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Discotic Triphenylene Twins Linked through Thiophene Bridges: Controlling Nematic Behavior in an Intriguing Class of Functional Organic Materials

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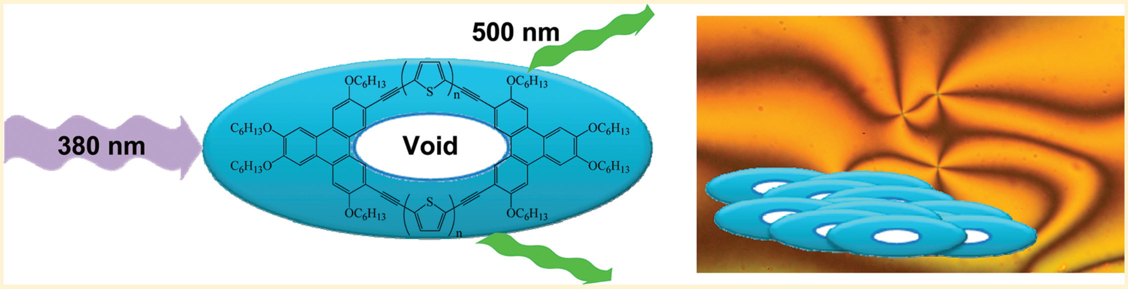
Ⓢ *Supporting Information*



ABSTRACT: Substituted triphenylenes and similar discotic molecules have a strong tendency toward columnar organization. Nematic mesophases are much less commonly observed in discotic systems. We have demonstrated a general strategy whereby discotic triphenylenes can be twinned to form stable, boardlike materials that display only nematic mesophases. The dominant structural feature that leads to nematic behavior is an enforced void region in the center of the macrocycle that results from bridging through the triphenylene 3,6-positions. This precludes simple columnar assembly because it would lead to free space through the center of each stack. Selection of appropriate bridging units allows materials to be designed which combine molecular features, such as the optoelectronic properties of electron-rich triphenylenes and conjugated thiophene units, with the processability, self-healing, and alignment features inherent in nematic mesophases. In addition, communication across twinned structures can lead to additional enhancement of optoelectronic behavior. This is particularly apparent in fully conjugated, planar twin **12** which is formally expected to have some antiaromatic character. This character is manifested in its spectral properties, and particularly noteworthy is its strong, Stokes shifted emission at around 500 nm.

1. INTRODUCTION

Discotic liquid crystals, first discovered by Chandrasekhar in 1977,[1] have become the subject of intense investigation.[2] Early work was mostly fundamental and curiosity-driven in nature, leading to expansion in the number of molecular cores capable of showing discotic liquid crystallinity.[3] Although numerous cores have been shown to give mesophases, three main classes have received particular attention due to combinations of molecular properties, synthetic versatility, and robustness, namely those based on phthalocyanine,[4] coronene,[5] and triphenylene[6] (Figure 1). The most commonly observed and investigated mesophases are columnar in structure,[7] not least because this unique architecture naturally lends itself to device applications employing a combination of processability, self-assembly/self-healing, and aligned, directional conduction of either charge or energy.[8] Molecular electronic applications of columnar systems are diverse and include organic light-emitting diodes,[9] field-effect transistors,[10] and photovoltaic systems.[10c,11]

A significant research effort has focused on unraveling the structural factors that control columnar mesophase formation in discotic systems. We and others have paid particular attention to systems based on the triphenylene core because it combines synthetic versatility with the molecular robustness required for device applications.[6,12,13] Qualitative parameters have been established to aid in the design of systems forming columnar mesophases.[14,15]

The columnar phases of discotic materials can be likened to the smectic mesophases formed by conventional calamitic (rod-shaped) liquid crystals. Similarly, like their calamitic counterparts, discotics can also form less ordered nematic mesophases. Unlike calamitics, however, this behavior is only rarely observed, and structural factors leading to its formation are poorly understood.[16] Nevertheless, discotic nematics have found very important application as optical compensating films for liquid crystal displays.[17]

2. RESULTS AND DISCUSSION

We recently communicated an unconventional molecular architecture whereby typically columnar triphenylene substructures were twinned through their 3,6-positions to create a rigid, conjugated structure with a central void region.[18]

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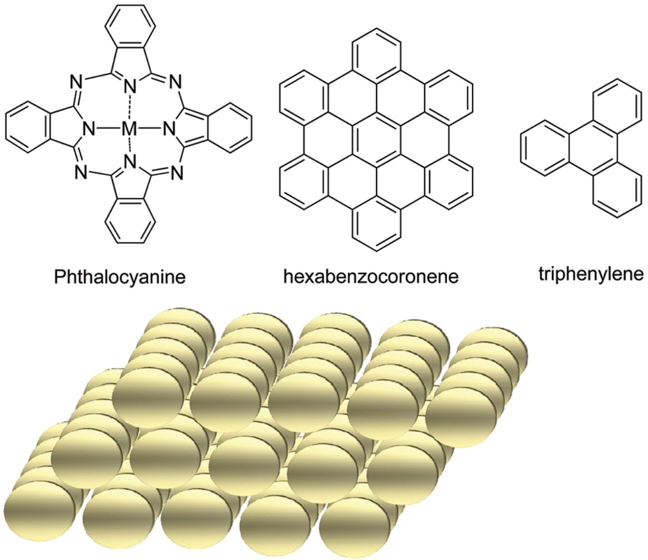


Figure 1. Three most common molecular cores that give rise to discotic columnar mesophase formation and a cartoon of the molecular arrangement in a columnar hexagonal mesophase.

Columnar organization of such structures would lead to free space through the core of the column and is therefore not possible. A switch to nematic behavior is therefore observed, allowing side chains from one unit to occupy the void of another. Indeed, precisely this mode of packing is observed in the crystal structure leading to a unique zigzag arrangement that corresponds to electronic communication in two dimensions but not the third (Figure 2).

Twinned triphenylenes, linked through their 3,6-positions, therefore could offer an intriguing general platform for organic materials design due to the combination of potential communication across the whole molecule and the incorporation of a nematogenic structural feature in the form of enforced free space at the molecular core. This paper describes examples of such twinned triphenylenes that were designed to interrogate the generality of the design feature and expand the application scope of the organic materials. To this end, we sought to incorporate aryl bridges across triphenylene twins, and the general structure is depicted in Figure 3. It is immediately apparent that introduction of such bridging units expands the central molecular cavity and the choice of bridge will further determine whether a planar conformation is expected through a balance between angle strain and conjugation.

In the first materials we targeted twins linked through phenylene bridges. It is clear from inspection of the generic structure in Figure 3 that bridging through a 1,3-substituted benzene moiety would lead to a twin with minimal angle strain and an expanded cavity. A fully planar core is expected, enforcing efficient conjugation between individual phenyl and triphenylene units. The synthesis of the twin is shown in Scheme 1.

Diethynyltriphenylene **3**[18] was coupled[19] with an excess of 1,3-diiodobenzene **4** to yield the bisiodophenyl intermediate **5**, which itself displayed a stable, wide range columnar mesophase. Crystals suitable for X-ray diffraction were obtained, and the structure, also shown in Scheme 1, shows that the cores of the molecules adopt an essentially planar conformation in the crystal with the discotic molecules forming offset columnar stacks. The target twinned structure was achieved by coupling diiodide **5** with the precursor triphenylene diacetylene **3** under palladium-free coupling conditions.[20] It is worth noting that this stepwise procedure proved more efficient than the single-step coupling−macrocyclization between diacetylene **3** and 1,3-diiodobenzene. The twinned triphenylene **6**, and indeed all of the twins described in this paper, displayed a strong tendency to aggregation leading to broadened signals and concentration-dependent chemical shifts observed for the aromatic protons in some ^{1}H NMR spectra, and it was not possible to obtain useful ^{13}C NMR data. ^{1}H NMR spectra were therefore recorded at the lowest reasonable concentration (typically 10^{-4}−10^{-5} M), and sample precipitation frequently occurred on standing.

