

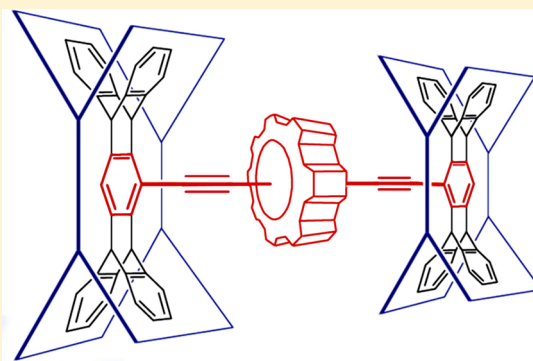
Toward Crystalline Molecular Rotors with Linearly Conjugated Diethynyl-Phenylene Rotators and Pentiptycene Stators

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Supporting Information

ABSTRACT: A strategy for the construction of crystalline molecular rotors involves the assemblage of chemical structures that emulate the elements of macroscopic rotary devices, such as those found in macroscopic gyroscopes and compasses. In this report, we describe an efficient and short synthetic route for preparation of molecular rotors with two pentiptycene-units linked at their central benzene ring by triple bonds to a linearly conjugated phenylene rotator. Five analogous compounds with phenol, alkoxy, or alkoxycarbonyl substituents were synthesized and fully characterized in solution and in the solid-state through various methods, such as cross-polarization magic angle spinning (CPMAS) ^{13}C NMR and single crystal X-ray diffraction. Molecular and packing structures obtained from single crystal X-ray diffraction and crystallization properties were analyzed with the goal of identifying the key parameters that may hinder or facilitate the formation of dynamically functional, crystalline molecular rotors.



INTRODUCTION

The field of artificial molecular machines has attracted the attention of many chemists over the last 20–30 years.¹ Initial efforts were centered on molecules that bear structural or analogic similarities to macroscopic machines or machine components, and an emphasis was placed on a detailed understanding of their dynamic stereochemistry,^{1,2} chemical bistability,³ and photocontrolled unidirectional rotation⁴ in solution. More recently, it has been recognized that useful, machine-like functions are likely to require the control of stereodynamic and chemical processes in molecules bound to surfaces⁵ and in bulk materials.⁶ We proposed that amphidynamic crystals, made up with molecules that experience rapid internal mobility, should be ideal candidates to design molecular machines.⁷ In search of promising amphidynamic crystal-forming molecules, we have explored a number of structures with components analogous to those of macroscopic compasses and gyroscopes, with a central rotator linked to a shielding stator that generates some free volume and guides the assembly for crystallization.⁶ Using structures with 1,4-phenylenes acting as rotators linked by alkynes to bulky trityl or trypticene stators, we have shown that Brownian rotation may reach frequencies as high 10^{10} s^{-1} ,⁸ depending on molecular and crystal structures. Knowing that bulky pentiptycenes are a relatively rigid and effective structural element that prevents the aggregation of linearly conjugated poly(phenyleneethynylene)s, as demonstrated by Swager,⁹ we decided to explore the synthesis and solid state properties of molecular rotors with phenylene rotators and pentiptycene stators. These structures are of interest to us because they generate linearly conjugated 1,4-*para*-phenylethynyl-benzene chromophores (highlighted in

red in Figure 1), which we and others have shown to possess remarkable photophysical properties as a function of the angle

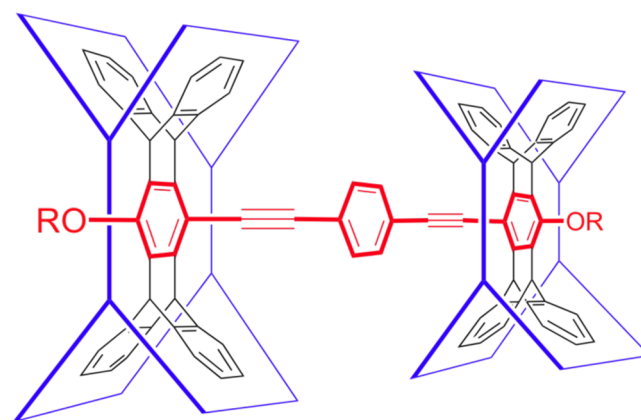
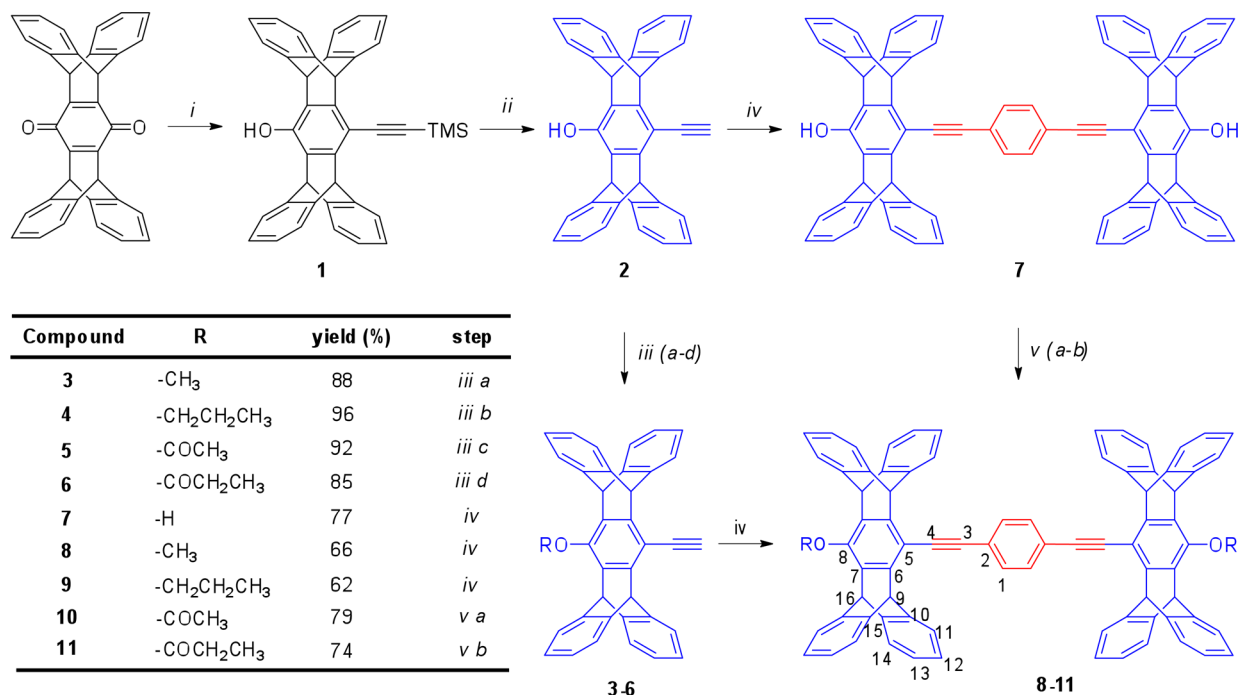


