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Triptycene-containing bis(phenylethynyl)benzene nematic liquid crystals[†]

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We report the synthesis of a new class of nematic liquid crystals with triptycenes built into a *p*-dialkoxy-bis(phenylethynyl)benzene mesomorphic core. Triptycenes are appended on the center or terminal ring of the mesogen, leading to symmetric liquid crystals and reduced symmetry liquid crystals, respectively. Both types displayed monotropic behavior, with the asymmetric compounds having unusual phase behavior, lacking distinct crystallization transitions, and forming a glassy mesophase. A chiral analogue was found to be non-mesomorphic, but induced chiral nematic phases when doped into achiral triptycene-containing analogues. Rotation is physically hindered normal to the director and, hence, this new liquid crystal architecture may allow for the synthesis of a single component liquid crystal that displays a biaxial nematic phase.

Introduction

With the discovery of a biaxial nematic phase in a lyotropic potassium laurate–1-decanol–water system,[1] serious efforts have been invested toward the discovery of the same in a single component thermotropic liquid crystalline system. In a conventional (uniaxial) nematic phase, all molecules lie, on average, with their long axes along a single director. Due to the inherent anisotropy in the index of refraction introduced by this arrangement, nematic liquid crystals have long been exploited to produce the optical effects that are the basis of conventional liquid crystal displays.[2] However, the switching time due to the electrical switching of the nematic phase is limited by the need to reorient the entire molecule *via* rotation along its major axis. Biaxial nematic phases, which could switch by rotation about the long axis of the molecule, offer an opportunity to generate switching on a shorter time scale.

Molecules in a biaxial nematic phase have a preferred organization in the direction normal to the classical nematic director.[3] This organization allows, in principle, for switching between two optically different states by rotation around the director, an overall faster molecular motion. A number of groups have been in pursuit of such a phase through a variety of designs with the hope of hindering molecular rotation to "freeze out" this second level of organization. However, the existence of a biaxial nematic phase in a single component system remains a subject of debate.[4] Designs include rods that are laterally attached to disks,[5] banana-shaped molecules, with or without laterally attached dipoles to inhibit free rotation,[6,7] and molecular-based biaxiality introduced in metallomesogens.[8]

During the course of our research on triptycenes and their ability to increase molecular ordering, we became aware that one of the compounds designed as a guest dye in our study was, in fact, liquid crystalline. Although, this was not the first liquid crystal based on a triptycene mesogen,[9] its design is distinctly different and could offer another entry into biaxial nematic phases.

Previous triptycene-based liquid crystals contained five long paraffinic chains distributed among the three aromatic rings.[9] However, symmetric triptycenes with six chains were found to be crystalline, high melting, and had poor solubilities. All of these materials were shown to undergo multiple phase transitions and were assigned to smectic A phases with hexagonal ordering of the triptycene cores within the lamellae.

In the new structures reported here, a classical nematogen based upon the bis(phenylethynyl)benzene calamitic core is appended with a triptycene on one of the benzene rings. We considered that the attachment of the triptycene allows for a physical "gearing" within the phase. Such a correlation of triptycene motion has already been exploited in the design of molecular gears and ratchets.[10] The fact that face-to-face disposition of the triptycenes is sterically unfavorable could lead to local head-to-tail correlations of the triptycenes normal to the director plane. If such ordering were induced over extended domains, a biaxial phase could be formed.

Synthesis

Two series of triptycene-based liquid crystals were synthesized, differing only in the position of the triptycene within the mesogen. One carries the triptycene on the center ring of a *p*-bis(phenylethynyl)benzene core, yielding a symmetric mesogen. In the other, the triptycene is attached to one of the outer rings, thereby reducing the symmetry of the system. This comparison was made to examine the effect of decreased symmetry on the mesophase behavior.

1 Symmetric triptycene liquid crystals

The synthetic pathway to the symmetric compounds is summarized in Scheme 1. Two literature compounds are coupled to build the core of the symmetric triptycene liquid crystals: coupling of 1,4-diiodotriptycene[11] to 4-tetrahydropyranyl-1-ethynylbenzene[12] *via* standard Sonogashira–Hagihara[13] conditions at room temperature provided compound **1** in 97% yield. Deprotection of the tetrahydropyranyl protecting groups, with *p*-TsOH in a mixture of dichloromethane and methanol, cleanly afforded the bisphenol compound **2** in 99% yield. Alkylation of the free phenols with alkyl bromides or iodides *via* modified a Williamson ether synthesis with Cs_2CO_3 (the Cs^+ cation increases the nucleophilicity of the phenoxide anion)[9c] in DMF yielded compounds CTO*n* (n = 4–14) in 41–82% yields. A chiral analogue, CTOS, was synthesized under

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[†] Electronic supplementary information (ESI) available: spectroscopic data for CTO4–14, CTOS, and ETO6–12. See http://www.rsc.org/suppdata/jm/b2/b203160d/

