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SYNTHESIS, STRUCTURE, AND PROPERTIES OF 2,5,8,11,14,17-HEXAMETHYLTRIPHENYLENO[2,1-*b*:3,4-*b*':6,5-*b*'':7,8-*b*''':10,9-*b*'''':11,12-*b*''''']HEXATHIOPHENE

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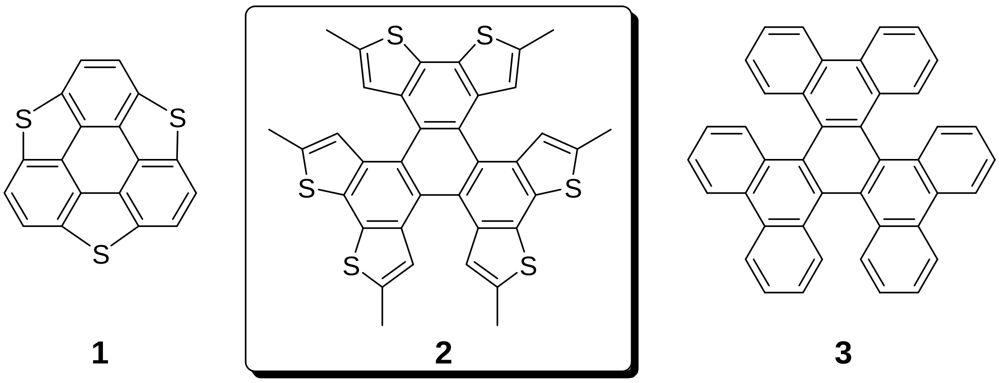
Dedicated to Prof. R. Noyori at the occasions of his 70th birthday

Abstract – 2,5,8,11,14,17-Hexamethyltriphenyleno[2,1-*b*:3,4-*b*':6,5-*b*'':7,8-*b*''':10,9-*b*'''':11,12-*b*''''']hexathiophene has been synthesized by an iron(III)-mediated oxidative cyclization of hexakis(2-methyl-4-thienyl)benzene, and its structure has been determined by an X-ray crystallographic analysis. Electronic properties were investigated by spectroscopic and electrochemical measurements.

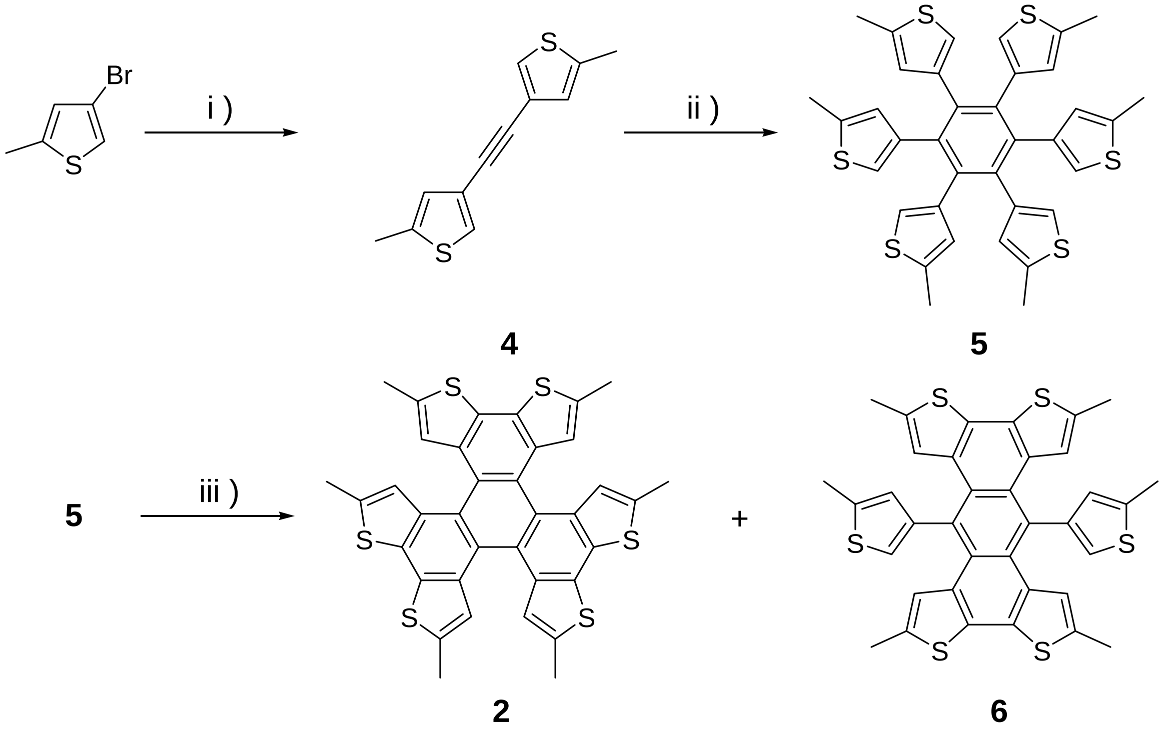
Polycyclic aromatic hydrocarbons (PAHs) represent an important class of fundamental π-systems.[1] Triphenylene, one of the simplest framework of PAHs, and its derivatives have been extensively investigated in terms of their unique structures and properties.[2] To further modulate their inherent structural and electronic features, many benzo derivatives have been synthesized.[3] On the other hand, the incorporation of thiophene rings onto PAHs exhibits considerable success in the design of unique organic semiconductors.[4] In this context, we have previously reported the synthesis, properties, and



