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Novel Ladder π-Conjugated Materials—Sila-Pentathienoacenes: Synthesis, Structure, and Electronic Properties

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Abstract: A novel series of ladder π-conjugated materials—sila-pentathienoacenes (**Si-PTA**) are synthesized and characterized. Crystal structures of the compounds show that the length of alkyl chains substituting on the thiophene ring has a significant influence on molecular packing. A densely packed structure with an interfacial distance of about 3.66 Å between the adjacent molecules is observed for the compound with shorter alkyl chains. However, a large interfacial distance (7.99 Å) is obtained for another compound because of the insertion of long alkyl chains between two planes. The investigation of the optical and electrochemical properties shows that the silylene bridge incorporated into the pentathienoacene framework exerts a clear effect on the electronic properties by the σ*–π* conjugation. Although only a slight enhancement is observed for the HOMO levels, with respect to that of pentathienoacene, the LUMO levels are significantly lowered. The observed electronic properties are consistent with the theoretical calculations.

Keywords: conjugation · ladder compounds · polycycles · semiconductors · silicon

Introduction

The design and synthesis of new molecular building blocks in the field of organic electronics are attracting much attention because of their application in organic field-effect transistors (OFETs),[1] organic light-emitting diodes (OLEDs),[2] and photovoltaic cells.[3] Ladder π-conjugated systems with fused polycyclic skeletons are an important class of compounds for organic-electronic materials because of their effective extension of the π-conjugation without any conformational disorder.[4] Among various ladder π-conjugated systems, fused thiophene aromatics have recently been developed as new organic semiconductors, which are one of the most promising candidates for organic field-effect transistors (OFETs) because of their high hole mobility.[5–7] Furthermore, several recent reports have shown that a high hole mobility[8] and power conversion efficiency (PCE)[9] are attained by introducing fused thiophene aromatics into the π-conjugated polymers.

The incorporation of silylene into the π-conjugated framework forming silole rings is a powerful strategy for the design of new promising functional molecules applicable for organic electronics.[10] The electronic properties of the whole π-conjugated system will be remarkably modified by the silole substructure, because the LUMO is significantly lowered arising from the effective σ*–π* conjugation between an exocyclic σ* orbital on the silicon atom and the π* orbital of the butadiene moiety.[11] In this context, we have designed and synthesized new π-conjugated systems obtained by replacing the central sulfur atom of pentathienoacene (**PTA**) with a silylene moiety (sila-pentathienoacene, **Si-PTA**). By introducing long alkyl chains on two terminal thiophene rings, the soluble sila-pentathienoacene was obtained (Scheme 1). However, the crystal structure showed that the unexpected molecular-packing structure was formed because of the insertion of the long alkyl chains between the adjacent molecular planes. For the sake of densely face-to-face stacking of the new fused polycyclic skeleton in the solid state, the other sila-pentathienoacene compound with two methyl groups was also synthesized (see Scheme 1). The length of alkyl chains has a clear influence on the molecular-packing structures. Systematic studies of their electronic properties have shown that the HOMO and LUMO levels, and the optical properties in solution are very different from

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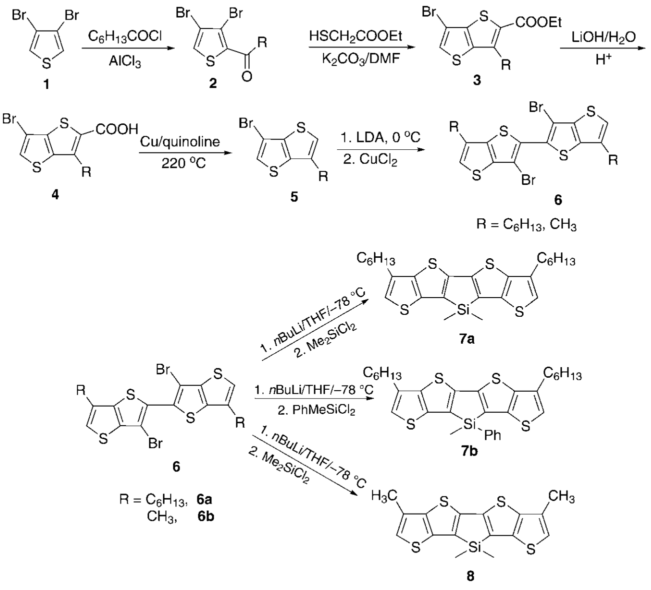

Scheme 1. Synthetic routes for **Si-PTA**.

those of PTA and the related π-conjugated system, bis(benzothieno)silole (**BBTS**) that have recently been synthesized by Ohshita and Kunai.[12] Like chemically modified small dithienosiloles (**DTS**)[8a,b,9a,13] and tetrathienoacenes,[8c] **Si-PTA** is a promising building block in π-conjugated polymers and oligomers for FET and photovoltaic applications.

