Antiaromatic twinned triphenylene discotics showing nematic phases and 2-dimensional π-overlap in the solid state†

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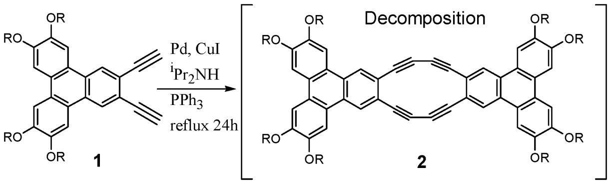
Construction of formally antiaromatic discotic twins based on dehydroannulene cores linked through non-adjacent positions on triphenylenes gives stable molecules with intriguing molecular and supramolecular properties and, unlike the majority of discotic triphenylenes and similar materials, the twins form nematic mesophases on heating.

Triphenylene derivatives are among the most widely studied discotic liquid crystals.[1–3] Many derivatives form stable columnar mesophases that demonstrate anisotropic conduction and lend themselves to diverse applications in molecular electronics.[4] Discotic nematic systems are much rarer but currently find application as compensating films for displays.[5] Simple twinned triphenylenes have received recent attention and a general observation is that linking two discotic triphenylene units *via* an appropriately lengthed, rigid spacer can yield nematic material.[6] Flexible spacers can preserve columnar mesophase formation or destroy mesophase behaviour completely depending on length and nature of the tether.[7–9] In all such simple twins, communication between the triphenylenes is minimal or non-existent so the basic properties of the discotic system are not modified or enhanced.

We were intrigued to interrogate the properties of rigidly fused discotic twins and reasoned that such structures would present a flattened, board-shaped architecture and that the resulting conjugated systems would show significant electronic perturbation. Our initial design focused on twinned dehydroannulene structure **2**. It can be seen that the structure is severely constrained to be planar at the core, yet presents a formally antiaromatic system. This antiaromatic twin, however, is expected to have poor thermal stability due to facile decomposition pathways made possible by the 1,2-substitution pattern in the annulene (*e.g.* pericyclic processes). This did indeed prove to be the case and preliminary experiments on the dimerization of **1** showed MALDI-MS evidence for traces of the product but dominant decomposition (Scheme 1).

Synthetic advances in our group and in others, however, provide access to triphenylene derivatives with almost any substitution pattern.[3,10–12] Dehydroannulene formation through the triphenylene 3,6-positions, **3**, appeared particularly attractive because the key conjugated antiaromatic core is maintained yet decomposition *via* pericyclic reactions is essentially impossible (Fig. 1). Synthesis of twin **3a** was achieved following the sequence shown in Scheme 2. Dibromide **4** was coupled with protected acetylene under Sonogashira coupling conditions.[13] Deprotection (NaH) yielded triphenylene diacetylene **6**. Formation of dehydroannulene twin **3a** was achieved in low yield by treatment of **6** with Pd/Cu(I)/PPh$_3$ in refluxing diisopropyl amine. Reaction conditions were optimised[14] to give twin **3a** in 27% yield along with higher cyclic dehydroannulene oligomers (Scheme 3).



Scheme 1 Attempted synthesis of dehydroannulene-twinned triphenylenes linked conventionally through *ortho*-sites.

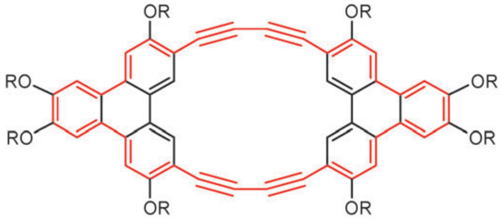


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Fig. 1 Dehydroannulene-twinned triphenylenes linked through 3,6-positions; a conjugated (a 36 π-electron, formally antiaromatic) pathway is shown in red.

Twins **3** are particularly interesting from both a molecular and supramolecular sense and their behaviour and properties are distinctly different from typical triphenylene discotics, their non-cyclic counterparts **7** (Scheme 2, synthesized in a stepwise manner—see ESI†) and the higher oligomers. By design the molecular conformation of **3** is forced to be planar and fully conjugated at the core and the molecule presents a board-like profile. Chemical characterisation supports this structure in solution. For example, ^{1}H NMR spectroscopy shows a characteristic signal at low field for the proton located within the formally antiaromatic π-system (9.23 ppm compared to 8.64 for the corresponding proton of **7**). Outer protons are shifted upfield as expected.

Electronic absorption spectra show further evidence of conjugation with **3a** giving a complex absorption spectrum with the longest wavelength band red-shifted by around 25 nm to 425 nm when compared to model compounds **6** and **7**.