Figure 1. A molecular rotor with a phenylene rotator linked by acetylene linkages to two pentiptycene stators. Using a central phenylene as a rotator brings the three-ring system in and out of conjugation as a function of the rotator motion.

made among the three conjugated rings.^{10,11} In this article we report the synthesis and characterization of molecular rotors 7–11 (Scheme 1) with a common 1,4-diethynylphenylene rotator and different substituents (R = H, Me, Propyl, COMe and COEt, respectively) in the two pentiptycene units. The latter substituents were added to explore potential trends in

Received: June 21, 2012

Published: August 6, 2012

Scheme 1. Synthesis of Precursors 1–6 and Molecular Rotors 7–11^a

^a(i) Lithium trimethylsilyl acetylene, Zn⁰, acetic acid. (ii) TBAF, THF, 50 °C. (iii) (a) Iodomethane, K₂CO₃, acetone; (b) 1-bromopropane, KI, K₂CO₃, acetone; (c) acetic anhydride, pyridine; (d) propionic anhydride, pyridine. (iv) 1,4-Diiodobenzene, [Ph₃P]₄Pd, (*i*-Pr)₂NH, toluene, 80 °C. (v) (a) Acetic anhydride, pyridine; (b) propionic anhydride, pyridine.

crystallization and physical properties. We also describe here the solid state characterization of compounds 7 and 10 by solid state CPMAS ¹³C NMR, and compounds 7, 10 and 11 by single crystal X-ray diffraction.¹²

RESULTS AND DISCUSSION

Synthesis and Characterization. We completed the synthesis of pentiptycene rotors 7–11 and compounds 3–6 starting from the alkynyl-substituted pentiptycene precursor 2 (Scheme 1). Compound 2 was obtained in two steps and in good yield (ca. 90%) by reaction of pentiptycene quinone^{9,13} with lithium trimethylsilyl acetylide followed by deoxygenation and removal of the trimethylsilyl group with tetrabutyl ammonium fluoride. Compound 2 was converted into derivatives 3–6 in good yields (>80%) by treatment with iodomethane, 1-bromopropane, acetic anhydride, and propionic anhydride, respectively. Molecular rotor 7 was synthesized by coupling compound 2 with 1,4-diiodobenzene (Scheme 1). For the synthesis of molecular rotors 8–11 we have explored two alternative pathways, i.e., Sonogashira coupling¹⁴ of precursors 3–6 with diiodobenzene or postfunctionalization of compound 7. Methoxy and propoxy substituents increased the solubility of the precursors, and thus the initial route was used. In the case of the esters, the addition of the substituents after the coupling increased the yields. Only the route affording the best yields is included in the table inset in Scheme 1.

Spectral patterns characteristic of the pentiptycene core were observed in the ¹H and ¹³C NMR spectra of compounds 2–6. In the case of 2, this includes ¹H NMR signals at 3.59 ppm for the acetylenic hydrogen and two singlets for the bridgehead hydrogens H16 and H9 at 5.65 and 5.86 ppm, respectively (for atom numbering, please see Scheme 1). The aromatic

hydrogens at H11–H14 result in four sets of signals, and their detailed coupling constants were estimated by taking advantage of spectral simulations using the program MestreC (Figure S1, Supporting Information). A doublet of doublets assigned to H11 at 7.44 ppm is described by $J_{ortho} = 5.16$, $J_{meta} = 3.3$, and $J_{para} = 1.05$ Hz. The signal for H12 at 6.98 ppm could be simulated as a doublet of doublet of doublets with $J_{ortho} = 5.16$ and 5.07 Hz and $J_{meta} = 3.46$ Hz, and that for H13 at 6.97 ppm with $J_{ortho} = 5.22$ and 5.06 Hz, and $J_{meta} = 3.46$ Hz. The calculated signal for H14 generates a similar pattern with J values of 5.22, 3.46, and 1.05 Hz corresponding to *ortho*-, *meta*-, and *para*-hydrogens. Analogous patterns were observed for all the asymmetric pentiptycenes. The ¹³C NMR spectra of compound 2 displayed ethynyl signals for C3 and C4 at 79.5 and 82.0 ppm, respectively, and the bridgeheads carbons C16 and C9 appeared at 47.3 and 52.2 ppm. The aromatic quaternary carbons C6, C10, C15 and C7 give rise to signals at 145.8, 145.1, 144.8, and 129.5 ppm. The protonated pentiptycene carbons C11–C14 are assigned at 125.3, 125.2, 124.0, and 123.4 ppm. A signal corresponding to C5 in the central aromatic ring resonates at 107.2 ppm while the phenolic carbon C8 at 146.6 ppm. Signals corresponding to the alkyl or acyl groups of compounds 2–6 were observed in the expected regions of the spectra. In the case of molecular rotors 7–11 the central phenylene displayed a single ¹H NMR signal generated by the four symmetric aromatic protons (H-1 in Scheme 1) at 7.90 ppm. It should be mentioned that ¹H and ¹³C resonances were assigned by ¹H and ¹³C NMR spectra in conjunction with heteronuclear techniques such as HMBC (please see the Supporting Information). Further characterization by high resolution time-of-flight electrospray mass spectrometry supported the structural characterization of molecular rotors 7–11 as the corresponding ammonium ion adducts [M +