In accordance with the design feature, when heated the new twinned structure forms only a nematic mesophase, underlining the link between the molecular structural motif and balance between columnar and nematic behavior. The high transition temperature into the mesophase, which could, no doubt, be lowered by simple side-chain modification, further indicates efficient packing in the crystal, an observation that is not surprising in light of the crystal structure observed for precursor **5**. Although **6** is an intriguing structure that provides a strain-free molecular void region in the center of the twin, the 1,3-phenylene link groups do not allow communication across the whole structure, and this results in optoelectronic properties that essentially mirror their monomeric precursors. Conjugated linkers are therefore required, and we first briefly investigated the isomeric twin linked through 1,4-phenylene bridges. Such systems would provide a strained macrocyclic twin, but it was recognized that synthesis would be much more challenging. Furthermore, simple molecular modeling[21] indicated that 1,4-phenylene-bridged twins could adopt a more favorable conformation where the benzene bridges lie essentially perpendicular to the core π-systems, breaking the conjugation pathway and communication between the two halves of the twin. Nevertheless, synthesis was attempted following the same strategy developed for 1,3-phenylene-bridged twin **6**

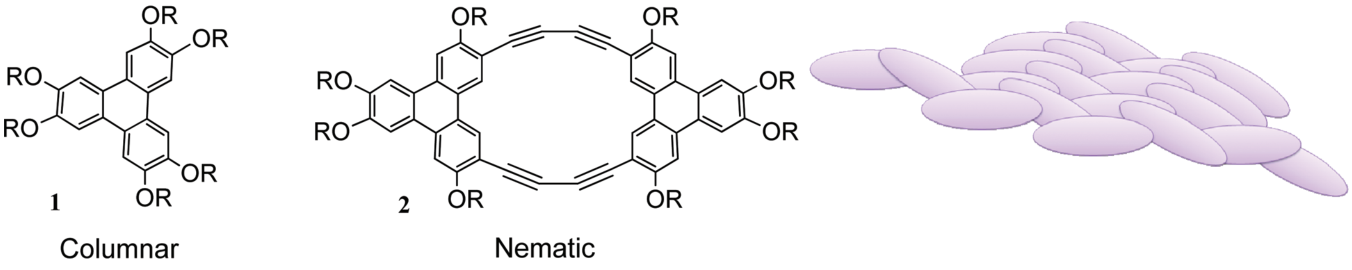


Figure 2. Columnar hexaalkoxytriphenylene **1** and its dehydroannulene twinned variant **2** that shows only nematic mesophase behavior, plus the zigzag arrangement present in the crystal.[18]

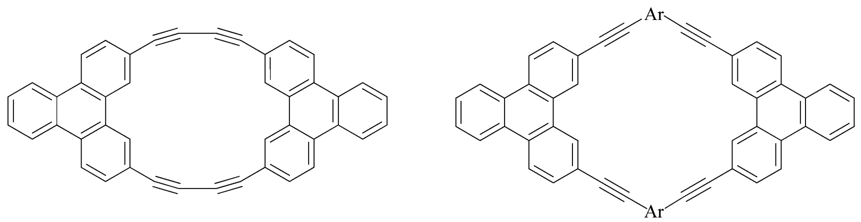
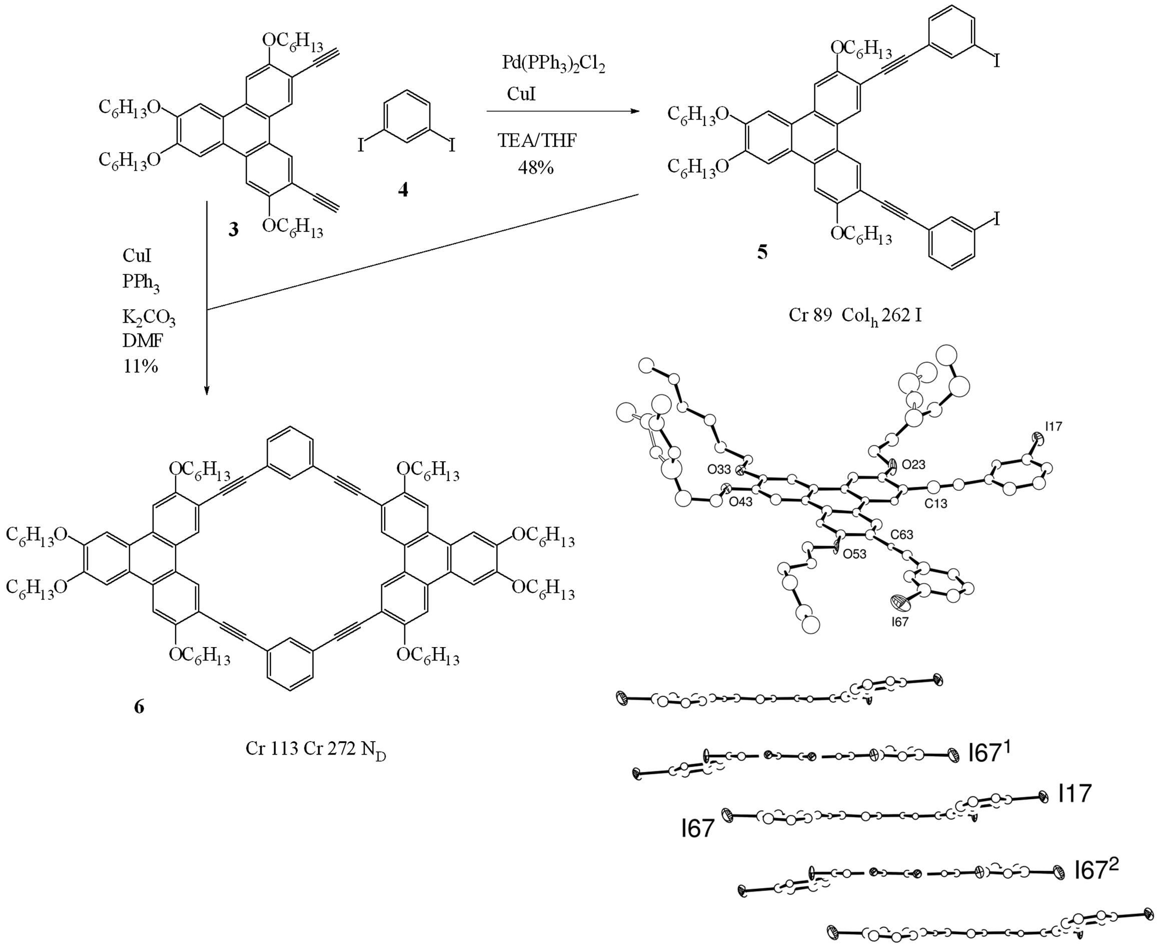


Figure 3. Triphenylene twins linked through their 3,6-positions; dehydroannulene twins (left) and arylene-bridged twins (right).

Scheme 1. Synthesis of 1,3-Phenylene-Bridged Twin 6 and the X-ray Crystal Structure of Intermediate 5[a]



