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Hexathienocoronenes: Synthesis and Self-Organization

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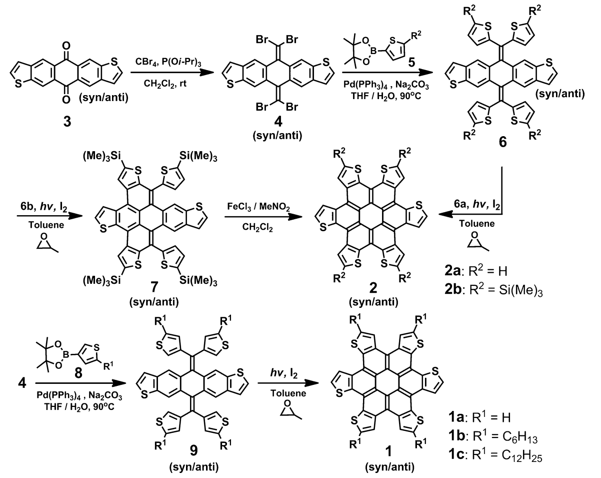
S *Supporting Information*

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 $cm^2\ V^{-1}\ s^{-1}$.

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 coronene[12] 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 tetrathiophene-fused version of the previously reported contorted hexabenzocoronene[13] (*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 (**4**). The conventional Corey−Fuchs (CF) reaction of anthradithiophene-5,11-dione (**3**) with PPh_3 and CBr_4 either in dichloromethane with stirring at room temperature[14] or refluxing in toluene[15] failed or gave only trace amounts of product because of the low reactivity of **3**. However, with a slightly modified procedure using $(i\text{-PrO})_3P$[16] instead of PPh_3, 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 dehydrogenated[17] 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

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



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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) showed three well-resolved absorption bands (α, β, p) characteristic of large PAHs. The absorption maximum of **2b** (β band, 370 nm, $\varepsilon = 2.48 \times 10^5$ M^{-1} cm^{-1}) exhibited a significant bathochromic shift (20 nm) relative to the corresponding band of TMS-TTC (350 nm, $\varepsilon = 1.83 \times 10^5$ M^{-1} cm^{-1}). The same bathochromic shift was observed for the α band of **2b** (476 nm) relative 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).

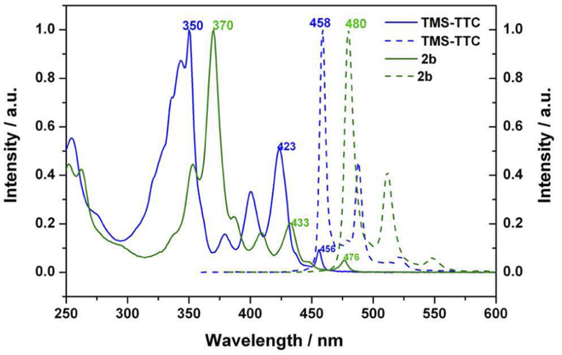

Figure 1. Normalized UV/vis spectra (solid) and photoluminescence (PL) spectra (dashed) of TMS-TTC (blue) and **2b** (green) (1.0×10^{-6} M in CH_2Cl_2). Three distinct emission bands with maxima at 458, 488, and 522 nm and at 480, 512, and 548 nm were observed in the PL spectra of **TMS-TTC** and **2b**,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

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 PAHs[26](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 °C/min resulted in a highly birefringent fanlike texture (Figure 2a), as observed for discotic liquid-crystalline (LC) phases.[20] With more rapid thermal processing (1 °C/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.

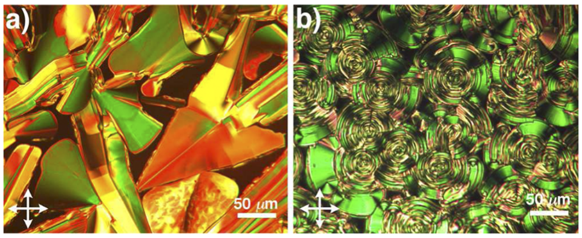

Figure 2. POM images of **1c** at cooling rates of (a) 0.1 and (b) 1 °C/min.

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 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 Å, 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,

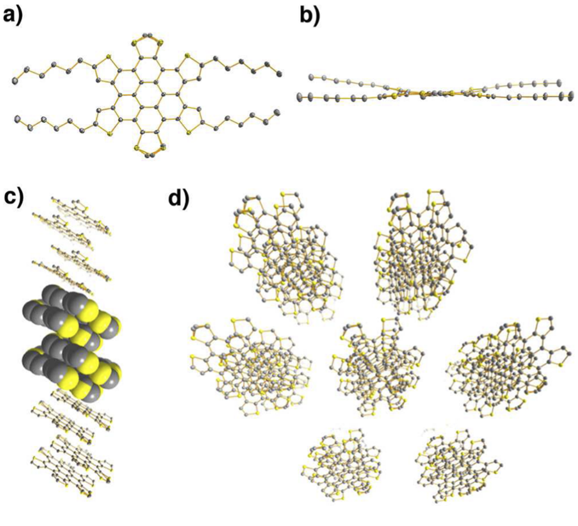

Figure 3. Crystal structure of **1b** obtained from *p*-xylene. (a) Top and (b) side views shown as ORTEP plots. (c) Side view of columnar packing with interlayer distances of 3.37 Å in the dimer stack and 3.5 Å between the dimers. (d) Eclipsed interlayer packing in the distorted hexagonal columnar arrangement.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

dimers are packed in a graphite-like AB fashion (Figure 3c). Within the dimer stacks, the $\pi-\pi$ 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 $\pi-\pi$ interactions with an expanded interlayer distance of 3.5 Å, with no obvious $\pi-\pi$ 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 ^{13}C 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 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 Cerius^2 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) ≈ 45°]. 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 ~45° [arccos(3.0/4.2) ≈ 45°]. The decreased order is related to the LC phase observed by POM.

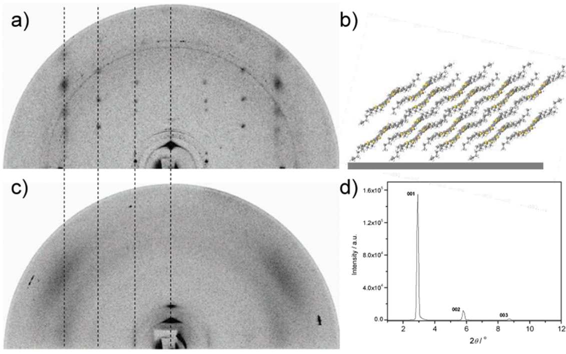

Figure 4. (a) GIWAXS pattern of a thin film of **1b** and (b) corresponding schematic illustration of the molecular organization on the surface. (c) GIWAXS pattern and (d) XRD of a thin film of **1c**. Dashed lines are guides for the reflections positioned on scattering lines.

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 SiO_2/AlO_x gate dielectric functionalized with a fluoroalkylphosphonic acid self-assembled monolayer[24] 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 $cm^2\ V^{-1}\ s^{-1}$ for **1a** and 0.001 $cm^2\ V^{-1}\ s^{-1}$ for **1b**. These mobilities are notably smaller than the best mobilities reported for TFTs based on oligoacenes[25] 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-annelated 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 annelated thiophenes on the anthradithiophene 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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■ REFERENCES

(1) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.

(2) (a) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (c) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.

(3) (a) Matena, M.; Stöhr, M.; Riehm, T.; Björk, J.; Martens, S.; Dyer, M. S.; Persson, M.; Lobo-Checa, J.; Müller, K.; Enache, M.; Wadepohl, H.; Zegenhagen, J.; Jung, T. A.; Gade, L. H. *Chem.—Eur. J.* **2010**, *16*, 2079. (b) Draper, S. M.; Gregg, D. J.; Madathil, R. *J. Am. Chem. Soc.* **2002**, *124*, 3486. (c) Takase, M.; Enkelmann, V.; Sebastiani, D.; Baumgarten, M.; Müllen, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5524. (d) Bunz, U. H. F. *Chem.—Eur. J.* **2009**, *15*, 6780.

(4) (a) Chernichenko, K. Y.; Sumerin, V. V.; Shpanchenko, R. V.; Balenkova, E. S.; Nenajdenko, V. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7367. (b) Sun, Y.; Tan, L.; Jiang, S.; Qian, H.; Wang, Z.; Yan, D.; Di, C.; Wang, Y.; Wu, W.; Yu, G.; Yan, S.; Wang, C.; Hu, W.; Liu, Y.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 1882. (c) Jiang, W.; Zhou, Y.; Geng, H.; Jiang, S.; Yan, S.; Hu, W.; Wang, Z.; Shuai, Z.; Pei, J. *J. Am. Chem. Soc.* **2010**, *133*, 1. (d) Zöphel, L.; Enkelmann, V.; Rieger, R.; Müllen, K. *Org. Lett.* **2011**, *13*, 4506.

(5) (a) Wu, D.; Pisula, W.; Haberecht, M. C.; Feng, X.; Müllen, K. *Org. Lett.* **2009**, *11*, 5686. (b) Wu, D.; Zhi, L.; Bodwell, G. J.; Cui, G.; Tsao, N.; Müllen, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5417.

(6) (a) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604. (b) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224. (c) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024. (d) Niimi, K.; Shinamura, S.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 8732. (e) Zschieschang, U.; Kang, M. J.; Takimiya, K.; Sekitani, T.; Someya, T.; Canzler, T. W.; Werner, A.; Blochwitz-Nimoth, J.; Klauk, H. *J. Mater. Chem.* **2012**, *22*, 4273.

(7) (a) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273. (b) Kashiki, T.; Shinamura, S.; Kohara, M.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H. *Org. Lett.* **2009**, *11*, 2473. (c) Nielsen, C. B.; Fraser, J. M.; Schroeder, B. C.; Du, J.; White, A. J. P.; Zhang, W.; McCulloch, I. *Org. Lett.* **2011**, *13*, 2414.

