

Hexathienocoronenes: Synthesis and Self-Organization

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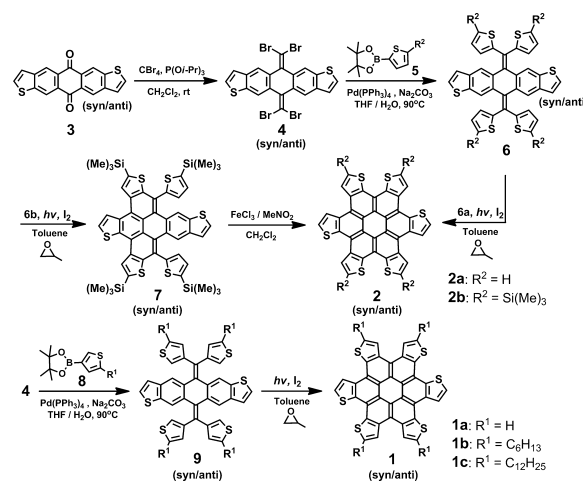
S Supporting Information

ABSTRACT: Here we report hexathienocoronenes (HTCs), fully thiophene-annelated coronenes in which six double bonds in the periphery are thieno-fused. The derivatives tetrasubstituted with hexyl and dodecyl chains show a phase formation that strongly depends on the chain length. HTCs are remarkably stronger donors than the known thiophene-annelated coronenes but do not readily assemble into well-ordered films when deposited from the vapor phase. Thus, thin-film transistors fabricated by vacuum deposition have only modest field-effect mobilities of 0.002 cm² V⁻¹ s⁻¹.

Polycyclic aromatic hydrocarbons (PAHs) can be regarded as two-dimensional graphene segments. Because of their optoelectronic and self-assembling properties,¹ PAHs have served as active components of organic electronic devices such as field-effect transistors, light-emitting diodes, and solar cells.² Compared with their all-hydrocarbon analogues, PAHs containing heteroatoms such as N,³ S,⁴ or O^{5a} in the aromatic skeleton, either neutral or positively charged,⁵ exhibit unprecedented chemical and physical properties. Increasing attention has been paid to heterocyclic PAHs, especially those containing thiophene units.⁶ To date, multiple-thiophene-fused benzene,⁷ naphthalene,⁸ anthracene,^{9,18} triphenylene,¹⁰ pyrene,^{4d} tetracene,^{11a–e} pentacene,^{11f} and coronene¹² have been developed. We are particularly interested in thiophene-annelated coronenes for their interesting assembly behavior. Nuckolls^{12a} described a contorted dibenzotetrathienocoronene (*c*-DBTTC), a tetrathienophene-fused version of the previously reported contorted hexabenzocoronene¹³ (*c*-HBC), although *c*-DBTTC is flatter than its analogue *c*-HBC. Spurred by the beautiful structure of the first fully heterocyclic circulene, “sulflower” (octathio[8]-circulene),^{4a} which has eight S atoms pointing out of the molecular plane, here we report hexathienocoronenes (HTCs), fully thiophene-annelated coronenes wherein six double bonds in the periphery are thieno-fused. The HTCs were obtained as inseparable mixtures of syn and anti isomers derived from the regioisomers of the anthradithiophene quinone precursor. To investigate the effect of the regioisomerism on the molecular packing and physical properties, a syn form, HTC *syn*-1b, was synthesized. The organization was studied by X-ray scattering of thin films. For two derivatives with hexyl and dodecyl substituents, the order and phase formation strongly depend on the length of the alkyl side chains.