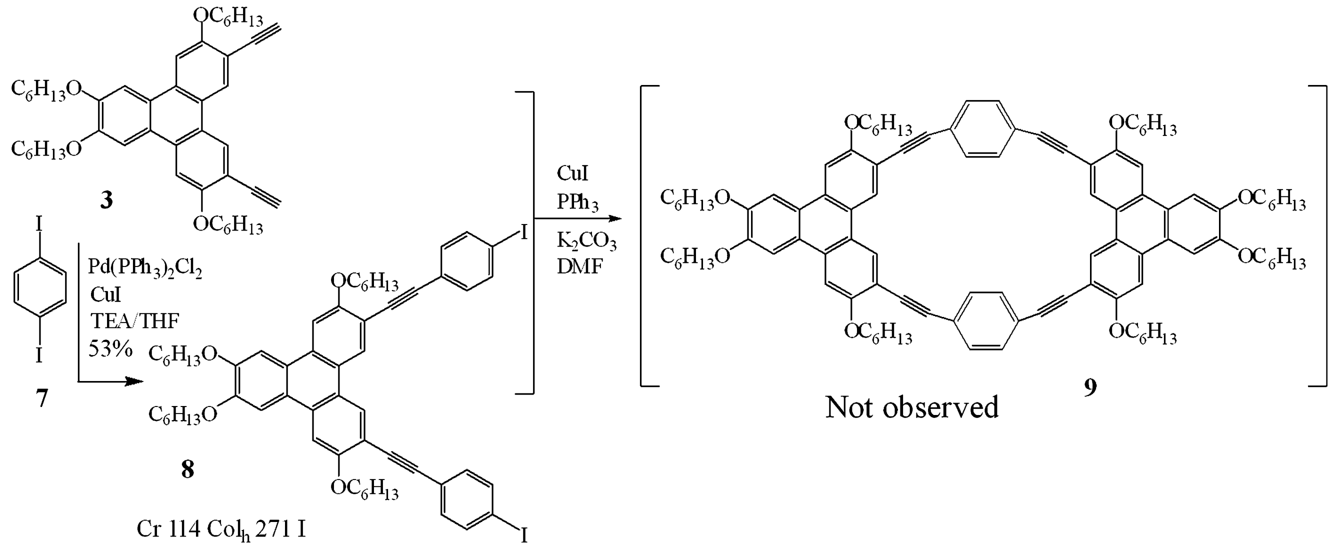
[a] Note: there is site disorder in two of the *n*-hexyl chains; hexyl side chains have been omitted from the stacking diagram but they do not all lie in the plane of the core; thermal ellipsoids and spheres are drawn at the 50% probability level.

(Scheme 2). Consequently, triphenylene diacetylene **3** was coupled with 1,4-diiodobenzene to give diiodide intermediate **8** that again displayed a stable, wide-range columnar mesophase. The final coupling between diiodide **8** and its precursor **3**, however, failed to yield any trace of the twin **9**.

We therefore sought to design bridging units that would reduce the overall strain (leading to achievable macrocyclization) but retain communication across the whole structure so that enhanced molecular properties could be combined with the self-assembly properties that would also be driven by the twinning motif. Thiophene bridges were recognized as being able to fulfill all of these requirements. 2,5-Linked thiophenes provide a near-perfect bonding angle (Figure 4), and more importantly, oligothiophene motifs feature in some of the most important emerging organic materials, spanning applications across optoelectronic materials.[10c,22]

The synthesis of thiophene-bridged twin **12** is shown in Scheme 3 and follows a similar route to the one successfully employed for 1,3-phenylene-bridged twin **6**. The stepwise route was once again required to synthesize the macrocylized product with low yields obtained even under high dilution conditions. Like **6**, and further verifying the design protocol, the 2,5-thiophene-bridged twin **12** shows only nematic behavior when heated, giving a highly mobile schlieren texture when observed by polarizing optical microscopy. The molecular properties of the two compounds **6** and **12**, however, differ significantly as a result of the conjugation that is possible in the latter twin. The conjugation pathway mapped across the macrocycle and cores gives a 4n electron count and describes a formally antiaromatic pathway. One 36e pathway is shown in red on twin **12** in

Scheme 2. Attempted Synthesis of 1,4-Phenylene-Bridged Twin 9



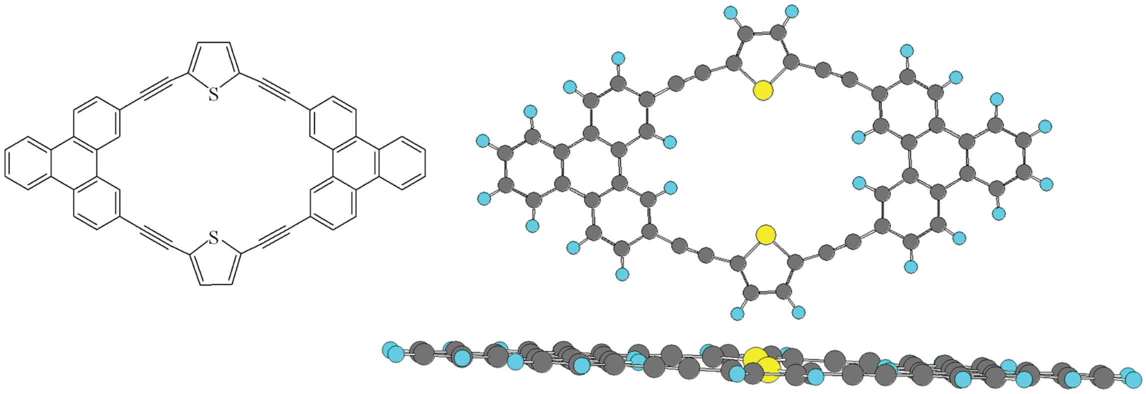
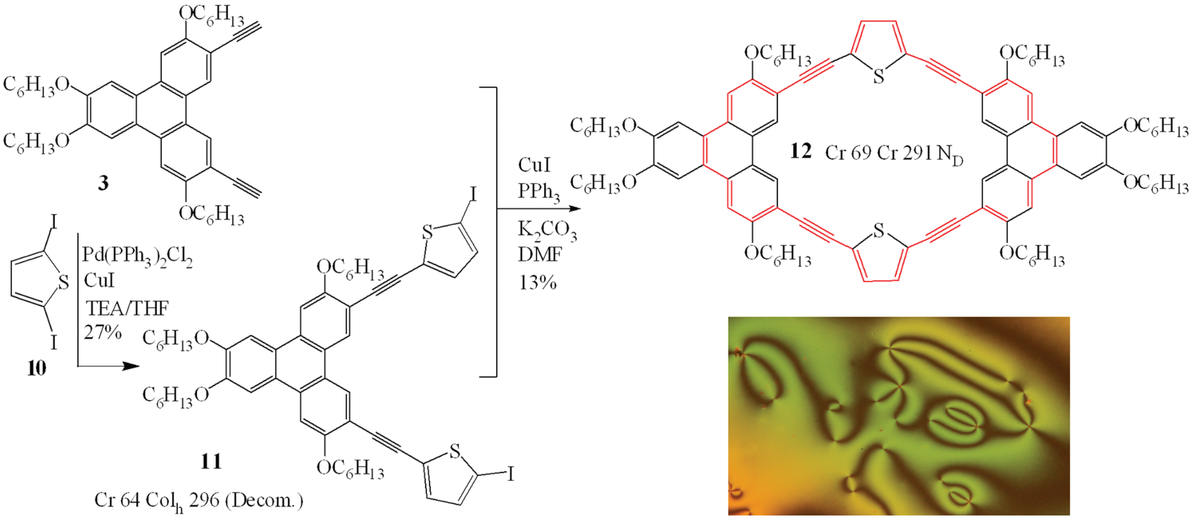


Figure 4. Triphenylene twin linked through 2,5-thiophene bridges and a simple molecular model showing the expected planar conformation.

Scheme 3. Synthesis of 2,5-Thiophene-Bridged Twin 12 and Its Nematic Texture Viewed by Polarizing Optical Microscopy



Scheme 3, but all others similarly give a 4n electron count. This character can be used as one way to rationalize the observed spectroscopic data. In the proton NMR spectrum of **12**, a significant downfield shift is observed for the proton located inside the macrocycle compared to its position in the precursor, consistent with antiaromatic character (Figure 5). Furthermore, the conjugated twin is highly luminescent and gives a large Stokes shift (ca. 60 nm difference between λ_{max} of the longest wavelength absorption band and the high-intensity emission band) indicative of significant reorganization in the excited state (Figure 6).