Results and Discussion

Synthesis

Scheme 1 depicts the synthetic route to sila-pentathienoacenes **7a**,**b**, and **8**. A key intermediate **6** was synthesized using the reported methodology.[14] Through the five-step reaction, **6** was synthesized with an acceptable yield (total yield: 17%) starting from 3,4-dibromothiophene. The target compounds were obtained according to the classical method from **6**. Thus, **6** was treated with two equivalents of *n*BuLi to produce the corresponding dianion, which was then quenched with the corresponding dichlorosilane. All sila-pentathienoacene derivatives were obtained in moderate yields.

The structure and purity of **7a**,**b**, and **8** were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR, and MALDI–HRMS. A singlet at about $\delta = 6.90$ ppm, a triplet in the region of $\delta = 2.69$–2.74 ppm, and a singlet at higher fields than $\delta = 1.0$ ppm (0.53 ppm and 0.77 ppm for **7a** and **7b**, 0.52 ppm for **8**) observed in the ^{1}H NMR spectra of **7a**,**b**, and **8** are assigned to be the terminal thiophene ring protons, methylene protons attached to the thiophene rings, and Si–CH$_3$ protons, respectively. All the signals showed relative integration values expected for their structures. A ^{13}C NMR signal at below −4.0 ppm (−4.12 ppm and −4.18 ppm for **7a** and **8**, respectively) is assigned to the Si–CH$_3$ carbons in these **Si-PTAs**. When one of the methyl group was replaced with a phenyl group (**7b**), the signal of Si–CH$_3$ was shifted to −4.97 ppm. Similarly, the ^{29}Si NMR signal at −8.13 for SiMe$_2$ in **7a** was shifted reasonably to $\delta = -13.9$ ppm for SiMePh in **7b**.

Crystal Structures of 7a and 8

Single crystals of **7a** and **8** suitable for X-ray analysis were obtained by slow evaporation from a hexane/CH$_2$Cl$_2$ mixed solvent at room temperature. As shown in Figure 1, the molecular structure of **7a** shows that the ring skeleton is almost planar, and the alkyl chains adopt an extended trans zig-zag conformation. In the crystal structure, the ring planes stack face-to-face but the distance between two adjacent molecular planes (7.99 Å) is very large because of the insertion of long alkyl chains between the two planes. However, it is interesting that the crystal structure of **8** is clearly different from that of **7a** (see Figure 2). The close π-stacking was formed with an interfacial distance of 3.66 Å between the adjacent molecules. Because of the tetracoordinate silicon bridge, all adjacent molecules stack with trans configurations to form a densely packed structure. This might be beneficial for achieving high carrier mobility. Remarkably, the length of the alkyl chains has a pronounced influence on the mo-

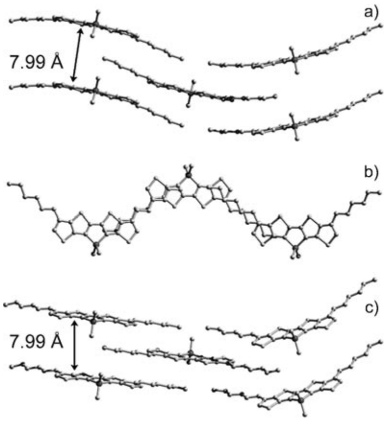

Figure 1. Crystal packing of **7a**. a) Molecular arrangement in a single crystal; b) side view; c) top view.

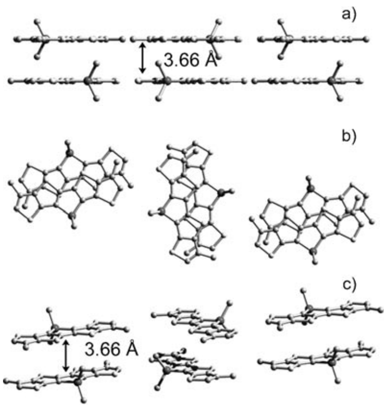

Figure 2. Crystal packing of **8**. a) Molecular arrangement in a single crystal; b) side view; c) top view.

lecular-packing structures. To the best of our knowledge, the significant effect of alkyl length on the molecular-packing structure is seldom reported as yet.[15]

