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A π-Extended Donor−Acceptor−Donor Triphenylene Twin Linked via a Pyrazine Bridge

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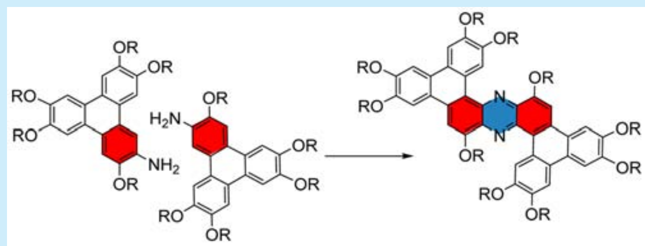
Supporting Information

ABSTRACT: *β*-Amino triphenylenes can be accessed via palladium catalyzed amination of the corresponding triflate using benzophenone imine. Transformation of amine **6** to benzoyl amide **18** is also straightforward, and its wide mesophase range demonstrates that the new linkage supports columnar liquid crystal formation. Amine **6** also undergoes clean aerobic oxidation to give a new twinned structure linked through an electron-poor pyrazine ring. The new discotic liquid crystal motif contains donor and acceptor fragments and is more oval in shape rather than disk-like. It forms a wide range columnar mesophase. Absorption spectra are strong and broad; emission is also broad and occurs with a Stokes shift of ca. 0.7 eV, indicative of charge-transfer character.



Discotic liquid crystals have attracted considerable attention from both a theoretical and applications point of view.[1] Two general classes of liquid crystal phase are formed from disc-shaped molecules. Columnar phases are formed when the individual molecules stack on top of each other, and the lattice arrangement of the resulting columns defines the subclass of mesophase.[2] Columnar phases are important because the stacking arrangement provides π-overlap in one direction only, leading to 1D conduction of charge and/or energy.[3] Nematic phases,[4] where the molecules retain orientational order only, are much rarer, but also find important applications, most notably as optical compensating films in LCDs.[5]

Triphenylenes are the most widely studied discotic liquid crystals, with substituted derivatives showing strong tendency toward columnar mesophase formation. Indeed, synthesis advances have allowed a wide range of symmetrical and unsymmetrically substituted derivatives to be prepared and qualitative structural parameters and boundaries have been defined for mesophase formation.[6] Nematic behavior is observed for a small number of triphenylene derivatives when columnar packing is disfavored, for example, in rigid, twinned structures such as **2** (Figure 1).[7]

Twinning and linking triphenylene discogens provides a route for the introduction of functionality into a processable liquid crystalline matrix, and one example from our previous work is the triphenylene−perylene−triphenylene triad **3**,[8] where matching of the core−core separation preserves columnar mesophase formation. In this triad the electronic nature of the triphenylene is also preserved, and identical to the ubiquitous hexaalkoxy triphenylenes (**1**).

Separately, significant synthesis effort has been deployed to modify the electronic character of the triphenylene core, i.e. switching from an electron-rich (p-type) to an electron-deficient (n-type) system. The most successful strategy to date has involved replacement of one or more of the benzenoid fragments of triphenylene with pyrazine units,[9] and examples of this approach include derivatives **4** and **5** (Figure 2). The syntheses of these heteroaromatic cores typically involve multiple diketone−diamine condensations.

As part of our work toward new diad, triad, and twinned triphenylene systems[7,8] we targeted replacement of the standard ether linked systems (e.g., **3**) with amides or imides, requiring access to discotic, all *β*-substituted monoamino-pentaalkoxy triphenylenes such as **6**.

An obvious route to the amine **6** is by reduction of the corresponding nitrotriphenylene **7**. However, although bromination of pentaalkoxy triphenylene **8** occurs exclusively in the remaining *β*-site, nitration gives only *α*-substitution[10] regardless of the temperature at which the reaction is performed. Indeed dibromination[6] and dinitration[11] of tetraalkoxy-triphenylene **9** gives similar, surprising results (exclusive *β*-bromination and *α*-nitration respectively), Scheme 1.