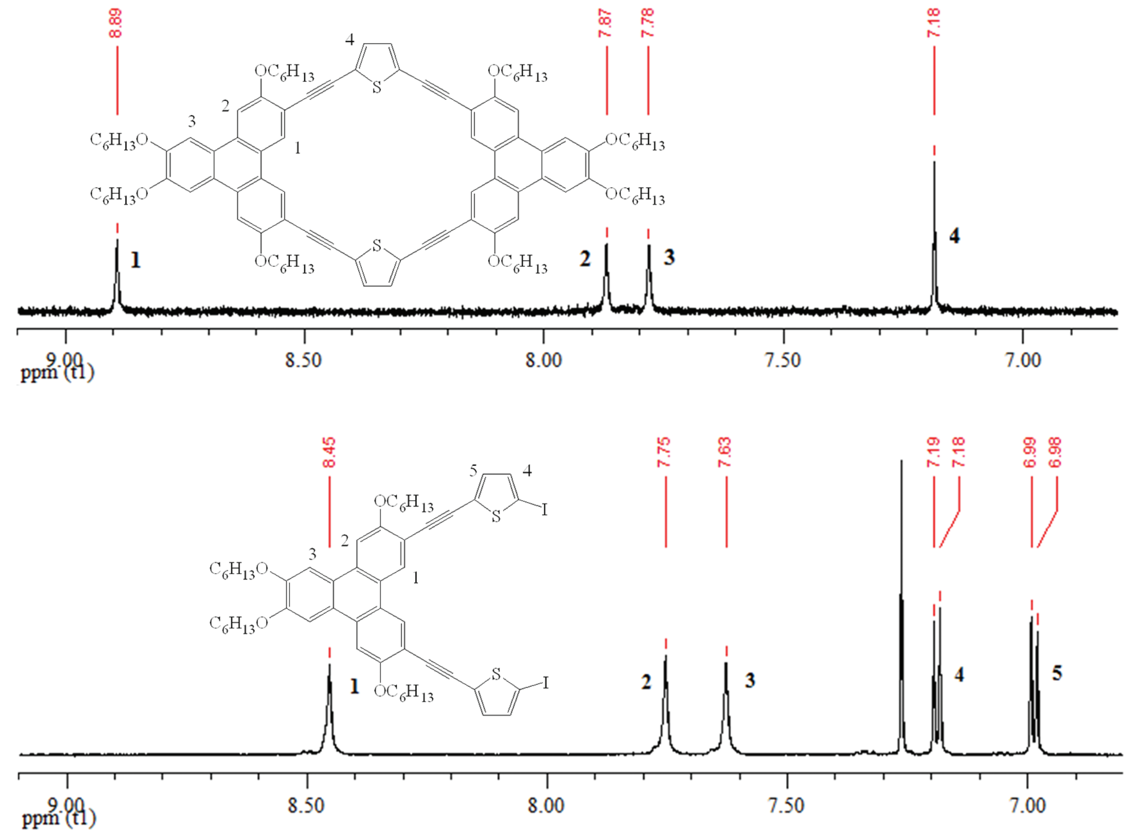


Figure 5. Comparison of the ^{1}H NMR spectra of formally antiaromatic twin **12** with its precursor **11**.

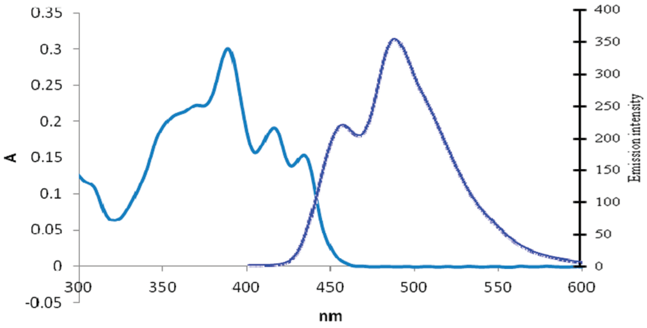


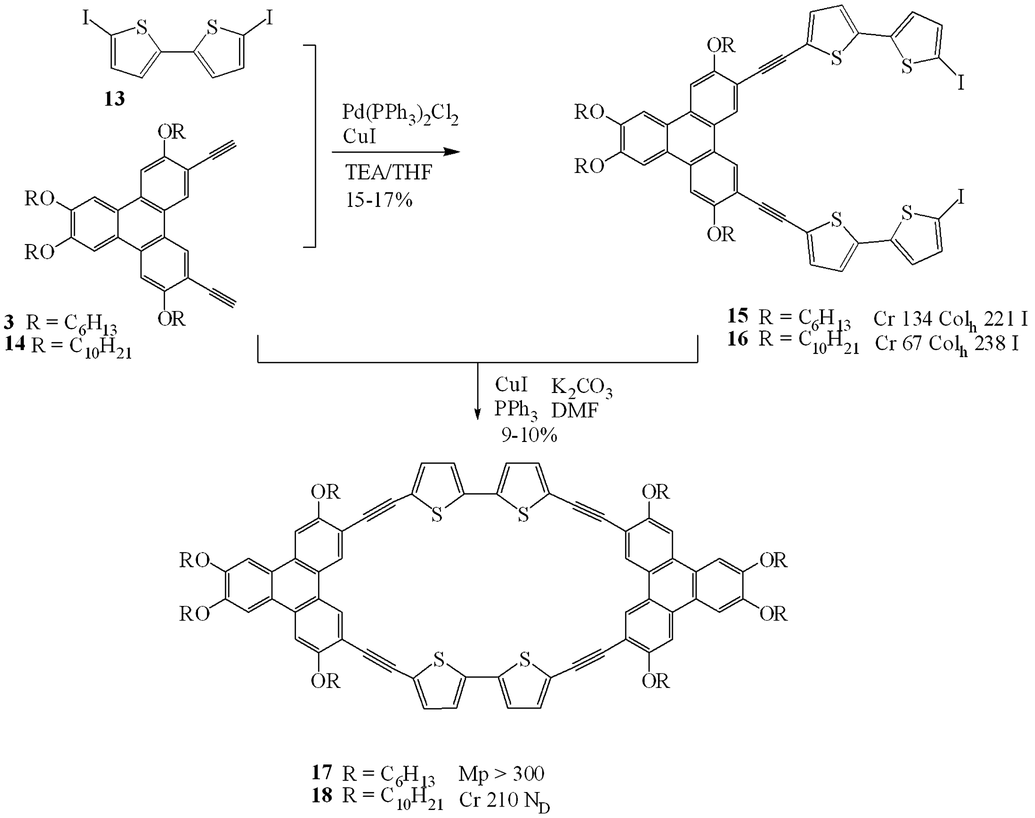
Figure 6. Absorption (6.6×10^{-7} M) and emission (6.6×10^{-8} M) spectra of twin **12** (excitation at 380 nm) recorded in dichloromethane.

The design protocol was pushed a further step forward by inserting bithiophene bridges to form the twin. Conjugation in such a system would be expected to shift the absorption and fluorescence deeper into the red and open the cavity within the macrocycle. In these structures, however, the bond angles are no longer ideal in the planar conformation. Synthesis was straightforward (Scheme 4) following our established methodology and sequence and produced twin **17** that failed to melt below 300 °C. As previously stated, successful protocols for tuning-phase transition temperatures are established, and in our case simply extending the alkoxide side chains (replacing hexyloxy- by decyloxy-) lowered the melting point sufficiently to reveal that nematic mesophase behavior is also exclusively observed in these greatly expanded twinned derivatives. It is unlikely, however, that these expanded systems favor a planar (and therefore conjugated) conformation. The proton NMR spectra of the twins show only a marginal downfield shift for the inner proton (Supporting Information). The absorption spectrum is broad, and fluorescence is weaker in **17** compared to both **12** and, significantly, its precursor **15**, showing two broad but distinct bands of almost equal intensity with the second one again significantly Stokes shifted (Supporting Information).

A strategy to encourage planarity, and therefore conjugation across the complete framework, would be to design a twin with a macrocylic *aromatic* system. This requires an unsymmetrical core with a 4n + 2 electron count, such as the one depicted in Figure 7.