NH_4^+ except molecular rotor **9**, which was observed as $[\text{M}]^+$ ion using the LIFDI technique.

X-ray Single Crystal Studies. Pure samples of molecular rotors **7–11** were highly insoluble in most solvents. Crystallization tests were limited to dichloromethane or chloroform, or binary systems containing one of them. Single crystals suitable for X-ray diffraction of diphenol **7**, acetyl derivative **10**, and propionyl ester **11** were grown by slow evaporation from dichloromethane/methanol, dichloromethane/chloroform and pure dichloromethane, respectively, with the resulting crystals desolvating very rapidly when removed from the mother liquor. The ORTEP diagrams derived from data acquired at 100 K are illustrated in Figure 2.

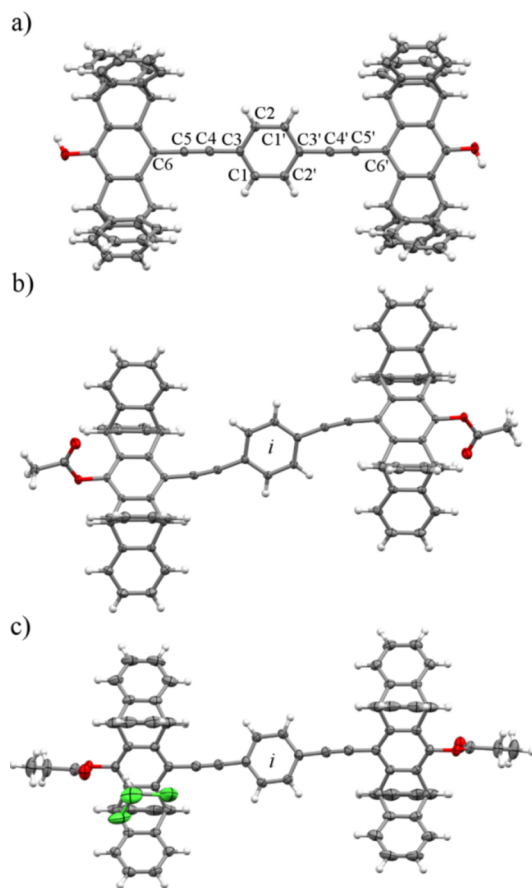


Figure 2. Molecular structures determined by single crystal X-ray diffraction. (a) Diphenol **7**. (b) Acetyl derivative **10**. (c) Propionyl ester **11** with one disordered chloroform molecule shown. All non-H atom ellipsoids are displayed at a 50% probability.

The crystallographic acquisitions and refinement data are included in the Supporting Information. All three compounds form crystals with two molecules per unit cell, each molecule having an inversion center that lies in the centroid of the rotator, with the planes of the two pentyptycenes in the structure adopting a parallel orientation.

The crystal structure of compound **7** was solved in the space group $P2_1/n$ with solvent molecules removed with the SQUEEZE algorithm.¹⁵ A similar treatment was carried out with the crystal structure of compound **10**, which was solved in the same space group. The structure of compound **11** was solved in the $P2_1/c$ space group with two chloroform molecules disordered over three positions. The structures of the

pentyptycene fragments showed no significant differences as compared with those of analogous compounds.¹⁶ Further analysis revealed that although the pentyptycene frameworks confer rigidity to the molecule, the molecular axes formed by the 1,4-diethynylphenylene linkages have a deviation from the linearity, ideally denoted by the $\text{C6–C4–Ph}_{\text{centroid}}$ angle of 180° . While in compounds **7** and **11** (Figure 2a and c) the distortion is small with angles of 178° and 175° , respectively, compound **10** has a rather severe deviation, as denoted by an $\text{C6–C4–Ph}_{\text{centroid}}$ angle of 165.4° (Figure 2b).

The packing structures of molecular rotors **7**, **10** and **11** occur in a manner that the central phenylene rotators experience close contacts with the pentyptycene blades from neighboring rotors. The central ring of compound **7** has edge-to-face interactions (carbon–centroid distances of 3.62 \AA) as shown in Figure 3a. Similarly, the central phenylene rotator in compound **10** is involved in face-to-face (centroid–centroid distances 3.81 \AA) and edge-to-face (carbon–centroid distances of 3.74 \AA) interactions with neighboring molecules, as shown in Figure 3b, suggesting a crowded environment around this ring. Finally, the central rotator in compound **11** presents edge-to-face interactions with the aromatic rings of the adjacent rotors with centroid–centroid distances of 3.77 \AA . Similar intermolecular interactions among pentyptycenes and aromatic rings have been observed in a relatively small number of X-ray single crystal structures with pentyptycene fragments containing at least one ethynyl group.^{11a,14a,17}