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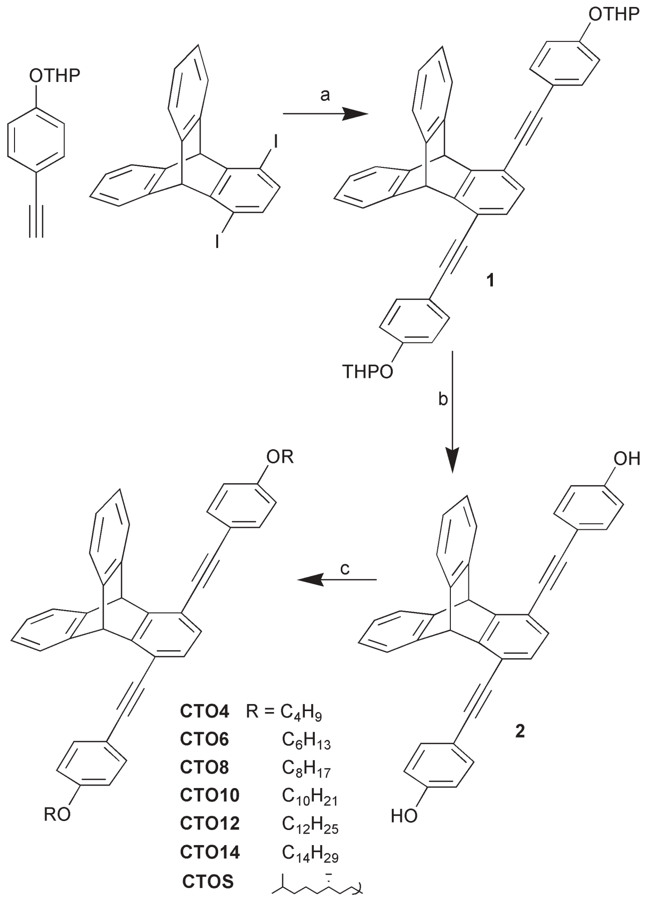


Scheme 1 (a) $PdCl_2(PPh_3)_2$, CuI, THF, $^{i}Pr_2NH$, 97%; (b) *p*-TsOH, CH_2Cl_2, MeOH, 99%; (c) RX, Cs_2CO_3, DMF, 41–82%.

the same alkylation conditions using (3*S*)-3,7-dimethyl-1-bromooctane.

2 Reduced symmetry triptycene liquid crystals

Triptycene-based liquid crystals with reduced symmetry were produced by a slightly longer but convergent synthesis. This synthetic pathway is summarized in Scheme 2. The general synthetic strategy centered on the palladium-catalyzed coupling of compounds **5** and **6** to build the mesomorphic core.

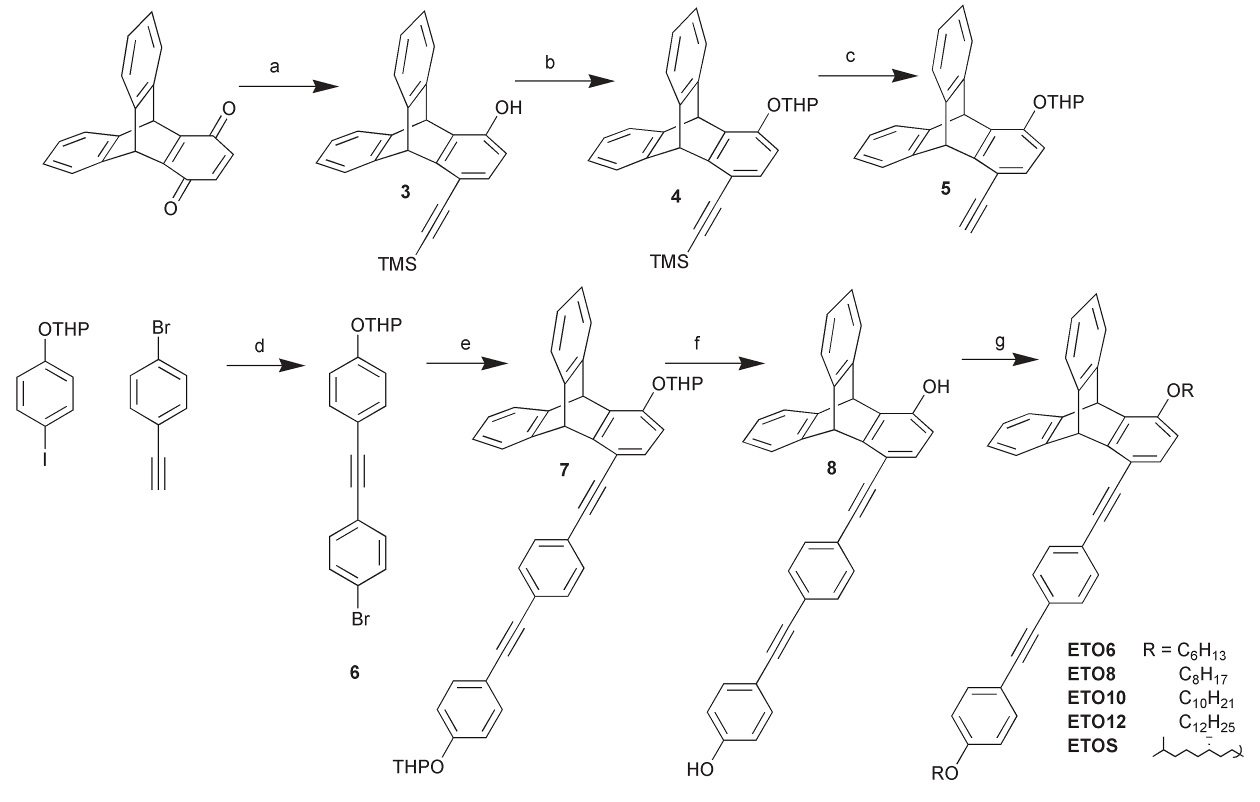
Compound **5** was synthesized in three steps from the readily available 1,4-triptycene quinone.[14] Slow addition of lithium trimethylsilylacetylide at low temperature, followed by the trapping of the intermediate adduct with trimethylsilyl chloride and reduction with zinc dust in the presence of acetic acid, afforded compound **3** in high yield and in one pot.[15] Protection of the free phenol as the tetrahydropyranyl ether, **4**, and removal of the trimethylsilyl group with potassium carbonate in tetrahydrofuran and methanol yielded acetylene **5**.