Optical Absorption and Fluorescence Behavior

UV/Vis absorption spectra of **7a**,**b**, and **8** in toluene solutions and those of thin films prepared by a drop-casting method are shown in Figures 3 and 4, respectively. In solution, **7a** shows two distinct absorption bands with maxima at 292 and 392 nm. A similar two-band feature was observed for **7b** in toluene, but the two bands are slightly red-shifted with maxima at 294 and 397 nm, indicating that Si−Ph extends the molecular conjugation to a certain degree. The absorption spectra of the films of **7a** and **7b** are similar to the corresponding spectra in toluene solution, but show a slight red-shift and clear broadening compared to those in solution, suggesting a weak intermolecular interaction. There is no dependence of the absorption maxima on the solvent polarity. The spectrum of **7a** in THF is the same as that in toluene (Figure 3a). It is expected that the absorption of **8** in dilute toluene exhibited no difference compared to that of **7a** as shown in Figure 4. However, a large blue shift (30 nm) and broadening in the absorption spectra of the solid film of **8** was observed with the absorption band exhibiting a maximum at about 358 nm. The absorption band with maximum at about 290 nm exhibited no clear shift besides broadening. Based on the exciton-coupling theory, a pronounced blue shift of the absorption with remarkable spectrum broadening strongly suggests the formation of H-aggregates with face-to-face stacking of the fused polycyclic skeleton.[16] Apparently, this point is consistent with its crystal structure.

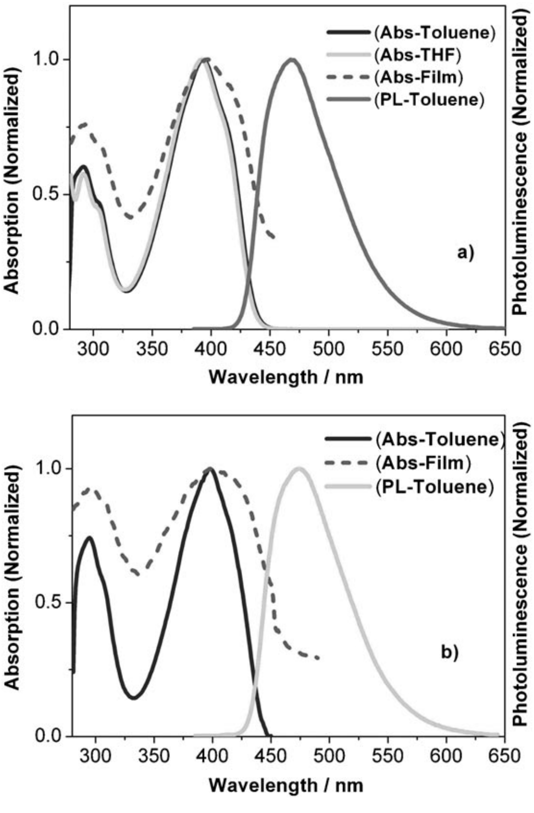

Figure 3. Absorption and photoluminescence spectra of a) **7a** and b) **7b** in different environments. The concentration of all the solutions is kept to be 1×10^{-4} mol L^{-1}. The films were prepared by drop-casting from a solution of toluene.

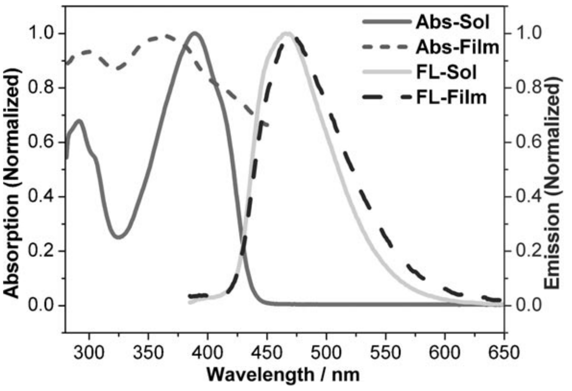

Figure 4. Absorption and photoluminescence spectra of **8** in different environments. The concentration of all the solutions is kept to be 1×10^{-4} mol L^{-1}. The films were prepared by drop-casting from a solution of toluene.

Fluorescence spectra of **7a**,**b**, and **8** in solution and film states are also shown in Figures 3 and 4, respectively. In toluene, all compounds exhibit only one maximum emission at around 470 nm. The emission of **8** in film showed a slight red shift (5 nm) in comparison with that in solution. In Table 1, the absorption, emission, and estimated band gap data are summarized.

The absorption spectra of **Si-PTAs** are evidently different from those of pentathienoacene (**PTA**) and **FT5** reported by Liu and He, which show only one broad absorption band in the region of 250–360 nm with distinct vibronic fine structure.[5a,14] The emission maxima of **7** and **8** are far longer than that of **PTA** (407 nm). All these results demonstrate that replacing the central sulfur in **PTA** with a silylene, results in unexpectedly large effects on the electronic structure of the whole π-system arising from the effective σ*–π* conjugation in the silole moiety. Fluorescence quantum yields of **7a** and **7b** in solution (0.7 and 0.81) are remarkably high in comparison to that of **PTA** (0.27), whereas the emission of the solid films of the **Si-PTA** is very weak, similar to that of the oligothiophene films.

