

Articles

Synthesis and Characterization of a Tetrathiafulvalene-Based Polymer

Sehyun Lee, Lei Wang,[†] Seok-Ho Hwang,[‡] Myong-Hoon Lee,* and Kwang-Un Jeong*

Department of Polymer-Nano Science Technology and Polymer Materials Fusion Research Center,
Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea

*E-mail: kujeong@jbnu.ac.kr (K.-U. Jeong); mhlee2@chonbuk.ac.kr (M.-H. Lee)

[†]Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, China

[‡]Department of Polymer Science and Engineering, Dankook University, Yongin 448-701, Korea

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A novel tetrathiafulvalene (TTF)-based main-chain polymer (6TTF-polymer) was successfully synthesized *via* a condensation polymerization between a newly synthesized dihydroxy TTF derivative and a malonyl chloride, and its chemical structure was characterized by spectroscopic techniques. Molecular weight of the 6TTF-polymer (9,030 g/mol by gel permeation chromatography) was large enough to form the ductile film. The electrochemical and optical properties of the 6TTF-polymer were further estimated by cyclic voltammetry, ultraviolet and photoluminescence spectroscopes. The highest occupied molecular orbital level ($E_{\text{HOMO}} = -4.79$ eV) and band-gap energy ($E_{\text{g}} = 1.91$ eV) of the 6TTF-polymer suggested that TTF-based polymer could act as a good electron donating material for the optoelectronic applications.

Key Words : Polymer, Tetrathiafulvalene, Fullerene, Synthesis

Introduction

Tetrathiafulvalene (TTF)-based molecules have been of great interests because of their unique photophysical and electrochemical behaviors, which makes it possible to apply them as organic charge transfer materials in the field of molecular switches,¹ sensors,² self-assembled redox-active supramolecules³ and organic field-effect transistors (OFETs).⁴ Especially, TTF derivatives have been considered as promising active materials for organic photovoltaics (OPV) due to their excellent electron donating properties.⁵

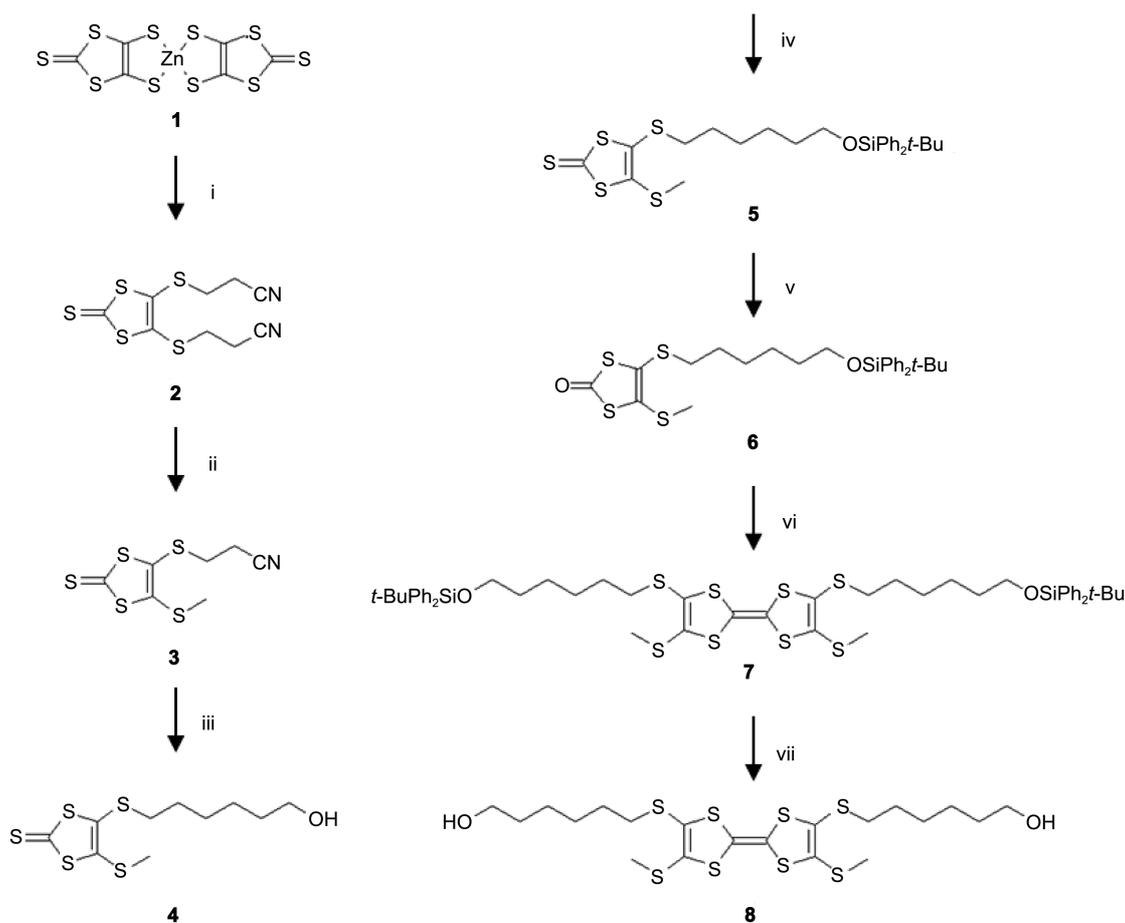
Due to the several advantages of bulk heterojunction (BHJ) OPVs, such as low cost and good processability, many BHJ materials containing electron donating and/or accepting moieties have been synthesized and characterized.⁶ Even though the charge separation in the BHJ materials is successfully achieved by introducing the interpenetrated network morphology, the total energy conversion efficiency of the solar cell is fairly limited in the consequence of the poor current collection which originates from the poorly organized path for charge flows and the mismatches between the absorption of the conjugated materials and the solar irradiation.⁷