The synthesis of the HTCs is shown in Scheme 1. The key building block is 5,11-bis(dibromomethylene)anthradithiophene-

Scheme 1. Synthesis of HTCs 1 and 2 Based on 3



phene (4). The conventional Corey–Fuchs (CF) reaction of anthradithiophene-5,11-dione (3) with PPh₃ and CBr₄ either in dichloromethane with stirring at room temperature¹⁴ or refluxing in toluene¹⁵ failed or gave only trace amounts of product because of the low reactivity of 3. However, with a slightly modified procedure using (*i*-PrO)₃P¹⁶ instead of PPh₃, the CF reaction of 3 smoothly afforded 4 in 67% yield. Subsequently, fourfold Suzuki cross-coupling of 4 with thiophene- α -boronic esters 5 afforded the bisolefin skeletons 6 in high yields (86–89%). In contrast to Nuckolls' case, photocyclization of trimethylsilyl (TMS)-substituted 6b gave only the half-closed product 7,¹⁷ while nonsubstituted 6a afforded the nonsubstituted, fully cyclodehydrogenated HTC 2a in 88% yield. On the other hand, 7 could be further dehydrogenated¹⁷ using ferric chloride to obtain 2b. For comparison, a TMS-substituted tetrathieno- $[a,c,j,l]$ coronene (TMS-TTC) was also synthesized [Scheme S1 in the Supporting Information (SI)]. Toward a facile and efficient synthesis of HTCs, we used Suzuki coupling of thiophene- β -boronic ester 8 with 4 followed by photocyclization to afford the target HTCs 1 directly in high yields (65–92%). To investigate the effect of the regioisomerism on the molecular packing and physical properties, we also synthesized the

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isomerically pure HTC *syn*-**1b** using *syn*-**3**¹⁸ as the precursor (Scheme S2).

HTCs **1** and **2** were fully characterized by NMR spectroscopy, MALDI-TOF mass spectrometry, UV/vis absorption spectroscopy. MALDI-TOF mass spectra of **1** and **2** revealed single species with isotopic distributions in accordance with calculations (Figure S1 in the SI). UV/vis spectra of **2b** (Figure 1)

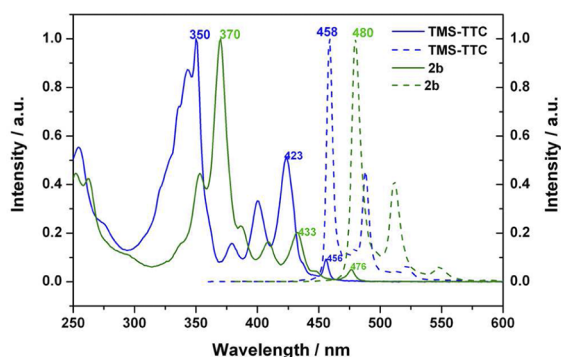


Figure 1. Normalized UV/vis spectra (solid) and photoluminescence (PL) spectra (dashed) of TMS-TTC (blue) and **2b** (green) (1.0×10^{-6} M in CH_2Cl_2). Three distinct emission bands with maxima at 458, 488, and 522 nm and at 480, 512, and 548 nm were observed in the PL spectra of TMS-TTC and **2b**, respectively.

showed three well-resolved absorption bands (α , β , p) characteristic of large PAHs. The absorption maximum of **2b** (β band, 370 nm, $\epsilon = 2.48 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) exhibited a significant bathochromic shift (20 nm) relative to the corresponding band of TMS-TTC (350 nm, $\epsilon = 1.83 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). The same bathochromic shift was observed for the α band of **2b** (476 nm) relative to TMS-TTC (456 nm). However, a small bathochromic shift (10 nm) was found for the p band of **2b** (433 nm) relative to TMS-TTC (423 nm). **1** and **2** showed almost identical absorption bands, although the four thiophenes are annelated at different positions (Figure S2a). The absorption spectra of spin-coated films exhibited bathochromic shifts of 16 nm for both **1b** and **1c** and spectral broadening, indicating that the HTCs have a strong tendency to aggregate in the solid state (Figure S2b).