The UV absorption and emission maxima of bis(benzothieno)siloles (BBTS) are reported to be approximately 40 and 35 nm longer than those of DTS, respectively.[10e,12] Interestingly, the absorption and emission of **7a** and **7b** occur at wavelengths 10 nm longer than those of BBTS. Namely, terminal thieno groups are more effective to extend the π-delocalization of DTS than terminal benzo groups.

Electrochemical Properties

The oxidation properties of **7a** and **8** were determined by cyclic voltammetry in CH_2Cl_2 solutions (1 mM) of tetrabutyl-

Table 1. Photophysical data and the band gaps derived from different approaches.

Compound	Absorption λ [nm]			Emission λ [nm]		Oxidation Potential	Band Gap [eV]	
	Toluene[a]	THF[a]	Film[b]	Toluene[a]	Φ [%][c]	E_{pa}/E_{pc}[d]	$E_{g_{opt}}$[e]	E_g[f]
7a	292, 392	292, 392	292, 392	467	70	0.62/0.39	2.76	2.83
7b	294, 397	N[g]	296, 404	473	81	N	2.74	N
8	291, 389	N	290, 358	466	N	0.61/0.35	2.77	2.83

[a] Measured in solution (1×10^{-4} M). [b] Measured in solid thin film on quartz plates prepared by spin-coating from solution. [c] 9,10-Diphenylanthracene standard. [d] E_{pa} and E_{pc} stand for anodic peak potential and cathodic peak potential, respectively. [e] Optical band gap derived from the onset of UV/Vis absorption spectra of solutions. [f] Cyclic voltammetric band gap derived from the difference between HOMO and LUMO energy levels, HOMO/LUMO $= E_{onset}$ +4.7 eV. [g] Not measured.

ammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) using a Pt wire as the counter electrode and a $Ag/AgNO_3$ (0.1 M) as the reference electrode. The detailed data are listed in Table 1, and the cyclic voltammograms are given in Figure 5.

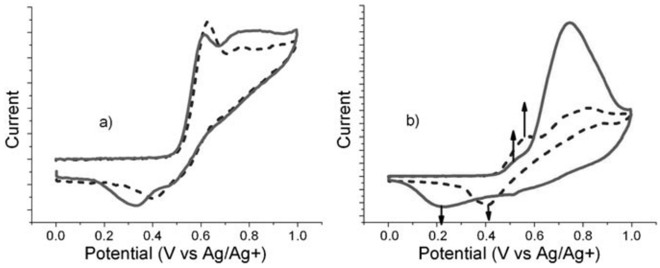

Figure 5. Cyclic voltammograms of **7a** (-----) and **8** (——), a) in CH_2Cl_2 solution and b) in film. Scan rate: 100 mV s^{-1}.

On sweeping anodically, **7a** undergoes two quasireversible oxidation peaks. The first oxidation potential with $E_{\text{onset}}^{\text{Ox}}$ is 0.51 eV versus Ag/Ag^+. The HOMO energy level of **7a** is estimated from the onset of oxidation wave to be −5.21 eV. The HOMO level is lower than that of pentacene (−4.60 eV),[17] being in accord with the more stable nature of **7a** against oxygen than pentacene. Compared with the HOMO of pentathienoacene (−5.33 eV), the slight enhancement of HOMO level for **7a** may be ascribed to silylene bridge. It is expected that the redox properties of **8** in solution would exhibit no clear difference compared with that of **7a**.

Generally, the orbital interaction between the silylene bridge and π-conjugated framework mainly affects the LUMO level through the σ*–π* conjugation. Furthermore, the oxidation potential of **7a** is shifted by 0.22 V toward less positive values with respect to that of bis(benzothieno)silole with analogous structure.[12]

To investigate the influence of molecular-packing structure on the electrochemical properties, the oxidation properties of **7a** and **8** in solid film (drop-casting on Pt disk electrode from toluene solution) were also measured using cyclic voltammetry in MeCN (see Figure 5b). The molecules in dilute solution are mostly present as single molecules and almost no aggregation occurs. As for films, both compounds undergo two quasireversible oxidation peaks. The first oxidation potential, $E_{\text{onset}}^{\text{Ox}}$, is around 0.45 eV versus Ag/Ag^+, which is shifted negatively by 0.06 eV. The cathodic peak potential ($E_{\text{pc}}^{\text{film}} = 0.21$ eV) of film for **8** is remarkably lower than that ($E_{\text{pc}}^{\text{sol}} = 0.33$ eV) of solution. In view of the existence of densely face-to-face stacking in single crystal of **8**, this point strongly suggests that the resulting oxidation state in a film is more stable because of the delocalization of electron in the whole π–π system. As for **7a**, the expected small difference for the cathodic peak potential (E_{pc}) between solution and film is observed because of the weak molecular interaction in the film.