In this aspect, utilizing the organic materials with excellent processability and good mechanical, chemical and thermal stabilities, the photo-efficiencies of solar cells can be significantly improved by controlling the structure and morphology of BHJ organic materials.⁸ However, in the low molecular weight organic systems, macroscopic phase

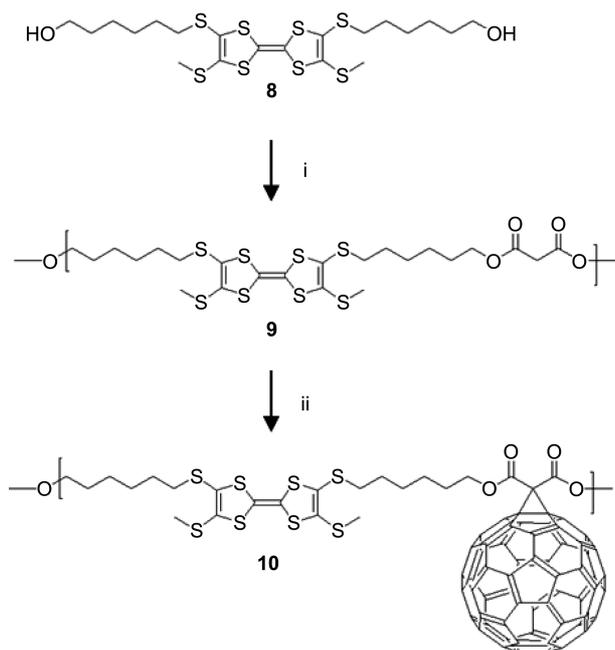
separations and defects such as cracks may occur during and after the solution coating, which results in a poor energy conversion.⁹ Therefore, it is desirable to synthesize a new polymer containing electron donor or/and acceptor. To satisfy this purpose, a new polymer (6TTF-polymer) containing electron donating (TTF) moiety was designed and synthesized and its electro-optical properties were investigated.

Result and Discussion

A new polymer (6TTF-polymer) containing electron-rich tetrathiafulvalene (TTF, electron donor) was successfully synthesized *via* coupling reactions. The detailed synthetic strategies were described in Scheme 1 and 2. To synthesize the targeted TTF-based monomer (**8**), the key starting compound **4** was prepared by the three-step reactions according to the literature.¹⁰ The hydroxyl group of **4** was protected by the reaction with *tert*-butyldiphenylsilyl chloride in the presence of imidazole to afford compound **5**. Then, TTF derivative **7** was obtained by the reaction of compound **6** in the presence of triethylphosphate. Deprotection of compound **7** with tetra-*n*-butyl-ammonium fluoride resulted in the targeted TTF-based monomer having two hydroxyl groups (**8**). All the synthesized compounds were purified by repeated column chromatographies and/or recrystallizations, and their chemical structures and purities were confirmed by proton (¹H) nuclear magnetic resonance (NMR, JNM-EX 400) in deuterated chloroform (CDCl₃), as shown in Figure 1. Chemical structure of compound **2** was verified by the