Compound **6** can be easily prepared under standard Sonogashira coupling conditions starting from 4-tetrahydropyranyl-1-iodobenzene[12] and commercially available 4-bromo-1-ethynylbenzene. Coupling of **5** and **6** in the presence of catalytic $Pd_2(dba)_3$ and CuI, with the addition of triphenylphosphine, in triethylamine in a sealed tube at 100 °C gave **7** in 73% yield, despite coupling to an electron-rich aryl bromide. Removal of the tetrahydropyranyl ethers in the presence of catalytic *p*-TsOH gives the free bisphenol, **8**, which was alkylated under the same conditions as for the symmetric triptycenes, to give the corresponding asymmetric triptycene compounds ETO*n* (n = 6–12).

Results and discussion

Mesomorphic behavior

1 Symmetric triptycene liquid crystals (CTO*n*). All symmetric compounds displayed monotropic behavior, indicating



Scheme 2 (a) 1. Lithium trimethylsilylacetylide, THF; 2. TMSCl; 3. Zn, AcOH, 86%; (b) dihydropyran, *p*-TsOH, CH_2Cl_2, 64%; (c) K_2CO_3, THF, MeOH, 99%; (d) $PdCl_2(PPh_3)_2$, CuI, THF, $^{i}Pr_2NH$, 68%; (e) **5**, $Pd_2(dba)_3$, PPh_3, CuI, Et_3N, 73%; (f) *p*-TsOH, CH_2Cl_2, MeOH, 80%; (g) RX, Cs_2CO_3, DMF, 63–86%.

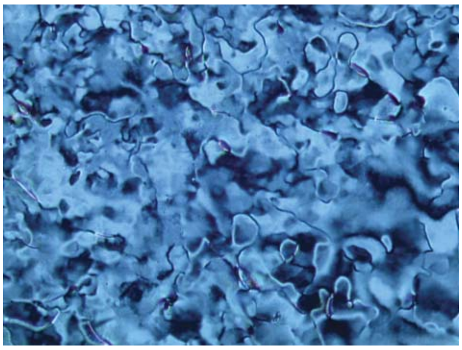


Fig. 1 Marbled texture exhibited by CTO8 on cooling (100× magnification, 133 °C).

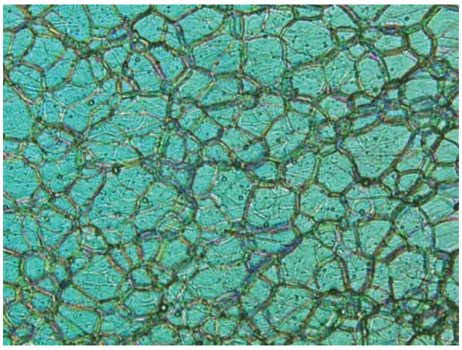


Fig. 2 Chiral nematic phase at the boundary of a contact preparation of CTO8 and CTOS (200× magnification, 128 °C).

Table 1 Mesophase behavior of symmetric triptycene derivatives CTO*n*[a]

Compound	T_I[b]/°C (ΔH/ kJ mol^{-1}; $\lvert\Delta S/R\rvert$)	T_N[c]/°C (ΔH/ kJ mol^{-1}; $\lvert\Delta S/R\rvert$)	T_K[d]/°C
CTO4[e]	205.3 (31.0)	—	187.8
	209.2 (23.6)		178.8
CTO6	181.8 (44.7)	158.5[f]	158.5
CTO8	177.2 (42.6; 12.3)	143.8 (−2.3; 0.7)	122.5
CTO10	147.7 (39.6; 11.3)	134.6 (−2.2; 0.7)	108.1
CTO12	145.4 (43.3; 12.5)	122.1 (−2.3; 0.7)	102.6
CTO14	141.4 (55.2; 16.0)	114.9 (−4.7; 1.5)	110.5
CTOS	138.9 (43.2)	—	93.0

[a] All compounds display monotropic behavior. [b] Clearing temperature on heating. [c] Transition temperature from isotropic melt to nematic phase on cooling. [d] Typical crystallization temperature on cooling. [e] Crystal–crystal transitions on heating and cooling. [f] Phase visible under polarized microscopy; nematic transition does not resolve on DSC.

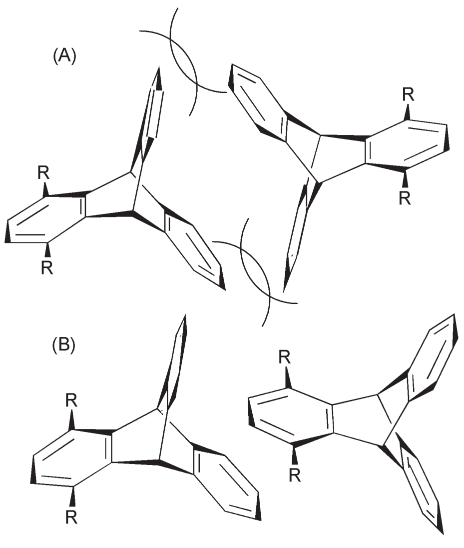
that all liquid crystalline phases are kinetically accessible, but not thermodynamically stable. Only nematic mesophases were displayed and polarized microscopy revealed classic droplet formation and coalescence to give marbled textures, characteristic of a nematic phase, as shown for CTO8 in Fig. 1. The mesophase behavior of the series CTO*n* is summarized in Table 1. Increasing the alkyl chain length decreased the clearing temperatures, although at a chain length longer than ten carbons, the effect drops off dramatically. In all cases, there is a hysteresis on cooling ranging from 13 to 33 °C. On cooling, transitions from the isotropic to liquid crystalline state were found to be typical for an isotropic to nematic transition, falling in the range 2–4 kJ mol^{-1}. As the isotropic to biaxial nematic transition has been predicted to be second order,[16] transition entropies ($\Delta S/R$) were determined and found to be quite low, ranging from 0.7 to 1.5, at the lower limit of values (0.5–6.0) found for isotropic to nematic transitions in the literature.[17]

