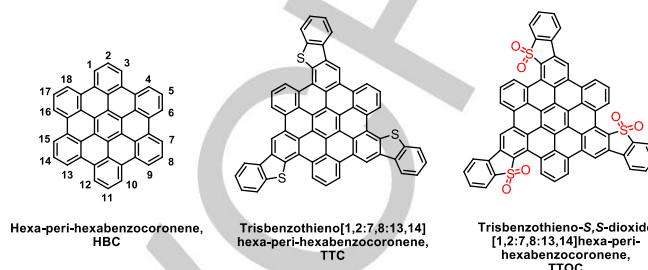


Derivatizing Tribenzothiophene Fused Hexa-*peri*-hexabenzocoronenes with Tunable Optoelectronic Properties

Yi Liu⁺,^[a] Tomasz Marszalek⁺,^[a] Klaus Müllen,^[a] Wojciech Pisula^{*, [a,b]} and Xinliang Feng^{*, [c]}

Abstract: A series of Trisbenzothieno[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronenes were synthesized and characterized by a combination of NMR, 2D NMR, MALDI-TOF MS, UV/Vis absorption spectroscopy, and 2D-WAXS measurement. By structural modulation like decoration of electro-donating alkoxy chain, and conversion from electron-rich thiophene ring into electron-poor thiophene-S,S-dioxide moiety, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the hexabenzocoronenes derivatives can be effectively tuned which is further verified by the DFT calculations and cyclic voltammetry.



Scheme 1. Representative structure of hexa-*peri*-hexabenzocoronene, trisbenzothieno[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronene and trisbenzothieno-S,S-dioxide[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronene.

Polycyclic aromatic hydrocarbons (PAHs), such as triphenylenes and hexa-*peri*-hexabenzocoronenes (HBCs),^[1] have attracted enormous attention in the fields of synthetic chemistry and organic semiconducting materials because of their unique optoelectronic properties^[2] and supramolecular behavior^[3]. For example, HBCs bearing long aliphatic side chains can self-organize into one-dimensional columnar superstructures in the solid state, which is highly promising for organic field-effect transistors. The fusion of thiophene rings at the periphery of PAHs offers the opportunity to tune their electronic energy levels, packing motifs and charge transport properties^[4], which is widely used in the design of novel organic semiconductors^[5]. Therefore, by combining these two types of fascinating π -conjugated structures, we have previously synthesized a tribenzo[b,b',b'']tribenzo[2,3:6,7:10,-11]coroneno[1,12-fg:5,4-f'g'-:9,8-f''g'']tris[1]benzothiophene (Trisbenzothieno[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronene, TTC Scheme 1)^[6], in which three benzothiophene rings are fused to the HBC periphery with a C3 symmetric architecture. Fusion with benzothiophene moieties renders an HBC derivative with extended π -conjugation and offers the potential for further chemical modification on S atoms, like oxidation of the thiophene ring into thiophene-S,S-dioxide^[7]. However, the poor solubility of unsubstituted TTC has hindered detailed studies of its optoelectronic properties and supramolecular behaviors.

Herein, a series of TTC derivatives bearing alkoxy and alkyl chains were successfully synthesized, and showed good solubility in common organic solvents (like dichloromethane, tetrahydrofuran). Of particular interest, we developed a new protocol to modulate the electronic energy level and self-assembly behavior of TTC via the oxidation of S atoms into the thiophene-S,S-dioxide moieties (Trisbenzothieno-S,S-dioxide[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronene, TTOC, Scheme 1), which are integrated into the π -conjugated skeleton. Both the decoration of electron-donating alkoxy chains and conversion from the electron-rich thiophene ring into electron-poor thiophene-S,S-dioxide units would be capable of tuning the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. Furthermore, unique helical packing in bulk with a relatively long pitch (3.4 nm) was achieved for alkyl chain-substituted TTCs.

The synthesis of TTCs **6** bearing linear or branched alkoxy chains was based on the key building block, 1,3,5-tris-(2'-bromo-4'-methoxyphenyl)benzene (**2**)^[8], which was readily obtained via acid-catalyzed condensation of 2-bromo-4-methoxyacetophenone (**1**, Scheme 2). The synthetic route consisted of Suzuki coupling of **2** with 4-dibenzothiophenylboronic acid, BBr_3 induced deprotection of the methoxy group, and then a substitution reaction with the desired alkyl bromide to afford the oligophenylene precursor (**5a-e**) with various alkoxy chains. An intramolecular oxidative cyclodehydrogenation reaction of **5a-e** was then performed with FeCl_3 as the Lewis acid and oxidant to provide targeted compounds **6a-e** substituted with different alkoxy chains (linear or branched) as orange powder. The products were well soluble in common organic solvents, including dichloromethane (DCM), toluene, and tetrahydrofuran (THF). MALDI-TOF mass spectrometry (Figure S1-S5 in Supporting Information) of **6a-e** indicated a single species with desired molecular weight and isotopic distributions consistent with the calculation. ^1H NMR spectra further validated the chemical identity of **6a-e** (see Supporting Information).