Scheme 1. Reagents and conditions: (i) $\text{Br}(\text{CH}_2)_2\text{CN}$, acetone, reflux, overnight; (ii) $\text{CsOH}\cdot\text{H}_2\text{O}$, dimethylformamide, methanol, iodomethane, $20\text{ }^\circ\text{C} \rightarrow 60\text{ }^\circ\text{C}$; (iii) $\text{CsOH}\cdot\text{H}_2\text{O}$, methanol, then, $\text{Br}(\text{CH}_2)_6\text{OH}$, $20\text{ }^\circ\text{C}$, 12 h; (iv) $t\text{-BuPh}_2\text{SiCl}$, imidazole, N,N -dimethylformamide, $20\text{ }^\circ\text{C}$; (v) $\text{Hg}(\text{OAc})_2$, 0.5 h; (vi) $\text{P}(\text{OEt})_3$, $130\text{ }^\circ\text{C}$, 3 h; (vii) TBAF in THF, tetrahydrofuran, $20\text{ }^\circ\text{C}$, 24 h.



Scheme 2. Reagents and conditions: (i) malonyl chloride, triethylamine, dichloromethane; (ii) DBU, tetrabromomethane, toluene, $70\text{ }^\circ\text{C}$, 40 h.

proton chemical shift at $-\text{S}-\text{CH}_2-$ (2.8 ppm). Protons of the methyl group exhibited a resonance signal ($\text{S}-\text{CH}_3$) at 2.5 ppm. After the substitution reaction of 6-bromohexan-1-ol to the compound **3**, new peaks corresponding to the alkyl protons of compound **4** appeared in the range of 1–2 ppm, and the peak at 3.7 ppm was identified as the methylene protons adjacent to hydroxyl group. Protection and deprotection reactions were evidenced by the chemical shifts of aromatic protons appearing in the range of 7–8 ppm.

As schematically illustrated in Scheme 2, the reaction of TTF-based dihydroxy monomer (**8**) with malonyl chloride resulted in the 6TTF-polymer (**9**). The number average molecular weight of 6TTF-polymer estimated by gel permeation chromatography (GPC) was 9,030 g/mol, which corresponded to the average degree of polymerization (n) = 8. The chemical structure of 6TTF-polymer was also identified by ^1H NMR, as represented in Figure 1(b). The chemical shift at 12 ppm corresponding to the carboxylic acid in the 6TTF-polymer indicated that the 6TTF-polymer was terminated mainly with carboxylic acid groups probably generated from the reaction of malonyl chloride with residual water molecules. Therefore, it was suggested that 6TTF-polymer with a higher molecular weight could be achieved if the water were completely removed from the