An alternative approach was therefore required, and we turned to palladium catalyzed amination.[12] The reaction could

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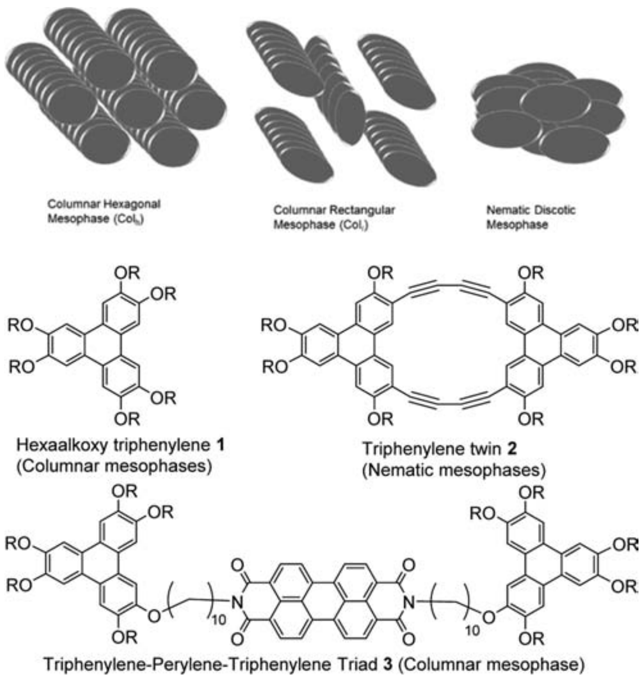


Figure 1. Structures of the columnar and nematic mesophases, and mesogenic triphenylenes.

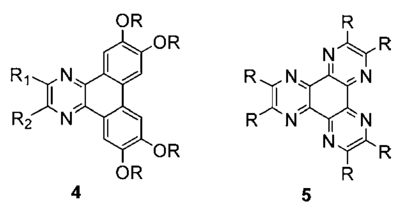
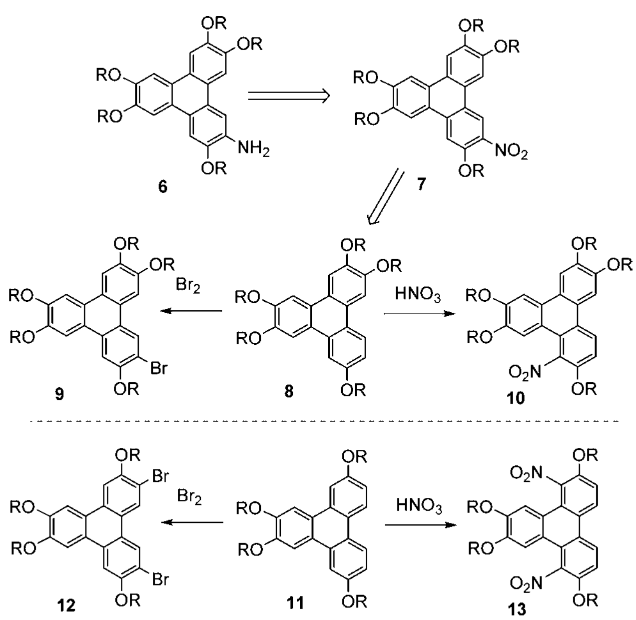


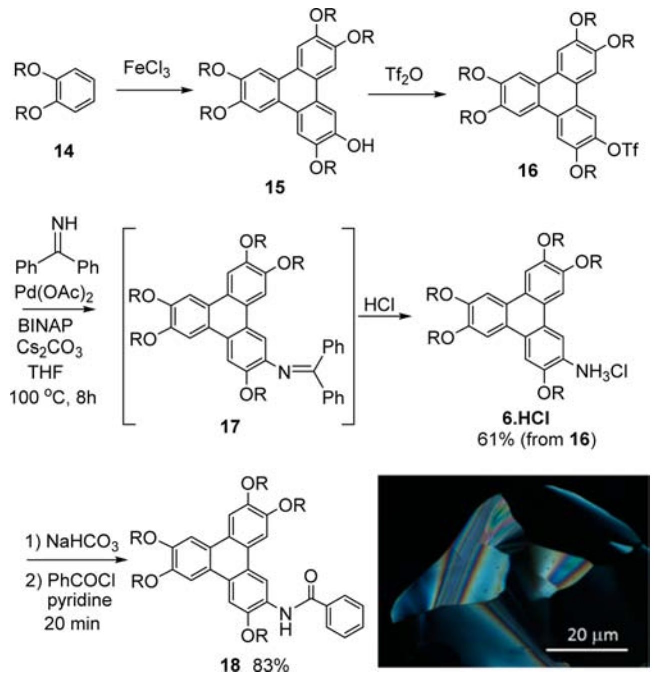
Figure 2. Electron-deficient azatriphenylenes.