(8) (a) Osaka, I.; Abe, T.; Shinamura, S.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2010**, *132*, 5000. (b) Shinamura, S.; Osaka, I.; Miyazaki, E.; Nakao, A.; Yamagishi, M.; Takeya, J.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 5024. (c) Osaka, I.; Abe, T.; Shinamura, S.; Takimiya, K. *J. Am. Chem. Soc.* **2011**, *133*, 6852. (d) Loser, S.; Bruns, C. J.; Miyauchi, H.; Ortiz, R. P.; Facchetti, A.; Stupp, S. I.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 8142. (e) Sanjaykumar, S. R.; Badgujar, S.; Song, C. E.; Shin, W. S.; Moon, S.-J.; Kang, I.-N.; Lee, J.; Cho, S.; Lee, S. K.; Lee, J.-C. *Macromolecules* **2012**, *45*, 6938. (f) Loser, S.; Miyauchi, H.; Hennek, J. W.; Smith, J.; Huang, C.; Facchetti, A.; Marks, T. J. *Chem. Commun.* **2012**, *48*, 8511.

(9) (a) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (c) Mamada, M.; Minamiki, T.; Katagiri, H.; Tokito, S. *Org. Lett.* **2012**, *14*, 4062. (d) Nakano, M.; Niimi, K.; Miyazaki, E.; Osaka, I.; Takimiya, K. *J. Org. Chem.* **2012**, *77*, 8099.

(10) Endou, M.; Ie, Y.; Aso, Y. *Heterocycles* **2008**, *76*, 1043.

(11) (a) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002. (b) Yuan, Q.; Mannsfeld, S. C. B.; Tang, M. L.; Toney, M. F.; Lüning, J.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 3502. (c) Tang, M. L.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 6064. (d) Tang, M. L.; Mannsfeld, S. C. B.; Sun, Y.-S.; Becerril, H. A.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 882. (e) Tang, M. L.; Reichardt, A. D.; Wei, P.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 5264. (f) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 3325.

(12) (a) Chiu, C.-Y.; Kim, B.; Gorodetsky, A. A.; Sattler, W.; Wei, S.; Sattler, A.; Steigerwald, M.; Nuckolls, C. *Chem. Sci.* **2011**, *2*, 1480. (b) Gorodetsky, A. A.; Chiu, C.-Y.; Schiros, T.; Palma, M.; Cox, M.; Jia, Z.; Sattler, W.; Kymissis, I.; Steigerwald, M.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 7909. (c) Li, Z.; Zhi, L.; Lucas, N. T.; Wang, Z. *Tetrahedron* **2009**, *65*, 3417.

(13) (a) Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M. L.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 7390. (b) Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 10700. (c) Guo, X.; Xiao, S.; Myers, M.; Miao, Q.; Steigerwald, M. L.; Nuckolls, C. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 691. (d) Plunkett, K. N.; Godula, K.; Nuckolls, C.; Tremblay, N.; Whalley, A. C.; Xiao, S. *Org. Lett.* **2009**, *11*, 2225.

(14) Hwang, G. T.; Son, H. S.; Ku, J. K.; Kim, B. H. *J. Am. Chem. Soc.* **2003**, *125*, 11241.

(15) Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2004**, *126*, 3108.

(16) Fang, Y.-Q.; Lifchits, O.; Lautens, M. *Synlett* **2008**, 413.

(17) Zhang, X.; Jiang, X.; Zhang, K.; Mao, L.; Luo, J.; Chi, C.; Chan, H. S. O.; Wu, J. *J. Org. Chem.* **2010**, *75*, 8069.

(18) (a) Lehnherr, D.; Hallani, R.; McDonald, R.; Anthony, J. E.; Tykwinski, R. R. *Org. Lett.* **2012**, *14*, 62. (b) Lehnherr, D.; Waterloo, A. R.; Goetz, K. P.; Payne, M. M.; Hampel, F.; Anthony, J. E.; Jurchescu, O. D.; Tykwinski, R. R. *Org. Lett.* **2012**, *14*, 3660. (c) Tylleman, B.; Vande Velde, C. M. L.; Balandier, J.-Y.; Stas, S.; Sergeyev, S.; Geerts, Y. H. *Org. Lett.* **2011**, *13*, 5208.

(19) (a) Gorodetsky, A. A.; Chiu, C.-Y.; Schiros, T.; Palma, M.; Cox, M.; Jia, Z.; Sattler, W.; Kymissis, I.; Steigerwald, M.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 7909. (b) Kang, S. J.; Kim, J. B.; Chiu, C.-Y.; Ahn, S.; Schiros, T.; Lee, S. S.; Yager, K. G.; Toney, M. F.; Loo, Y.-L.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 8594.

(20) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Gele, C. H.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832.

(21) (a) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067. (b) Destrade, C.; Foucher, P.; Gesparoux, H.; Nguyen, H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

(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.

(23) Liu, C.; Liu, Z.; Lemke, H. T.; Tsao, H. N.; Naber, R. C. G.; Li, Y.; Banger, K.; Müllen, K.; Nielsen, M. M.; Sirringhaus, H. *Chem. Mater.* **2010**, *22*, 2120.

(24) Zschieschang, U.; Ante, F.; Schlörholz, M.; Schmidt, M.; Kern, K.; Klauk, H. *Adv. Mater.* **2010**, *22*, 4489.

(25) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053.

(26) Pisula, W.; Tomovic, Z.; Simpson, C.; Kastler, M.; Pakula, T.; Müllen, K. *Chem. Mater.* **2005**, *17*, 4296.

(27) Balandier, J.-Y.; Quist, F.; Stas, S.; Tylleman, B.; Ragoen, C.; Mayence, A.; Bouzakraoui, S.; Cornil, J.; Geerts, Y. H. *Org. Lett.* **2011**, *13*, 548.

Supporting Information

Hexathienocoronene: Synthesis and self-Organization

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Section 1. Materials and Methods

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker DPX 250, and Bruker DRX 500. UV-visible spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a dichloromethane solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature. A Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, the reference electrode, and the working electrode, respectively. Crystal-structure determinations were carried out on a Nonius KCCD diffractometer with graphite monochromated Mo K radiation. The structures were solved by direct methods (SHELXS-97). Refinements were performed as full-matrix least-squares refinements with anisotropic temperature factors for the non-hydrogen atoms. H atoms were included with fixed isotropic temperature factors in the riding mode. The distances of the atoms in the disordered thiophene rings are very close. Thus, their distances were constrained to standard bond lengths. DSC was measured by Mettler DSC 30 with a heating rate of 10 K/min from 20 °C to 250 °C. The optical textures of the compound were investigated using a Zeiss microscope with polarizing filters equipped with a Hitachi KP-D50 Colour digital CCD camera. The samples were sandwiched between two glass slides and then thermally treated on a Linkam hot stage regulated with a Linkam TMS 91 temperature controller. GIWAXS measurements were performed using a custom setup consisting of rotating anode X-ray source (Rigaku Micromax). By orienting the substrate surface at or just below the critical angle for total reflection with respect to the incoming X-ray beam (~0.2°), scattering from the deposited film is maximized with respect to scattering from the substrate. The GIWAXS data were acquired using a camera comprising an evacuated sample chamber with an X-ray photosensitive image plate. A rotating Cu-anode operating at 42 kV and 20 mA (Cu Kα, λ = 1.5418 Å) was used as X-ray source, focused, and monochromatized by a 1D multilayer. Unless otherwise noted, all starting materials were purchased from Aldrich, Acros and use as received without further purification. Thiophene boronic ester **5a**, **8a** were purchased from Alfa Aescar, while **5b**,[S1] **8b**,[S2] **8c**[S2] and **10**[S3] were prepared followed the reported procedures.

Section 2. Synthesis

Anthra[*2,3-b*:*6,7-b'*]dithiophene-*5,11*-dione and anthra[*2,3-b*:*7,6-b'*]dithiophene-*5,11*-dione (3)

Thiophene-2,3-dicarboxaldehyde (2.0 g, 14.3 mmol) was dissolved in EtOH (200 mL) in a 500-mL round-bottom flask with a stirring bar, followed by the addition of 0.73 g 1,4-cyclohexanedione (6.5 mmol). Upon addition of a 15 % KOH solution (8 mL), precipitate began to form immediately. The mixture was stirred for an additional hour, then filtered to yield 1.93 g (6.0 mmol, 93 %) of quinone **3** as a yellow powder that was identical to previously reported compound.[S4]

5,11-Bis(dibromomethylene)-anthra[*2,3-b*:*6,7-b'*]dithiophene and *5,11*-Bis(dibromomethylene)-anthra[*2,3-b*:*7,6-b'*]dithiophene (4)

A solution of $P(O\text{-}i\text{Pr})_3$ (7.3 mL, 32 mmol) in dichloromethane (10 mL) was added dropwise under Ar to a suspension of quinone **3** (1.282 g, 4.0 mmol) and CBr_4 (7.96 g, 24.0 mmol) in dichloromethane (200 mL) at 0^{o}C. The mixture was then stirred at room temperature under Ar overnight. The reaction mixture was filtered, washed with dichloromethane. The filtrate was collected and evaporated, the residue was purified by Si gel chromatography (hexane/ dichoromethane = 1/1 as eluent). The first fraction was collected, evaporated and dried under vacuum afford compound **4** as an off-white solid

1.69 g (2.68 mmol, 67%). ^{1}H NMR (250 MHz, CD_2Cl_2), δ (ppm): 8.33 (s, 2H), 8.28 (s, 2H), 7.57 (d, J = 5.0 Hz, 2H), 7.39 (d, J = 5.0 Hz, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm): 140.55, 140.44, 140.33, 139.03, 138.84, 133.16, 133.04, 132.80, 132.68, 129.27, 129.25, 124.50, 123.17, 122.21. FD-MS (8 KV): m/z 632.2, cacld.: 632.02 (M^+). Elemental analysis: Calculated: C 38.01, H 1.28, Br 50.57, S 10.15; Found: C 38.13, H 1.30.