1 2 3

Figure 1. Structures of **1**, **2**, and **3**

bowl-shaped structure of triphenyleno[1,12-*bcd*:4,5-*b*'*c*'*d*':8,9-*b*''*c*''*d*'']trithiophene (**1**)[5] that is formally isoelectronic with coronene. Here, we report on the synthesis, structure, and properties of novel six-thiophene-annelated triphenylene **2**, which is isoelectronic with hexabenzotriphenylene **3**.[6,7]



Scheme 1. Synthesis of 2,5,8,11,14,17-hexamethyltriphenyleno[2,1-*b*:3,4-*b*':6,5-*b*'':7,8-*b*''':10,9-*b*'''':11,12-*b*''''']hexathiophene (**2**)

Conditions

i) $PdCl_2(PPh_3)_2$, CuI, ethynyltrimethylsilane, DBU, H_2O, toluene, 80 ºC, 95%;
ii) $Co_2(CO)_8$, 1,4-dioxane, 140 ºC, 87%;
iii) 1) $Fe(ClO_4)_3 \cdot nH_2O$; 2) $H_2NNH_2 \cdot H_2O$, $CHCl_3$/MeCN, rt, **2**: 13%, **6**: 3%.

Although most of triphenylene derivatives have been synthesized by cyclotrimerizations of arynes,[3] our synthesis of 2,5,8,11,14,17-hexamethyltriphenyleno[2,1-*b*:3,4-*b*':6,5-*b*'':7,8-*b*''':10,9-*b*'''':11,12-*b*''''']-hexathiophene (**2**) is based on oxidative cyclization[8] of hexathienylbenzene (**5**) as outlined in Scheme 1. Firstly, bis(2-methyl-4-thienyl)ethyne (**4**) was prepared by the modified Sonogashira coupling reaction in 95% yield.[9] Cobalt-catalyzed cyclotrimerization of **4** gave hexakis(2-methyl-4-thienyl)benzene (**5**) in 87% yield. Oxidative cyclization of **5** by $Fe(ClO_4)_3 \cdot nH_2O$ resulted in the formation of a mixture of **2** and **6**. Finally, recrystallization of the mixture from a toluene solution gave single crystals of **2**, whose structure was unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS measurements as well as an X-ray crystallographic analysis. As shown in Figure 2,[10] molecular structure of **2** proves to be a nonplanar conformation with C_2 symmetry, and it exhibits bond alternation between the *exo* (1.45–1.47 Å) and *endo* (1.40–1.41 Å) bonds in the central benzene ring. Similar nonplanar conformation and bond alternation (*exo*: 1.44–1.45 Å; *endo*: 1.39–1.41 Å) have been observed on hexabenzotriphenylene **3**.[7]