The range over which nematic mesophases persist is narrow in the case of CTO6 and CTO14. For CTO6, the nematic phase can be observed with polarized microscopy on cooling, but rapidly crystallized on standing. This was also reflected in its differential scanning calorimetry (DSC) measurements, as the nematic transition was not resolved from the crystallization peak. The hexyl side chains were the shortest length that displayed mesophases; CTO4 crystallized on cooling. Interestingly, CTOS, containing chiral (3*S*)-3,7-dimethyloctyl groups, also crystallized on cooling. However, a contact preparation of CTOS with CTO8 yielded a chiral nematic phase at the contact boundary, exhibiting the plane texture shown in Fig. 2.

The parent bis(phenylethynyl)benzene liquid crystals are known from the literature to show a number of uncharacterized smectic phases.[18] Unlike the previously reported triptycene-based smectic liquid crystals, in which the mesogen lacks a calamitic element, our materials only show highly fluid nematic phases. We believe that this difference in phase behavior is due to the extension of the mesomorphic core, *via* incorporation of the triptycene into a bis(phenylethynyl)benzene core. Any organization in a layered phase would generate large degrees of internal free volume. Free volume is not energetically favored so the system organizes to efficiently fill space in the liquid crystalline phases. This is consistent with our previous demonstrations that triptycenes have a propensity to "nest" other molecules in the convex surfaces defined by faces of their aromatic rings.[19] This is also consistent with previous approaches toward introducing structural anisotropy, such addition of lateral alkyl chains[20] or metal carbonyl fragments.[21]

Packing considerations, as shown in Scheme 3, of the sterically bulky triptycenes may also have an effect. Tail-to-tail packing [Scheme 3(A)] is more sterically crowded and creates free volume, thereby prohibiting smectic phase formation. Head-to-tail packing [Scheme 3(B)] displays steric complementarity and spacial regularity. This bias in packing is a potential mechanism for inducing a biaxial nematic phase with a preferred head-to-tail arrangement of triptycenes.

2 Reduced symmetry triptycene liquid crystals (ETO*n*). To decrease the symmetry of the CTO*n* series, the triptycene was moved to one of the terminal benzene rings in the bis(phenylethynyl)benzene system. It was hoped that this decreased symmetry would extend the mesophase range. The mesophase behavior of the ETO*n* series was found to be highly complex. On heating, cold crystallization peaks could be observed before



Scheme 3 R = 4-Alkoxyphenylethynyl. (A) Steric hindrance and free volume created by tail-to-tail orientation of triptycenes (rotation or translation of either triptycene yields head-to-tail packing). (B) More facile packing of head-to-tail orientation.

Table 2 Mesophase behavior of reduced symmetry triptycene derivatives, ETO*n*[a]

Compound	$T_I{}^b$/°C (ΔH/ kJ mol^{-1}; $\lvert\Delta S/R\rvert$)	$T_N{}^c$/°C (ΔH/ kJ mol^{-1}; $\lvert\Delta S/R\rvert$)	$T_K{}^d$/°C (ΔH/ kJ mol^{-1})
ETO6	179.4 (39.2; 10.4)	140.1 (−1.5; 0.4)	46.3 br (−34.3)
ETO8	164.3 (46.0; 12.7)	134.3 (−1.8; 0.5)	87.1 br (−18.5)
ETO10	129.3 (39.9; 11.9)	121.6 (−2.4; 0.7)	36.8 (−4.1)
ETO12	136.0 (50.5; 14.8)	119.5 (−2.1; 0.6)	40.8 br (−24.1)

[a] All compounds display monotropic behavior. [b] Clearing temperature on heating. [c] Transition temperature from isotropic melt to nematic phase on cooling. [d] Typical crystallization temperature on cooling; br, broad transition.

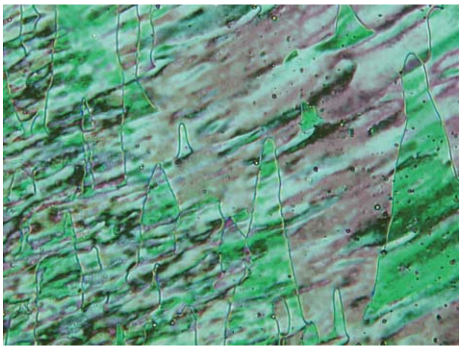


Fig. 3 Marbled texture exhibited by ETO10 on cooling (200× magnification, 116 °C).

melting to an isotropic phase. There was a subtle decrease in the clearing temperatures with respect to the same length chain in the symmetric series. The mesophase behavior of the series ETO*n* is summarized in Table 2. However, we did not succeed in obtaining enantiotropic behavior. The hysteresis on cooling remained in the range 8 to 39 °C. A typical marbled texture exhibited by this series is shown in Fig. 3.