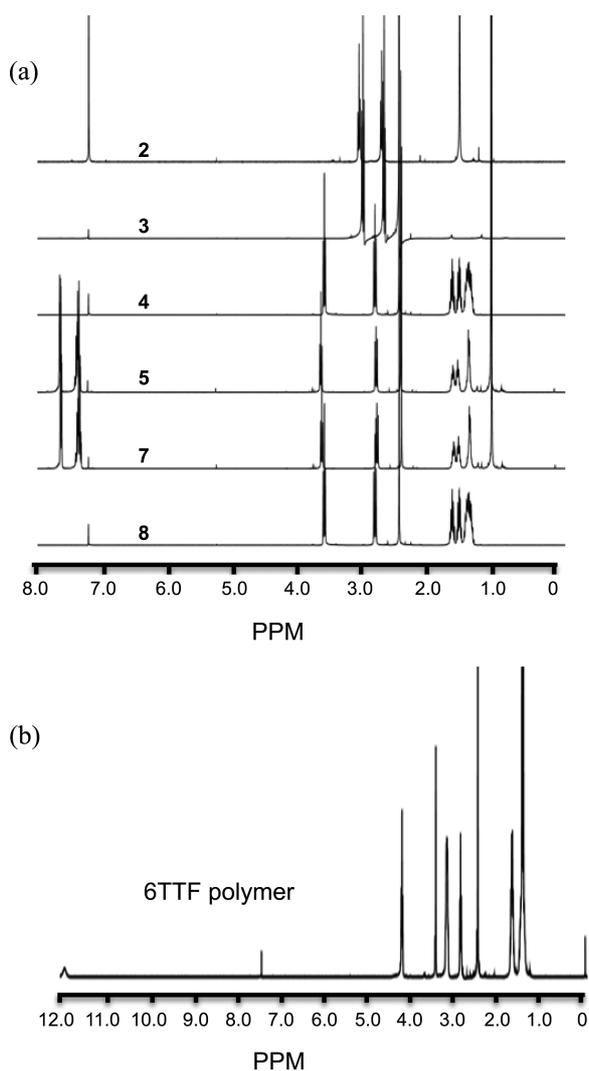


Figure 1. (a) ^1H NMR spectra of the synthesized compounds from **2** to **9**. (b) ^1H NMR spectrum of the 6TTF-polymer.

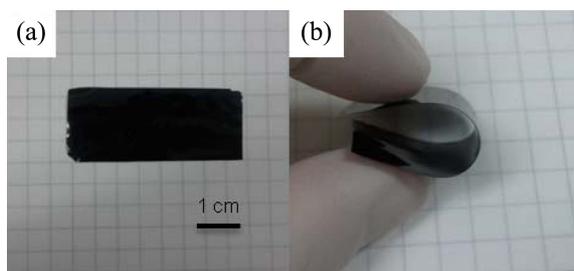


Figure 2. Photographic images of the free (a) and bent (b) 6TTF-polymer films.

reaction system before and during the polymerization. 6TTF-polymer was soluble in common organic solvents, such as toluene, hexane, dichloromethane and tetrahydrofuran, which allowed us to fabricate the robust thin films by a simple solution casting. As shown in Figure 2, the cast 6TTF-polymer films were bendable and ductile, indicating that the molecular weight of synthesized 6TTF-polymer was high enough.

To obtain 6TTF- C_{60} polymer (**10**) containing both electron donor (TTF) and acceptor (C_{60}) moieties in the polymer chain, we attempted to introduce the fullerene moiety (C_{60}) to the 6TTF-polymer (**9**) main chain by the malonate- C_{60} coupling reaction. However, the resulting 6TTF- C_{60} polymer was not soluble in any of organic solvents, and hence, precipitated out during the polymer reaction (Scheme 2). The poor solubility of 6TTF- C_{60} polymer should be originated from the chemical crosslinking at the C_{60} moiety. It was reported that the reaction between C_{60} and malonate moiety resulted in only 40% of mono-substituted product, and the rest of C_{60} was substituted by more than two malonate groups.¹¹ Therefore, it is believed that a large number of C_{60} molecules have participated in the chemical crosslinking during the polymer reaction of 6TTF-polymer. To avoid the insolubility of 6TTF- C_{60} polymer, more sophisticated reaction conditions should be taken into account, which will be investigated further in the future.

To explore the electro-optical properties of the resulting 6TTF-polymer as a candidate material for OPV, electrochemical, optical and photoelectric properties were investigated by utilizing cyclic voltammetry (CV), ultraviolet-visible (UV-vis) spectroscopy and photoluminescence (PL) spectroscopy, respectively. Electrochemical properties of the 6TTF-polymer were first studied by CV, and their results were represented in Figure 3 and tabulated in Table 1. Additionally, the CV data for TTF itself were also included in Table 1 for the comparison.¹²⁻¹⁴ It was found that redox

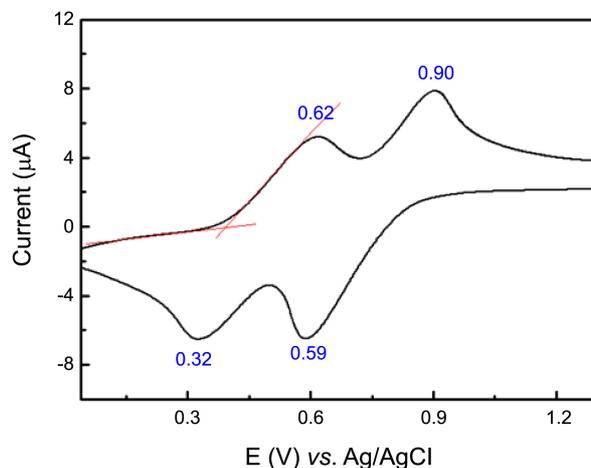


Figure 3. Cyclic voltammogram of the 6TTF-polymer (0.01 mM in CH_2Cl_2). Here, Bu_4ClO_4 (0.1 M) worked for a supporting electrolyte. A glass carbon electrode, an Ag/AgCl electrode and a platinum wire were also used as a working electrode, a reference electrode and a counter electrode, respectively.