The synthesis of such unsymmetrical twins is clearly more complex than their symmetrical counterparts, and two general macrocyclization sequences were considered (Figure S1, Supporting Information). Simple modeling again indicated that the proposed twin would have modest strain, and therefore the two approaches were considered equally viable. The synthesis of unsymmetrical twin **26** is shown in Scheme 6. The synthesis required initial preparation of a singly protected triphenylene diacetylene derivative **22**, and this synthesis is shown in Scheme 5. 3,6-Dibromotriphenylene **19** was coupled first with 2-propanol-protected acetylene and then with TMS-acetylene to give the differentially protected analogue **21**. Treatment with sodium hydroxide in dry toluene smoothly afforded the (mono) TMS-protected derivative **22**. Two equivalents of **22** reacted with 5,5′-diiodo-2,2′-bithiophene **13** to give the protected open twin **23** that was easily deprotected by treatment with potassium carbonate in THF−methanol (giving **24**). The final macrocyclization was achieved by careful coupling with bis(iodothiophenyl)acetylene **25**,[23] albeit again in low yield even under high dilution conditions.

Scheme 4. Synthesis of Expanded 5,5′-Bithiophene-Bridged Twins 17 and 18



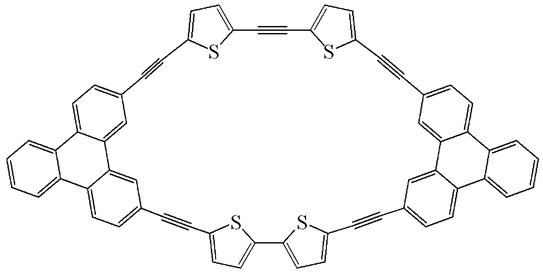


Figure 7. Unsymmetrical, expanded twin structure with formally aromatic electron count.

Unsymmetrical twin **26** does not display any mesophase behavior below 300 °C. Its transition temperatures could again be reduced through chain modification, and nematic behavior would again be expected, but this was not considered useful because the molecular properties of **26** show little evidence for communication across the structure. In the proton NMR spectrum, the signals for the inner protons appear at essentially the same chemical shift as the equivalent proton in formally antiaromatic twin **17**, suggesting that both systems lack significant conjugation (Supporting Information). The absorption and fluorescence spectra are broad and featureless supporting this conclusion (Supporting Information).

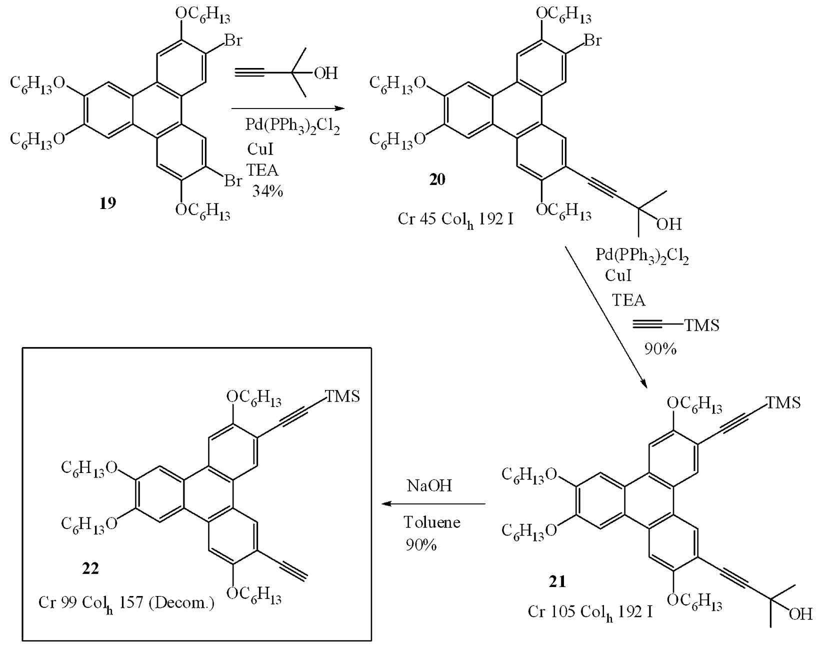
3. SUMMARY AND OUTLOOK

We have demonstrated a general strategy whereby discotic triphenylenes, which have a strong tendency toward columnar organization, can be twinned to form stable, boardlike materials that display only nematic mesophases. The dominant structural feature that leads to nematic behavior is an enforced void region in the center of the macrocycle that results from bridging through the triphenylene 3,6-positions which precludes simple columnar assembly because it would lead to free space through the middle of each stack. In this study, we have focused on the use of thiophene units to bridge between the discotic triphenylenes, and this leads to interesting and potentially important organic materials that can combine the known, favorable properties associated with oligothiophenes with the processability, alignment, and self-healing qualities of nematic mesophases. In addition, communication across twinned structures can lead to enhanced and novel features to optimize optoelectronic behavior. This is particularly apparent in twin **12** which is clearly fully conjugated and therefore is formally expected to have some antiaromatic character. This character is manifested in its spectral properties, and particularly noteworthy is its strong, Stokes-shifted fluorescence at around 500 nm. The structural motif can therefore be exploited for designing processable organic materials for targeted optoelectronic applications.

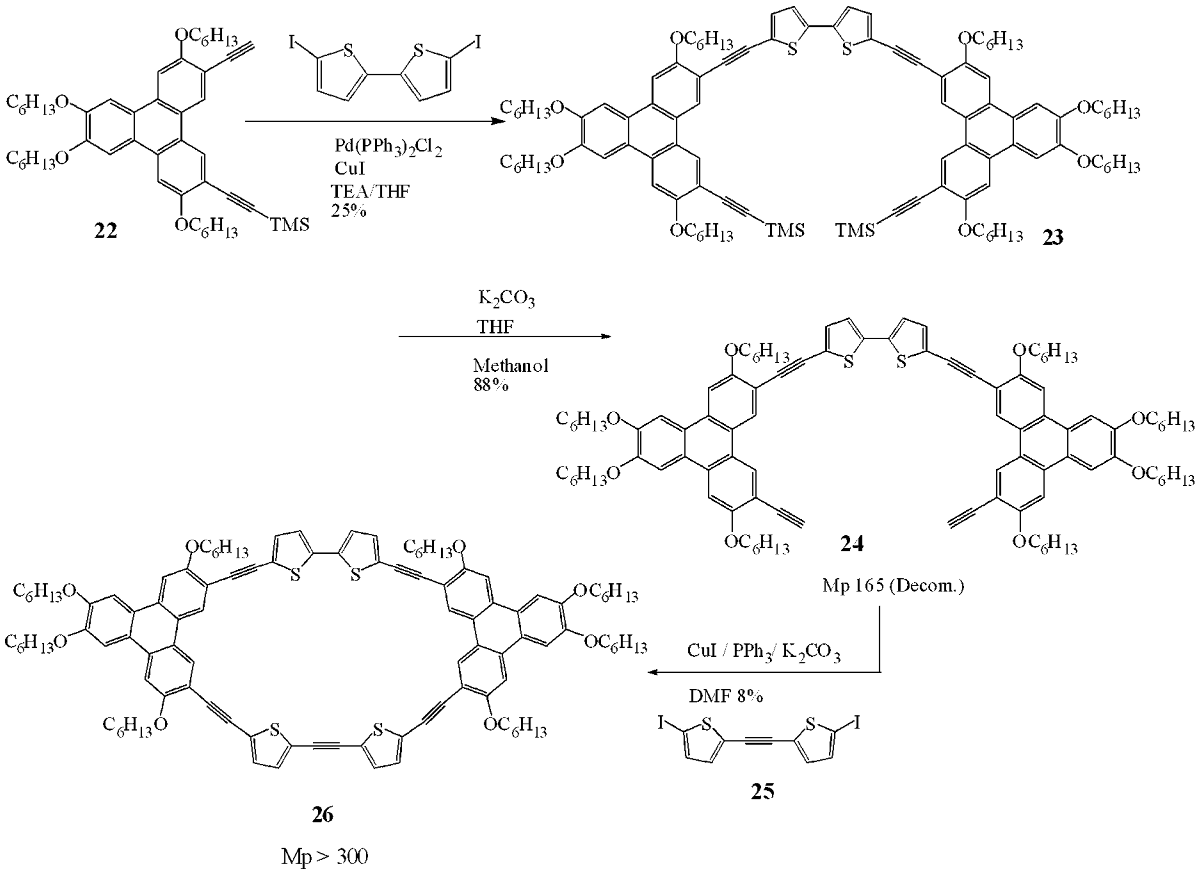
4. EXPERIMENTAL SECTION

General Procedure for the Synthesis of Intermediate Bis(iodoarylethynyl)triphenylenes 5, 8, 11, 15, and 16. Diiodide (**4**, **7**, **10**, **13**) (ca. 4 mmol) and $Pd(PPh_3)_3Cl_2$ (0.06 mmol) in a mixture of freshly distilled triethylamine (10 mL) and THF (5 mL) were stirred at room temperature for 15 min. CuI (ca. 0.2 mmol) was then added, followed by triphenylene diacetylene **3** or **14** (ca. 0.6 mmol) dissolved in THF (5 mL). After addition, the mixture was heated at 50 °C for 17–24 h and then evaporated to dryness in vacuo. The residue was subjected directly to purification by silica gel chromatography to yield the title compounds.