The reduced symmetry of this series does appear to change the crystallization behavior. No members of the series displayed a distinct crystallization exotherm on cooling, exhibiting only broad transitions in their DSC thermograms. The phases remain fluid over a wide range before becoming highly viscous. Under polarized microscopy, regions of local crystallization were seen throughout and were very slow to advance into the fluid regions. Isotropic to nematic transition entropies in the series were found to be lower than for the CTO*n* series, ranging from 0.4-0.7, indicating a lower first-order nature to the transition. When cooled rapidly (30 °C min^{-1}) from the nematic phase, ETO*n* was trapped in a glassy state, as evident from the T_g step transition on reheating followed by a cold crystallization. The presence of a glassy phase was also indicated by the large difference in melting *versus* crystallization enthalpies in ETO8–12.

Conclusion

Two series of triptycene-containing bis(phenylethynyl)benzene liquid crystals were synthesized and determined to display monotropic nematic phases. Chiral variants were found to be crystalline, but upon doping into another liquid crystal in the series, showed a chiral nematic phase. Local gearing of the triptycenes and threading of their sidearms through the triptycene void spaces explain the absence of smectic phases. Variants with reduced symmetry display slightly lower clearing points, do not show distinct crystallization peaks on cooling, and the order of the mesophase can be trapped by rapid cooling in a glass. The structural elements in these compounds may be useful for the creation of a single component biaxial liquid crystal phase due to the physical inhibition of rotation caused by triptycene. Triptycenes also provide a convenient location for further funcationalization to incorporate dipoles into the molecules to aid in switching and further inhibit rotation. Continuing studies in our laboratories seek to develop new materials that exploit the potential of triptycene elements in liquid crystals.

Experimental

Thermal studies were carried out *via* differential scanning calorimetry (DSC) and measured on a Perkin-Elmer DSC 7 under argon at a scan rate of 10 °C min^{-1}. Microscopic textures were viewed on a Leica DM RXP optical microscope, with a Linkham 350 hot stage controlled by a Linkham TP 92 temperature controller used to vary the sample temperature. All synthetic manipulations were performed under an argon or nitrogen atmosphere in flame-dried glassware. High resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) using a peak matching protocol to determine the mass and error range of the molecular ion.

General procedure for alkylation of bisphenols

To a solution of 100 mg (0.206 mmol) of a bisphenol in 2 ml DMF was added 3–6 equivalents of the appropriate 1-iodo- or 1-bromoalkane and the solution purged with Ar. Cs_2CO_3 (167 mg, 0.618 mmol) was added and the solution was heated at 75 °C for 3 h. After cooling, the solution was diluted with dichloromethane and washed sequentially with water, NH_4Cl (aq.), dilute NaOH (aq.), water, and saturated NaCl (aq.). After drying over $MgSO_4$ and filtration, removal of the solvent *in vacuo* yielded the crude product. Purification can be effected by either repeated recrystallization from acetone (twice; symmetric triptycenes) or adsorbtion onto silica gel (asymmetric triptycenes) followed by column chromatography with 5 : 1 hexanes–dichloromethane eluent. All yields are reported after purification.

1,4-Bis(4″-tetrahydropyranyloxyphenylethynyl)-9,10[1′,2′]-benzeno-9,10-dihydroanthracene (1). 1,4-Diiodotriptycene (1.518 g, 3 mmol), 4-tetrahydropyranyloxy-1-ethynylbenzene (1.30 g, 6.5 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and CuI (30 mg, 0.15 mmol) were combined and placed under Ar. Sequentially, 15 ml THF and 3 ml diisopropylamine were added. The solution was stirred at room temperature for 2.5 h. The reaction solution was then filtered through Celite and the Celite was rinsed with dichloromethane. After removal of the solvent *in vacuo*, the residue was flushed through a plug of silica gel with dichloromethane to remove the catalyst. Removal of the solvent *in vacuo* yielded an orange solid that was heated with 100 ml acetone, cooled, and filtered off, to yield **1** (1.28 g) as a tan solid. Evaporation of the filtrate *in vacuo* yielded a brown solid that was purified *via* gradient column chromatography with 1 : 1 hexanes–dichloromethane to pure dichloromethane to yield an additional 640 mg of **1** (total yield: 1.92 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, 4H, J = 8.7), 7.43 (dd, 4H, J = 5.3, 3.1), 7.09 (d, 4H, J = 8.7), 7.00 (dd, 4H, J = 5.3, 3.1), 5.96 (s, 2H), 5.49 (t, 2H, J = 3.0 Hz), 3.91 (m, 2H), 3.64 (m, 2H), 2.02 (m, 2H), 1.95–1.55 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 146.9, 144.8, 133.1, 127.9, 125.5, 124.1, 118.7, 116.7, 116.3, 96.4, 94.1, 86.0, 62.3, 52.4, 30.6, 25.5, 19.0. FT-IR (KBr) ν/cm^{-1}: 2941, 2870, 2202, 1602, 1510, 1239, 960. HRMS (ESI) *m*/*z*: calcd. for $C_{46}H_{38}O_4$, 655.2843 ([M + H]$^+$), found 655.2840. M.p. 230–233 °C (with decomp.).