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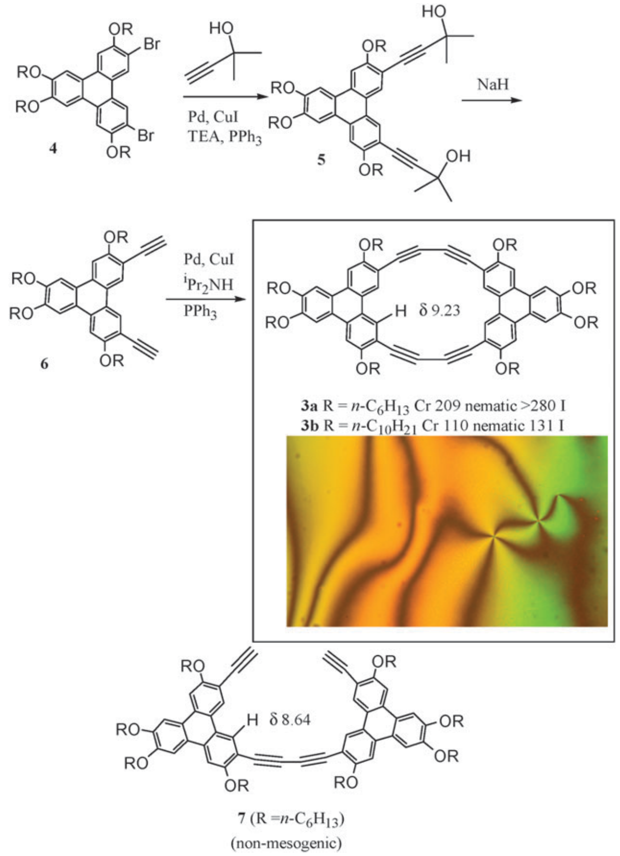
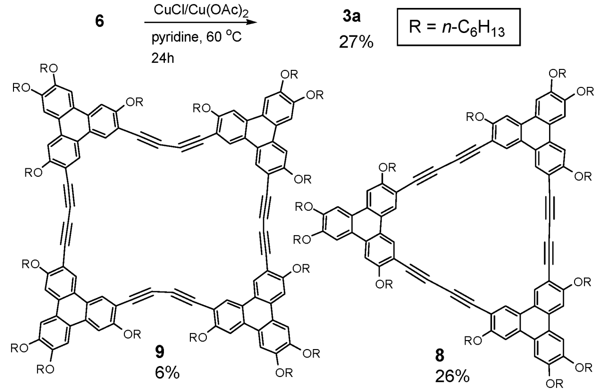
† Electronic supplementary information (ESI) available: Full experimental, characterisation details and spectra of **3a**. CCDC 769122. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00311e



Scheme 2 Synthesis of dehydroannulene-twinned triphenylenes **3** and nematic phase of **3a** as observed by polarising optical microscopy (216 °C, 200×).



Scheme 3 Optimised synthesis of twin **3a** and higher cyclic oligomers.

The emission spectrum of twin **3a** is particularly distinctive and shows a very large Stokes shift of *ca.* 70 nm and broadened peaks, whereas the emission of the model **7** is sharp and shifted by only *ca.* 10 nm (Fig. 2). The peak shape and shift suggest significant reorganisation of **3** in its excited state.

Unlike the majority of discotic triphenylenes and similar materials, twin **3a** forms a nematic mesophase on heating and displays characteristic textures when observed by polarising optical microscopy (Scheme 2). It is interesting to note that open twin **7** and higher cyclic oligomers **8** and **9**, each able to adopt non-planar conformations, are non-mesogenic. The corresponding longer chain derivative, **3b**, was synthesized

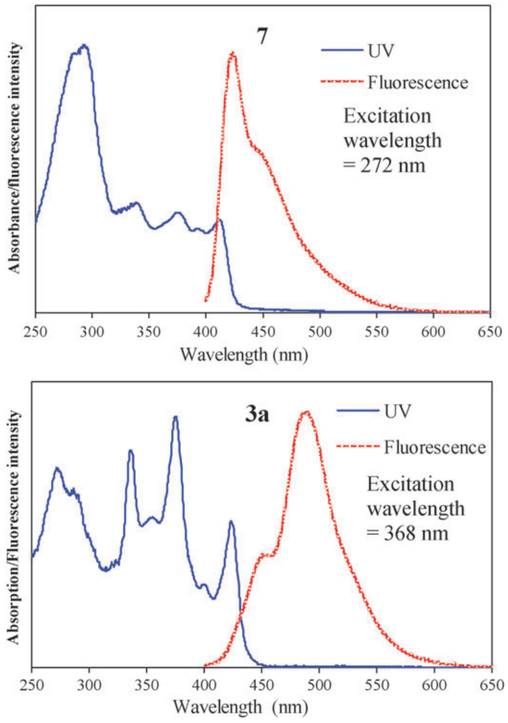


Fig. 2 Absorption (7.4×10^{-6} M) and fluorescence (7.4×10^{-8} M) spectra of **3a** and **7** in dichloromethane.

