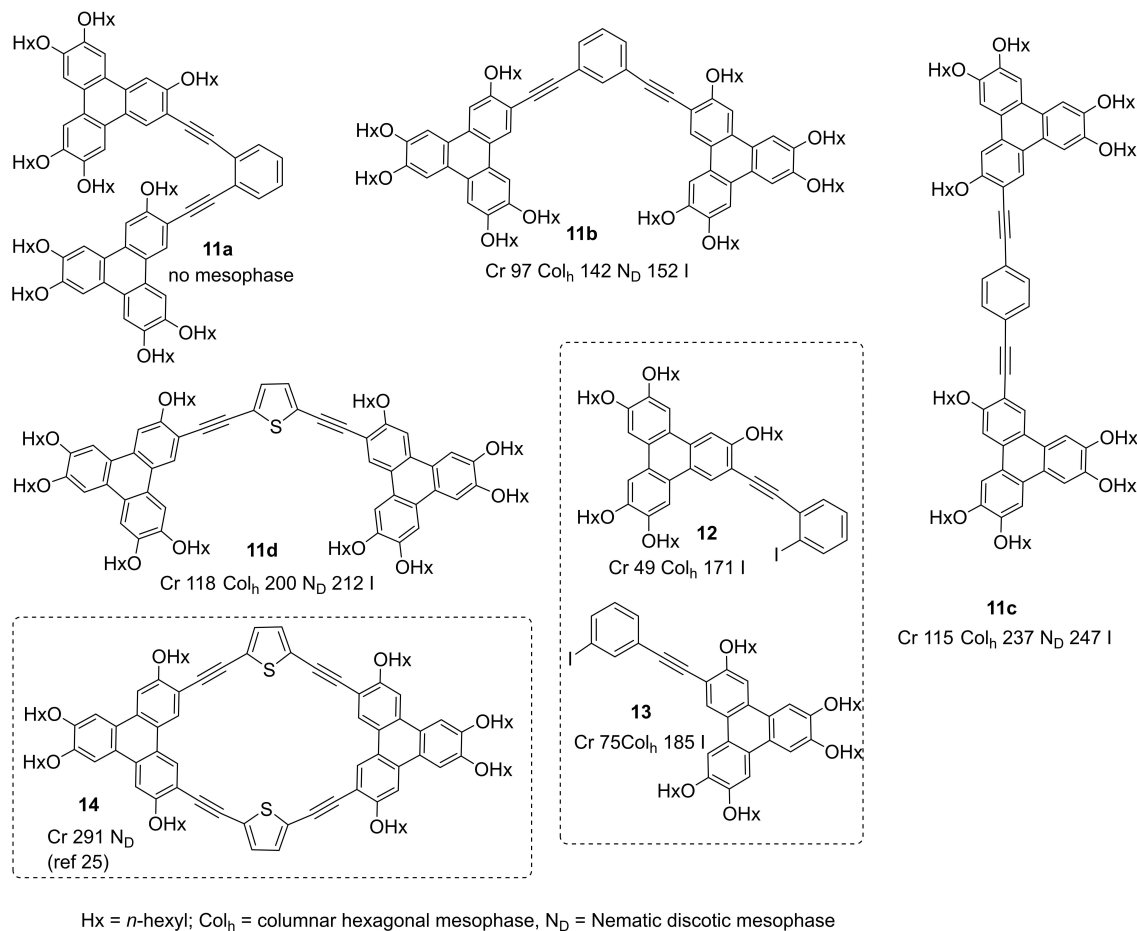


Figure 3. Structures and mesophase behaviour of alkyne-arylalkyne bridged triphenylene dimers.

Conclusion

In conclusion we have demonstrated that mesophase formation in rigid discotic dimers can be predictably controlled through careful choice of bridging unit. The balance is subtle, and significant disruption to the ideal columnar packing through a bent bridge shortens the discogen-discogen separation and reduces conformational freedom such that mesophase formation is somewhat disfavoured for both columnar and nematic assemblies. While the constrained 1,2-phenylene bridged dimer prevents organised assembly to such an extent that neither mesophase formation nor crystallisation is observed, opening the bridge angle leads to progressively more stable, higher temperature mesophases. In these cases, the technologically useful phase sequence isotropic-nematic-columnar-glass is followed on cooling. Samples of 1,4-phenylene system **11c** spontaneously and rapidly align homeotropically between glass slides. The behaviour complements and contrasts that of the related rigid twins that form only nematic phases.

Experimental Section

The general procedure for the synthesis of dimers **11a–d** is illustrated for *meta*-dimer **11b**. Pd (PPh₃)₂Cl₂ (0.007 g, 0.0099 mmol, 0.06 eq.), CuI (0.0022 g, 0.011 mmol, 0.07 eq.), triphenyl phosphine (0.0052 g, 0.0199 mmol, 0.12 eq.) and 1, 3-diiodobenzene (0.055 g, 0.166 mmol, 1 eq.) were stirred in freshly distilled triethylamine (40 ml) under nitrogen. Ethynyl triphenylene **10** (0.275 g, 0.365 mmol, 2.2 eq.) was dissolved in dry TEA (10 ml) and added slowly by syringe pump at 0.5 ml per hour to the above mixture. The resulting solution was further refluxed overnight. The reaction was worked up by addition of water and then extracted with DCM (3 × 100 ml), dried (MgSO₄) and the solvent was evaporated under reduced pressure, to give a crude product which was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to give a solid which was recrystallized from DCM/EtOH (1:1) to obtain dimer **11b** (0.0754 g, 29%) as a pale yellow solid. Triphenylene **13** was also isolated from the chromatography column as an off-white solid (20 mg, 13%).

Acknowledgements

Funding for AOA from the Ministry of Education, Saudi Arabia is gratefully acknowledged. We thank Jacob Gretton for assistance with molecular modelling and estimation of core-core separation in triphenylene dimers.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Alkynes · Cross-Coupling · Discotic nematic · Liquid Crystals · Triphenylenes

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Manuscript received: August 23, 2022

Revised manuscript received: September 13, 2022

Accepted manuscript online: September 14, 2022