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis[(3-iodophenyl)ethynyl]-triphenylene (5): pale yellow solid (385 mg, 48%); transition temperatures Cr 89 °C Col_h 262 °C I; IR (ATR, cm^{-1}) 3017, 2970, 2925, 2857, 2212, 1608, 1582, 1427, 1376; ^1H NMR (400 MHz, Scheme 5. Synthesis of Singly Protected Triphenylene Intermediate 22



Scheme 6. Synthesis of the Formally Aromatic, Unsymmetrical Twin 22



CDCl$_3$) δ 8.52 (s, 2H), 7.98 (t, J = 1.6 Hz, 2H), 7.76 (s, 2H), 7.68 (m, 2H), 7.65 (s, 2H), 7.56–7.58 (m, 2H), 7.12 (t, J = 8.0 Hz, 2H), 4.27–4.22 (m, 8H), 2.02–1.91 (m, 8H), 1.70–1.58 (m, 8H), 1.49–1.38 (m, 16H), 0.96–0.92 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.7, 149.9, 140.1, 137.0, 130.7, 130.1, 129.8, 128.2, 125.9, 124.3, 122.1, 112.2, 107.1, 104.1, 93.7, 92.0, 88.0, 69.5, 68.9, 31.8, 31.7, 29.41, 29.37, 26.0, 25.9, 22.8, 22.7, 14.14, 14.07; MALDI-MS 1080.45 (M$^+$). Anal. Calcd for $C_{58}H_{66}I_2O_4$: C, 64.45; H, 6.15. Found: C, 64.40; H, 6.10.

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis[(4-iodophenyl)ethynyl]-triphenylene (8): yellow solid (465 mg, 53%); transition temperatures Cr 114 °C Col$_h$ 271 °C I; IR (ATR, cm^{-1}) 3017, 2924, 2856, 2212, 1609, 1425, 1377; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.55 (s, 2H), 7.78 (s, 2H), 7.72 (d, J = 8.4, 2H), 7.67 (s, 2H) 7.34 (d, J = 8.4, 2H), 4.28–4.21 (m, 8H), 2.02–1.90 (m, 8H), 1.69–1.55 (m, 8H), 1.46–1.32 (m, 16H), 0.97–0.91 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 150.1, 137.6, 133.2, 130.2, 128.4, 124.5, 123.4, 122.3, 122.2, 112.6, 107.5, 104.4, 93.9, 92.9, 88.0, 69.6, 69.0, 31.6, 29.3, 25.8, 25.76, 22.59, 22.56, 13.9; MALDI-MS 1080.43 (M^+). Anal. Calcd for $C_{58}H_{66}I_2O_4$: C, 64.45; H, 6.15. Found: C, 64.51; H, 6.25.

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis[2-(5-iodothiophene-2-yl)ethynyl]triphenylene (11): yellow solid (172 mg, 27%); transition temperatures Cr 64 °C Col_h 296 °C dec; IR (ATR, cm^{-1}) 3017, 2970, 2924, 2856, 2212, 1607, 1583, 1427, 1377; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 2H), 7.75 (s, 2H), 7.63 (s, 2H), 7.19 (d, J = 3.6 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 4.23 (t, J = 6.3 Hz, 8H), 2.01–1.89 (m, 8H), 1.68–1.56 (m, 8H), 1.46–1.38 (m, 16H), 0.96–0.92 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 157.7, 150.1, 137.3, 133.1, 130,4, 130.32, 130.26, 129.4, 128.0, 124.55, 124.49, 122.3, 122.2, 112.2, 111.7, 107.4, 104.4, 92.5, 85.9, 81.5, 80.7, 69.7, 69.24, 69.2, 31.92, 31.87, 29.6, 29.5, 29.4, 26.1, 26.0, 22.93, 22.89, 22.86, 14.33, 14.29; MALDI-MS 1092.46 (M^+). Anal. Calcd for $C_{54}H_{62}I_2S_2O_4$: C, 59.34; H, 5.72. Found: C, 59.39; H, 5.75.

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis[(5′-iodo-2,2′-bithiophene-5-yl)ethynyl]triphenylene (15): yellow solid (415 mg, 17%); transition temperatures Cr 134 °C Col_h 221 °C I; IR (ATR, cm^{-1}) 3068, 2920, 2853, 2196, 1607, 1537, 1425, 1378; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.60 (s, 2H), 7.85 (s, 2H), 7.76 (s, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 2H), 7.08 (d, J = 4.0 Hz, 2H), 6.91 (d, J = 4.0 Hz, 2H), 4.29 (t, J=6.4 Hz, 4H), 4.24 (t, J = 6.4 Hz, 4H), 2.01–1.88 (m, 8H), 1.69–1.52 (m, 8H), 1.47–1.36 (m, 16H), 0.96–0.92 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 157.5, 150.0, 142.6, 137.9, 137.3, 132.4, 130.0, 127.7, 125.4, 124.1, 124.0, 123.0, 121.9, 112.0, 106.9, 104.0, 91.9, 86.3, 72.3, 69.2, 68.8, 31.52, 31.47, 29.2, 29.1, 25.7, 25.6, 22.5, 22.4, 13.62, 13.55; MALDI-MS 1256.32 (M^+).

2,7,10,11-Tetrakis(decyloxy)-3,6-bis[(5′-iodo-2,2′-bithiophene-5-yl)ethynyl]triphenylene (16): yellow solid (643 mg, 15%); transition temperatures Cr 67 °C Col_h 238 °C I; IR (ATR, cm^{-1}) 3066, 2917, 2850, 2194, 1603, 1535, 1423; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 2H), 7.80 (s, 2H), 7.70 (s, 2H), 7.22 (d, J = 3.9 Hz, 2H), 7.17 (d, J = 3.9 Hz, 2H), 7.04 (d, J = 3.9 Hz, 2H), 6.88 (d, J = 3.9 Hz, 2H), 4.23 (m, 8H), 2.04–1.88 (m, 8H), 1.71–1.56 (m, 8H), 1.51–1.19 (m, 48H), 0.96–0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 149.7, 142.8, 137.7, 137.3, 132.4, 129.90, 127.6, 125.2, 124.2, 123.9, 123.1, 122.0, 112.0, 106.9, 103.9, 92.1, 86.7, 72.5, 69.4, 68.8, 32.0, 29.78, 29.76, 29.7, 29.67, 29.5, 29.4, 26.33, 26.30, 22.7, 14.18, 14.16; MALDI-MS 1480.55 (M^+).

General Procedure for the Synthesis of Twinned Triphenylenes 6, 12, 17, and 18. CuI (5.7 mg, 0.03 mmol), PPh_3 (7.8 mg, 0.03 mmol), and K_2CO_3 (41.5 mg, 0.30 mmol) in freshly distilled DMF (60 mL) were stirred at room temperature for 15 min. Triphenylene diiodide (**5**, **8**, **11**, **15** or **16**) (0.10 mmol) and triphenylene diacetylene (**3** or **14**) (0.12 mmol) were added. The reaction was stirred and heated at 150 °C for 24 h, and then the mixture was poured into saturated aqueous NH_4Cl (50 mL), followed by methanol (200 mL). The product was filtered and washed thoroughly with methanol. A portion of the solid was then subjected to careful silica gel chromatography to yield an analytical sample of the twin. [The samples' low solubility and aggregation prevented acquisition of informative ^{13}C NMR data.]