Arising from the invisible signal of cyclic voltammograms for the reduction potential in THF solution, the reduction potential of **7a** and **8** were estimated from the cyclic voltammograms measured in films (see Supporting Information). Both compounds displayed irreversible reduction processes with $E_{\text{onset}}^{\text{(R)}}$ at −2.33 eV. According to the $E_{\text{onset}}^{\text{(R)}}$, the LUMO level can be obtained to be −2.38 eV. It is expected that the LUMO level of sila-pentathienoacene is clearly lower than that of pentathienoacene (−2.04 eV). Apparently, σ*–π* conjugation caused by a silylene bridge exerts a significant impact on LUMO levels. The band gap is derived as the difference between the HOMO and the LUMO energy levels as determined by cyclic voltammetry. The band gap (E_g = 2.83 eV) is very close to that ($E_{g_{opt}}$ = 2.76 eV) determined by the onset of the UV/Vis absorption spectra.

Theoretical Calculations

To get further insight into the electronic structures of the polycyclic π-electron systems, the density functional theoretical calculations (B3LYP)[18] were performed for model-ring systems, **Si-PTA**, **PTA**, **DTS**, and **BBTS** at the 6-31G* level using the Gaussian 03 program.[19] The contours of the HOMO and LUMO of **7a** are plotted in Figure 6b. The calculated HOMO levels shown in Figure 6a are in good accord with those determined by electrochemical measurements, whereas the agreement for the LUMO levels is marginal. The reason is ascribed in part to the less than satisfactory reversibility of the reduction of **Si-PTA** and other systems. The theoretical calculations indicate that the HOMO of **Si-PTA** is higher than that of **PTA**. The difference between **Si-PTA** and **PTA** could be caused by the inductive effects of the central group. An electropositive Me_2Si group raises the HOMO, while electronegative sulfur lowers the HOMO. The LUMO level of **Si-PTA** is even lower than that of **PTA** because of the effective σ*–π* conjugation in

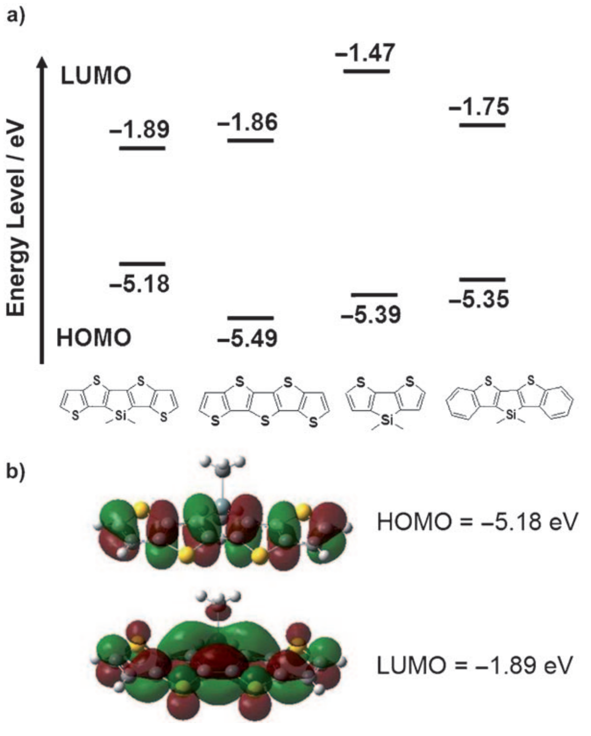

Figure 6. DFT calculations of several π-conjugated ring systems (B3LYP/6-31G): a) Kohn–Sham HOMO and LUMO energy levels and b) pictographical presentation of the Kohn–Sham HOMO and LUMO of **7a**.

the silole moiety, though the inductive raising of the LUMO should be operative in **Si-PTA**. As a result, the HOMO/LUMO energy gap of **Si-PTA** is much smaller than that of **PTA** and the smallest among the systems investigated here.

Conclusions

A novel series of ladder π-conjugated materials—sila-pentathienoacenes (**Si-PTA**) are synthesized and characterized. The length of alkyl chains substituting on the thiophene ring has a significant influence on molecular packing. For both **7a** and **8**, the fused polycyclic skeletons form face-to-face packing structures in single crystals. However, a large interfacial distance (7.99 Å) is obtained for **7a** because of the insertion of long alkyl chains between the two planes. A densely packed structure with an interfacial distance of about 3.66 Å for the adjacent molecules is observed for **8** with shorter alkyl chains. We find that the silylene bridge incorporated into the pentathienoacene framework exerts a clear effect on the electronic properties because of the σ*–π* conjugation. The HOMO/LUMO gap of the new extended π-systems is even smaller than that of the related extended silole systems like BBTS. The novel π-conjugated system is a good candidate as a building block incorporated to π-conjugated polymers for FET and photovoltaic applications. Studies on the synthesis of the polymers with low band gap based on sila-pentathienoacene are now in progress.