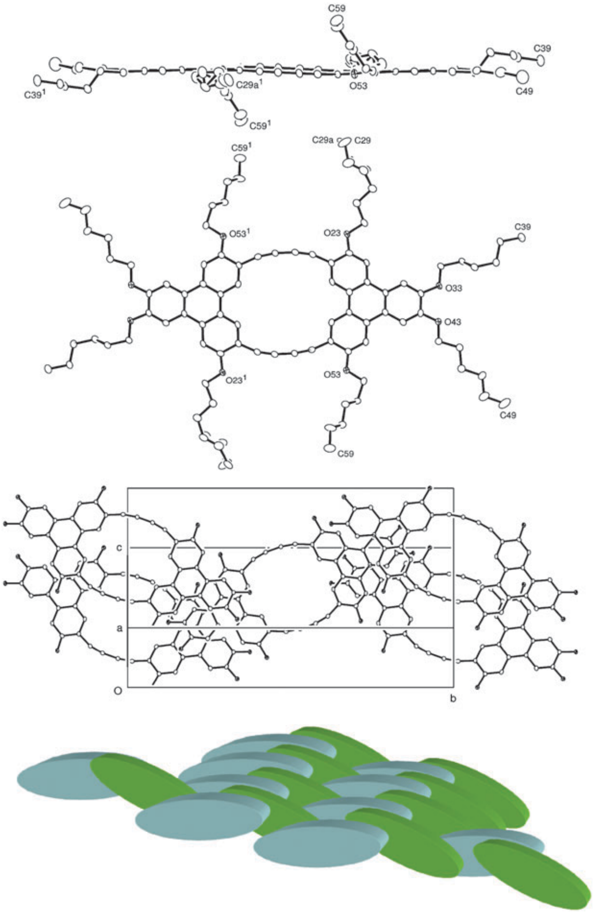


Fig. 3 X-Ray crystal structure of **3a** and cartoon showing inter- and intracolumnar communication in the solid.

in order to lower the transition temperatures and is found to form a stable nematic phase from 110–131 °C.

Crystals of **3a** suitable for X-ray diffraction[15] were obtained by slow evaporation from hexane/THF. The crystal structure, Fig. 3, reveals the anticipated near-planar molecular conformation. Most interesting, however, is the molecular packing in the crystal. It can be seen that the two triphenylene units from each twin stack in adjacent columns with an intracolumnar triphenylene–triphenylene separation of 3.48 Å, leading to a unique supramolecular arrangement where there is now electronic communication both along *and* across the stacks. Face-to-face columnar organisation of the whole molecules is prevented because it would leave a void within the core and this no doubt accounts for the observed exclusive nematic behaviour of twins **3**.

In conclusion we have prepared a new class of formally antiaromatic discotic twins based on dehydroannulene cores linked through non-adjacent positions on triphenylenes. Construction in this fashion gives stable, planar, board-like molecules with intriguing molecular and supramolecular properties. The X-ray crystal structure of twin **3a** shows the molecule to exist in the expected near-planar conformation and its packing is particularly intriguing, giving an arrangement where there is now electronic communication both along and across the stacks.

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15 Crystal data for **3a** (CCDC 769122): $C_{92}H_{116}O_8$, M = 1349.8. Monoclinic, space group $P2_1/a$ (equiv. to no. 14), a = 8.8608(6), b = 27.2688(16), c = 16.3205(12) Å, β = 95.592(2)°, V = 3924.6(5) Å^3, Z = 2, D_c = 1.142 g cm^{-3}, $F(000)$ = 1464, T = 120(2) K, μ(Mo-Kα) = 0.7 cm^{-1}, λ(Mo-Kα) = 0.71073 Å. Crystals are yellow plates. Intensity data measured by thin-slice ω- and φ-scans on a Bruker-Nonius KappaCCD diffractometer (at EPSRC National Crystallography Service) with Mo-Kα radiation and 10 cm confocal mirrors monochromator. Total no. of reflections recorded, to θ_{max} = 22.5°, was 21 077 of which 5106 unique (R_{int} = 0.070); 3735 'observed' with $I > 2\sigma(I)$. Data processed with DENZO/SCALEPACK,[16] with absorption corrections in SADABS.[17] Structure determined by direct methods in SHELXS,[18] and refined in SHELXL.[18] Final wR_2 = 0.141 and R_1 = 0.100[18] for all 5106 reflections weighted $w = [\sigma^2(F_o^2) + (0.0239P)^2 + 5.09P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for 'observed' data only, R_1 = 0.066. In final difference map, highest peak *ca.* 0.22 eÅ^{-3}.

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