General Procedure for the Suzuki-Miyaura Coupling (**6a-6b**; **9a-9c**). The synthesis of **9b** is used as an example, with the other compounds prepared in identical procedure. Compound **4** (204 mg, 0.32 mmol), thiophene-β-boronic ester **8b** (475 mg, 1.61 mmol) and $Pd(PPh_3)_4$ (38 mg, 32 μmol) were put into a 100 mL two-necked flask. A degassed THF (12 mL) was added under argon, the resulted solution was degassed by freeze-pump-thaw cycles. An aqueous solution (3 mL) of Na_2CO_3 (274 mg, 2.58 mmol) was added under argon. The mixture was further degassed by freeze-pump-thaw cycles and then stirred at 90°C overnight. The mixture was cooled to room temperature, THF was evaporated and the resulted residue was extracted with CH_2Cl_2. The organic phase was washed with water and brine, dried with anhydrous Na_2SO_4. Compound **9b** was isolated by column chromatography (Hexane/CH_2Cl_2 = 3:1) as a light yellow solid in 85% yield. ^{1}H NMR (250 MHz , CD_2Cl_2), δ (ppm): 7.60 (s, 2H), 7.55 (s, 2H), 7.28 (d, J = 5.0 Hz, 2H), 7.03 (d, J = 5.0 Hz, 2H), 6.95 (brs, 4H), 6.67 (brs, 4H), 2.70 (t, J = 7.5 Hz, 8H), 1.24 (m, 24H), 0.87 (t, J = 7.5 Hz, 12H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 146.15, 146.10, 145.99, 145.95, 142.22, 142.13, 142.03, 138.08, 137.97, 136.34, 136.22, 136.12, 135.58, 135.42, 130.45, 130.36, 130.26, 127.07, 126.98, 126.92, 124.23, 122.93, 121.85, 121.80, 121.74, 32.28, 32.24, 32.11, 32.09, 30.54, 30.51, 29.20, 29.14, 23.08, 14.48. FD-MS (8 KV): m/z 981.06, cacld.: 981.57.

***5,11*-Bis(bis(thiophen-2'-yl)methylene)-anthra[*2,3-b*:*6,7-b'*]dithiophene and *5,11*-Bis(bis(thiophen-2'-yl)methylene)-anthra[*2,3-b*:*7,6-b'*] dithiophene (6a).** 86%.^{1}H NMR (CD_2Cl_2): δ (ppm) 7.80 (s, 2H), 7.75 (s, 2H), 7.24 (d, J = 5.0 Hz, 2H), 7.28-7.24 (m, 4H), 7.15-7.12 (m, 4H), 7.08 (d, J = 5.0 Hz, 2H), 6.99-6.95 (m, 4H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 143.76, 143.68, 143.58, 139.32, 139.15, 138.31, 135.13, 134.97, 134.83, 128.99, 127.66, 127.12, 127.07, 126.53, 126.44, 125.10, 124.23, 122.78, 121.77.

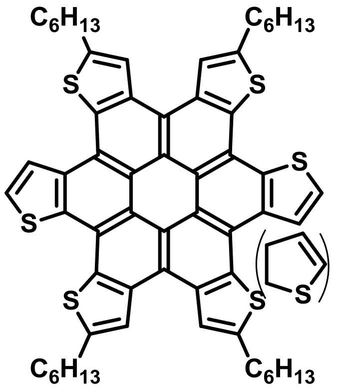
FD-MS (8 KV): m/z 644.50, cacld.: 644.93.

***5,11*-Bis(bis(5'-trimethylsilyl-thiophen-2'-yl)methylene)-anthra[*2,3-b*:*6,7-b'*]dithiophene and *5,11*- Bis(bis(5'--trimethylsilyl-thiophen-2'-yl)methylene)-anthra[*2,3-b*:*7,6-b'*] dithiophene (6b).** 89%. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.75 (s, 2H), 7.70 (s, 2H), 7.35 (d, J = 5.0 Hz, 2H), 7.17-7.11 (m, 8H), 7.07 (d, J = 5.0 Hz, 2H), 0.30 (s, 36H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 149.30, 149.16, 149.02, 141.66, 141.51, 139.04, 138.26, 135.08, 134.93, 134.14, 129.96, 129.85, 127.38, 125.47, 124.13, 122.66, 121.59, 120.50, 0.00. FD-MS (8 KV): m/z 932.90, cacld.: 933.66.

***5,11*-Bis(bis(thiophen-3'-yl)methylene)-anthra[*2,3-b*:*6,7-b'*]dithiophene and *5,11*-Bis(bis(thiophen-3'-yl)methylene)-anthra[*2,3-b*:*7,6-b'*] dithiophene (9a).** 93%. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.59 (s, 2H), 7.54 (s, 2H), 7.32-7.25 (m, 10H), 7.05-7.00 (m, 6H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 142.43, 142.34, 142.25, 138.01, 137.93, 136.53, 135.35, 135.29, 135.20, 135.14, 129.53, 129.33, 127.25, 125.79, 125.75, 125.69, 125.66, 124.51, 124.42, 124.14, 122.92, 121.80. FD-MS (8 KV): m/z 644.11, cacld.: 643.99.

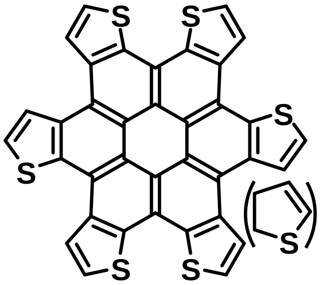
***5,11*-Bis(bis(5'-dodecylthiophen-3'-yl)methylene)-anthra[*2,3-b*:*6,7b'*]dithiophene and *5,11*- Bis(bis(5'-dodecylthiophen-3'-yl)methylene)-anthra[*2,3-b*:*7,6-b'*] dithiophene (9c).** 87%. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.64 (s, 2H), 7.59 (s, 2H), 7.32(d, J = 5.0 Hz, 2H), 7.07 (d, J = 5.0 Hz, 2H), 7.00 (brs, 4H), 6.70 (brs, 4H), 2.74 (t, J = 7.5 Hz, 8H), 1.60-1.55(m, 8H), 1.32-1.28 (m, 72H), 0.91(t, J = 7.5 Hz, 12H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 145.97, 145.92, 145.81, 145.77, 142.04, 141.95, 141.85, 137.90, 137.80, 136.15, 136.04, 135.92, 135.40, 135.25, 130.28, 130.18,130.08, 126.81, 124.07, 122.77, 121.64, 32.36, 32.18, 32.13, 30.36, 30.13, 29.94, 29.80, 29.38, 29.34, 23.12, 14.30. FD-MS (8 KV): m/z 1317.80, cacld.: 1318.21.

General Procedure for the Synthesis of Hexathienocoronenes (2a, 1a-1c). The synthesis of **1b** is used as an example, with the other compounds prepared in identical procedures. A mixture of **9b** (220 mg, 0.22 mmol), iodine (284 mg, 1.12 mmol) and propylene oxide (6 mL) in anhydrous toluene (200 mL) was irradiated with UV light at 300 nm wavelength overnight. The solvent was removed under reduced pressure and the solid was washed with small amount of DCM, further purified by recrystallization from THF to afford **1b** as a yellow solid in 68% yield.



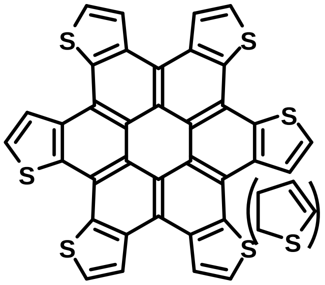
^{1}H NMR (d_8-THF, 500MHz, 333K): δ (ppm) 8.76 (d, J = 5.0Hz, 2H), 8.21 (s, 1H), 8.13 (s, 1H), 8.11 (s, 1H), 8.04 (s, 1H), 7.96 (d, J = 5.0Hz, 2H), 3.23 (t, J = 7.5 Hz, 4H), 3.17 (t, J = 7.5 Hz, 4H), 2.08-1.97 (m, 8H), 1.71-1.62 (m, 8H), 1.58-1.44 (m, 16H), 1.04-1.00 (m, 12H); ^{13}C NMR ($C_2D_4Cl_4$, 500MHz, 373K): 146.11, 145.51, 134.14, 133.50, 132.34, 125.38, 122.69, 120.21, 31.53, 31.32, 31.22, 31.01, 30.78, 28.95, 22.44, 13.82. MALDI-TOF-MS (TCNQ as matrix): m/z 973.08, cacld.: 973.51. Elemental analysis: Calculated: C 74.03, H 6.21, S 19.76; Found: C 73.97, H 6.18, S 19.69.

Coroneno[2,1-b:3,4-b':5,6-b'':8,7-b''':9,10-b'''',11,12-b''''']hexathiophene and Coroneno[2,1-b:3,4-b':6,5-b'':8,7-b''':9,10-b'''',11,12-b''''']hexathiophene (2a).



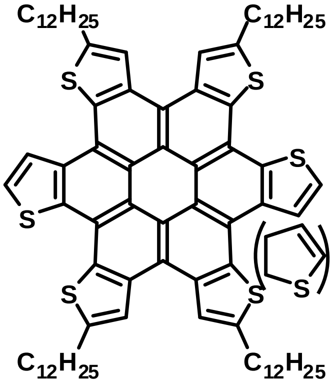
88%. ^{1}H NMR, ^{13}C NMR could not be obtained due to the poor solubility of the compound. MALDI-TOF-MS (TCNQ as matrix): m/z 636.49, cacld.: 636.87. Elemental analysis: Calculated: C 67.89, H 1.90, S 30.21; Found: C 67.65, H 1.86, S 30.26.