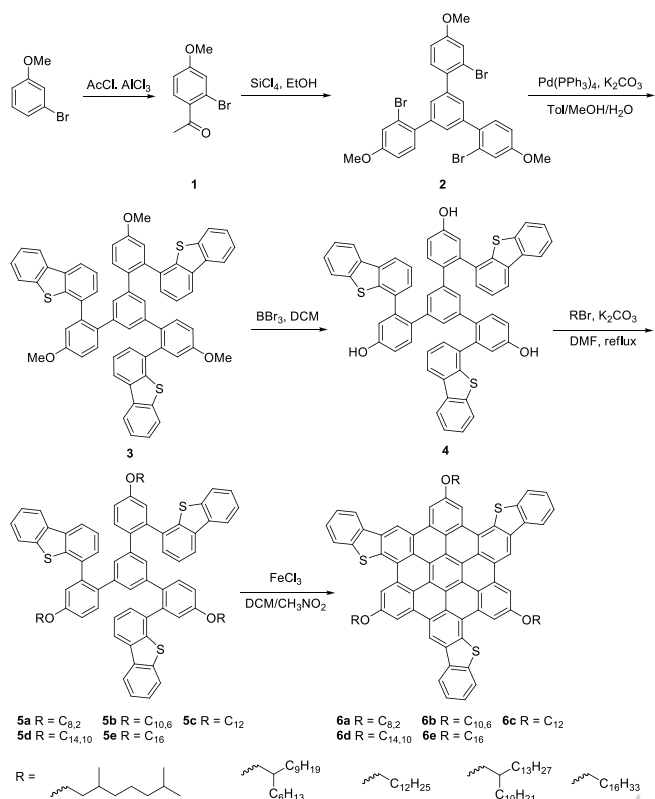
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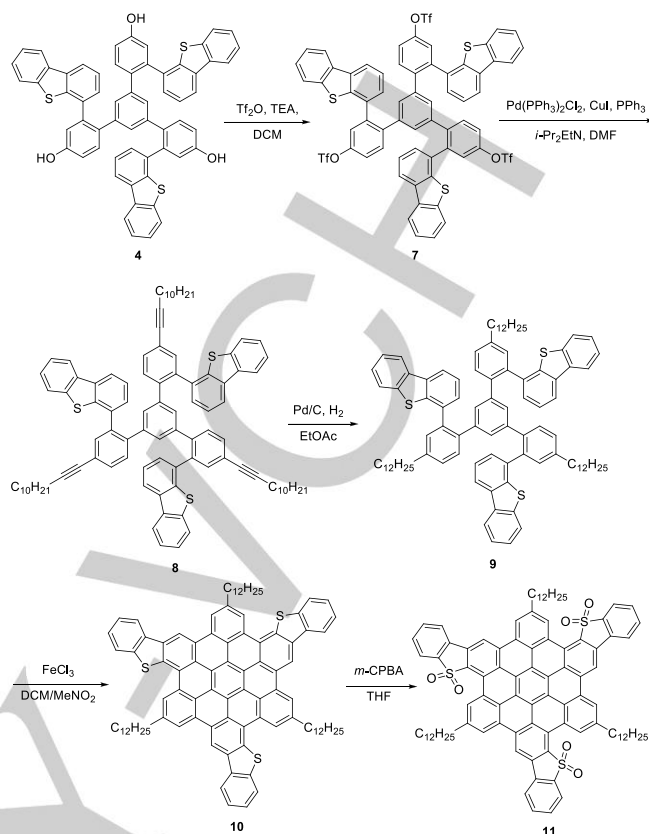
[+] These authors contributed equally to this work.

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Scheme 2. Synthetic routes towards TTCs **6** bearing alkoxy chains.