To elucidate the influence of the peripheral thiophenes on the molecular energy levels of the coronene core, the HOMO energies of the HTCs were obtained via cyclic voltammetry (Figure S3). For example, **2b** showed four quasi-reversible oxidation waves, with the onset of the first oxidation indicating a HOMO energy of -5.08 eV, which is in good agreement with calculations (-4.93 eV; Figure S4) and comparable to the values reported for $[a,g,m]$ TTC (-5.51 eV)^{12c} and *c*-DBTTC (-5.10 eV).^{12a} The HOMO energies of **1b** and **1c** are -5.00 and -4.97 eV, respectively (Table S1 in the SI). Thus, the new HTCs are stronger donors than $[a,g,m]$ TTC and *c*-DBTTC and might serve as efficient active layers in photovoltaic devices.¹⁹

The bulk thermotropic properties of HTCs **1b** and **1c** were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). **1b** and **1c** showed only one main phase transition during cooling, related to their solidification from the isotropic melt. The transition temperatures were 232°C for **1b** and 128°C for **1c**, indicating the effect of the alkyl side chains on the thermal properties, as observed previously for other discotic PAHs²⁶ (Figure S5). An additional peak at 38°C for **1c** was assigned to reorganization of the

substituent alkyl chains. The phase was further characterized by means of POM on thin films cooled from the isotropic phase. Slow cooling at $0.1^\circ\text{C}/\text{min}$ resulted in a highly birefringent fanlike texture (Figure 2a), as observed for discotic liquid-

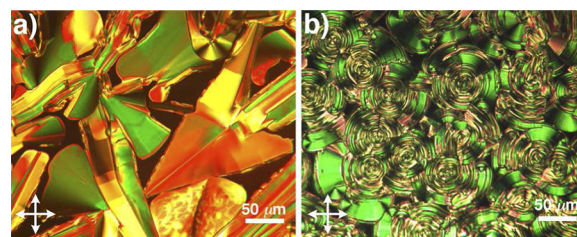


Figure 2. POM images of **1c** at cooling rates of (a) 0.1 and (b) $1^\circ\text{C}/\text{min}$.

crystalline (LC) phases.²⁰ With more rapid thermal processing ($1^\circ\text{C}/\text{min}$), the shape of the texture changed to spiral, indicating that the columns were approximately parallel to the glass slides and that the molecules were tilted with respect to the column axis (Figure 2b).²¹ This is in agreement with the structural analysis discussed below.

To provide a better understanding of the nature of the HTC molecules and their intermolecular interactions, single crystals of **1b** were grown from *p*-xylene solutions by slow evaporation at room temperature. Although these HTC materials existed as inseparable mixtures of *syn* and *anti* isomers, this did not significantly interfere with the packing in the crystal,^{11f} as shown in Figure 3.^{22a} In contrast to *c*-DBTTC, because of the relatively

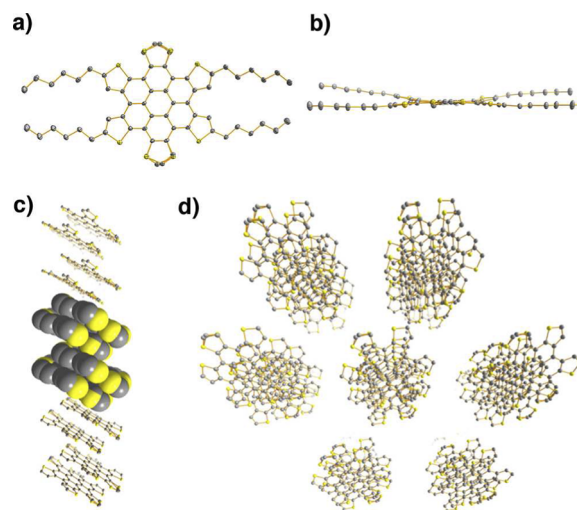


Figure 3. Crystal structure of **1b** obtained from *p*-xylene. (a) Top and (b) side views shown as ORTEP plots. (c) Side view of columnar packing with interlayer distances of $3.37 \text{ \AA}$ in the dimer stack and $3.5 \text{ \AA}$ between the dimers. (d) Eclipsed interlayer packing in the distorted hexagonal columnar arrangement. H atoms and the hexyl side chains in (c) and (d) have been removed for clarity. C, gray; S, yellow.