Solid State NMR and Powder X-ray Diffraction Experiments. The ^{13}C CPMAS solid state NMR technique is a powerful tool to identify different solid forms, including polymorphs, solvates, and amorphous systems, and to investigate the internal dynamics of solid samples by means of line-shape analysis. Polycrystalline samples of molecular rotors **7** and **10** were prepared using the binary solvent systems described above. Unfortunately, bulk crystallization tests consistently afforded solids that did not match the powder X-ray patterns calculated from their corresponding single crystal structures. In the case of compound **7** the powder pattern obtained from the bulk solid after slow evaporation from dichloromethane/methanol presented only weak Bragg reflections and a main, broad featureless signal in the range $5\text{--}55^\circ$ (2θ). Conversely, the powder patterns obtained from bulk samples of compound **10** after slow evaporation of dichloromethane/chloroform (or hexanes/dichloromethane), suggested crystalline solids with poor crystallinity, as evident from the broad but distinct Bragg reflections between 5 and 40° (2θ), with a certain amount of an amorphous component, responsible for the broad background (Supporting Information). The concomitant presence of crystalline and amorphous components was attributed to the low stability of the samples upon air exposure, which modifies the amount of included dichloromethane.

As anticipated from the PXRD measurements, the CPMAS ^{13}C NMR spectrum of molecular rotor **7** exhibited broad signals with full width at half-maximum (fwhm) between 180 and 350 Hz that confirmed a significant contribution of an amorphous component in the sample. Nonquaternary suppression experiments were used to remove the signals belonging to static protonated carbon atoms (Supporting Information). In general, the CPMAS ^{13}C NMR spectrum resembles the one observed in solution, with two signals in the aliphatic region corresponding to the bridgehead carbons and small broad signals coming from the alkyne fragment between

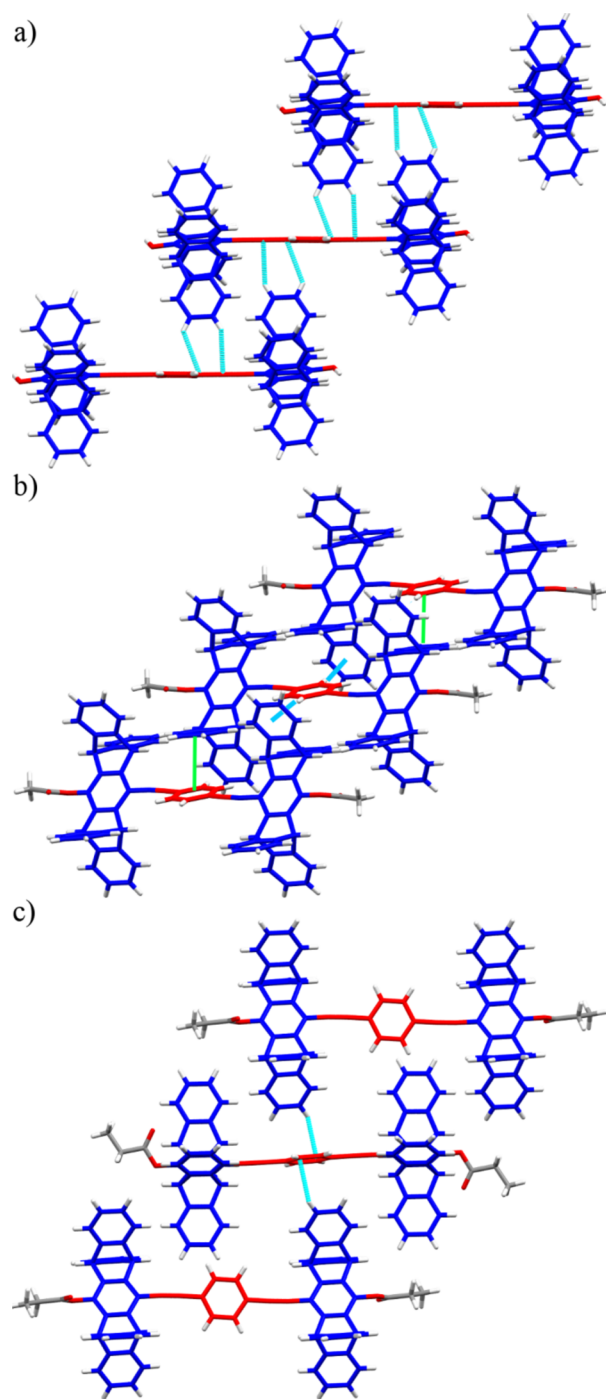


Figure 3. Packing diagrams of the molecular rotors illustrating the recurring intermolecular close contacts among the central phenylene in red and their closest neighbor rotors in blue. (a) Light blue lines indicate a edge-to-face interactions with carbon-centroid distance of 3.62 Å in compound **7**. (b) In compound **10**, vertical green lines indicate π - π interactions (centroid-centroid distance of 3.81 Å), and blue lines indicate an edge-to-face interaction with carbon-centroid distance of 3.74 Å. (c) In compound **11** blue lines designate an edge-to-face interaction with centroid-centroid distance of 3.77 Å.

85 and 100 ppm. However, the strongly overlapping signals in the aromatic region prevent the exploration of rotational motion by site exchange and coalescence analysis using variable temperature experiments.