Coroneno[1,2-b:4,3-b':5,6-b'':7,8-b''':10,9-b'''',11,12-b''''']hexathiophene and Coroneno[1,2-b:4,3-b':6,5-b'':7,8-b''':10,9-b'''',11,12-b''''']hexathiophene (1a).



92%. ^{1}H NMR, ^{13}C NMR could not be obtained due to the poor solubility of the compound. MALDI-TOF-MS (TCNQ as matrix): m/z 636.02, cacld.: 636.87. Elemental analysis: Calculated: C 67.89, H 1.90, S 30.21; Found: C 67.63, H 1.88, S 30.22.

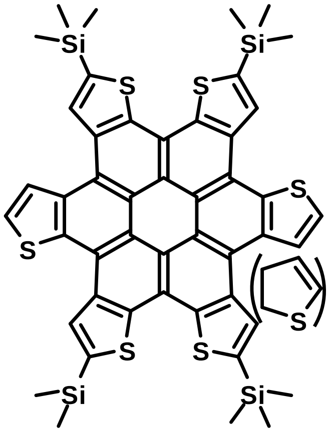
2,5,11,14-tetra(dodecyl)coroneno[1,2-b:4,3-b':5,6-b'':7,8-b''':10,9-b'''',11,12-b''''']hexathiophene and 2,8,11,17-tetra(dodecyl)coroneno[1,2-b:4,3-b':6,5-b'':7,8-b''':10,9-b'''',11,12-b''''']hexathiophene (1c)



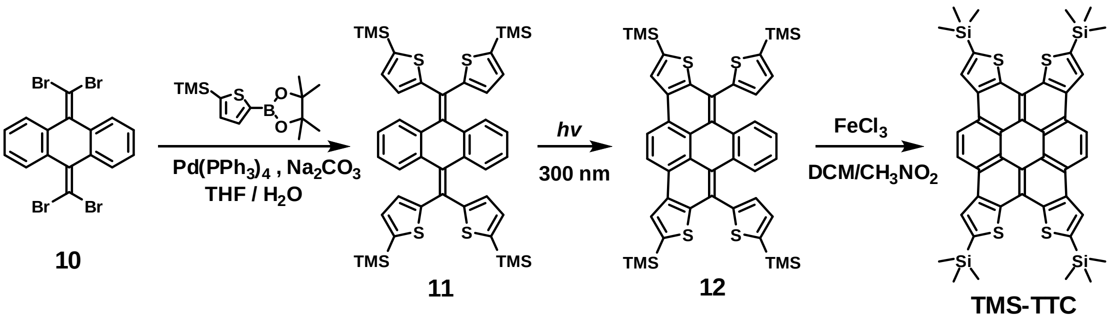
65%. ^{1}H NMR ($C_2D_4Cl_4$, 295K): δ (ppm) 8.62 (d, J = 5.0Hz, 2H), 8.01 (s, 1H), 7.92 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 3.23 (t, J = 7.5 Hz, 4H), 3.15 (t, J = 7.5 Hz, 4H), 1.97-1.84 (m, 8H), 1.62-1.30 (m, 8H), 0.90 (t, 12H);^{13}C NMR ($C_2D_4Cl_4$, 500MHz, 373K): 146.19, 145.50, 134.23, 133.91, 133.59, 132.33, 125.35, 122.72, 122.61, 120.22, 119.98, 31.63, 31.34, 31.25, 31.03, 30.80, 29.45, 29.38, 29.32, 29.02, 22.31, 13.61. MALDI-TOF-MS (TCNQ as matrix): m/z 1309.69, cacld.: 1310.15. Elemental analysis: Calculated: C 77.01, H 8.31, S 14.68; Found: C 77.10, H 8.26, S 14.62.

2,8,11,17-tetra(trimethylsilyl)coroneno[2,1-b:3,4-b':5,6-b'':8,7-b''':9,10-b'''',11,12-b''''']hexathiophene and 2,8,11,17-tetra(trimethylsilyl)coroneno[2,1-b:3,4-b':6,5-b'':8,7-b''':9,10-b'''',11,12-b''''']hexathiophene (2b)

Compound **6b** (200 mg, 0.21 mmol) was photo-cyclodehydrogenated using the procedure for **1b,** the reaction mixture was washed with sodium sulfite solution and extract with DCM, dried over Na_2SO_4, evaporated to afford the partial fused intermediate **7** and used for next step without further purification. Compound **7** was dissovled in anhydrous CH_2Cl_2 (100 mL) and bubbled with argon for 20 minutes. Then a solution of $FeCl_3$ (170 mg, 1.05 mmol) in CH_3NO_2 (2.0 mL) was added dropwise. The reaction mixture was further stirred at room temperature with argon bubbling for 30 min. Methanol was added, the resulted precipitate was collected by filtration, washed by methanol to afford **2b** as a yellow solid (161 mg) in 83% yield.



^1H NMR (CD_2Cl_2): δ (ppm) 9.28 (s, 2H), 8.99(s, 2H), 8.65(d, J = 5.0 Hz, 2H), 8.04(d, J = 5.0 Hz, 2H), 0.81(s, 18H), 0.77 (s, 18H); ^{13}C NMR ($C_2D_2Cl_4$, 500MHz, 393K): 144.96, 144.32, 140.24, 134.69, 134.28, 132.64, 132.62, 126.22, 121.34, 120.22, 29.36, -0.02. MALDI-TOF-MS (TCNQ as matrix): m/z 924.55, cacld.: 924.08. Elemental analysis: Calculated: C 62.29, H 4.79, S 20.79; Found: C 62.51, H 4.73, S 20.66.

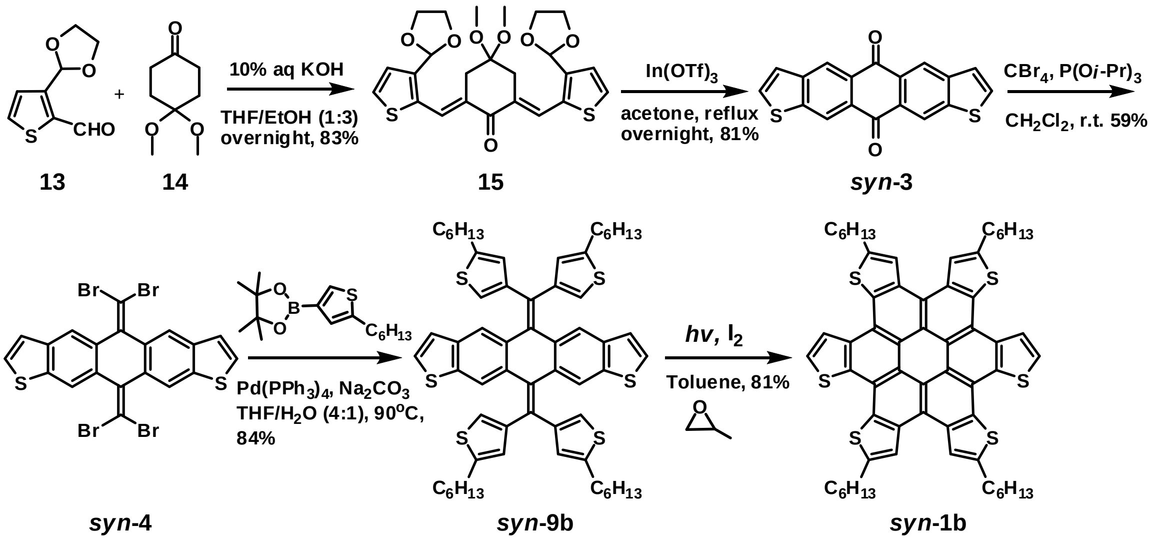


Scheme S1. Synthesis of **TMS-TTC**.

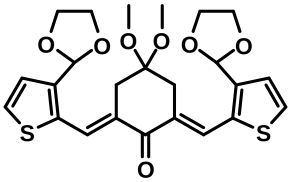
9,10-bis(bis(5-(trimethylsilyl)thiophen-2-yl)methylene)-9,10-dihydroanthracene (11). Compound **11** was synthesized using identical conditions with that of **6b** from **10** and **5b** in 88% yield as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.24-7.20 (m, 4H), 7.13 (m, 8H), 6.93-6.89 (m, 4H), 0.33 (s, 36H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 149.15, 141.53, 138.78, 138.04, 134.00, 129.67, 127.61, 126.03, 0.00. FD-MS (8 KV): m/z 821.10, cacld.: 821.49.

Compound **12** was synthesized using identical condition with that of **1b**. Toluene was evaporated, the residue was purified by column chromatography (Hexane/CH_2Cl_2 = 3:1), collected the first bright yellow fraction. Evaporated and dried under vaccum afford compound **12** as a light yellow solid in 87% yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.82 (s, 2H), 8.45 (s, 2H), 7.94-7.90 (m, 2H), 7.70 (d, J = 5.0 Hz, 2H), 7.51(d, J = 5.0 Hz, 2H), 7.06-7.02 (m, 2H), 0.54 (s, 18H), 0.45 (s, 18H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 149.94, 146.53, 144.74, 143.36, 136.79, 135.38, 132.84, 130.10, 129.81, 126.95, 125.92, 125.88, 125.34, 123.98, 123.87, 0.18, 0.00. FD-MS (8 KV): m/z 816.67, cacld.: 817.45.