Scheme 1. Different Regiochemical Outcomes from Bromination and Nitration of Triphenylenes 8 and 11 (R = *n*-Hexyl)



be achieved via bromide **9**, but for synthetic convenience we developed the synthesis via triflate **16** as shown in Scheme 2,

Scheme 2. Synthesis of Triphenylene Amine 6 and Its Conversion to Amide 18 (Inset Shows the Polarizing Optical Microscopy Image of 18 in the Columnar Hexagonal Mesophase at 165 °C)



exploiting the facile single-step synthesis of monohydroxytriphenylene **15**.[13] Consequently bishexyloxybenzene **14** was treated with $FeCl_3$ (5 equiv) to give **15** which was converted to the triflate **16** using Tf_2O. Cross-coupling with benzophenone imine[14] proceeded smoothly to give imine **17** which was immediately hydrolyzed by addition of 2 M HCl to a THF solution, resulting in precipitation of the amine as its HCl salt (**6·HCl**). Addition of saturated $NaHCO_3$, separation, and extraction with DCM gave crude amine **6** which was rapidly purified by column chromatography. The isolated amine could be stored under nitrogen or used immediately. Efficient amide formation was demonstrated by treatment with benzoyl chloride in DCM/pyridine, smoothly yielding the expected amide **18**.

Amide **18** displays a wide range columnar hexagonal mesophase. On cooling from the isotropic liquid the mesophase forms at 168 °C and persists until crystallization at 36 °C. The mesophase is characterized as columnar hexagonal based on its distinctive texture when observed by polarizing optical microscopy. However, it should be noted that slow cooling results in good (homeotropic) alignment of the sample. The triphenylene amides are therefore potentially very useful materials, and it is clear that this mode of amide linkage is compatible with preserving (and indeed enhancing) mesophase stability.[10]

The most interesting result, however, was obtained when the crude precursor amine **6** was left stirring in the open atmosphere. The solution became red/orange and fluorescent, and after stirring at room temperature for 1 h a new product was observed alongside the unreacted amine. The new product was isolated (chromatography) and characterized as **19** where a new pyrazine ring links the triphenylene units (Scheme 3). Oxidative coupling of aryl amines to give (benzo)pyrazine fragments are known, but typically employ

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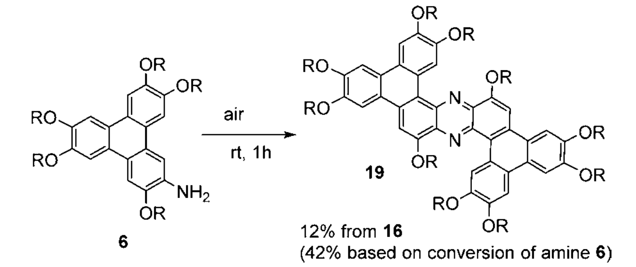
Scheme 3. Synthesis of Pyrazine-Linked Twin 19 through Aerobic Oxidative Coupling of Amine 6



strong oxidants such as superoxide or DDQ to achieve the transformation.[15] Clearly the electron-rich nature of the triphenylene amine **6** drives this clean oxidative coupling using just air as the oxidant.

Fused triphenylene twin **19** is a deep red material, and it exhibits a broad absorption between 400 and 550 nm with an extinction coefficient of ca. 10^4 M^{-1} cm^{-1}. Its emission spectrum is similarly broad with a Stokes shift of ca. 0.7 eV (Figure 3). The behavior is similar to that observed in related

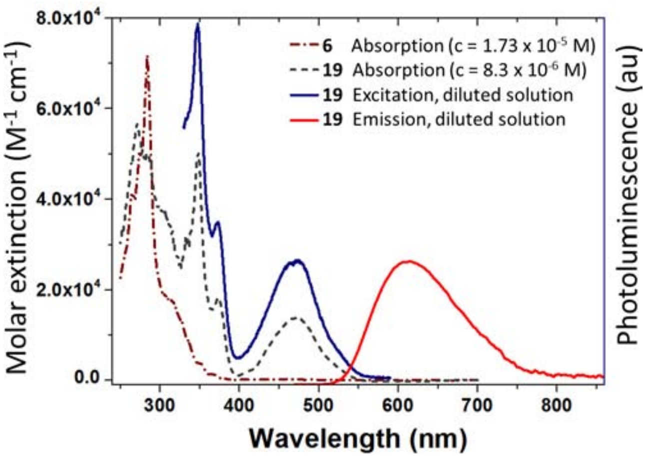


Figure 3. UV−vis absorption spectra of amine **6** and twin **19** plus photoluminescence spectra of **19**. The excitation was monitored at 614 nm, and the emission was excited at 450 nm; all in DCM solutions.