By comparison, the CPMAS ^{13}C NMR spectrum of solid samples of compound **10** obtained from hexane/dichloromethane presented sharper signals with fwhm between 60 and 160 Hz (Figure 4b), which agree with the higher crystallinity of

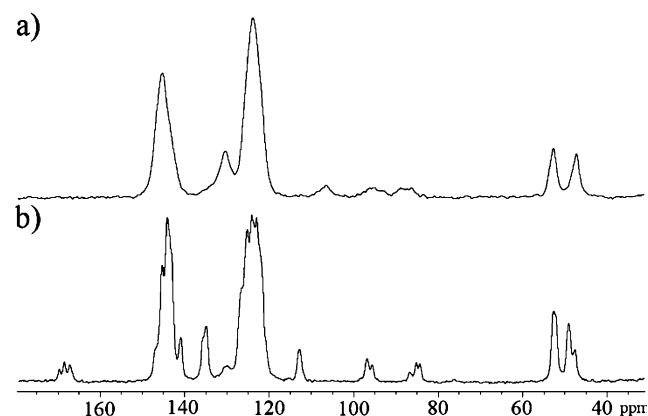


Figure 4. (a) CPMAS ^{13}C NMR spectrum of compound **7** showing broad overlapping signals, particularly in the aromatic region. (b) CPMAS ^{13}C NMR spectrum of molecular rotor **10** showing the signal tentatively assigned to the rotator at 130 ppm.

the sample deduced from the PXRD. The bridgehead carbons in the aliphatic region were removed (dephased) with the nonquaternary suppression technique (Supporting Information), and more resolved signals from the alkyne segment were observed. Although the carbon signal coming from the central phenylene may be tentatively assigned to the signal at 130 ppm by analogy with the solution NMR assignments, significant overlap with signals from a set of pentiptycene carbons makes variable temperature coalescence analysis highly impractical.

CONCLUSIONS

The construction of molecular rotors with efficient rotary dynamics for potential dielectric and electrooptic applications require crystal lattices with parallel molecular alignment for rotation and response to be directionally congruent. While this requirement was met in single crystals of compounds **7**, **10** and **11**, none of their structures provide the necessary shielding and free volume necessary for reorientational and rotational movement in the solid state. Analysis of the packing structures in crystals of compounds **7**, **10** and **11** revealed that intermolecular contacts among the central phenylene rotators and the pentiptycene blades from neighboring molecules hinder the rotational motions of the former. While the structural features of compounds **7**, **10** and **11** are not optimal to produce efficient rotating structures, we expect that bulky groups at the periphery of the pentiptycene blades will help prevent the edge-to-face interactions and interdigitation observed in the current structures. Synthetic and crystallization studies with compounds meeting these design features are currently in progress.

EXPERIMENTAL SECTION

General Remarks. Tetrakis(triphenylphosphine)palladium(0), pyridine, acetic anhydride, propionic anhydride and diisopropylamine are commercially available and were used without further purification. Commercially available acetone was dried over potassium carbonate. Toluene and tetrahydrofuran were distilled by refluxing them over traces of sodium metal using benzophenone as indicator. Sonogashira cross coupling reactions (air sensitive) were performed under argon atmosphere. Yields of products refer to chromatographically purified

products unless otherwise stated. The reaction products were isolated by flash chromatography performed on 230–400 mesh silica gel.

NMR spectra were recorded in CDCl_3 solutions in 300, 400, and 500 MHz spectrometers using the residual solvent as internal standard. Splitting patterns are described as s = singlet, t = triplet, q = quartet, ddd = doublet of doublet of doublets, and the chemical shifts are stated in ppm. Infrared spectra were recorded on a FT-IR spectrometer as solid samples using the attenuated total reflectance (ATR) technique, and bands are stated in cm^{-1} . Mass spectra were obtained using electrospray ionization or liquid introduction field desorption mass (LIFDI) technique using a time-of-flight detector.

9,10-Dihydro-9,10-*o*-benzanthracene-1,4-dione and 5,6,7,12,13,14-hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6,13-dione were synthesized according to previously reported methods^{9a} with 82 and 96%, respectively. Also reported 5,6,7,12,13,14-hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-hydroxy-13-ethynyltrimethylsilane (Compound 1) was obtained in 92%.^{11a}

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-hydroxy-13-ethynyltrimethylsilane (1). Under an atmosphere of argon, 10.0 mL of *n*-butyllithium in hexanes (2.5 M, 24.9 mmol) was added dropwise to a solution of trimethylsilyl acetylene (2.8 mL, 20 mmol) in THF (100 mL) at -10°C , and the mixture was then stirred 30 additional minutes. The solution of lithium trimethylsilyl acetylide was transferred to another flask containing 5,6,7,12,13,14-hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6,13-dione (8.0 g, 17 mmol) dissolved in 100 mL of THF, and the mixture was then stirred 3 more hours at -10°C . Then, trimethylsilyl chloride (2.0 mL, 17 mmol), zinc powder (3.0 g, 46 mmol), and 11 mL of acetic acid were added successively. The mixture was kept at room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was dissolved in DCM and washed with brine. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 9:1 hexanes:EtOAc to give 8.6 g (92%) of 1 as a white solid: mp decomposes above 300°C ; ^1H NMR (300 MHz, CDCl_3) δ 7.34 (ddd, $J = 6.69, 2.75, 1.07$ Hz, 4H), 7.31 (ddd, $J = 5.94, 2.48, 1.07$ Hz, 4H), 6.96 (ddd, $J = 7.8, 6.69, 2.48$ Hz, 4H), 6.93 (ddd, $J = 7.8, 5.94, 2.75$ Hz, 4H), 5.79 (s, 2H), 5.61 (s, 2H), 0.48 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.3, 145.5, 145.2, 144.9, 129.3, 125.3, 125.2, 124.0, 123.4, 108.6, 101.1, 99.5, 52.4, 47.3, 0.5; IR (solid, cm^{-1}) 3520, 3020, 2956, 2146, 1702, 1593, 1578, 1458, 1248, 1196, 986, 838, 741.