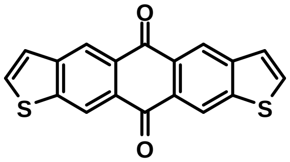
2,5,8,11-tetra(trimethylsilyl)coroneno[2,1-b:3,4-b’:8,7-b’’:9,10-b’’’]tetra-thiophene (TMS-TTC). Compound **12** (90 mg, 0.11 mmol) was dissovled in anhydrous CH_2Cl_2 (30 mL) and bubbled with argon for 20 minutes. Then a solution of $FeCl_3$ (89 mg, 0.55 mmol) in CH_3NO_2 (1.0 mL) was added dropwise. The reaction mixture was further stirred at room temperature with argon bubbling for 30 min. Methanol was added, the resulted precipitate was collected by filtration, washed by methanol to afford **TMS-TTC** as a yellow solid (74 mg) in 85 % yield. ^{1}H NMR (CD_2Cl_2): δ (ppm) 8.96 (s, 4H), 8.71 (s, 4H), 0.82 (s, 36H); ^{13}C NMR (CD_2Cl_2): δ (ppm) 142.33, 137.72, 136.37, 129.59, 123.95, 122.03, 121.79. 0.00. MALDI-TOF MS (TCNQ as matrix): m/z 812.17, cacld.: 812.14. . Elemental analysis: Calculated: C 64.97, H 5.45, S 15.77; Found: C 64.78, H 5.63, S 15.68.



Scheme S2. Synthesis of isomerically pure ***syn*-1b**. Compound **13**,[S5] **14**[S6] were prepared according the reported procedures.

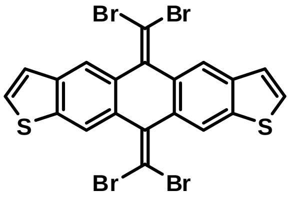


15: To a solution of **13** (653mg, 3.55 mmol) and **14** (267 mg, 1.69 mmol) in THF (4 ml) and EtOH (12 ml) was added an aqueous solution of 10% KOH (0.1 ml). The mixture was stirred at r.t. overnight. The resulted precipitate was collected by filtration, washed with EtOH (2×5 ml), dried under vacuum to afford **15** (683 mg, 83%) as a bright yellow solid. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.25 (s, 2H), 7.46 (d, J = 5.0 Hz, 2H), 7.27(d, J = 5.0Hz 2H), 6.09 (s, 2H), 4.16-4.00 (m, 8H), 3.21 (s, 6H), 3.15(brs, 4H).^{13}C NMR (CD_2Cl_2): δ (ppm) 187.76, 142.17, 136.56, 130.05, 128.72, 128.54, 127.59, 99.36, 98.54, 65.63, 48.75, 35.81. FD-MS (8 KV): m/z 490.32, cacld.: 490.59.

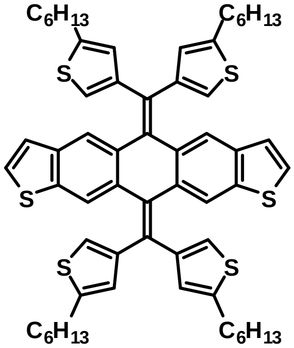


***syn*-3:** To a mixture of compound **15** (235 mg, 0.48 mmol) and In(OTf)$_3$(66 mg, 0.12 mmol) was added anhydrous acetone 10 ml, the resulted suspension was heated to reflux overnight. The reaction mixture was cooled to r.t., filtered and washed with acetone (10 ml) and CH_2Cl_2 (5 ml) to afford syn-3 as a yellow solid (124 mg, 81%).

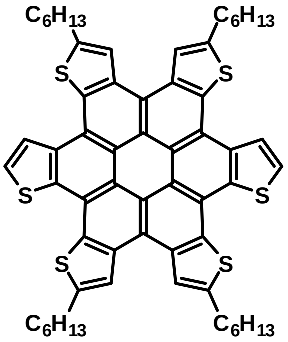
^1H NMR ($CDCl_3$): δ (ppm) 8.90 (s, 2H), 8.82 (s, 2H), 7.77 (d, J = 5.0 Hz, 2H), 7.59 (d, J = 5.0Hz 2H). This compound was insufficiently soluble for ^{13}C NMR measurement. FD-MS (8 KV): m/z 319.97, cacld.: 320.38.



***syn*-4:** A solution of P(O-*i*Pr)$_3$ (0.4 mL, 1.60 mmol) in dichloromethane (10 mL) was added dropwise under Ar to a suspension of quinone ***syn*-3** (65 mg, 0.20 mmol) and CBr_4 (530 mg, 1.60 mmol) in dichloromethane (20 mL) at 0°C. The mixture was then stirred at room temperature under Ar overnight. The reaction mixture was filtered, washed with dichloromethane. The filtrate was collected and evaporated, the residue was purified by Si gel chromatography (hexane/dichoromethane = 1/1 as eluent). The first fraction was collected, evaporated and dried under vacuum afford compound ***syn*-4** (76 mg, 67%) as an off-white solid ^1H NMR (250 MHz, CD_2Cl_2), δ (ppm): 8.31 (s, 2H), 8.26 (s, 2H), 7.56 (d, J = 5.0 Hz, 2H), 7.39 (d, J = 5.0 Hz, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm): 140.55, 140.33, 139.03, 138.84, 133.18, 132.70, 129.27, 124.46, 123.18, 122.23. FD-MS (8 KV) : m/z 631.93, cacld.: 632.02.



***syn*-9b:** Compound ***syn*-4** (63 mg, 0.1 mmol), thiophene-β-boronic ester **8b** (177 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (12 mg, 10 μmol) were put into a 100 mL two-necked flask. A degassed THF (6 mL) was added under argon, the resulted solution was degassed by freeze-pump-thaw cycles. An aqueous solution (1.5 mL) of Na_2CO_3 (85 mg, 0.8 mmol) was added under argon. The mixture was further degassed by freeze-pump-thaw cycles and then stirred at 90°C overnight. The mixture was cooled to room temperature, THF was evaporated and the resulted residue was extracted with CH_2Cl_2. The organic phase was washed with water and brine, dried with anhydrous Na_2SO_4. Compound ***syn*-9b** (82 mg, 84%) was isolated by column chromatography (Hexane/CH_2Cl_2 = 3:1) as a light yellow solid.^{1}H NMR (250 MHz , CD_2Cl_2), δ (ppm): 7.60 (s, 2H), 7.55 (s, 2H), 7.29 (d, J = 5.0 Hz, 2H), 7.03 (d, J = 5.0 Hz, 2H), 6.95 (brs, 4H), 6.67 (brs, 4H), 2.70 (t, J = 7.5 Hz, 8H), 1.24 (m, 24H), 0.88 (t, J = 7.5 Hz, 12H); δ (ppm) 146.12, 145.93, 142.19, 142.00, 138.05, 137.94, 136.30, 136.08, 135.55, 135.38, 130.42, 130.22, 127.07, 126.98, 126.88, 124.21, 122.92, 121.84, 121.78, 121.71, 32.27, 32.22, 32.09, 32.07, 30.52, 30.49, 29.18, 29.12, 23.07, 14.47. FD-MS (8 KV): m/z 981.33, cacld.: 981.57.



***syn*-1b:** A mixture of ***syn*-9b** (60 mg, 0.06 mmol), iodine (76 mg, 0.30 mmol) and propylene oxide (1.6 mL) in anhydrous toluene (60 mL) was irradiated with UV light at 300 nm wavelength overnight. The solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane/DCM = 3:1) to afford ***syn*-1b** (49 mg, 81%) as a brownish yellow solid. ^{1}H NMR (d_8-THF, 500MHz, 333K): δ (ppm) 8.78 (d, J = 5.0Hz, 2H), 8.24 (s, 2H), 8.07 (s, 2H), 7.98 (d, J = 5.0Hz, 2H), 3.23 (t, J = 7.5 Hz, 4H), 3.15 (t, J = 7.5 Hz, 4H), 2.03-1.96 (m, 8H), 1.72-1.60 (m, 8H), 1.53-1.43 (m, 16H), 0.99-0.95 (m, 12H); ^{13}C NMR (d_8-THF, 500MHz, 373K): 145.96, 135.11, 134.75, 134.47, 133.26, 126.27, 126.18, 123.91, 123.71, 121.04, 32.94, 32.74, 32.60, 32.07, 31.84, 30.34, 23.78, 14.64. MALDI-TOF-MS (TCNQ as matrix): m/z 971.99, cacld.: 972.30. Elemental analysis: Calculated: C 74.03, H 6.21, S 19.76; Found: C 73.91, H 6.13, S 19.53.