Twin **6**: off-white solid (16 mg, 11%); transition temperatures Cr 113 °C Cr 272 °C N_D; IR (ATR, cm^{-1}) 3016, 2927, 2854, 1609, 1425, 1378; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 4H), 8.10 (s, 2H), 7.87 (s, 4H), 7.76 (s, 4H), 7.56 (dd, J = 7.6 Hz, J = 1.6 Hz, 4H), 7.39 (t, J = 7.6 Hz, 2H), 4.32–4.25 (m, 16H), 3.38 (s, 1H), 2.06–1.93 (m, 16H), 1.76–1.57 (m, 16H), 1.51–1.26 (m, 32H), 0.99–0.93 (m, 24H); UV–vis (CH_2Cl_2) λ_{max} (log ε) 312 (5.32), 343 (5.12), 397 (4.58) nm; MALDI-MS 1502.15 (M^+).

Twin **12**: bright yellow solid (20 mg, 13%); transition temperatures Cr 69 °C Cr 291 °C N_D 300 °C; IR (ATR, cm^{-1}) 2925, 2856, 2197, 1604, 1519, 1425, 1377; ^{1}H NMR (400 MHz, $C_6D_5CD_3$, 85 °C) δ 8.94 (s, 4H), 8.04 (s, 4H), 7.89 (s, 4H), 4.21–4.18 (t, J = 6.4 Hz, 16H), 1.96–1.86 (m, 16H), 1.68–1.53 (m, 16H), 1.45–1.39 (m, 32H), 1.01–0.96 (m, 24H); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.88 (s, 4H), 7.85 (s, 4H), 7.77 (s, 4H), 7.17 (s, 4H), 4.31 (t, J = 6.4 Hz, 8H), 4.25 (t, J = 6.4 Hz, 8H), 2.11–1.89 (m, 16H), 1.65–1.54 (m, 16H), 1.46–1.39 (m, 32H), 0.97–0.91 (m, 24H); UV–vis (CH_2Cl_2) λ_{max} (log ε) 277 (5.54), 389 (5.65), 416 (5.45), 434 (5.36) nm; MALDI-MS 1514.31 (M^+).

Twin **17**: orange solid (10 mg, 10%); mp > 300 °C; IR (ATR, cm^{-1}) 2922, 2854, 2194, 1607, 1425, 1376; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (s, 4H), 7.82 (s, 4H), 7.72 (s, 4H), 7.27 (m, 8H), 4.29 (t, J = 6.4 Hz, 8H), 4.25 (t, J = 6.4 Hz, 8H), 2.11–1.89 (m, 16H), 1.65–1.54 (m, 16H), 1.46–1.39 (m, 32H), 0.97–0.91 (m, 24H); UV–vis (CH_2Cl_2) λ_{max} (log ε) 294 (5.06), 373 (5.10), 419 (5.17) nm; MALDI-MS 1677.95 (M^+).

Twin **18**: orange solid (12 mg, 9%); transition temperatures Cr 210 °C N_D; IR (ATR, cm^{-1}) 2920, 2851, 2193, 1605, 1424, 1375; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.61 (s, 4H), 7.76 (s, 4H), 7.66 (s, 4H), 7.24 (s, 8H), 4.26 (t, J = 6.4 Hz, 8H), 4.22 (t, J = 6.4 Hz, 8H), 2.04–1.89 (m, 16H), 1.74–1.55 (m, 16H), 1.46–1.24 (m, 96H), 0.98–0.93 (m, 24H); MALDI-MS 2126.03 (M^+).

2,7,10,11-Tetrakis(hexyloxy)-3-bromo-6-(3-methyl-3-hydroxybutynyl)triphenylene (20). Dibromotriphenylene **19** (1.00 g, 1.27 mmol), $Pd(PPh_3)_3Cl_2$ (45 mg, 0.0635 mmol), and CuI (12 mg, 0.0635 mmol) in freshly distilled triethylamine (20 mL) were heated at 50 °C for 20 min. 2-Methyl-3-butyn-2-ol (118 mg, 1.40 mmol) was added dropwise and the suspension was heated at 50 °C for 3 h. The reaction mixture was evaporated to dryness in vacuo, and the residue subjected directly to silica gel chromatography (DCM/petroleum ether = 1:1–9:1) to yield the title compound **20** as an off-white solid (0.34 g, 34%): transition temperatures Cr 45 °C Col_h 192 °C I; IR (ATR, cm^{-1}) 3413 (br), 2954, 2926, 2858, 2330 (w), 1604, 1497, 1424; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.29 (s, 1H), 7.76 (s, 1H), 7.75 (s, 1H), 7.64 (s, 1H), 7.58 (s, 1H), 4.26–4.17 (m, 8H), 2.18–1.91 (m, 8H), 1.72 (s, 6H), 1.65–1.53 (m, 8H), 1.45–1.35 (m, 16H), 0.96–0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.7, 149.9, 149.84, 129.9, 128.9, 128.1, 127.6, 124.3, 124.2, 123.6, 121.5, 112.5, 112.2, 107.58, 107.51, 105.3, 104.0, 98.5, 79.1, 70.0, 69.7, 69.5, 68.9, 65.9, 51.1, 32.0, 31.93, 31.88, 31.8, 29.6, 29.4, 26.1, 26.0, 22.93, 22.90, 22.87, 14.33, 14.28; HRMS (ES) m/z $[M + H]^+$ calcd for $C_{47}H_{65}BrO_5$ 789.4088, found 789.4082. Anal. Calcd for $C_{47}H_{65}BrO_5$: C, 71.46; H, 8.29. Found: C, 71.37; H, 8.33.

2,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilylethynyl)-6-(3-methyl-3-hydroxybutynyl)triphenylene (21). Triphenylene **20** (700 mg, 0.90 mmol), $Pd(PPh_3)_3Cl_2$ (156 mg, 0.22 mmol), and CuI (42.3 mg, 0.22 mmol) in freshly distilled triethylamine (20 mL) were heated at 60 °C for 20 min. Trimethylsilyl acetylene (354 mg, 3.60 mmol) was then added dropwise. The suspension was heated at 60 °C for 18 h. The reaction mixture was evaporated to dryness in vacuo, and the residue was subjected directly to silica gel chromatography (DCM/petroleum ether = 2:3–4:1) to yield the title compound **21** as an off-white solid (645 mg, 90%): transition temperatures Cr 105 °C Col_h 192 °C I; IR (ATR, cm^{-1}) 3443 (br), 2955, 2929, 2859, 2150, 1610, 1503, 1468, 1426; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.52 (s, 1H), 7.82 (s, 1H), 7.80 (s, 1H), 7.69 (s, 1H), 7.67 (s, 1H), 4.26–4.19 (m, 8H), 2.24 (s, 1H) 2.00–1.90 (m, 8H), 1.71 (s, 6H), 1.65–1.53 (m, 8H), 1.45–1.35 (m, 16H), 0.96–0.92 (m, 12H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 157.7, 149.84, 149.80, 130.0, 129.8, 128.7, 128.4, 124.4, 124.3, 122.2, 122.16, 122.13, 112.7, 112.2, 107.4, 107.3, 104.3, 104.2, 101.6, 98.9, 98.2, 78.8, 69.5, 68.9, 68.8, 65.8, 31.7, 31.62, 31.60, 31.5, 29.6, 29.31, 29.28, 29.25, 25.78, 25.77, 22.62, 22.58, 14.04, 14.02, 14.0, 0.0; HRMS (ES) m/z $[M + H]^+$ calcd for $C_{52}H_{74}O_5Si$ 807.5378, found 807.5383. Anal. Calcd for $C_{52}H_{74}O_5Si$: C, 77.37; H, 9.24. Found: C, 77.30; H, 9.26.