Experimental Section

General Methods

All starting materials were obtained from commercial suppliers and used as received. Reagent-grade solvents were dried and purified according to the following procedures: methylene chloride (MC) and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride. THF and diisopropylamine were dried over sodium metal and distilled. NMR spectra were recorded on a Bruker DPX 400 (^{1}H NMR 400 MHz and ^{13}C NMR 100 MHz) spectrometer. The mass spectra were obtained using the IonSpec 4.7 T HiResMALDI instrument. The luminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer (the pathlength of the quartz cell is 1 cm). The emission bandwidth was 3 nm. UV absorption spectra were obtained using a scinco S-3150 UV/Vis spectrophotometer.

Single crystals of **7a** and **8** were obtained by slow evaporation of hexane/CH_2Cl_2 solution at room temperature. Diffraction data were obtained with $Cu_{K\alpha}$ ($\lambda = 1.54184$ nm) radiation for **7a** and $Mo_{K\alpha}$ ($\lambda = 0.71073$ nm) for **8** at 293 K using an Oxford Diffraction X-Calibur CCD system. **7a**: monoclinic, $P2_1/c$, crystal size: $0.36 \times 0.20 \times 0.06$ mm^3, cell dimensions: $a = 25.0751(11)$ Å; $b = 8.1932$ (5) Å; $c = 14.0853$ (6) Å; alpha = 90.00°; beta = 103.088 (4)°; gamma = 90.00°; $Z = 4$, GOF = 0.997, $R_1 = 0.0414$, $wR_2 = 0.1113$. CCDC: 772506 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. **8**: monoclinic, $P2_1/m$, crystal size: $0.40 \times 0.20 \times 0.18$ mm^3, cell dimensions: $a = 11.2504$ (19) Å; $b = 7.3279$ (10) Å; $c = 21.376$ (3) Å; alpha = 90.00°; beta = 91.536 (13)°; gamma = 90.00°, $Z = 4$, GOF = 1.050 , $R_1 = 0.0974$, $wR_2 = 0.2704$, CCDC: 772507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

1-(3,4-Dibromothiophen-2-yl)heptan-1-one (**2**): Heptanoyl chloride (4.75 g, 32 mmol) was added dropwise to a mixture of 3, 4-dibromothiophene (**1**) (7.20 g, 30 mmol) and $AlCl_3$ (9.25 g, 69 mmol) in CH_2Cl_2 (30 mL) with stirring at 0 °C under argon. The mixture was stirred for 4 h and then poured into HCl (50 mL, 0.6 M). The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine and water, then dried over $MgSO_4$, and concentrated. Chromatography on silica gel (petroleum ether) afforded the pure product **2** (9.66 g, 91 %). ^{1}H NMR (400 Hz, $CDCl_3$): $\delta = 7.60$ (s, H), 3.06–3.02 (t, 2 H), 1.77–1.71 (m, 2 H), 1.40–1.30 (m, 6 H), 0.91–0.87 ppm (t, 3 H); ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 191.98$, 139.76, 129.19, 117.03, 116.99, 41.26, 31.63, 28.88, 24.02, 22.52, 14.06 ppm; GC–MS: *m*/*z* (%): 354.8.

6-Bromo-3-hexylthieno[3,2-b]thiophene-2-carbonic ester (**3**): Ethyl mercaptoacetate (3.28 mL, 30 mmol) and then a catalytic amount of 18-crown-6 (20 mg) were added dropwise to a mixture of **2** (10.62 g, 30 mmol) and K_2CO_3 (19.67 g, 143 mmol) in DMF (25 mL) with stirring under argon. The resulting mixture was heated at 60–70 °C overnight. The mixture was then poured into water. After filtration, the solid was washed with water. The collected solid (**3**) was further washed with methanol and used directly for the next reaction (9.20 g, 82 %). ^{1}H NMR (400 Hz, $CDCl_3$): $\delta = 7.43$ (s, H), 4.39–4.34(q, 2 H), 3.15–3.11 (t, 2 H), 1.72–1.68 (m, 2 H), 1.41–1.29 (m, 6 H), 0.89–0.86 ppm (t, 3 H); ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 162.70$, 143.92, 141.85, 140.17, 128.64, 127.28, 103.19, 61.14, 31.59, 29.35, 29.28, 29.09, 22.59, 14.33, 14.08 ppm; GC–MS: *m*/*z* (%): 375.9.

