

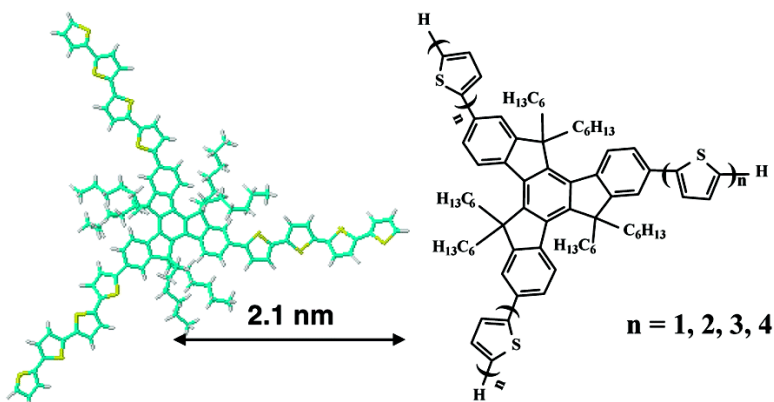
Communication

Star-Shaped Polycyclic Aromatics Based on Oligothiophene-Functionalized Truxene: Synthesis, Properties, and Facile Emissive Wavelength Tuning

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Star-Shaped Polycyclic Aromatics Based on Oligothiophene-Functionalized Truxene: Synthesis, Properties, and Facile Emissive Wavelength Tuning

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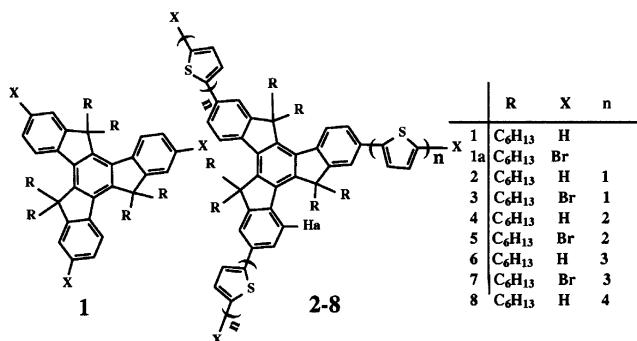
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Most recently, new synthetic methodologies and novel structures have been extensively devoted to investigating thiophene-based electronic materials due to the special intrinsic physical properties of structural and chemical disorder,¹ and the easy modification of the thiophene structure.² The physical properties of π -conjugated organic materials can be tuned by utilizing special structures, effective conjugation length, stereochemistry, or substituents. Such chemical variations not only control the molecular electronic structure, but also undoubtedly alter the collective interactions between chromophores and therefore modify the properties in solid states. The incorporation of thiophene rings onto polycyclic aromatic frameworks also exhibited considerable success when applied to the design and synthesis of unique organic semiconductors.³ Among many polycyclic compounds, the heptacyclic polyarene 10,15-dihydro-5*H*-diindeno[1,2- α ;1',2'-*c*]fluorene (truxene) has been recognized as a potential starting material for the construction of larger polyarenes and a bowl-shaped fragment of the fullerenes and of C_3 tripods materials in asymmetric catalysis and chiral recognition due to the polyarene and planar system.⁴ Some *syn*-trialkylated truxene derivatives exhibited special self-association behavior through arene-arene interaction.⁵ To our best knowledge, although some planar C_3 -symmetric 2,3,7,8,12,13-hexahydroxytruxene derivatives (esters or ethers) have been studied in the field of liquid crystals,⁶ there are no reports on the synthesis and investigation of the optical properties of π -conjugated materials based on the truxene skeleton.

In this Communication, we describe a strategy to obtain precisely well-defined and readily pure luminescent materials of intermediate molecular size (4 nm) with excellent yields, which is a family of well-defined star-shaped compounds with two chromophores (truxene as the core and oligothiophenes as the branches) for understanding the effect of conjugation length and side chains on preventing the self-association through arene-arene interaction to improve the amorphous property of resulting materials. For this purpose, new molecules containing a heptacyclic polyarene with high C_3 -symmetry and thiophene segments have been prepared and characterized to exhibit exceptional optical properties with a stepwise increase of the thiophene ring.

The synthetic approach to desired materials is outlined in Scheme 1. The full alkylation of the anions of the truxene lithium salts afforded **1**. The bromination of **1** afforded 2,7,12-tribromo-5,5',-10,10',15,15'-hexahexyltruxene **1a**. The parent compound in the series, **2**, was obtained via Suzuki cross-coupling reactions of **1a** with 2-thiopheneboronic acid. Reactions were carried out under conditions as we previously reported.^{2f} Treatment of **2** with NBS (3.1 equiv) afforded **3**. Longer thiophene arms were obtained by coupling **3** with 2-thiopheneboronic acid to yield **4**; the repetitive bromination and cross-coupling reactions finally gave the yellow and freely soluble **8**, a star-shaped thiophene-functionalized truxene derivative. The conjugated homologues through Suzuki cross-coupling were isolated in excellent yields of over 90%. Not only did we obtain appropriated ¹H and ¹³C NMR and analytical data,

Scheme 1



we also employed a MALDI-TOF/MS measurement to characterize the structure and molecular weight of new compounds.