Section 3. MALDI-TOF MS Spectral Profiles

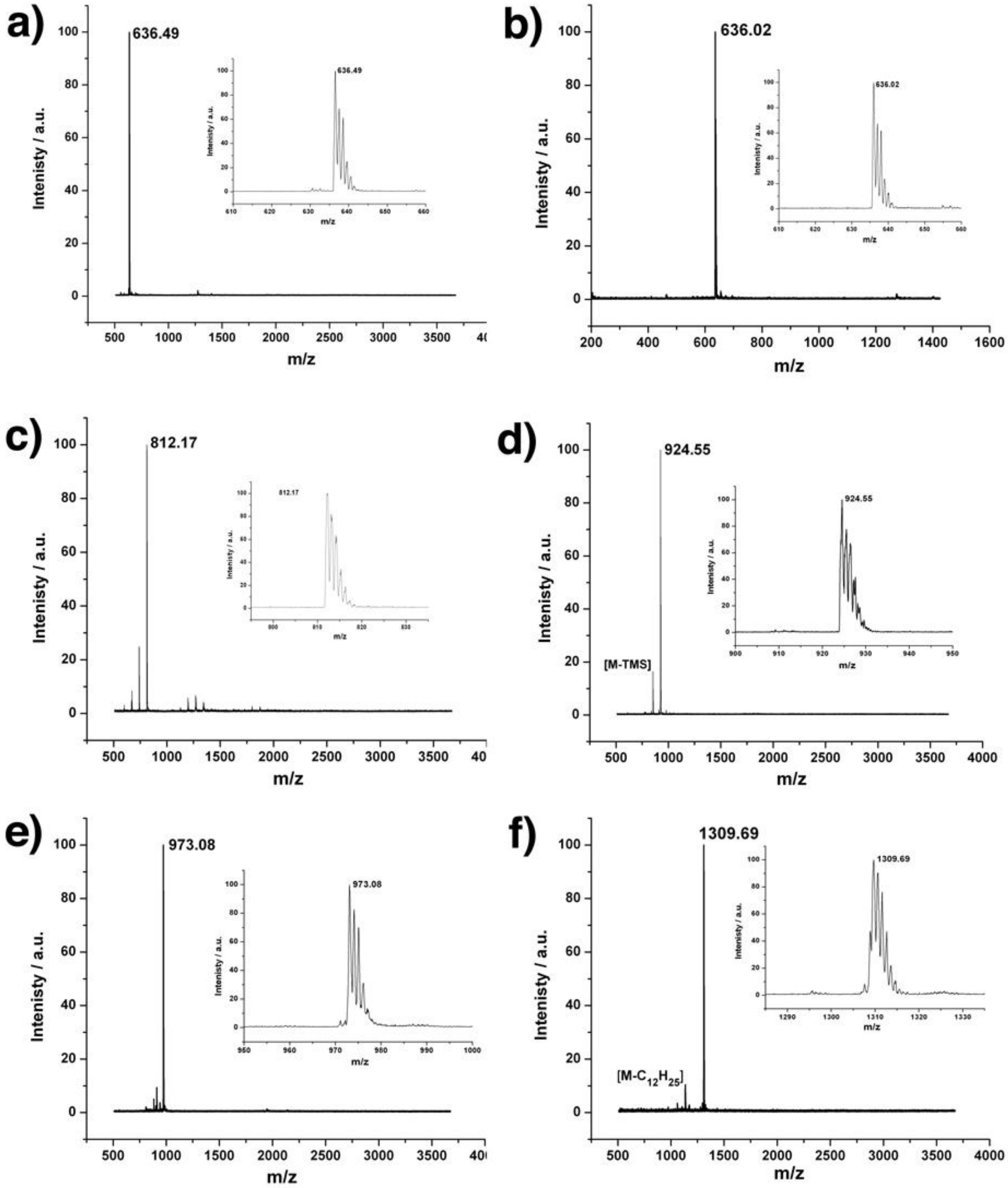


Figure S1. MALDI-TOF MS Spectral Profiles of a) **2a**, b) **1a**, c) **TMS-TTC**, d) **2b**, e) **1b** and f) **1c**.

Section 4. UV/Vis Spectra of HTC 1 and 2

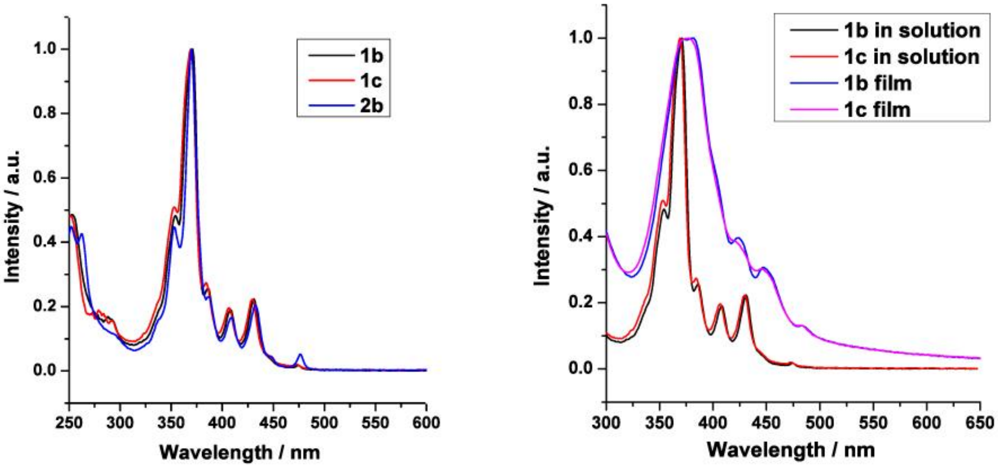


Figure S2. a) Normalized UV/Vis spectra of HTCs **1b**, **1c** and **2b** in CH_2Cl_2 (1.0×10^{-6} M); b) UV/Vis spectra of HTCs **1b**, **1c** in CH_2Cl_2 solution (1.0×10^{-6} M) and spin coated film from toluene (1.0×10^{-3} M). When compared to parent coronene (*p* band, 342 nm; *α* band, 428 nm),[S7] HTCs reveals a bathochormic shift of 91 nm for the *p* band and 48 nm for the α band. These results suggest that fusion of additional four or six thiophene rings to the coronene core leads to an extended π-conjugation.

Section 5. Cyclic Voltammetry and Energy levels

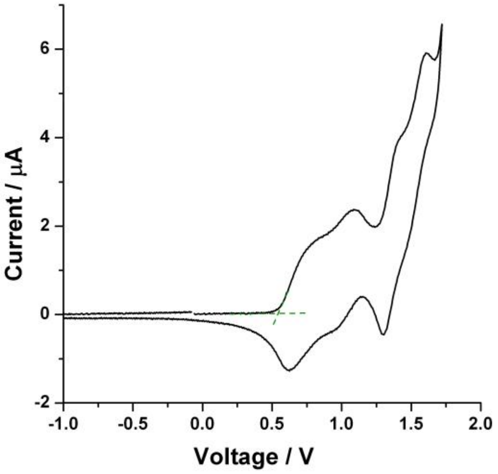


Figure S3. Cyclic voltammetric profile of compound **2b** in dichloromethane solution (0.5 mM) containing 0.1 M Bu_4NPF_6. Potentials are reported versus the Fc/Fc^+ redox couple as an internal standard, scan rate = 100 mV/s.

Table S1. Optical and redox data of HTC **1** and **2**.

Compounds	λ_{abs} **[nm]**[a]	E_{gap} **[eV]**[b]	$E_{ox/onset}$ - $E_{ox/onset(Fc/Fc+)}$ **[V]** [c]	**HOMO[eV]**[d]	**LUMO[eV]**
2b	370	2.57	0.28	-5.08	-2.51
1b	371	2.58	0.20	-5.00	-2.42
1c	369	2.57	0.17	-4.97	-2.40
***c*-DBTTC**[f]	371	2.50	--	-5.10	-2.30

[a] In $CHCl_2$, 1×10^{-5} M, 295K. [b] Determined from the onset of absorption(1×10^{-5} M). [c] In CH_2Cl_2, 0.5 mM, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 100 mV/s, versus Fc/Fc^+. [d] Determined from $E_{HOMO} = -(E_{ox/onset} + 4.80)$ (eV). [e] Calculated from $E_{LUMO} = E_{HOMO} + E_{gap.}$ [f] Data from Ref.S8.

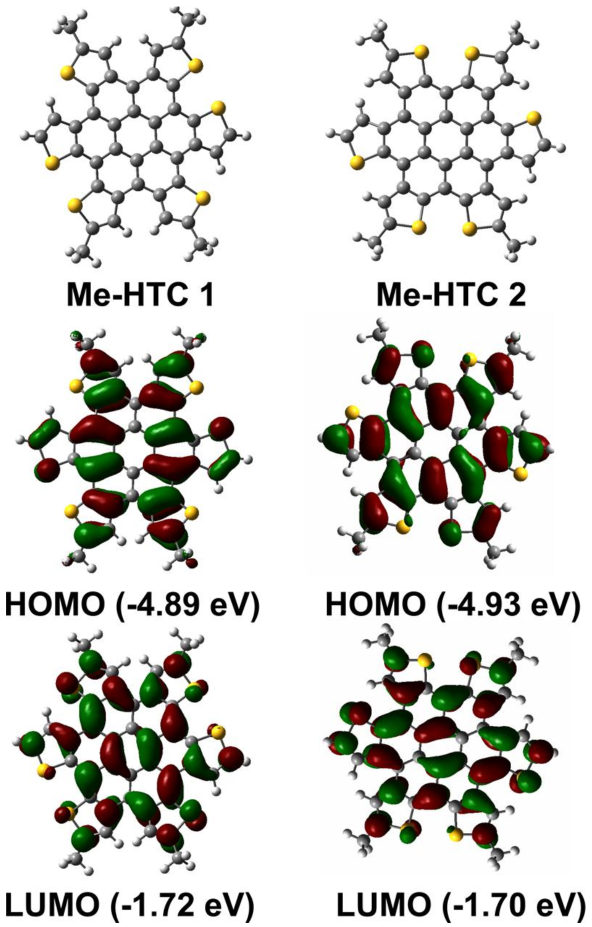


Figure S4. Calculated molecular structures and frontier molecular orbital profiles for Me-HTC **1** (*anti*-form) and Me-HTC **2** (*anti*-form).

Section 6. Differential Scanning Calorimetry (DSC) Traces

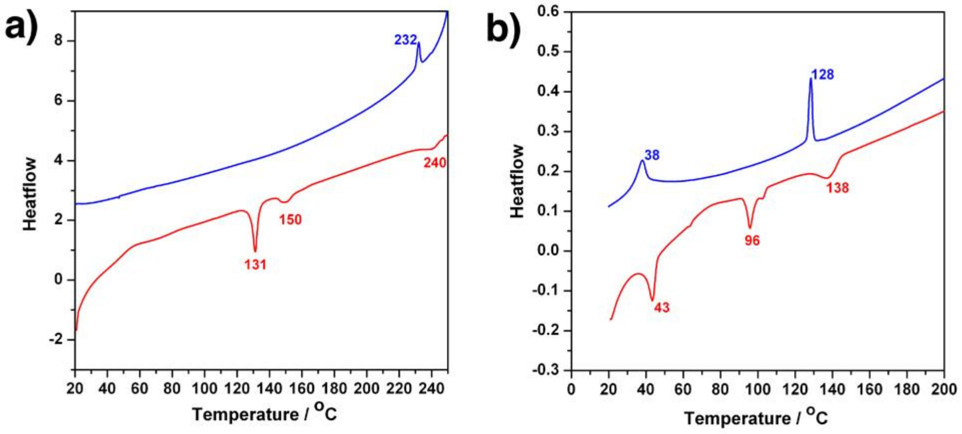


Figure S5. a) DSC traces of **1b** on second heating (red line)/cooling (blue line) (rate: 10 K/min); b) DSC traces of **1c** on second heating (red line)/cooling (blue line) (rate: 10 K /min).