6-Bromo-3-hexylthieno[3,2-b]thiophene-2-carboxylic acid (4): **3** (9.724 g, 26 mmol) was dissolved into a mixture of THF (40 mL), methanol (5 mL), and LiOH (10 mL, 10 % solution). The resulting mixture was refluxed overnight and poured into concentrated hydrochloric acid. The acidic mixture was then diluted with water (to 100 mL). The resulting precipitate was filtered and washed with water, then washed with methanol and dried under vacuum overnight (8.55 g, 95 %). ^{1}H NMR (400 Hz, $CDCl_3$): $\delta = 7.49$ (s, H), 3.18–3.14 (t, 2 H), 1.75–1.72 (t, 2 H), 1.41–1.30 (m, 6 H), 0.90–0.87 ppm (t, 3 H); ^{13}C NMR (100 Hz, $CDCl_3$): $\delta = 168.57$, 145.92, 143.11, 140.35, 128.30, 127.68, 103.32, 31.56, 29.32, 29.29, 29.23, 22.57, 14.11 ppm; GC–MS: *m*/*z* (%): 303.9.

3-Bromo-6-hexylthieno[3,2-b]thiophene (5): Copper powder (0.628 g), as a catalyst, was added into a mixture of **4** (3.46 g, 10 mmol) and quinoline (12 mL). The mixture was heated to 220–230 °C until no gas bubbles were observed. After slightly cooling the solution, the mixture was filtered and hexane (20 mL) was added to the filtrate. The organic solution was washed with a solution of HCl (10 %) until it turned clear. The organic solution was washed with water until the washes were neutral. After drying over anhydrous MgSO$_4$, the solution was concentrated. Chromatography on silica gel (petroleum ether) afforded the pure product **5** (2.14 g, 71 %). ^{1}H NMR (400 Hz, DMSO): $\delta = 7.77$ (s, 1 H), 7.41(s, 1 H), 2.67–2.64 (t, 2 H), 1.65–1.62 (t,2 H), 1.25 (m, 6 H), 0.84–0.81 ppm (t, 3 H); ^{13}C NMR (100 Hz, CDCl$_3$): $\delta = 139.97$, 139.10, 135.93, 123.36, 122.67, 103.02, 31.62, 29.72, 29.03, 28.64, 22.64, 14.15 ppm; GC–MS: *m*/*z* (%): 303.8 (M-COOH)$^+$; MS (ESI): *m*/*z* (%): 345.04.

3-Bromo-2-(3-bromo-6-hexylthieno[3,2-b]thiophen-2-yl)-6-hexylthieno-[3,2-b]thiophene (6a): Fresh LDA was prepared by the reaction of diisopropylamine (0.44 g, 4 mmol) in dry THF (10 mL) with *n*BuLi (2.5 mL, 1.60 M in hexane) at 0 °C under argon. To the LDA solution stirred at 0 °C for 15 min, **5** (1.21 g, 4 mmol) in THF (6 mL) was added dropwise. After stirring at 0 °C for 1 h, CuCl$_2$ (0.62 g, 4 mmol) powder was added to the mixture. The final mixture was stirred overnight, and the reaction was then quenched with water. After evaporating most of the THF, the residue was extracted with hexane, washed with brine and water, and dried over MgSO$_4$. After evaporating hexane, the residue was recrystallized from ethanol to give **6** as a crystalline solid (1.09 g, 45 %). **6a**: ^{1}H NMR (400 Hz, CDCl$_3$): $\delta = 7.10$ (s, 2 H), 2.74–2.70(t, 4 H), 1.79–1.73 (m, 4 H), 1.41–1.33 (m, 12 H), 0.91–0.88 ppm (t, 6 H); ^{13}C NMR (100 Hz, CDCl3): $\delta = 140.53$, 138.92, 135.92, 129.74, 122.86, 105.62, 105.62, 31.58, 29.77, 29.02, 28.64, 22.64, 14.12 ppm; MS (ESI): *m*/*z* (%): 604.89.

3-bromo-2-(3-bromo-6-methylthieno[3,2-b]thiophen-2-yl)-6-methylthieno[3,2-b] thiophene (6b): A mixture of diisopropylamine (0.44 g, 4 mmol) and dry THF (10 mL) was stirred under argon. *n*BuLi (2.5 mL, 1.60 M) was added dropwise at 0 °C. The freshly made LDA was stirred at 0 °C for 15 min, and then 3-bromo-6-methylthieno[3,2-b]thiophene (0.93 g, 4 mmol) in THF (6 mL) was added dropwise. The mixture then was stirred at 0 °C for one hour, and CuCl$_2$ (0.618 g, 4 mmol) powder was added. The final mixture was stirred overnight, and the reaction was then quenched with water. After evaporating most of the THF, the residue was extracted with hexane, washed with water and brine, and dried over MgSO$_4$. After evaporating hexane, the residue was recrystallized from ethanol to give **6b** as a crystalline solid (0.31 g, 33 %).^{1}H NMR (400 Hz, CDCl$_3$): $\delta = 7.09$ (s, 2 H), 2.37(s, 6 H) ppm; MS (EI): *m*/*z* (%): 465.63.