Table 1. Electrochemical potentials and energy levels of the 6TTF-polymer

	E_1^a/V	E_2^a/V	$\lambda_{\text{UV}}/\text{nm}$	E_g^b/eV	HOMO ^c /eV
TTF	0.34	0.73	-	-	-
6TTF-polymer	0.47	0.75	381	2.27	4.79

^a E_1 and E_2 stand for the half wave oxidation potentials. ^b E_g means the optical band gap energy. ^c E_{HOMO} is defined as $-(E_{\text{onset}}^{\text{ox}} + 4.4 \text{ eV})$. Here $E_{\text{onset}}^{\text{ox}}$ means the onset potential for the oxidation.¹⁴

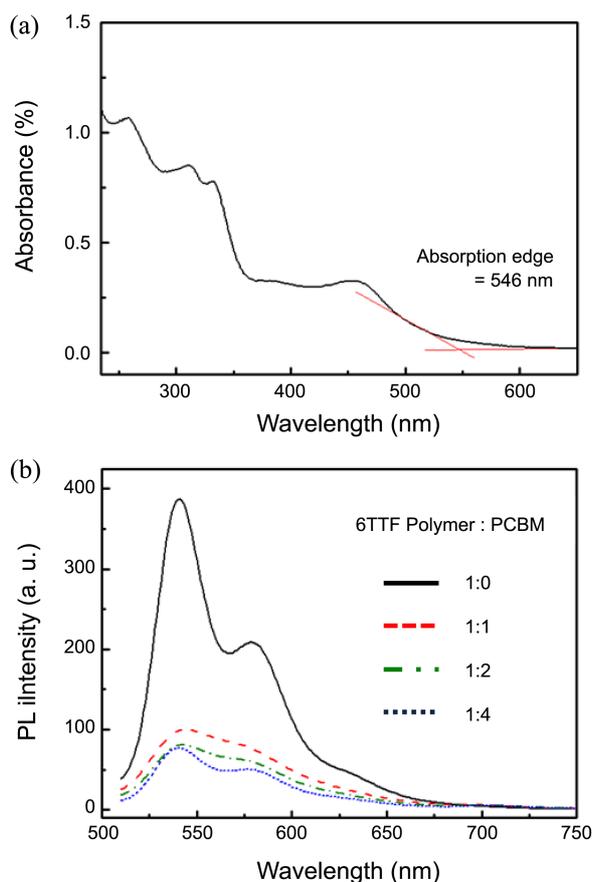


Figure 4. (a) UV-vis absorption spectrum of the 6TTF-polymer in dichloromethane. (b) PL spectra of the 6TTF-polymer/PCBM/chlorobenzene solutions at room temperature when they were excited with the 560 nm pumping light.

properties of the 6TTF-polymer did not change significantly from those of TTF.¹² Since TTF-derivative salts keep the high symmetric planar conformation and undergo oxidation at mild potentials to generate a stable radical cation, TTF-derivative salts can exhibit high electrical conductivity.¹²⁻¹⁴ Two reversible oxidation peaks appearing at 0.47 (cation radical TTF⁺) and 0.75 V (dication TTF²⁺) for TTF itself were detected at 0.62 and 0.90 V for the 6TTF-polymer, respectively. The difference of electrochemical potentials could be due to the combined effects of the electro-donating effect from the disulfide groups and the molecular aggregation.¹³ Slight increase in the oxidation potentials implied that the TTF moiety becomes more stable to the air/light oxidation reaction which is one of the main drawbacks of TTF molecules for the practical application.¹⁴

To investigate optical properties of the 6TTF-polymer, UV-vis absorption was also monitored in dichloromethane (Figure 4(a)), and the results were tabulated in Table 1. The 6TTF-polymer exhibited two absorption bands between 270 and 350 nm and a wide absorption band in the range of 450-550 nm. Absorptions between 270 and 350 nm corresponds to the absorptions of the malonyl group in the 6TTF-polymer, and a wide absorption in the range of 450-550 nm is contributed by the TTF moiety in the polymer.¹⁵ Based on

the UV result and CV analysis, the HOMO level and band-gap energy (E_g) of the 6TTF-polymer were estimated to be -4.79 and 1.91 eV, respectively. Compared with the HOMO levels of typical *p*-type organic semiconductors (4.9-5.5 eV), the 6TTF-polymer showed slightly higher energy indicating that the TTF moiety is more stable to air/light oxidation as mentioned in the discussions of optical properties based on the UV spectral results.¹⁵ Additionally, it is worth to note that the 6TTF-polymer possesses a relatively low band gap which is promising as a good electron donor for the OPV applications.