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-hydroxy-13-acetylene (2). 5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-hydroxy-13-ethynyltrimethylsilane 1 (8.50 g, 15.8 mmol) and 200 mL of dry THF were added to a two neck flask under argon atmosphere. A solution of tetrabutyl ammonium fluoride in THF (1.0 M, 23.5 mL, 23.5 mmol) was added to the mixture, which was then stirred 2 additional hours at 50°C . Then, the solvent was removed in vacuo, and the resulting solid was dissolved in DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 9:1 hexanes:EtOAc to give 7.0 g (95%) of 2 as a white solid: mp decomposes above 350°C ; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (ddd, $J = 5.16, 3.30, 1.05$ Hz, 4H), 7.34 (ddd, $J = 5.22, 3.46, 1.05$ Hz, 4H), 6.97 (ddd, $J = 5.07, 5.16, 3.46$ Hz, 4H), 6.95 (ddd, $J = 5.06, 5.22, 3.30$ Hz, 4H), 5.85 (s, 2H), 5.65 (s, 2H), 3.59 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 145.8, 145.1, 144.9, 129.5, 125.3, 125.2, 124.0, 123.4, 107.2, 82.0, 79.5, 52.2, 47.3; IR (solid, cm^{-1}) 3615, 3567, 3306, 3067, 3019, 2978, 2103, 1593, 1577, 1458, 1404, 1309, 1227, 1188, 1147, 1108, 1069, 1046, 871, 853, 801, 747, 676, 665; ESI-TOF(+) calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{36}\text{H}_{23}\text{O}$ 471.1743, found 471.1750.

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-methoxy-13-acetylene (3). A mixture of compound 2 (1.0 g, 2.1 mmol), potassium carbonate (0.68 g, 4.9 mmol) and 40 mL of dry acetone was added in a two neck flask under argon atmosphere, and the mixture was then stirred 10 additional minutes. Then, iodomethane (0.20 mL, 2.6 mmol) was added to the mixture,

which was stirred overnight at room temperature. The mixture was diluted with DCM and washed with brine. The organic layer was dried over MgSO_4 , filtered and washed and concentrated. The resulting solid was purified by flash chromatography using 9:1 hexanes:EtOAc to give 0.90 g (88%) of 3 as white solid: mp decomposes above 315°C ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (ddd, $J = 7.96, 1.87, 1.04$ Hz, 4H), 7.44 (ddd, $J = 7.91, 1.81, 1.04$ Hz, 4H), 7.05 (ddd, $J = 7.96, 6.06, 1.81$ Hz, 4H), 7.03 (ddd, $J = 6.06, 7.91, 1.87$ Hz, 4H), 5.95 (s, 2H), 5.80 (s, 2H), 3.91 (s, 3H), 3.70 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 146.8, 145.2, 145.0, 135.4, 125.40, 125.38, 124.1, 123.5, 110.2, 82.8, 79.4, 62.9, 52.3, 48.1; IR (solid, cm^{-1}) 3299, 2922, 1724, 1574, 1458, 1255, 1082, 906, 748; ESI-TOF(+) calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{37}\text{H}_{25}\text{O}$ 485.1900, found 485.1900.

6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-propoxy-13-acetylene (4). A mixture of 2 (1.0 g, 2.1 mmol), 1-bromopropane (0.2 mL, 2.6 mmol), potassium carbonate (0.68 g, 4.9 mmol) KI (0.43 g, 2.6 mmol) and 40 mL of dry acetone was refluxed for 18 h. After this time, the solvent was removed under reduced pressure. The residue was dissolved in DCM and washed with brine. The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 95:5 hexanes:EtOAc to give 1.0 g (96%) of 4 as white solid: mp decomposes above 350°C ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (ddd, $J = 8.01, 2.30, 0.76$ Hz, 4H), 7.41 (ddd, $J = 7.52, 2.14, 0.76$ Hz, 4H), 7.05 (ddd, $J = 7.92, 8.01, 2.14$ Hz, 4H), 7.02 (ddd, $J = 7.92, 7.52, 2.3$ Hz, 4H), 5.94 (s, 2H), 5.78 (s, 2H), 4.02 (t, $J = 6.81$ Hz, 2H), 3.69 (s, 1H), 2.10 (sextet, $J = 7.20$ Hz, 2H), 1.38 (t, $J = 7.20$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 146.5, 145.1, 144.9, 135.4, 125.3, 125.2, 123.9, 123.4, 109.8, 82.6, 79.3, 77.6, 52.1, 48.2, 23.8, 11.1 IR (solid, cm^{-1}) 3282, 3023, 2951, 2926, 2871, 1781, 1580, 1456, 1259, 1182, 1076, 904, 759, 742; ESI-TOF(+) calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{39}\text{H}_{29}\text{O}$ 513.2213, found 513.2220.

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-acetoxy-13-acetylene (5). A mixture of 2 (1.0 g, 2.1 mmol) and 10 mL of pyridine was added into a two neck flask and stirred 10 min. Then, acetic anhydride (0.30 mL, 3.2 mmol) was added, and the mixture was stirred 16 additional hours at room temperature. The reaction mixture was quenched by adding 10 mL of distilled water and stirred for 1 h. The crude of the reaction was dissolved with DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 95:5 hexanes:EtOAc to give 1.0 g (92%) of 5 as a white solid: mp decomposes above 300°C ; ^1H NMR (300 MHz, CDCl_3) δ 7.44 (ddd, $J = 7.45, 2.81, 1.07$ Hz, 4H), 7.35 (ddd, $J = 6.76, 2.86, 1.07$ Hz, 4H), 7.02 (ddd, $J = 7.52, 7.45, 2.86$ Hz, 4H), 6.99 (ddd, $J = 7.52, 6.76, 2.81$ Hz, 4H), 5.93 (s, 2H), 5.39 (s, 2H), 3.69 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.5, 146.8, 144.9, 144.4, 141.2, 134.9, 125.5, 125.4, 124.1, 123.8, 111.8, 83.4, 79.0, 52.2, 48.7, 20.9; IR (solid, cm^{-1}) 3282, 3067, 3041, 3022, 2921, 2840, 1904, 1764, 1457, 1369, 1182, 1063, 902, 757, 742; ESI-TOF(+) calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{38}\text{H}_{25}\text{O}_2$ 513.1849, found 513.1838.