After the bromination, the specific double signal in the aromatic range belonging to the three α -thiophene protons disappeared in ¹H NMR spectra (Table S2), and then the specific singlet signal at about δ 111 ppm appeared due to the three α -thiophene carbons in ¹³C NMR spectra. For proton NMR spectra of all oligothiophene-functionalized truxene derivatives, it is astonishing that chemical shifts belonging to methylene groups moved more upfield than those of methyl groups. These chemical shift values (about 0.5–0.6 ppm) were quite lower than those of normal methyl and methylene groups. Some research showed that the self-association by arene stacking for *syn*-5,10,15-trialkylated truxene derivatives in solutions was observed while chemical shifts of **Ha** (protons at the 4-, 9-, and 14-position of truxene) in CDCl₃ were dependent on the concentration, which moved upfield as the concentration increased.^{5b} However, it is worth noting that the chemical shifts of **Ha** for our compounds did not exhibit any change with an increase of the concentration, which indicated that hexahexyl groups efficiently reduced such self-association. Our results described provided a versatile strategy for controlling the morphology of truxene derivatives.

The absorption and emission spectra for compounds **1**, **2**, **4**, **6**, and **8** in THF solution are shown in Figure 1. Oligothiophenes show a strong π - π^* electron absorption band in the visible region, which is progressively red-shifted with increasing chain length. On the basis of the spectroscopic investigation of oligothiophenes, the effective conjugation length is not much longer than 11 repeat units.⁷ As is shown in Table S1, the continuous red shifts of the absorption spectra were observed with a successive increase of thiophene rings in the investigation of the oligothiophene-functionalized truxene derivatives. Compounds **2**, **4**, **6**, and **8** exhibited a maximum absorption at 341, 383, 411, and 424 nm, which was substantially red-shifted relative to those of thiophene, bithiophene (302 nm), terthiophene (354 nm), and quaterthiophene (396 nm), respectively. The electronic absorption maximum for compound **8** (424 nm) is quite close to that of the regioregular polyalkylthiophenes (434 nm). The results suggested the formation of a highly extended π -delocalized system through the truxene core. Moreover, the results all

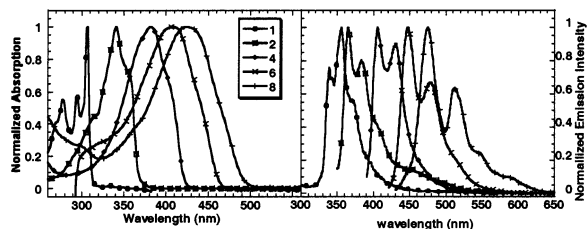
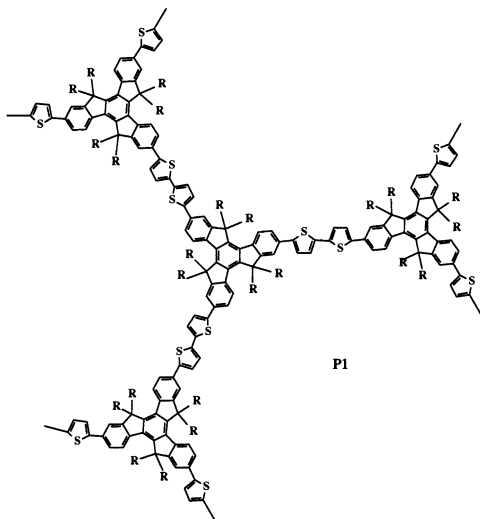


Figure 1. Absorption (left) and emission (right) spectra for compounds in THF solution.

Scheme 2



demonstrated that the emission spectra of truxene derivatives were liable to be tuned by introducing oligothiophene segments. Figure S1 shows plots of the lowest energy transition versus the inverse numbers of thiophene rings for the truxene-core series in THF solution. The linear equations showed a saturation limit for ΔE versus the number (n) of the thiophene rings. The curve about the lowest energy transition versus the numbers of thiophene rings suggested this trend. The PL spectrum of every compound exhibited a maximum with a well-defined vibronic feature, and the difference of peaks was enlarged with an increase of thiophene rings.

We also synthesized a soluble dendritic hyperbranched polymer **P1** utilizing **2** by employing the FeCl_3 mediated oxidative polymerization in chloroform shown in Scheme 2. In Figure S3, we presented the room-temperature absorption and emission spectra of **P1** in THF solution. Both spectra were red-shifted with respect to **2** because of the increase of conjugation length after polymerization. The absorption spectrum peaked at 352 nm with a high shoulder at 405 nm, red-shifted about 11 and 64 nm in comparison with that of **2**; however, the emission spectra exhibited the maximum at 491 nm with another peak (467 nm), which was close to that of **8**, although the absorption spectrum of **P1** was blue-shifted in comparison with those of **6** and **8**. Lack of vibration structure in both spectra was consistent with the disordered nature of the resulting polymer and suggested the existence of a broad distribution of ground- and excited-state molecular conformations. We considered that the large apparent Stokes' shift (about 1 eV) between the emission and absorption maximum also reflected this disorder.

In conclusion, we have shown a facile approach to soluble star-shaped C_3 -symmetric oligothiophene-functionalized polycyclic aromatics based on truxene. The long branches with four thiophene

rings (about 2.1 nm length from the center) were afforded through Suzuki cross-coupling with excellent yields. The ease of synthesis will provide a strategy for us to investigate larger star-shaped polycyclic aromatics. The investigation of ^1H and ^{13}C NMR spectra has indicated that the hexahexyl groups efficiently prevented the self-association through arene–arene stacking, which might improve the amorphous property of the materials in solid states. Chemical shifts belonging to methylene groups moved more upfield than those of methyl groups. These chemical shift values (about 0.5–0.6 ppm) were quite lower than those of normal methyl and methylene groups. We also synthesized a dendritic hyperbranched polymer through oxidative polymerization. The absorption and emission spectra of the desired materials were liable to be tuned by introduction of more thiophene rings. We have set up a platform to understand the photophysical properties of polycyclic conjugated polymers through the investigation of these star-shaped polycyclic aromatics.

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Supporting Information Available: Experimental procedures and all characterization data of new compounds **2–8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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