D−A−D systems containing pyrazine acceptor units[16] and indicates charge transfer character. DFT calculations, using the Gaussian 09 program using the B3LYP functional and 6-31G** basis set,[17] were performed on the twin (the octamethoxy analogue of **19** was used in calculations). The calculated HOMO and LUMO for the twin (Figure 4) further illustrate the charge transfer from donors (triphenylene components) to the acceptor (pyrazine) in the excited state.

On heating, the isolated crystalline material melts into a liquid crystal phase at 123 °C, clearing to the isotropic liquid at 227 °C. On cooling the mesophase develops a birefingent texture that unambiguously shows a columnar hexagonal phase is also formed by this oval-shaped twin (Figure 5). Significant supercooling is observed, and the mesophase persists down to 50 °C, where partial recrystallization occurs.

In summary, a straightforward sequence of steps allows synthesis of *β*-amino triphenylenes via palladium catalyzed amination of the corresponding triflate using benzophenone imine. Transformation of the amine to benzoyl amide **18** is

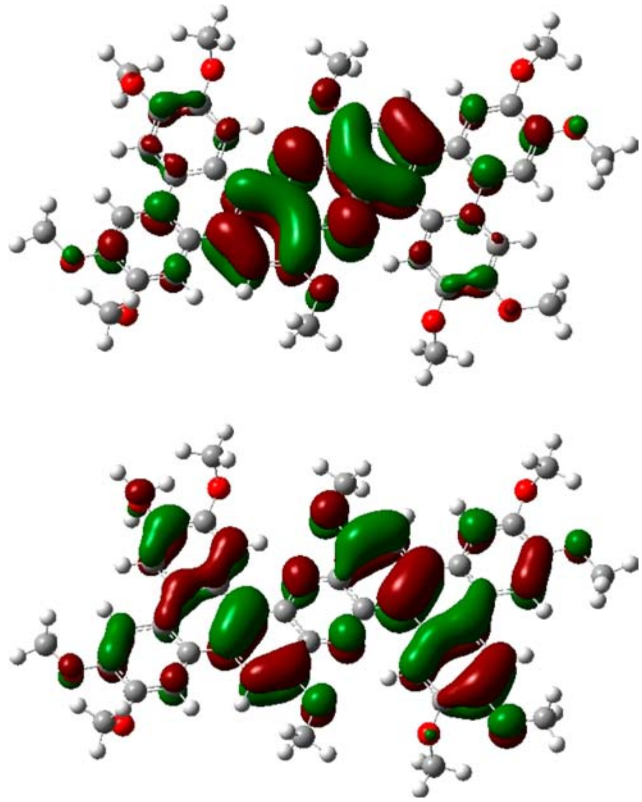


Figure 4. Calculated HOMO (bottom) and LUMO (top) for twin **19** (methoxy substituents were used for the calculation).

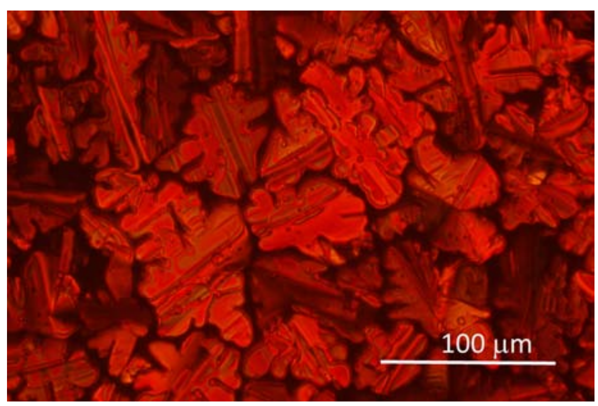


Figure 5. Mesophase texture of **19** in the columnar hexagonal phase at 220 °C.

also straightforward, and the resultant derivative demonstrates that the new linkage supports columnar liquid crystal formation. Precursor amine **6**, however, is unstable in air. A stirred solution smoothly couples to give a new twinned structure linked through an electron-poor pyrazine ring. The new discotic liquid crystal motif is more oval in shape rather than disk-like, and it forms a wide range columnar mesophase. The twin has both donor (alkoxytriphenylene) and acceptor (pyrazine) character, and it absorbs and emits strongly in the visible spectrum. Absorption and emission spectra are both broad, with emission occurring with a Stokes shift of ca. 0.7 eV, indicative of charge-transfer character.

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ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01444.

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Notes

The authors declare no competing financial interest.

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