weak steric congestion of the six outer thiophene rings, **1b** adopts an almost planar conformation (Figure 3a,b); the maximal deviation of the C and S atoms from the molecular plane is $0.56 \text{ \AA}$, and the angle between the plane of the outer thiophene and inner benzenoid rings is 7.4° . X-ray diffraction (XRD) also revealed the assembly of **1b**. Columnar packing was observed, with stacks of molecules oriented along the *a* axis. Interestingly, the repeating moiety with the stack is not the monomer; instead,

dimers are packed in a graphite-like AB fashion (Figure 3c). Within the dimer stacks, the π - π interactions dominate, with a distance of 3.37 Å between two molecules, while the distance between the dimers is expanded to ca. 3.5 Å. These molecular stacks are arranged in a distorted hexagonal arrangement of columns in the solid state (Figure 3d). Serendipitously, another crystal polymorph of **1b** was obtained from dilute toluene solution.^{22b} Interestingly, this crystal polymorph of **1b** forms dimers by π - π interactions with an expanded interlayer distance of 3.5 Å, with no obvious π - π stacking among the dimers. Furthermore, the aromatic plane of **1b** is much more twisted (Figure S6). On the other hand, single crystals of isomerically pure *syn*-**1b** were also obtained by slow evaporation from *p*-xylene.^{22c} However, the crystal structure of *syn*-**1b** was remarkably similar to that of the *syn*/anti mixture and also displayed disorder at two sulfur positions, probably because the molecules were simply flipped over in the lattice and present in equal abundance (Figure S7).²⁷ Comparison of the ¹³C NMR spectra of *syn*-**9b** and *syn*/anti-**9b** together with the ¹H NMR spectrum of *syn*-**1b** showed much better resolution of peaks than for *syn*/anti-**1b**, further confirming that the observed disorder was not a result of the presence of a mixture of *syn* and anti isomers but appeared because half of the molecules were inverted in the crystal lattice (Figure S8).

To gain further insight into the supramolecular organization of **1b** and **1c** on the surface, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements on thin films were performed. The samples were prepared by drop-casting from toluene solution (2 mg/mL) with subsequent annealing at 90 °C. The GIWAXS pattern of **1b** indicates a crystalline phase with molecules arranged edge-on, while the columnar stacks are parallel to the surface (Figure 4a). An identical organization was

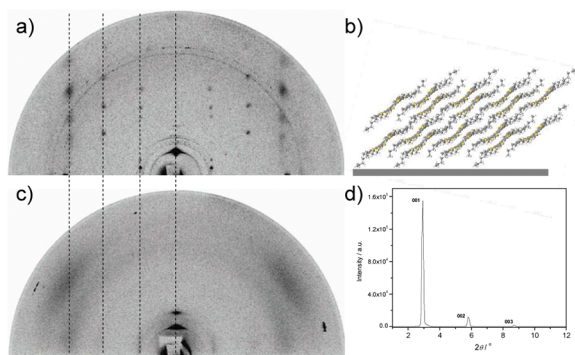


Figure 4. (a) GIWAXS pattern of a thin film of **1b** and (b) corresponding schematic illustration of the molecular organization on the surface. (c) GIWAXS pattern and (d) XRD of a thin film of **1c**. Dashed lines are guides for the reflections positioned on scattering lines.