To modulate the electronic structure of TTCs, oxidation of the sulfur atoms on compound **6a** was initially conducted. Decomposition of the alkoxy chain when oxidizing sulfur atoms using an oxidant like *meta*-chloroperoxybenzoic acid (*m*-CPBA), however, prohibited us from obtaining the desired compound with thiophene-*S,S*-dioxide units fused on the π -conjugation frameworks. Therefore, we turned to the synthesis of TTC **10** with alkyl substitutions based on the precursor **4** (Scheme 3). After conversion of the phenol group of **4** to aryl triflate, introduction of the alkyl chain on compound **7** via Sonogashira coupling and a hydrogenation reaction of **8** followed by intramolecular cyclodehydrogenation of precursor **9** produced a tridodecyl chain-substituted TTC **10** as an orange powder with an overall yield of 41% in just 4 steps. MALDI-TOF mass spectrometry of **10** revealed a single species with isotopic distribution, consistent with the calculation results, and the peak *m/z* of 1345.5 was also in good agreement with its molecular weight of 1345.98 g/mol (Figure S6). ¹H NMR in C₂D₂Cl₄ with a detailed proton signal assignment is given in the Supporting Information (Figure 1, Figure S7-S9), validating the chemical structure of the desired compound.



Scheme 3. Synthetic routes toward tridodecyl chain-substituted TTC **10** and TTC **11**.

Compound **10** was subsequently subjected to the reaction with *m*-CPBA in THF at room temperature. After quenching the reaction with methanol (MeOH), filtration, and thoroughly washing with MeOH, compound **11** was obtained as a red powder in high yield (85%). MALDI-TOF mass spectrometry of **11** showed a single peak at 1442.5, consistent with the targeted molecular weight of 1441.98 g/mol (Figure S6). Comparison with the simulated isotopic distribution is also shown in the inset of Figure S6.

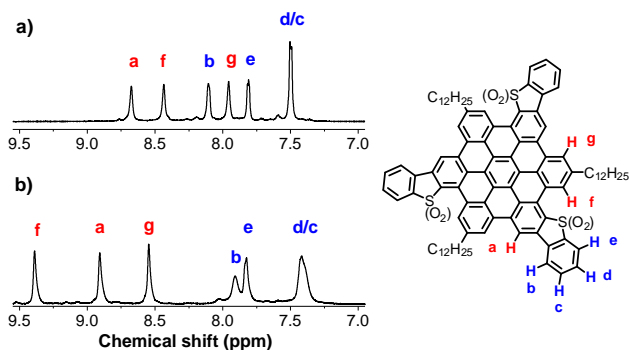


Figure 1. Detailed proton signal assignment of **10** (a) and **11** (b) in C₂D₂Cl₄ (Concentration: 2.3 mM) at 403K.

The chemical identity of **11** with selective oxidation on S atoms was further verified by combined analysis with ^1H NMR, ^1H - ^1H COSY, NOESY, and TOCSY spectra in $\text{C}_2\text{D}_2\text{Cl}_4$ at 403 K (Figure 1, Figure S10-S12), for which signals corresponding to all aromatic protons were rationally assigned. Obvious downfield shifts were observed for the three types of protons (H_a , H_f , H_g) on the HBC cores after oxidation of the S atoms. The signal of the proton H_a located at the phenyl ring where the benzothiophene units are fused showed a downfield shift from 8.67 (for **10**) to 8.91 (for **11**) after oxidation. The peak corresponding to two phenyl protons (H_f/H_g) beside the dodecyl chain shifted from 8.43/7.96 (for **10**) to 9.31/8.55 (for **11**), respectively. For the aromatic protons on the peripheral benzothiophene ring, a slight downfield shift was observed for the signal of the meta proton H_e from 7.81 (for **10**) to 7.83 (for **11**), which was attributed to the deshielding effect of the electron-withdrawing thiophene-S,S-dioxide unit. The signals of the peripheral phenyl protons H_c and H_d emerged into one broad peak, which exhibited an upfield shift from $\delta = 7.50$ for **10** to $\delta = 7.42$ for **11** after oxidation. Moreover, the proton H_b displayed a more pronounced upfield shift from 8.11 (for **10**) to 7.91 (for **11**) after oxidation.