Section 7. Crystal Polymorph of 1b from Toluene and *p*-Xylene

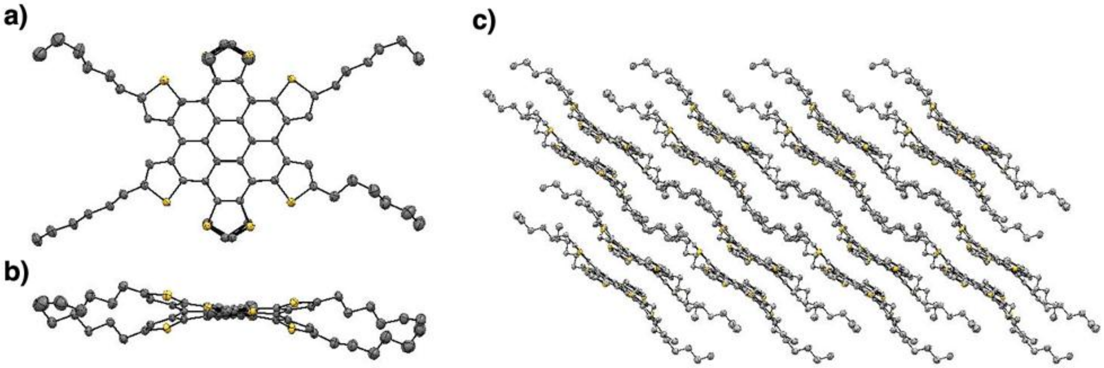


Figure S6-1. Crystal structure of HTC **1b** from toluene. a) Top and b) side views in ellipsoid drawing; c) Packing mode along *b* axis. Hydrogen atoms are not shown for clarity. Gray = carbon, yellow = sulphur. CCDC-876942: 010×0.18×0.36 mm; triclinic; space group *P-1*; a = 13.8948(9), b = 14.4076(8), c = 14.5193(7); α = 61.552(3), β = 70.858(3), γ = 74.447(3); V = 2392.3(2); Z = 2; T = 120 K; total reflections = 21994; unique reflections = 10316; full-matrix least-squares refinement on F; semiempirical absorption correction from equivalents; final R indices ($F_o > 4\sigma(F_o)$) are R_1 = 0.0693 and wR_2 = 0.0643 (R_1(all data) = 0.1133 and wR_2(all data) = 0.0822);

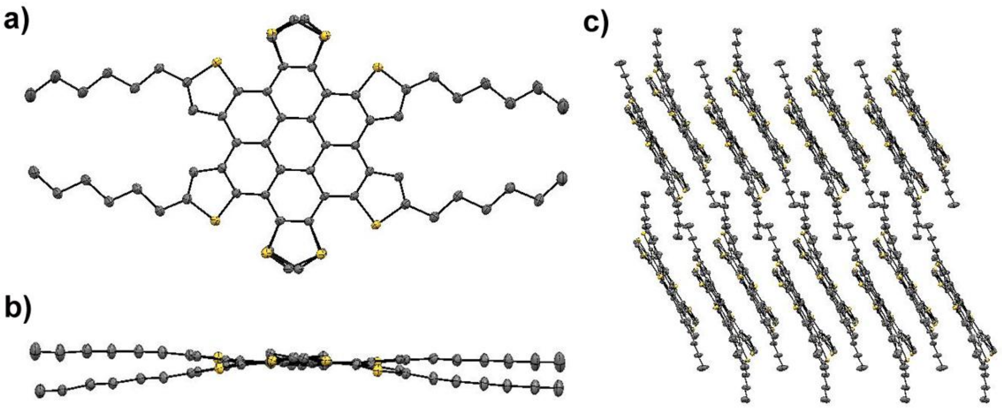


Figure S6-2. Crystal structure of HTC **1b** from *p*-xylene. a) Top and b) side views in ellipsoid drawing; c) Packing mode along *c* axis. Hydrogen atoms are not shown for clarity. Gray = carbon, yellow = sulphur. CCDC-869826: 0.14 ×0.20×0.39 mm; triclinic; space group *P-1*; a = 7.9721(3), b = 17.2319(8), c = 18.5026(9); α = 109.117(2), β = 91.667(3), γ = 93.427(3); V = 2394.12(19); Z = 2; T = 120K; total reflections = 28308; unique reflections = 13364; full-matrix least-squares refinement on F; semiempirical absorption correction from equivalents; final R indices ($F_o > 4\sigma(F_o)$) are R_1 = 0.0467 and wR_2 = 0.0554 (R_1(all data) = 0.0970 and wR_2(all data) = 0.0801).

Section 8. Crystal structure of *syn*-1b

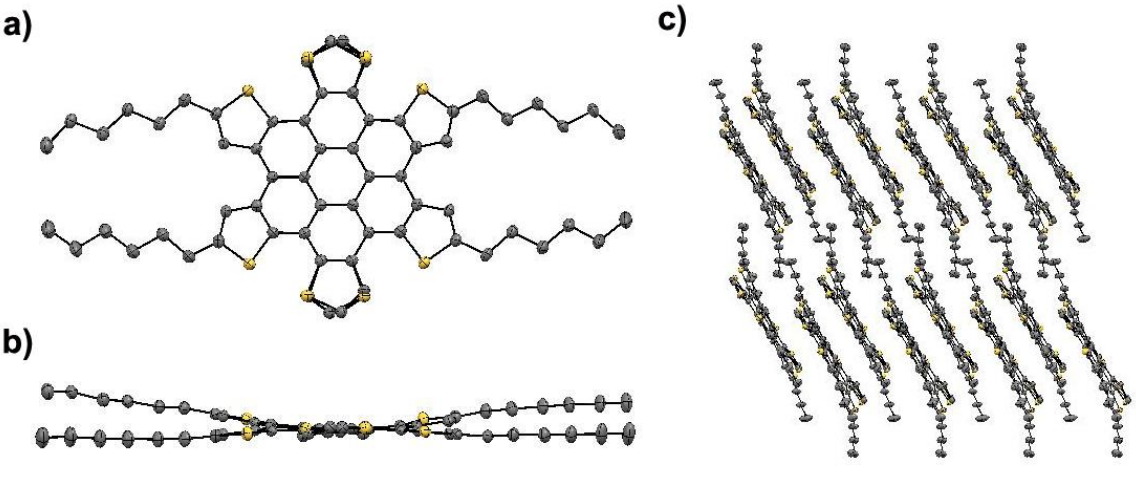


Figure S7. Crystal structure of *syn*-HTC **1b** from *p*-xylene. a) Top and b) side views in ellipsoid drawing; c) Packing mode along *c* axis. Hydrogen atoms are not shown for clarity. Gray = carbon, yellow = sulphur. CCDC-895213: a = 7.9799(2), b = 17.2385(6), c = 18.5251(6); α = 109.097(1), β = 91.517(2), γ = 93.589(9); V = 2400.39(13); Z = 2; T = 120K; total reflections = 30293; unique reflections = 12715; full-matrix least-squares refinement on F; semiempirical absorption correction from equivalents; final R indices

($F_o > 4\sigma(F_o)$) are $R_1 = 0.0539$ and $wR_2 = 0.0613$ (R_1(all data) = 0.0950 and wR_2(all data) = 0.0651).

Section 9. Comparison of the NMR spectra of *syn*/*anti*-9b and *syn*-9b and *syn*/*anti*-1b and *syn*-1b