1,4-Bis(4″-hydroxyphenylethynyl)-9,10[1′,2′]-benzeno-9,10-dihydroanthracene (2). **1** (981 mg, 1.5 mmol) was dissolved in a mixture of 25 ml dichloromethane and 15 ml methanol.

p-TsOH (35 mg, 0.2 mmol) was added and the solution stirred at room temperature for 1 h. The solvent was removed *in vacuo* and the residue purified *via* column chromatography over silica gel with 10 : 1 dichloromethane : ethyl acetate, to yield **2** (720 mg, 99%) as an off-white solid. Analytically pure samples of **2** were obtained by recrystallized from chloroform. ^{1}H NMR (300 MHz, CD_3CN): δ 7.59 (d, 4H, J = 8.7), 7.50 (dd, 4H, J = 5.6, 3.1), 7.36 (s, 2H), 7.11 (s, 2H), 7.03 (dd, 4H, J = 5.1, 3.3), 6.90 (d, 4H, J = 8.7 Hz), 6.08 (s, 2H). ^{13}C NMR (75 MHz, CD_3CN): δ 158.5, 147.6, 145.4, 134.2, 128.5, 126.3, 124.8, 119.2, 116.5, 114.7, 95.4, 85.4, 52.5. FT-IR (KBr) ν/cm^{-1}: 3419, 2968, 2208, 1605, 1514, 1164, 831. HRMS (EI) *m*/*z*: calcd. for $C_{36}H_{22}O_2$, 486.1614 (M^+), found 486.1608. M.p. 240–242 °C.

1,4-Bis(4″-butyloxyphenylethynyl)-9,10[1′,2′]-benzeno-9,10-dihydroanthracene (CTO4). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-iodobutane (0.070 ml, 0.617 mmol), yielded CTO4 (50 mg, 41%). Representative characterization for the CTO*n* series, the remaining characterization data are contained in the ESI. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, 4H, J = 6.9), 7.47 (dd, 4H, J = 5.3, 3. Hz), 7.12 (s, 2H), 7.03 (dd, 4H, J = 5.4, 3.3), 6.96 (d, 4H, J = 6.9), 5.99 (s, 2H), 4.03 (t, 4H, J = 6.6), 1.82 (pent., 4H, J = 6.8), 1.55 (m, 4H), 1.01 (t, 6H, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 147.0, 145.0, 133.4, 128.0, 125.6, 124.3, 118.8, 115.3, 114.9, 94.2, 85.9, 68.0, 52.4, 31.5, 19.5, 14.1. FT-IR (KBr) ν/cm^{-1}: 2951, 2925, 2967, 2210, 1604, 1512, 1248, 1167, 833. HRMS (EI) *m*/*z*: calcd. for $C_{44}H_{38}O_2$, 598.2866 (M^+), found 598.2846.

1,4-Bis(4″-hexyloxyphenylethynyl)-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (CTO6). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-iodohexane (0.092 ml, 0.617 mmol), yielded CTO6 (72 mg, 53%).

1,4-Bis(4″-octyloxyphenylethynyl)-9,10[1′,2′]-benzeno-9,10-dihydroanthracene (CTO8). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-bromooctane (0.212 ml, 1.2 mmol), yielded CTO8 (118 mg, 81%). Characterization matches that in ref. 17.

1,4-Bis(4″-decyloxyphenylethynyl)-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (CTO10). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-iododecane (0.131 ml, 0.617 mmol), yielded CTO10 (106 mg, 65%).

1,4-Bis(4″-dodecyloxyphenylethynyl)-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (CTO12). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-bromododecane (0.155 ml, 0.617 mmol), yielded CTO12 (139 mg, 82%).

1,4-Bis(4″-tetradecyloxyphenylethynyl)-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (CTO14). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), 1-bromotetradecane (0.357 ml, 1.2 mmol), yielded CTO14 (126 mg, 70%).

1,4-Bis{4″-[(3‴*S*)-3‴,7‴-dimethyloctyloxy]phenylethynyl}-9,10-[1’,2’]-benzeno-9,10-dihydroanthracene (CTOS). Prepared according to the general procedure: **2** (100 mg, 0.206 mmol), (3*S*)-3,7-dimethyl-1-bromooctane (0.250 ml), yielded CTOS (109 mg, 69%).

1-Hydroxy-4-trimethylsilylethynyl-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (3). A solution of trimethylsilyllithium was prepared *via* dropwise addition of *n*-BuLi (2.5 M in hexanes, 9.5 ml, 23.8 mmol) to a solution of trimethylsilylacteylene (3.40 ml, 24 mmol) in 60 ml THF at −40 °C. The solution was stirred for 10 min, and then allowed to warm to 0 °C. The trimethylsilyllithium solution was added dropwise *via* cannula to a −40 °C solution of triptycene-1,4-quinone (5.68 g, 20 mmol) in 60 ml THF over the course of 40 min. The solution was stirred at 0 °C for 1 h. Trimethylsilyl chloride (3.0 ml, 23.6 mmol) was added and the solution stirred for 30 min. Then, Zn dust (4.0 g, 61 mmol) and glacial AcOH (14 ml) were added to the solution, stirred at 0 °C for 1 h, and then the solution allowed to warm to room temperature overnight (15 h). The solution was filtered through Celite, which was washed with dichloromethane. The combined organic solutions were washed with water, $NaHCO_3$ (aq.), and NaCl (aq.). After drying over $MgSO_4$ and filtration, removal of the solvent *in vacuo* yielded a pale yellow solid which was dried *in vacuo*. Column chromatography over silica gel with dichloromethane yielded **3** (6.32 g, 86%) as a foamy cream-colored solid. Analytically pure **3** was obtained by recrystallization from hexanes. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 4H), 7.01 (m, 4H), 6.96 (d, 1H, J = 8.1), 6.35 (d, 1H, J = 8.1 Hz), 5.88 (s, 1H), 5.82 (s, 1H), 5.28 (s, 1H), 0.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.6, 150.3, 145.0, 131.6, 129.5, 125.4, 125.3, 124.2, 123.8, 112.9, 111.6, 103.3, 99.9, 96.0, 52.6, 47.3, 0.65. FT-IR (KBr) ν/cm^{-1}: 3268, 3072, 2957, 2150, 1582, 1487, 1459, 1249, 841. HRMS (EI) *m*/*z*: calcd. for $C_{25}H_{22}OSi$, 366.1434 (M^+), found 366.1449. M.p. 94–96 °C.