To investigate the impact of the oxidation of an S atom and substitution with an electron-donating alkoxy chain on the photophysical properties of TTC, UV/Vis absorption and fluorescence spectra of **6c**, **10**, and **11** were measured in THF (Figure 2). The absorption maximum of **6c** ($\lambda_{\text{abs}} = 390$ nm, $\epsilon = 0.96 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) exhibited a subtle bathochromic shift compared to that of **10** ($\lambda_{\text{abs}} = 387$ nm, $\epsilon = 1.10 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$), which was attributed to the electron-donating dodecyloxy chain that extends the conjugation.^[9] Compound **11** ($\lambda_{\text{abs}} = 389$ nm, $\epsilon = 0.73 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) also displayed a slightly red shift of the absorption maximum with respect to that of compound **10** due to integration of the electron-withdrawing thiophene-S,S-dioxide unit into the large π -system. Moreover, both compounds **6c** and **11** manifested broader absorption features than **10** with absorption tailing to about 500 nm. For the photoluminescence spectra, the bathochromic shift was more obvious after introduction of the electron-donating alkoxy chain ($\lambda_{\text{lum}} = 539$ nm for **6c**) or electron-withdrawing thiophene-S,S-dioxide unit ($\lambda_{\text{lum}} = 557$ nm for **11**) when compared with alkyl chain-substituted TTC (**10** ($\lambda_{\text{lum}} = 534$ nm)).

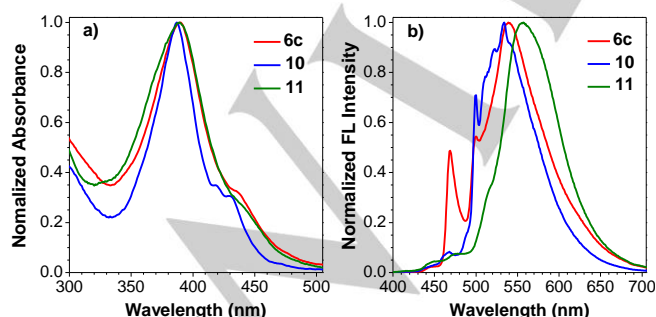


Figure 2. UV/Vis (a) and photoluminescence (b) spectra of **6c**, **10** and **11** (1.0×10^{-5} M in THF).

To further elucidate the photophysical properties, the energy levels of model compounds for **6c**, **10**, and **11** were calculated by the density functional theory (DFT) method at the B3LYP/6-31G(d)^[10] level of theory (Figure 3). After introduction of the alkoxy chain, the HOMO level of **6c** increased to -4.98 eV compared to its alkyl-substituted analog **10** (-5.06 eV), while the LUMO level also increased from -1.80 eV (**10**) to -1.74 eV (**6c**). Notably, the HOMO/LUMO level ($-5.58/-2.34$ eV) of **11** markedly decreased compared with that of **10** ($-5.06/-1.80$ eV) after converting the electron-rich benzothiophene ring into an electron-poor thiophene-S,S-dioxide unit. Nevertheless, the effect of oxidation of the sulfur atom on the band gap was subtle, which was confirmed by the similar absorption spectra for **10** and **11**. On the other hand, cyclic voltammetry measurements for **6c**, **10**, and **11** in DCM were obtained to determine the oxidation potential (Figure S14 in Supporting Information). The HOMO levels calculated from the first oxidation potential for **6c**, **10**, and **11** were -4.90 eV, -4.91 eV and -5.46 eV, respectively, consistent with the values based on DFT calculation. The decreased HOMO level for **11** compared with **10** strongly suggests the enhanced affinity of **11** to electrons, which may be promising for the development of new n-type semiconductors.

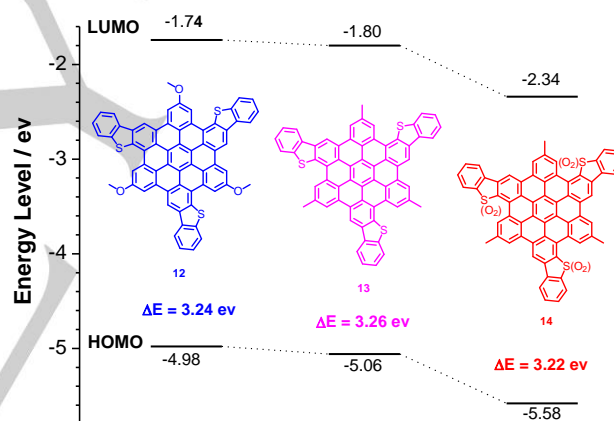


Figure 3. Molecular energy level of model compounds **12**, **13**, **14** for **6c**, **10**, and **11**, respectively, based on B3LYP/6-31G(d) level via DFT calculation (dodecyl chain was substituted with a methyl group to reduce the calculation time).