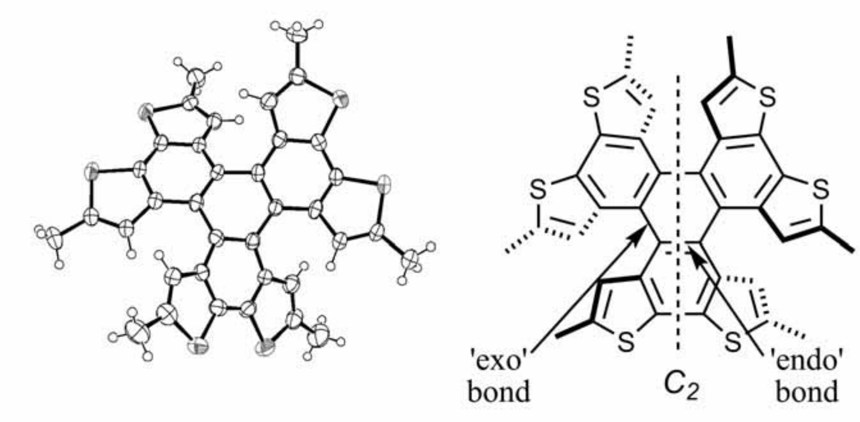


Figure 2. Molecular structure of **2**

Figure 3 shows UV–vis absorption and fluorescence spectra of **2** and **3** in CH_2Cl_2. They resemble each other in shape, reflecting the isoelectronic structures, but the absorption and fluorescence maxima of **2** are blue-shifted relative to those of **3**. The electrochemical properties of **2** and **3** were also investigated by means of cyclic voltammetry, and their voltammograms are shown in Figure 4. Hexathienotriphenylene **2** showed two reversible oxidation waves with half-wave potentials of +0.59 and +0.98 V vs. Fc/Fc$^+$ couple. The first oxidation potential of **2** is approximately 0.23 V more negative compared with that of hexabenzotriphenylene **3**, indicating that the introduction of thiophene units to triphenylene framework leads to increase electron-donating nature.[11]

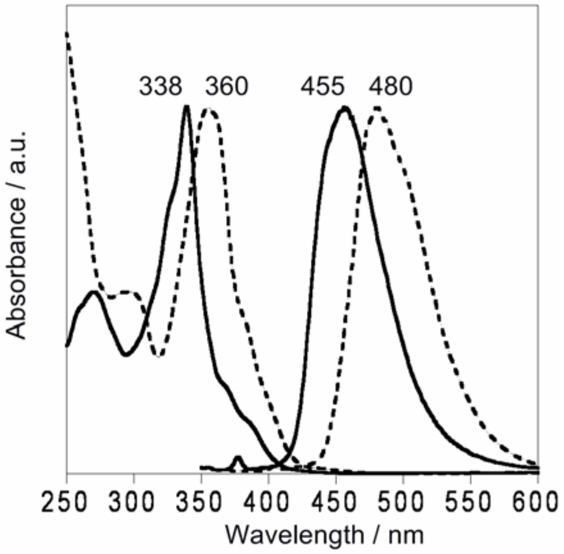


Figure 3. Electronic absorption and fluorescence spectra of **2** (solid line) and **3** (dashed line) in CH_2Cl_2

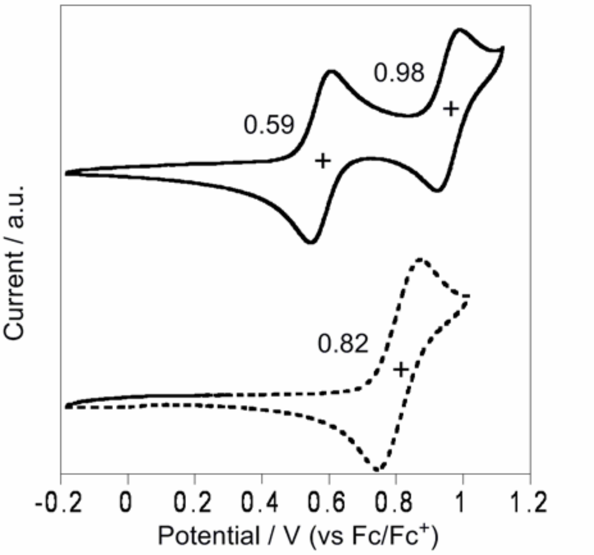


Figure 4. Cyclic voltammograms of **2** (solid line) and **3** (dashed line) in CH_2Cl_2

In conclusion, we report here a new class of heteroaromatic triphenylene derivative, hexathienotriphenylene **2**, prepared via oxidative cyclization of hexathienylbenzene. This study provides a useful synthetic route for a series of heteroaromatic-extended triphenylenes. Further investigations on the conformational study of **2** as well as the application to organic electronic devices will be reported in due course.

ACKNOWLEDGEMENTS

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10. Crystal Data for **2**: $C_{36}H_{24}S_6 \cdot 0.5C_7H_8$ $M = 695.02$, triclinic, Space Group P-1 (no. 2), $a = 8.3928(17)$ Å, $b = 14.338(2)$ Å, $c = 14.545(3)$ Å, $V = 1663.0(5)$ Å^3, $Z = 2$, $D_{\mathrm{calc}} = 1.388$ g·cm^{-3}, $F_{(000)} = 722.00$, $\mu = 4.404$ cm^{-1} (Mo K_α: 0.71069 Å), 12226 reflections measured, 7011 unique, $R = 0.0787$ for $I > 3\sigma(I)$, $wR = 0.1230$ for all data. The crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-687321.