7a: *n*BuLi (1.5 mL, 1.60 M in hexane) was added dropwise to a solution of **6** (0.60 g, 1 mmol) in dry THF (8 mL) at −78 °C under argon. After stirring the mixture at the same temperature for 15 min, dichlorodimethylsilane (0.129 g, 1 mmol) was added to the mixture. The resulting mixture was stirred overnight at room temperature and quenched with water. After evaporating most of solvent, the mixture was dissolved into hexane and washed with water. The organic phase was dried with anhydrous MgSO$_4$ and concentrated. Chromatography on silica gel (petroleum ether) afforded the pure **7a** (0.21 g, 42 %). **7a**: ^{1}H NMR (400 Hz, CDCl$_3$): $\delta = 6.92$(s, 2 H), 2.74–2.70 (t, 4 H), 1.79–1.73 (m, 4 H), 1.41–1.33 (m, 12 H), 0.90–0.88 (t, 6 H), 0.53 ppm (s, 6 H); ^{13}C NMR (100 Hz, CDCl$_3$): $\delta = 150.57$, 140.96, 141.33, 135.46, 133.2, 120.68, 127.5, 31.66, 30.15, 29.11, 28.69, 22.65, 14.16, −4.12 ppm; ^{29}Si NMR (CDCl$_3$): $\delta = -8.33$ ppm; HRMS (MALDI/DHB): *m*/*z* (%) calcd for $C_{26}H_{34}S_4Si$: 502.13; found: 502.1301 ± 0.002.

7b: *n*BuLi (1.5 mL, 1.60 M in hexane) was added dropwise to a solution of **6** (0.60 g, 1 mmol) in dry THF (8 mL) at −78 °C under argon. The mixture was then reacted at −78 °C for 15 min, and dichloromethylphenylsilane (0.191 g, 1 mmol) was added. The resulting mixture was stirred overnight at room temperature and quenched with water. After evaporating most of the THF, the mixture was dissolved into hexane and washed with water. The organic phase was dried with anhydrous MgSO$_4$ and concentrated. Chromatography on silica gel (petroleum ether) afforded the pure **7b** (0.22 g, 39 %). ^{1}H NMR (400 Hz, CDCl$_3$): $\delta = 7.69$–7.68(d, 2 H), 7.40–7.34(m, 2 H), 6.93(s, 2 H), 2.74–2.70 (t, 4 H), 1.79–1.71 (m, 4 H), 1.32–1.30 (m, 12 H), 0.89–0.85 (t, 6 H), 0.77 ppm (s,3 H); ^{13}C NMR (100 Hz, CDCl$_3$): $\delta = 151.26$, 141.46, 141.17, 135.50, 134.36, 132.49, 131.60, 130.37, 128.40, 120.92, 31.65, 30.15, 29.10, 28.69, 22.64, 14.15, −4.97 ppm; ^{29}Si NMR (CDCl$_3$): $\delta = -13.9$ ppm; HRMS (MALDI/DHB): *m*/*z* (%) calcd for $C_{31}H_{36}S_4Si$: 564.15; found: 564.1452 ± 0.002.

8: A mixture of **6b** (0.46 g, 1 mmol) and dry THF (8 mL) was stirred under argon. *n*BuLi (1.5 mL, 1.60 M) was added dropwise at −78 °C. The mixture was then reacted at −78 °C for 15 min, and dichlorodimethylsilane (0.13 g, 1 mmol) was added. The resulting mixture was stirred overnight at room temperature and quenched with water. After evaporating most of the THF, the mixture was dissolved into hexane, washed with water, and dried over anhydrous MgSO$_4$. After evaporation of hexane, chromatography on silica gel (petroleum ether) afforded the pure product **8** (0.11 g, 31 %). ^{1}H NMR (400 Hz, CDCl$_3$): $\delta = 6.92$ (s, 2 H), 2.37 (s, 6 H), 0.52 ppm (s, 6 H); ^{13}C NMR (100 Hz, CDCl$_3$): $\delta = 150.7$, 141.9, 141.2, 133.5. 130.1, 122.5, 121.3, 116.5, 15.1, −4.18 ppm; ^{29}Si NMR (100 Hz, CDCl$_3$): $\delta = -8.35$ ppm; HRMS (MALDI/DHB): *m*/*z* (%) calcd for $C_{16}H_{14}S_4Si$: 361.97; found: 361.9726 ± 0.002.

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