2,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilylethynyl)-6-ethynyltriphenylene (22). Freshly powdered sodium hydroxide (500 mg, 12.5 mmol) was added to triphenylene **21** (527 mg, 0.653 mmol) dissolved in anhydrous toluene (50 mL). The suspension was heated under reflux for 80 min. The mixture was filtered, and the filtrate was evaporated to dryness in vacuo. The residue was subjected directly to silica gel chromatography (DCM/petroleum ether = 1:1) to yield the title compound **22** as an off-white solid (440 mg, 90%): transition temperatures Cr 99 °C Col_h 157 °C dec; IR (ATR, cm^{-1})

3316, 2955, 2927, 2859, 2150, 2105, 1609, 1468, 1425; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.59 (s, 1H), 8.54 (s, 1H), 7.80 (s, 1H), 7.79 (s, 1H), 7.68 (s, 1H), 7.67 (s, 1H), 4.27−4.19 (m, 8H), 3.38 (s, 1H) 2.00−1.90 (m, 8H), 1.68−1.57 (m, 8H), 1.43−1.37 (m, 16H), 0.96−0.91 (m, 12H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 158.2, 158.1, 150.0, 149.9, 130.2, 130.0, 129.4, 128.8, 124.5, 124.3, 122.2, 122.0, 112.7, 111.6, 107.4, 107.3, 104.3, 101.5, 98.9, 94.4, 81.3, 80.4, 69.52, 69.47, 69.1, 68.9, 31.7, 31.60, 31.56, 29.7, 29.31, 29.26, 29.1, 25.8, 25.7, 22.63, 22.59, 22.56, 15.0, 14.1, 14.0, 0.0; HRMS calcd for $C_{49}H_{68}O_4Si$ 748.4881, found 748.4880. Anal. Calcd for $C_{49}H_{68}O_4Si$: C, 78.56; H, 9.15. Found: C, 78.59; H, 9.08.

5,5′-Bis[2,7,10,11-tetrakis(hexyloxy)-3-(trimethylsilylethynyl)triphenylen-6-yl]bithiophene (23). 5,5′-Diiodobithiophene (41.8 mg, 0.10 mmol), Pd(PPh$_3$)$_3$Cl$_2$ (7.0 mg, 0.01 mmol), and CuI (3.8 mg, 0.02 mmol) in freshly distilled triethylamine (5 mL) and THF (5 mL) were stirred at 50 °C for 20 min. Compound **22** (150 mg, 0.20 mmol) in THF (15 mL) was added at the rate of 5 mL/h to the solution, and then the reaction was stirred at 50 °C for 16 h. The reaction mixture was evaporated to dryness in vacuo, and the residue subjected directly to purification by silica chromatography (DCM/hexane = 3:7) to yield the title compound **150** as a pale orange semisolid (42 mg, 25%): IR (ATR, cm^{-1}) 2926, 2857, 2150, 1608, 1425, 1378; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.57 (s, 2H), 8.55 (s, 2H), 7.81 (s, 4H), 7.74 (s, 2H), 7.69 (s, 2H), 7.26 (d, J = 3.9 Hz, 2H), 7.18 (d, J = 3.9 Hz, 2H), 4.32−4.29 (t, J = 6.6 Hz, 4H), 4.26−4.22 (t, J = 6.6 Hz, 12H), 2.07−1.92 (m, 16H), 1.77−1.53 (m, 16H), 1.51−1.39 (m, 32H), 0.99−0.92 (m, 24H), 0.33 (s, 18H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 158.6, 158.0, 150.3, 150.2, 138.8, 133.1, 130.4, 130.3, 129.0, 127.9, 124.6, 124.5, 124.3, 123.9, 122.4, 122.2, 112.7, 107.1, 106.9, 104.4, 102.8, 99.0, 93.0, 87.5, 69.9, 69.5, 69.2, 32.5, 32.4, 32.3, 30.14, 30.10, 30.07, 26.7, 26.5, 26.45, 23.4, 23.28, 23.26, 14.6, 14.44, 14.39; MALDI-MS 1660.33 (M$^+$).

5,5′-Bis[2,7,10,11-tetrakis(hexyloxy)-6-ethynyltriphenylen-3-yl]bithiophene 24. Triphenylene **23** (40 mg, 0.024 mmol) and K$_2$CO$_3$ (32 mg, 0.24 mmol) were stirred in a mixture of THF (12 mL) and methanol (4 mL) at room temperature for 6 h. The mixture was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in DCM and recrystallized from methanol to yield the title compound **24** as a yellow solid (32 mg, 88%): mp 165 °C dec; IR (ATR, cm^{-1}) 3313, 2926, 2856, 2196, 2104, 1608, 1425, 1377; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.55 (s, 2H), 8.52 (s, 2H), 7.79 (s, 4H), 7.71 (s, 2H), 7.68 (s, 2H), 7.26 (d, J = 3.6 Hz, 2H), 7.17 (d, J = 3.6 Hz, 2H), 4.33−4.29 (t, J = 6.6 Hz, 4H), 4.26−4.22 (t, J = 6.6 Hz, 12H), 3.44 (s, 2H), 2.04−1.91 (m, 16H), 1.77−1.54 (m, 16H), 1.52−1.41 (m, 32H), 0.99−0.92 (m, 24H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 158.4, 158.0, 150.4, 150.2, 138.8, 133.1, 130.5, 130.3, 129.5, 127.9, 124.6, 124.5, 124.2, 123.9, 122.2, 122.1, 112.5, 111.4, 107.2, 106.9, 104.2, 93.0, 87.5, 81.5, 69.9, 69.6, 69.3, 32.5, 32.4, 32.3, 30.1, 30.05, 29.9, 26.6, 26.5, 26.45, 26.3, 23.4, 23.3, 14.5, 14.4; MALDI-MS 1515.87 (M$^+$). Anal. Calcd for $C_{100}H_{122}O_8S_2$: C, 79.22; H, 8.11. Found: C, 79.15; H, 8.13.

Twin **26**. CuI (1.7 mg, 0.009 mmol), PPh$_3$ (2.4 mg, 0.009 mmol), and K$_2$CO$_3$ (12.4 mg, 0.09 mmol) were stirred in freshly distilled DMF (45 mL) at room temperature for 20 min, and then 2,2′-bi(5,5′-diiodo)thienylacetylene **25** (prepared according to the literature reported by Pu^2) (6.6 mg, 0.015 mmol) and **24** (22.7 mg, 0.015 mmol) was added directly to the suspension. The reaction was heated at 150 °C for 24 h. The mixture was poured onto ice-cold water (50 mL), and methanol (200 mL) was added. The precipitate was filtered and washed thoroughly with methanol. The solid was then subjected to careful silica gel chromatography (×3) (DCM/cyclohexane = 3:7) to yield an analytical sample of the title compound **26** as an orange solid (ca. 2 mg, 8%): mp > 300 °C; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) 8.65 (s, 2H), 8.64 (s, 2H), 7.83 (s, 2H), 7.82 (s, 2H), 7.73 (s, 4H), 7.31 (d, J = 3.6 Hz, 2H), 7.27 (d, J = 3.6 Hz, 2H), 7.21 (d, J = 4.0 Hz, 2H), 7.18 (d, J = 4.0 Hz, 2H), 4.31−4.27 (t, J = 6.4 Hz, 8H), 4.26−4.23 (t, J = 6.4 Hz, 8H), 2.04−1.91 (m, 16H), 1.75−1.52 (m, 16H), 1.51−1.40 (m, 32H), 0.99−0.93 (m, 24H); UV−vis (CH$_2$Cl2) λ_{max} (log ε) 283 (4.65), 382(4.64), 416(4.63), 450(4.39) nm; MALDI-MS: 1701.96 (M$^+$). (The samples' low solubility and aggregation prevented acquisition of informative ^{13}C NMR data.)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization spectra for all new compounds including absorption and emission spectra, polarizing optical microscopy images for nematic materials and DSC traces, and X-ray crystal structure of **5**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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