11. **General Information.** Column chromatography was performed on silica gel (40–50 μm). TLC plates were visualized with UV. Preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-918 equipped with JAI-GEL 1H/2H columns. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet), coupling constant (Hz), integration. UV–vis spectra were recorded on a Shimadzu UV-3100PC. Fluorescence spectra were recorded using a Fluoromax-2 spectrometer in the photo-counting mode equipped with a Hamamatsu R928 photomultiplier. The bandpass for the emission spectra was 3.0 nm. All spectra were obtained in spectrograde solvents. The concentrations of solutions were adjusted to yield absorbance less than 0.1 in the absorption spectrum for any fluorescence experiments. Fluorescence quantum yield was determined using 9,10-diphenylanthracene (Φ_f = 0.90, in cyclohexane) as standard. Cyclic voltammetry was carried out on a BAS CV-50W voltammetric analyzer. High-resolution mass spectrum (HRMS) was obtained on JEOL JMS-700.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 4-Bromo-2-methylthiophene and dibenzo[*f*,*j*]phenanthro[9,10-*s*]picene **(3)** were prepared by reported procedure, and their ^{1}H NMR data were in agreement with those of the previously reported compounds.[6,12]

Bis(2-methyl-4-thienyl)ethyne (4). 4-Bromo-2-methylthiophene (1.77 g, 10.0 mmol), ethynyltrimethylsilane (589 mg, 6 mmol), water (88 mg, 4.9 mmol), DBU (9.13 g, 60.0 mmol), $PdCl_2(PPh_3)_2$ (181 mg, 0.257 mmol), and CuI (89 mg, 0.47 mmol) were placed in a test tube and dissolved with toluene (10 mL). The mixture was stirred at 80 ºC for overnight. Hexane was added to the reaction mixture, and the organic layer was washed with NH_4Cl aq and water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **4** (1.03 g, 95%). Colorless plates; mp 98–99 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (d, 6H, J = 1.1 Hz), 6.81 (quint-like, J = 1.2 Hz, 2H), 7.22 (d, 2H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 15.1, 83.7, 121.7, 126.5, 127.6, 139.5; Exact mass Calcd for $C_{12}H_{10}S_2$: 218.0224, Found: 218.0226.

Hexakis(2-methyl-4-thienyl)benzene (5). A solution of **4** (1.03 g, 4.72 mmol) in dioxane (20 mL) was degassed by Ar bubbling. To the solution was added $Co_2(CO)_8$ (270 mg, 0.79 mmol) in one portion. The mixture was stirred at 140 ºC for overnight. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:1 hexane/$CHCl_3$) to give **5** (0.90 g, 87%). Pale brown powder; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.24

(d, 18H, $J = 1.0$ Hz), 6.12 (quint-like, $J = 1.2$ Hz, 6H), 6.31 (d, 6H, $J = 1.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 15.0, 121.8, 128.2, 136.2, 136.6, 140.3; Exact mass Calcd for $C_{36}H_{30}S_6$: 654.0672, Found: 654.0678.

2,5,8,11,14,17-Hexamethyltriphenyleno[2,1-*b*:3,4-*b*':6,5-*b*'':7,8-*b*''':10,9-*b*'''':11,12-*b*''''']-hexathiophene (2). Hexakis(2-methyl-4-thienyl)benzene (**5**) (331 mg, 0.506 mmol) were placed in 200 mL round-bottomed flask and dissolved with MeCN (20 mL) and $CHCl_3$ (80 mL). To the mixture was added $Fe(ClO_4)_3 \cdot nH_2O$ (2.16 g, 6.0 mmol) in one portion. The resulting dark blue solution was stirred at rt for overnight. Hydrazine monohydrate (4 mL) was added, and the organic layer was washed with NH_4Cl aq and water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was passed through silica gel (2:1 hexane/$CHCl_3$). Recrystallization from toluene gave single crystals of **2** (44 mg, 13%). Purification of the filtrate by preparative GPC gave **6** (11 mg, 3%). **2**: Pale orange crystals; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.62 (d, 18H, $J = 1.1$ Hz), 7.47 (q, 6H, $J = 1.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 16.2, 124.2, 126.1, 133.3, 136.7; Exact mass Calcd for $C_{36}H_{24}S_6$: 648.0202, Found: 648.0208; UV/Vis (CH_2Cl_2) λ_{max}^{abs} 338 nm (log ε 5.08), λ_{max}^{ems} 455 nm (Φ_f 9.0 × 10^{-3}).

6: Pale orange powder; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.42 (d, 12H, $J = 1.1$ Hz), 2.66 (d, 6H, $J = 1.1$ Hz), 6.02 (q, 4H, $J = 1.1$ Hz), 6.83 (m, 2H), 6.98 (d, 2H, $J = 2.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 15.6, 16.1, 123.5, 125.9, 126.2, 129.2, 129.6, 132.9, 133.2, 134.2, 141.2, 144.3; Exact mass Calcd for $C_{36}H_{26}S_6$: 650.0359, Found: 650.0356.

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