recently determined for columnar terrylene diimides.²³ Meridional reflections along q_z for $q_{x,y} = 0$ are related to an intercolumnar out-of-plane spacing of 1.84 nm. Further scattering lines parallel to q_z suggest a complex intracolumnar packing of the molecules. To clarify the surface organization, the single-crystal data for both solvents (toluene and *p*-xylene) were used to simulate the scattering patterns with Cerius² for comparison to the experimental results. As expected, only the simulated pattern for the crystal from toluene was in good agreement with the GIWAXS pattern (Figure S9). In this way, it was possible to derive precisely the molecular packing of **1b** on the surface after thermal treatment. The molecules are arranged

with the alkyl chains pointing toward the substrate, and the aromatic cores are tilted ca. 45° toward the surface (Figure 4b). This correlates with the calculated molecular size of 2.58 nm [$\arccos(1.84/2.58) \approx 45^\circ$]. On the basis of these findings, the GIWAXS pattern of **1c** was then analyzed (Figure 4c). The reflections related to the intracolumnar arrangement for **1c** are significantly broader than those for **1b** but are located on identical scattering lines at identical positions. This indicates not only a lower crystallinity for **1c** because of the longer flexible alkyl side chains but also a similar molecular organization on the surface. This latter conclusion was drawn from the first scattering line in the middle-angle region and the wide-angle off-meridional reflections, all of which were located at the same scattering angles as for **1b**. The out-of-plane spacing of 3.0 nm determined from the XRD plot (Figure 4d) is in agreement with the meridional plane of the GIWAXS pattern and is attributed to molecules tilted by $\sim 45^\circ$ [$\arccos(3.0/4.2) \approx 45^\circ$]. The decreased order is related to the LC phase observed by POM.

Bearing in mind these highly ordered structures formed in the assemblies, we further investigated the charge transport properties in polycrystalline vacuum-deposited thin films of HTCs. **1a** and **1b** were selected for the first attempt because of their high crystallinity. Bottom-gate, top-contact thin-film transistors (TFTs) with a 110 nm thick SiO₂/AlO_x gate dielectric functionalized with a fluoroalkylphosphonic acid self-assembled monolayer²⁴ and a 30 nm thick vacuum-deposited semiconductor layer were fabricated. **1a** and **1b** were deposited at substrate temperatures of 100 and 120 °C, respectively. Figure S10 shows the output and transfer characteristics of the TFTs, which exhibited p-type behavior with field-effect mobilities of 0.002 cm² V⁻¹ s⁻¹ for **1a** and 0.001 cm² V⁻¹ s⁻¹ for **1b**. These mobilities are notably smaller than the best mobilities reported for TFTs based on oligoacenes²⁵ and thienoacenes.^{6c,11} The reasons for these relatively small mobilities are the self-assembly into one-dimensional columnar stacks and the poor crystallinity of the vacuum-deposited thin films, as revealed by atomic force microscopy (Figure S11a,c) and XRD (Figure S11b,d). The poor crystallinity of the vacuum-deposited films is in stark contrast to the excellent crystallinity of the drop-cast films (see Figure 4), which suggests that solution processing may be a more suitable deposition method for HTCs.

In summary, we have reported unprecedented sulfur-containing heterocyclic PAHs and established a facile synthetic method for these fully thiophene-annulated coronenes that allows various substituents to be introduced easily. They reveal remarkable self-assembly behavior in solution, the solid state, and at the solution–substrate interface. HTC **1c** forms a columnar mesophase over a wide temperature range close to room temperature, which is much lower than that for the well-investigated hexadodecylhexabenzocoronene,²⁶ and thus is good for processing in electronic devices. Moreover, compared with the reported *c*-DBTTCs, the tetrasubstituted HTCs leave the two α -positions of the annulated thiophenes on the anthradi-thiophene backbone open, allowing further functionalization and polymerization.²⁷ Investigations of the formation of charge transfer complexes with acceptor counterparts (e.g., TCNQ) and polymerization of HTCs are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic details and characterization data. 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.

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- (22) The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif: (a) *syn/anti-1b* formed in *p*-xylene: CCDC-869826. (b) *syn/anti-1b* formed in toluene: CCDC-876942. (c) *syn-1b* formed in *p*-xylene: CCDC-895213.
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