1-Tetrahydropyranyloxy-4-trimethylsilylethynyl-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (4). Dihydropyran (1.0 ml, 11 mmol) and *p*-TsOH (10 mg, 0.06 mmol) were added to a solution of **3** (3.67 g, 10 mmol) in 25 ml dichloromethane The solution was allowed to stir at room temperature for 4 h. Additional dihydropyran (0.25 ml) was added after 1.5 and 3 h. The reaction was then diluted with dichloromethane and washed with $NaHCO_3$ (aq.) and NaCl (aq.). After drying over $MgSO_4$ and filtration, removal of the solvent *in vacuo* yielded a pale yellow oil which was titurated with MeOH and filtered to yield **4** (2.88 g, 64%) as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (m, 4H), 7.06 (d, 1H, J = 8.3), 7.01 (m, 4H), 6.74 (d, 1H, J = 8.3), 5.91 (s, 1H), 5.89 (s, 1H), 5.24 (t, 1H, J = 3.0 Hz), 3.86 (m, 1H), 3.56 (m, 1H), 2.19 (m, 1H), 1.90-1.60 (m, 5H), 0.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 149.6, 145.3, 134.3, 129.4, 125.3, 124.1, 123.8, 123.7, 112.4, 112.3, 103.3, 96.7, 96.2, 62.3, 52.6, 47.6, 30.6, 25.5, 19.3, 0.7. FT-IR (KBr) ν/cm^{-1}: 2954, 2149, 1590, 1484, 1249, 856, 840. HRMS (EI) *m*/*z*: calcd. for $C_{30}H_{30}O_2Si$, 450.2010 (M^+), found 450.2011. M.p. 191–193 °C.

1-Tetrahydropyranyloxy-4-ethynyl-9,10-[1′,2′]-benzeno-9,10-dihydroanthracene (5). **4** (1.80 g, 4 mmol) was dissolved in a mixture of 25 ml THF and 8 ml methanol and the solution was purged with Ar for 30 min. K_2CO_3 (2.21g, 16 mmol) was added and the solution stirred at room temperature for 8 h. The solution was then filtered through Celite, which was washed with dichloromethane. Removal of the solvent *in vacuo* yielded **5** (1.50 g, 99%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (m, 4H), 7.11 (d, 1H, J = 8.7), 7.02 (m, 4H), 6.78 (d, 1H, J = 8.7), 5.94 (s, 1H), 5.93 (s, 1H), 5.44 (t, 1H, J = 3.0 Hz), 3.87 (m, 1H), 3.58 (m, 1H), 3.30 (s, 1H), 2.22 (m, 1H), 2.10-1.90 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 149.7, 145.2, 134.4, 130.0, 125.33, 125.29, 124.2, 123.8, 123.7, 112.5, 111.1, 96.7, 81.8, 79.1, 62.3, 52.3, 47.6, 30.6, 25.5, 19.3. FT-IR (KBr) ν/cm^{-1}: 3286, 2940, 2869, 2096, 1594, 1486, 1015. HRMS (EI) *m*/*z*: calcd. for $C_{27}H_{22}O_2$, 378.1614 (M^+), found 378.1626. M.p. 195–198 °C (with decomp.).

1-Bromo-4-(4′-tetrahydropyranyloxy-1′-ethynylphenyl)benzene (6). 4-Tetrahydropyranyloxy-1-iodobenzene (1.824 g, 6 mmol), 1-bromo-4-ethynylbenzene (1.086 g, 6 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.3 mmol), CuI (57 mg, 0.3 mmol) were combined and placed under Ar. To the solids was added 30 ml THF and 6 ml diisopropylamine, and the solution stirred at room temperature for 14 h. The solvent was then removed *in vacuo* and the residue flushed through a plug of silica gel with a solution of 2 : 1 dichloromethane–hexanes to remove the catalyst. After removal of the solvent *in vacuo*, the orange solid was triturated with methanol and filtered, to yield **6** (1.45 g, 68%) as a tan solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (m, 4H), 7.36 (d, 2H, J = 8.7),7.02 (d, 2H, J = 8.0), 5.45 (t, 1H, J = 3.0), 3.89 (dt, 1H, J = 10.4, 3.0 Hz), 3.62 (m, 1H), 2.10–1.55 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 133.2, 133.1, 131.8, 122.8, 122.3, 116.6, 116.0, 96.4, 90.8, 87.3, 62.3, 30.4, 25.3, 18.9. FT-IR(KBr) ν/cm^{-1}: 2947, 2213, 1599, 1508, 1240, 1078, 1037, 825. HRMS (ESI) *m*/*z*: calcd. for $C_{19}H_{17}BrO_2$, 379.0304 ([M + Na]$^+$), found 379.0312. M.p. 119–121 °C.