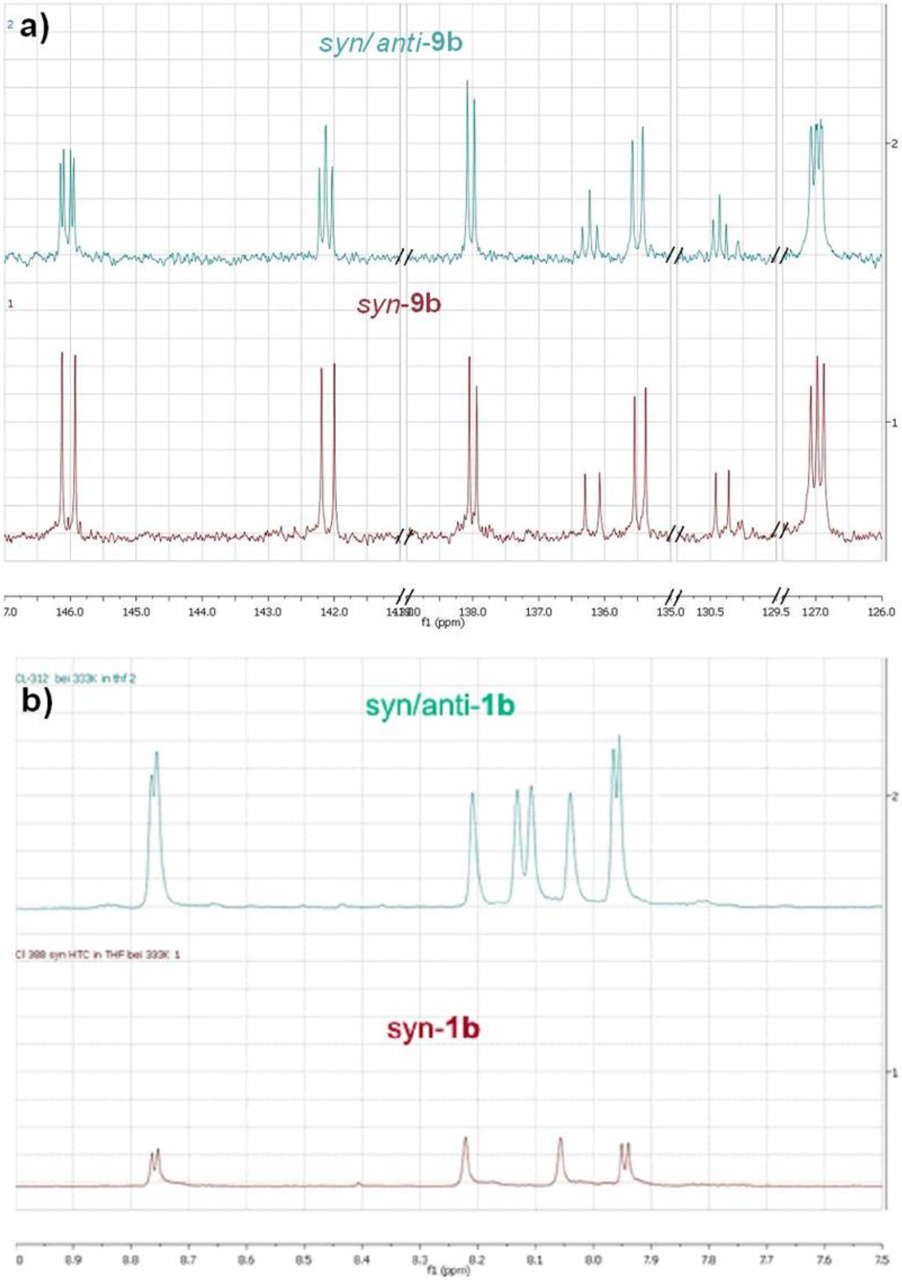


Figure S8. a) Comparison of selected window of ^{13}C NMR spectra of *syn*/*anti*-**9b** and *syn*-**9b**; b) Comparison of selected window of ^{1}H NMR spectra of *syn*/*anti*-**1b** and *syn*-**1b.**

Section 10. GIWAXS Patterns

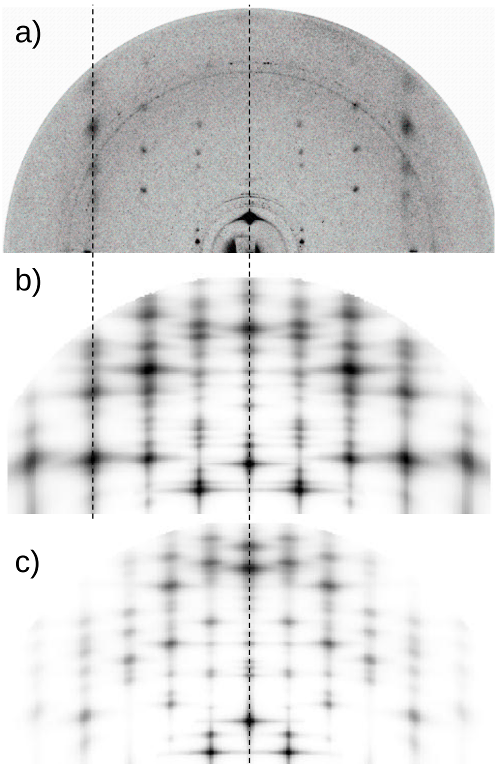


Figure S9. GIWAXS pattern of thin films of **1b**, simulated patterns of **1b** based on the single crystal data from b) toluene and c) *p*-xylene. Dashed lines are guides for the eye of same scattering lines.

Section 11. Output and transfer characteristics of vacuum deposited thin film transistors of HTC 1a and 1b.

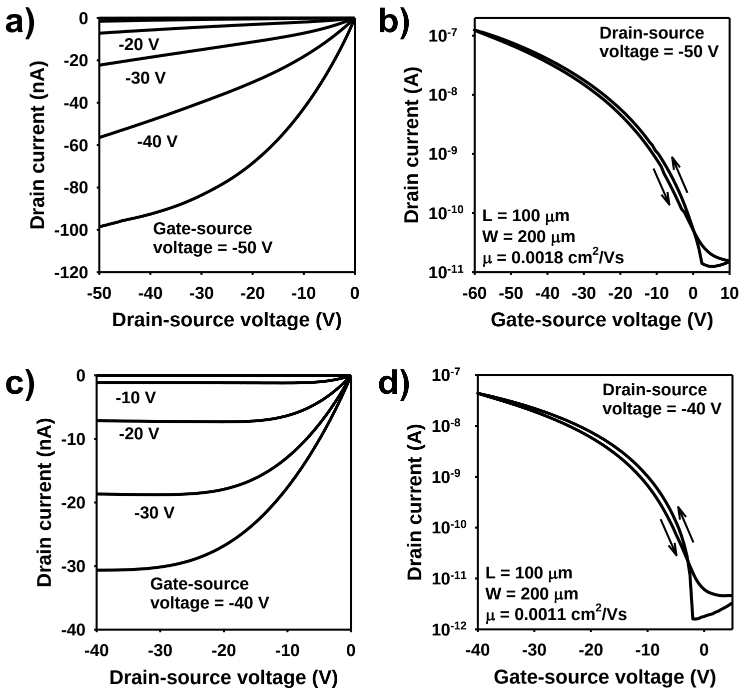


Figure S10. a) Output and b) transfer characteristics of a bottom-gate, top-contact transistor based on a vacuum-deposited layer of **1a**. c) Output and d) transfer characteristics of a bottom-gate, top-contact transistor based on a vacuum-deposited layer of **1b**. Both on/off current ratio of **1a** and **1b** were 10^4.

Section 12. AFM Images and PXRD Pattern of Vacuum Deposited Films of 1a and 1b

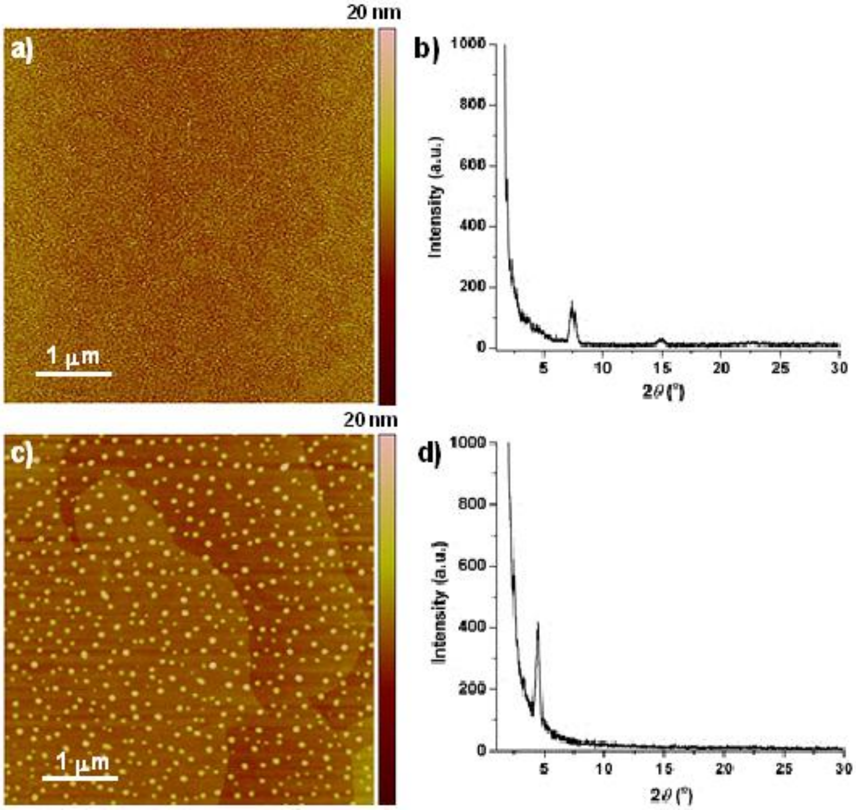


Figure S11. AFM images of the vacuum deposited films (30 nm) of a): **1a**, c): **1b**; PXRD pattern of vacuum deposited films (30 nm) of b): **1a**, d): **1b.**

Section 13. Supporting Referrences

S1. Chotana, G. A.; Kallepalli, V. A.; Maleczka Jr, R. E.; Smith Iii, M. R. *Tetrahedron* **2008**, *64*, 6103-6114.

S2. Brusso, J. L.; Hirst, O. D.; Dadvand, A.; Ganesan, S.; Cicoira, F.; Robertson, C. M.; Oakley, R. T.; Rosei, F.; Perepichka, D. F. *Chem. Mater.* **2008**, *20*, 2484-2494.

S3. Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2004**, *126*, 3108-3112.

S4. Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664-672.

S5. Hibino, S.; Kano, S.; Mochizuki, N.; Sugino, E., *J. Org. Chem.* **1984,** *49* (25), 5006-5008.

S6. Lehnherr, D.; Hallani, R.; McDonald, R.; Anthony, J. E.; Tykwinski, R. R., *Org. Lett.* **2012,** *14*, 62-65.

S7. Newman, M. S. *J. Am. Chem. Soc.* **1940**, *62*, 1683-1687.

S8. Chiu, C.-Y.; Kim, B.; Gorodetsky, A. A.; Sattler, W.; Wei, S.; Sattler, A.; Steigerwald, M.; Nuckolls, C. *Chem. Sci.* **2011**, *2*, 1480-1486.