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzene)pentacene-6-propanoyloxy-13-acetylene (6). A mixture of 2 (1.0 g, 2.1 mmol) and 10 mL of pyridine was added into a two neck flask and left stirring for 10 min. Then, propionic anhydride (0.40 mL, 3.2 mmol) was added, and the mixture was then stirred 16 additional hours at room temperature. The reaction mixture was quenched by adding 10 mL of distilled water, and the mixture was stirred for one additional hour. The whole mixture was dissolved with DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 95:5 hexanes:EtOAc to give 1.0 g (85%) of 6 as white solid: mp decomposes above 325°C ; ^1H NMR (300 MHz, CDCl_3) δ 7.45 (ddd, $J = 6.30, 1.89, 0.57$ Hz, 4H), 7.34 (ddd, $J = 6.26, 2.24, 0.57$ Hz, 4H), 7.02 (ddd, $J = 7.56, 6.30, 2.24$ Hz, 4H), 7.00 (ddd, $J = 7.56, 6.26, 1.89$ Hz, 4H), 5.94 (s, 2H), 5.39 (s, 2H), 3.70 (s, 1H), 2.98 (q, $J = 7.5$ Hz, 2H), 1.64 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.1, 146.7, 144.9, 144.4, 141.3, 134.9, 125.5, 125.4, 124.1, 123.8, 111.7,

83.4, 79.1, 52.2, 48.7, 27.9, 10.1; IR (solid, cm^{-1}) 3282, 3067, 3040, 3025, 2923, 1942, 1899, 1758, 1456, 1253, 1118, 1080, 1023, 759, 742; ESI-TOF(+) calcd for $[\text{M} + \text{H}]^+$ $\text{C}_{39}\text{H}_{27}\text{O}_2$ 527.2006, found 527.2001.

Bis-1,4-[5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzene)-pentacene-6,13-diol]-benzene (7). A mixture of **2** (0.70 g, 1.5 mmol), 1,4-diiodobenzene (0.25 g, 0.74 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.051 g, 0.039 mmol), 8 mL of diisopropylamine and 12 mL of toluene was stirred at 80 °C for 24 h. Then, the reaction mixture was dissolved with DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using hexanes:EtOAc 1:1:0.1 to give 0.60 g (77%) of **7** as a yellow solid: mp decomposes above 350 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.91 (s, 4H), 7.44 (ddd, $J = 5.99, 1.66, 0.31$ Hz, 8H), 7.36 (ddd, $J = 6.19, 1.54, 0.31$ Hz, 8H), 6.99 (ddd, $J = 7.45, 5.99, 1.54$ Hz, 8H), 6.97 (ddd, $J = 7.45, 6.19, 1.66$ Hz, 8H), 5.93 (s, 4H), 5.71 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.1, 145.9, 145.1, 144.9, 131.8, 129.7, 125.3 (2C), 125.2, 124.0, 123.5, 108.1, 94.1, 87.4, 52.6, 47.4; IR (solid, cm^{-1}) 3314, 3066, 2920, 2850, 2198, 1592, 1576, 1458, 1197, 743; ESI-TOF(+) calcd for $[\text{M} + \text{NH}_4]^+$ $\text{C}_{78}\text{H}_{50}\text{NO}_2$ 1032.3836, found 1032.3867.

Bis-1,4-[5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzene)-pentacene-6-methoxy-13-ethynyl]-benzene (8). A mixture of **3** (0.48 g, 1.0 mmol), 1,4-diiodobenzene (0.17 g, 0.52 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.07 g, 0.06 mmol), 8 mL of diisopropylamine and 12 mL of toluene was stirred at 80 °C for 24 h. Then, the reaction mixture was dissolved in DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 9:1 hexanes:EtOAc to give 0.40 g (66%) of **8** as a white solid: mp decomposes above 370 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.98 (s, 4H), 7.49 (ddd, $J = 6.84, 1.47, 0.34$ Hz, 8H), 7.43 (ddd, $J = 6.93, 1.43, 0.34$ Hz, 8H), 7.05 (ddd, $J = 6.84, 6.93, 1.43$ Hz, 8H), 7.02 (ddd, $J = 6.81, 6.93, 1.47$ Hz, 8H), 5.80 (s, 4H), 5.95 (s, 4H), 4.00 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.5, 146.1, 145.0, 144.9, 135.3, 131.8, 125.3, 125.2, 123.9, 123.6, 123.4, 110.9, 94.5, 87.1, 62.7, 52.4, 47.9; IR (solid, cm^{-1}) 2923, 1726, 1577, 1509, 1458, 1299, 1272, 1076, 748, 740; ESI-TOF(+) calcd for $[\text{M} + \text{NH}_4]^+$ $\text{C}_{80}\text{H}_{54}\text{NO}_2$ 1060.4149, found 1060.4198.