Compound 7. **5** (379 mg, 1.0 mmol), **6** (358 mg, 1.0 mmol), $Pd_2(dba)_3$ (45 mg, 0.05 mmol), triphenylphosphine (130 mg, 0.50 mmol), and CuI (10 mg, 0.05 mmol) were combined and placed under Ar. Triethylamine (10 ml) was added, the tube sealed with a Teflon plug, and the solution heated to 100 °C for 24 h. The reaction solution was cooled, diluted with dichloromethane, and filtered through a plug of Celite, which was rinsed with further dichloromethane. Removal of the solvent *in vacuo* yielded a yellow solid which was absorbed onto silica gel and purified *via* gradient column chromatography over silica gel with 2 : 1 to 1 : 2 hexanes–dichloromethane, to yield **7** (471 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, 2H, J = 8.1), 7.52 (d, 2H J = 8.1), 7.47 (d, 2H, J = 8.7), 7.41 (m, 4H), 7.09 (d, 2H, J = 8.4), 7.03 (d, 1H, J = 8.4), 6.99 (m, 4H), 6.77 (d, 1H, J = 8.7 Hz), 5.93 (s, 1H), 5.91 (s, 1H), 5.43 (m, 2H), 3.87 (m, 2H), 3.58 (m, 2H), 2.16 (m, 2H), 2.10–1.55 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.3, 152.0, 149.1, 145.2, 145.1, 134.5, 13.1, 131.5, 129.5, 125.3, 124.2; 123.8, 123.4, 116.5, 116.1, 112.6, 112.1, 96.8, 96.4, 91.5, 91.2, 88.2, 62.3, 52.6, 47.6, 30.7, 30.6, 25.54, 25.45, 19.3, 19.0. FT-IR (KBr) ν/cm^{-1}: 3040, 2941, 2870, 2214, 1600, 1515, 1238. HRMS (ESI) *m*/*z*: calcd. for $C_{46}H_{38}O_4$, 655.2843 ([M + H]$^+$), found 655.2826. M.p. 213–216 °C (with decomp.)

Compound 8. **7** (392 mg, 0.5 mmol) was dissolved in mixture of 12 ml dichloromethane and 6 ml methanol. *p*-TsOH (15 mg, 0.09 mmol) was added and the solution stirred at room temperature for 1 h. The solventwas removed *in vacuo* and the residue was purified *via* column chromatography over silica gel with 10 : 1 chloroform–ethyl acetate, to yield **8** (230 mg, 80%) as an off-white solid. Compound **8** was recrystallized from chloroform. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60(d, 1H, J = 8.1), 7.55 (d, 2H, J = 8.1), 7.47 (d, 2H, J = 9.0), 7.44 (m, 4H), 7.06 (d, 1H, J = 8.4), 7.02 (dd, 4H, J = 5.1, 3.1), 6.84 (d, 2H, J = 8.1), 6.45 (d, 1H, J = 8.7 Hz), 5.95 (s, 1H), 5.84 (s, 1H), 4.89 (s, 1H), 4.88 (s, 1H). ^{13}C NMR (75 MHz, CD_3CN): δ 158.3, 152.7, 150.2, 145.9, 145.7, 133.9, 133.8, 132.5, 133.3, 132.1, 130.2, 126.1, 126.0, 124.7, 124.4, 124.0, 123.8, 116.4, 114.7, 114.1, 110.7, 92.2, 91.5, 89.6, 88.0, 52.8, 47.5. FT-IR (KBr) ν/cm^{-1}: 3399, 3069, 2965, 2212, 1606, 1517. HRMS (EI) *m*/*z*: calcd. for $C_{36}H_{22}O_2$, 486.1614 (M$^+$), found 498.1623. M.p. 187–189 °C.

Compound ETO6. Prepared according to the general procedure: **8** (100 mg, 0.02 mmol), 1-iodohexane (0.184 ml, 1.2 mmol), yielded ETO6 (104 mg, 77%). Representative characterization for the ETO*n* series, the remaining characterization data are contained in the ESI. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 2H, J = 8.1), 7.55 (d, 2H, J = 8.1), 7.50 (d, 2H, J = 8.7), 7.45 (dd, J = 5.0, 3.2), 7.41 (dd, 2H, J = 5.0, 3.2), 7.13 (d, 1H, J = 8.4), 7.00 (dd, 4H, J = 5.3, 3.2), 6.89 (d, 2H, J = 9.0), 6.55 (d, 1H, J = 8.7 Hz), 5.94 (s, 1H), 5.92 (s, 1H), 3.99 (m, 4H), 1.83 (m, 4H), 1.60–1.30 (m, 12H), 0.94 (m, 6H).^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 154.2, 149.1, 145.33, 145.25, 133.8, 133.2, 131.5, 129.6, 125.3, 125.2, 124.1, 123.8, 123.4, 123.3, 115.0, 114.7, 110.9, 109.5, 91.6, 91.1, 89.4, 88.1, 68.7, 68.3, 52.6, 47.3, 31.9, 29.53, 29.47, 26.2, 26.0, 23.0, 22.9, 14.45, 14.42. FT-IR (KBr) ν/cm^{-1}: 3066, 2925, 2854, 2211, 1600, 1516, 1273, 1244. HRMS (EI) *m*/*z*: calcd. for $C_{48}H_{46}O_2$, 654.3492 (M$^+$), found 654.3467.

Compound ETO8. Prepared according to the general procedure: **8** (100 mg, 0.02 mmol), 1-bromooctane (0.212 ml, 1.2 mmol), yielded ETO8 (94 mg, 64%).

Compound ETO10. Prepared according to the general procedure: **8** (100 mg, 0.02 mmol), 1-bromodecane (0.250 ml, 1.2 mmol), yielded ETO10 (120 mg, 76%).

Compound ETO12. Prepared according to the general procedure: **8** (100 mg, 0.02 mmol), 1-bromododecane (0.310 ml, 1.2 mmol), yielded ETO12 (145 mg, 86%). Compound ETO12 was recrystallized from hexanes.

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