As shown in Figure 4(b), PL spectra were obtained from the 6TTF-polymer/PCBM blends with various weight ratios, indicating that the 6TTF-polymer can be used as a good electron donating polymer having a low band-gap for photovoltaic applications. For PL spectra of the 6TTF-polymer/PCBM blends, dilute solutions were prepared in chlorobenzene with 0.01 wt % concentration, and excited by pumping a 560 nm wavelength laser which was determined by UV-vis spectrum of 6TTF-polymer (Figure 4(a)). Furthermore, BHJ solar cell devices (ITO/PEDOT:PSS/6TTF-polymer:PCBM/Al) were fabricated by using the 6TTF-polymer/PCBM blends and the photo-conversion efficiencies were compared with respect to the 6TTF-polymer/PCBM ratio. Even though 6TTF-polymer was fairly well quenched by PCBM, the photo-conversion efficiency of the BHJ solar cell was low (0.01%). Therefore, to improve the photo-conversion efficiency, the HOMO level of 6TTF-polymer should be tuned by varying the conjugation length of TTF moiety and the molecular packing structure, and the morphology of 6TTF-polymer/PCBM blends should be optimized, which are under the investigations.

Conclusion

A novel 6TTF-polymer containing TTF moiety in the main chain was successfully synthesized *via* a condensation polymerization between dihydroxy TTF derivative and malonyl chloride, and its chemical structure was characterized by spectroscopic techniques. The resulting 6TTF-polymer was further functionalized by the reaction of the malonate group in the polymer chain with C₆₀ to obtain 6TTF-C₆₀ polymer, in which an electron donor (TTF) and electron acceptor (C₆₀) were covalently bound in the polymer main chain. While the 6TTF-polymer showed excellent solubility in common organic solvents, the 6TTF-C₆₀ polymer was insoluble in any of common organic solvents due to the chemical crosslinking caused by multiple substitutions at the C₆₀ moiety during the introduction of C₆₀ onto 6TTF-polymer. Number average molecular weight of the 6TTF-polymer was estimated to be 9,030 g/mol by GPC, and the resulting film was ductile to be bent. The electrochemical and optical analyses of the 6TTF-polymer by CV, UV-vis and PL spectroscopies revealed that the HOMO level (E_{HOMO}) and band-gap energy (E_g) of the 6TTF-polymer were -4.79 and 1.91 eV, respectively. The high HOMO level and low band-gap energy suggested that the 6TTF-polymer

could act as a good electron donor for the OPV applications. The BHJ solar cells fabricated with 6TTF-polymer/PCBM blends, however, displayed relatively low photo-conversion efficiencies.

Experimental Section

Materials. Column chromatography was performed on Merck silica gel (70-230 mesh). All reagents were of commercial qualities and used as supplied, otherwise we stated the purification processes. The compound **3** was prepared in our laboratory by the two-step reactions according to the reference 10.

4-(6-Hydroxyhexylthio)-5-(methylthio)-1,3-dithiole-2-thione (4). Under the nitrogen atmosphere at room temperature, compound **3** (3.0 g, 9.8 mmol) and cesium hydroxide monohydrate (3.8 g, 22 mmol) were dissolved in methanol (50 mL). After stirring for 2 h, 6-bromohexan-1-ol (2.22 mL, 16.5 mmol) was added into the mixture, and the solution was stirred for 12 h at room temperature. After the evaporation of solvent, the residue was purified by column chromatography by using ethyl acetate/methylene chloride as an eluent to obtain compound **4** (yellowish oil, 3 g, 76%). FT IR spectrum (KBr, cm^{-1}): 1060 (C=S), and 3270 (OH); $^1\text{H-NMR}$ (CDCl_3 , δ_{H}): 3.65 (2H, t), 2.87 (2H, t), 2.50 (3H, s), 1.66 (2H, m), 1.58 (2H, m), and 1.42 (4H, m).