The bulk thermotropic behavior of **6c**, **10**, and **11** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA exposed a decomposition temperature (corresponding to 5% weight lost) of about 423 °C, 455 °C and 422 °C for **6c**, **10**, and **11**, respectively, while the DSC analyses exhibited no phase transition over the investigated temperature range between 20 °C and 300 °C. The 2D-WAXS pattern of extruded fibers for **6c** in Figure S15c indicates a typical discotic columnar organization, which is observed for a broad range of PAHs in their liquid crystalline phase.^[11] In this state, the columns are characteristically arranged in a hexagonal unit cell with a packing parameter of $a_{\text{hex}} = 2.92$ nm, determined based on the positions of the equatorial reflections. This value is consistent with the molecular

size of **6c**. The position of reflections in the meridional axis of the pattern is attributed to the π -stacking distance of 0.34 nm of the non-tilted disc. The formation of a liquid crystalline at ambient temperature can be correlated with the C3 symmetry of the molecules and the attachment of the relatively flexible alkoxy side chains.^[12] Replacing these dodecyloxy substituents by dodecyls in **10** enhances the supramolecular order (Figure 4a). Although the molecules are also assembled in stacks (π -stacking distance 0.35 nm and orthogonal unit cell $a = 3.25$ nm and $b = 1.92$ nm), the multiple wide-angle meridional and small-angle off-meridional scattering intensities suggest the formation of a complex organization within the columns (Figure 4a). Typically, such scattering patterns are characteristic of helical packing with a relatively long pitch.^[13] In the case of **10**, the pitch length of 3.4 nm was derived from the position of the first scattering line (hk1). Taking into account the simple intermolecular distance of 0.35 nm and the C3 symmetry of the molecule, a rotation angle of 12° between neighboring discs can be concluded (Figure 4b). Simulations by Cerius2 suggested a 2D pattern, which is in good agreement with the experimental data and thus confirm the proposed model. We assume that the slight helical rotation could be triggered by the three benzothiophene units sticking out into the core periphery. Conversion of the planar thiophene ring into more bulky thiophene-S,S-dioxide for **11** slightly increases the π -stacking distance to 0.36 nm and induces a liquid crystalline phase identical to **6c** (Figure S16), but with a cubic intercolumnar arrangement ($a = 2.45$ nm) as the best fit.

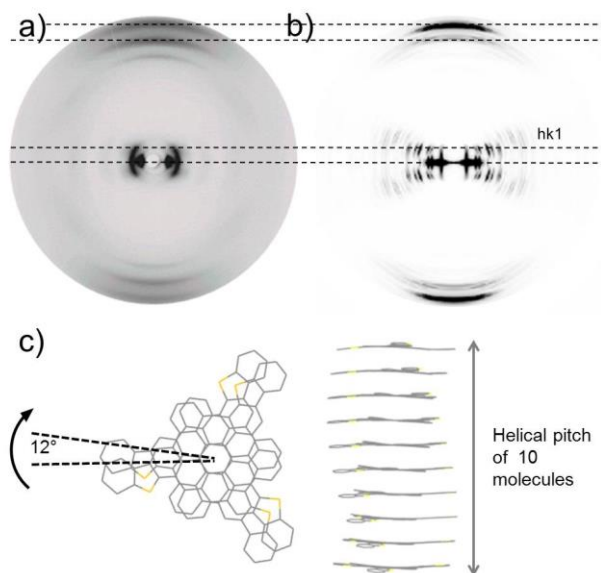


Figure 4. a) 2D-WAXS and b) Cerius2 simulation of **10**, c) packing model for **11** at the top and side view of a column.

In summary, a series of trisbenzothieno[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronenes (TTC) with flexible alkyl or alkoxy chains were readily synthesized. Detailed studies of their optoelectronic properties and supramolecular behavior were

conducted, and tridodecyl chains substituted TTC **10** exhibited unique helical packing in bulk with a relative long pitch (3.4 nm). Furthermore, the electron affinity and energy level of these TTC derivatives could be effectively modulated through converting oxidizing electron-rich thiophene rings into electron-poor thiophene-S,S-dioxide units. This strategy may provide a new pathway for developing organic semiconductors with tunable charge transport properties.

Acknowledgements

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Keywords: hexa-*peri*-hexabenzocoronenes • benzothiophene • oxidation • thiophene-S,S-dioxide • helical packing

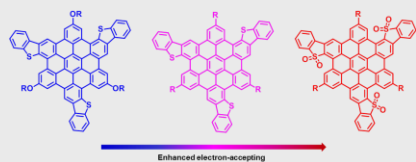
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COMMUNICATION



A series of Trisbenzothieno[1,2:7,8:13,14]hexa-*peri*-hexabenzocoronenes were synthesized. Their optoelectronic properties and supramolecular behavior can be effectively tuned through the attachment of electron-donating alkoxy chains or the conversion of electron-rich thiophene rings to electron-poor thiophene-*S,S*-dioxide moieties.

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