Bis-1,4-[5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzene)-pentacene-6-propoxy-13-ethynyl]-benzene (9). A mixture of **4** (0.45 g, 0.87 mmol), 1,4-diiodobenzene (0.14 g, 0.43 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.059 g, 0.051 mmol), 8 mL of diisopropylamine and 12 mL of toluene was stirred at 80 °C for 24 h. Then, the reaction mixture was dissolved in DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using hexanes:EtOAc 95:5 to give 0.30 g (62%) of **9** as a white solid: mp decomposes above 370 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 4H), 7.47 (ddd, $J = 7.62, 1.74, 0.76$ Hz, 8H), 7.38 (ddd, $J = 7.62, 1.34, 0.76$ Hz, 8H), 7.02 (ddd, $J = 7.62, 6.62, 1.34$ Hz, 8H), 7.00 (ddd, $J = 7.62, 6.50, 1.74$ Hz, 8H), 5.96 (s, 4H), 5.76 (s, 4H), 3.99 (t, $J = 6.8$ Hz, 4H), 2.08 (sextet, $J = 7.2$ Hz, 4H), 1.34 (t, $J = 7.6, 6\text{H}$); ^{13}C NMR (75 MHz, CDCl_3) δ 150.0, 146.1, 145.2, 145.1, 135.6, 131.9, 125.34, 125.3, 124.0, 123.8, 123.5, 110.8, 94.6, 87.3, 77.7, 52.5, 48.3, 23.9, 11.1. 52.5, 48.3, 23.9, 11.4; IR (solid, cm^{-1}) 3068, 3020, 2958, 2918, 2872, 2849, 1902, 1720, 1577, 1458, 1299, 1271, 1073, 751, 741; LIFDI-TOF(+) calcd for $[\text{M}]^+$ $\text{C}_{84}\text{H}_{58}\text{O}_2$ 1098.4437, found 1098.4431.

Bis-1,4-[5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzene)-pentacene-6-acetoxy-13-ethynyl]-benzene (10). In a round-bottom flask, compound **7** (0.10 g, 0.090 mmol) was suspended in 2 mL of pyridine, and the mixture was stirred 1 h at room temperature. Afterward, acetic anhydride (0.020 mL, 0.21 mmol) was added to the mixture, which was then stirred overnight. After 16 h, the reaction mixture was quenched by adding 10 mL of distilled water and then stirred one additional hour. The crude was extracted twice with DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 7:3 hexanes:EtOAc

to give 0.087 g (87%) of **10** as a white solid: mp decomposes above 300 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.92 (s, 4H), 7.44 (ddd, $J = 6.72, 1.16, 0.53$ Hz, 8H), 7.30 (ddd, $J = 7.05, 0.96, 0.53$ Hz, 8H), 6.98 (ddd, $J = 7.21, 6.72, 0.96$ Hz, 8H), 6.97 (ddd, $J = 7.21, 7.05, 1.16$ Hz, 8H), 5.93 (s, 4H), 5.36 (s, 4H), 2.66 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.6, 146.2, 144.9, 144.4, 141.2, 135.0, 132.1, 125.6, 125.5, 124.1, 123.9, 123.7, 112.7, 95.2, 86.9, 52.2, 48.8, 21.0; IR (solid, cm^{-1}) 3067, 3020, 2924, 2853, 1769, 1592, 1509, 1458, 1391, 1368, 1298, 1266, 1109, 1058, 1015, 883, 833, 749, 741; ESI-TOF(+) calcd for $[\text{M} + \text{NH}_4]^+$ $\text{C}_{82}\text{H}_{54}\text{NO}_4$ 1116.4047, found 1116.4080.

Bis-1,4-[5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzene)-pentacene-6-propanoyloxy-13-ethynyl]-benzene (11). In a round-bottom flask compound **7** (0.10 g, 0.089 mmol) was suspended in 2 mL of pyridine, and the mixture was stirred 1 h at room temperature. Afterward, 0.030 mL of propionic anhydride (0.23 mmol) was added to the mixture, which was then stirred overnight. After 16 h, the reaction mixture was quenched by adding 10 mL of distilled water and stirred one additional hour. The crude was extracted twice with DCM and washed with a saturated aqueous solution of NH_4Cl . The organic layer was dried over MgSO_4 , filtered and concentrated. The resulting solid was purified by flash chromatography using 7:3 hexanes:EtOAc to give 0.082 g (82%) of **11** as a white solid: mp decomposes above 300 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.92 (s, 4H), 7.44 (ddd, $J = 7.20, 1.21, 0.41$ Hz, 8H), 7.30 (ddd, $J = 6.78, 1.27, 0.41$ Hz, 8H), 7.00 (ddd, $J = 7.51, 7.20, 1.27$ Hz, 8H), 6.97 (ddd, $J = 7.51, 6.78, 1.21$ Hz, 8H), 5.93 (s, 4H), 5.36 (s, 4H), 2.95 (t, $J = 7.5$ Hz, 4H), 1.60 (q, $J = 7.5$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.0, 146.1, 144.8, 144.3, 141.2, 134.9, 131.9, 125.4, 125.3, 123.9, 123.8, 123.6, 112.5, 95.0, 86.9, 52.4, 48.7, 27.8, 10.1; IR (solid, cm^{-1}) 3067, 2923, 2849, 1765, 1509, 1458, 1298, 1260, 1178, 1121, 1079, 833, 751, 743; ESI-TOF(+) calcd for $[\text{M} + \text{NH}_4]^+$ $\text{C}_{84}\text{H}_{58}\text{NO}_4$ 1144.4360 found, 1144.440.

■ ASSOCIATED CONTENT

📄 Supporting Information

Spectroscopic data for all compounds, ^{13}C CPMAS and nonquaternary suppression spectra of compounds **7** and **10**, crystallographic parameters and crystallographic information files (cif) for compounds **7**, **10**, and **11**. This material 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.

■ ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation Grants CHE-1048804 and DMR1101934. B.R.-M. and E.E.-S. thank CONACYT (Mexico) and UC-Mexus for postdoctoral fellowships.

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