4-(6-(2,2-Dimethyl-1,1-diphenylpropoxy)hexylthio)-5-(methylthio)-1,3-dithiole-2-thione (5). To the solution of compound **4** (2.60 g, 8.33 mmol) in dimethylformamide (50 mL), the mixture of imidazole (6.0 g, 88 mmol) and *tert*-butyldiphenylsilyl chloride (2.29 g, 8.33 mmol) was added under the argon atmosphere at room temperature. The solution was stirred at room temperature for 12 h. After the evaporation of solvent, the residue was dissolved in dichloromethane, washed with water, and dried with magnesium sulfate. Column chromatographic purification with dichloromethane afforded compound **5** as an orange oil (4.0 g, 87%). $^1\text{H NMR}$ (CDCl_3 , δ_{H}): 7.68-7.64 (4H, m), 7.42-7.38 (6H, m), 3.65 (2H, t), 2.83 (2H, t), 2.47 (3H, s), 1.68 (2H, m), 1.56 (2H, m), 1.36 (4H, m), and 1.05 (9H, s).

4-(6-(2,2-Dimethyl-1,1-diphenylpropoxy)hexylthio)-5-(methylthio)-1,3-dithiol-2-one (6). Mercuric acetate (4.54 g, 14.3 mmol) was added to the solution of compound **5** (3.5 g, 6.54 mmol) in dichloromethane (50 mL). After stirring for 0.5 h at room temperature, the reaction mixture was filtered, and the solvent was evaporated. Column chromatographic purification of the residue with dichloromethane provided compound **6** as a pale green oil (3.0 g, 88%). $^1\text{H NMR}$ (CDCl_3 , δ_{H}): 7.67-7.64 (4H, m), 7.42-7.38 (6H, m), 3.65 (2H, t), 2.83 (2H, t), 2.47 (3H, s), 1.68 (2H, m), 1.56 (2H, m), 1.36 (4H, m), and 1.05 (9H, s).

4-(6-(*tert*-Butyldiphenylsilyloxy)hexylthio)-2-(4-(6-(*tert*-butyldiphenylsilyloxy)hexylthio)-5-(methylthio)-1,3-dithiole-2-ylidene)-5-(methylthio)-1,3-dithiole (7). The solution of compound **6** (2.5 g, 4.67 mmol) in triethylphosphate (20 mL) was stirred at 130 °C for 5 h. After gradually cooling the mixture to room temperature, the solvent was evapo-

rated. The residue was purified by a column chromatography with dichloromethane/hexane as an eluent to obtain compound **7** as a red orange oil (2.05 g, 88%). $^1\text{H NMR}$ (CDCl_3 , δ_{H}): 7.67-7.62 (8H, m), 7.41-7.36 (12H, m), 3.63 (4H, t), 2.83 (4H, t), 2.46 (6H, s), 1.68 (4H, m), 1.56 (4H, m), 1.36 (8H, m), and 1.05 (18H, s).

4-(6-Hydroxyhexylthio)-2-(4-(6-hydroxyhexylthio)-5-(methylthio)-1,3-dithiol-2-ylidene)-5-(methylthio)-1,3-dithiole (8). Tetrabutylammonium fluoride (1 M in THF, 11 mL, excess) was added to the solution of compound **7** (2.05 g, 1.97 mmol) under the argon atmosphere at room temperature. The reaction mixture was stirred for 12 h. After the evaporation of solvent, the residue was purified by column chromatography with ethyl acetate as an eluent to afford compound **8** (0.9 g, 81%). $^1\text{H NMR}$ (CDCl_3 , δ_{H}): 3.63 (4H, t), 2.87 (4H, t), 2.50 (6H, s), 1.66 (4H, m), 1.58 (4H, m), and 1.42 (8H, m).

6TTF-Polymer (9). Malonyl chloride (0.66 g, 4.7 mmol) was added to the solution of compound **8** (2.47 g, 4.82 mmol), triethylamine (0.52 g, 5.1 mmol) and dichloromethane (100 mL). The reaction mixture was stirred at room temperature for 20 h under the argon atmosphere. The residue was precipitated in hexane, and the resulting solid was dried in vacuum oven to obtain compound **9** (reddish power, 1.5 g, 48%).

6TTF-C₆₀ Polymer (10). Under the argon atmosphere, C₆₀ fullerene (0.11 g, 0.152 mmol) was added to a mixture of 6TTF-polymer **9** (0.055 g), tetrabromomethane (0.26 g, 0.76 mmol) and 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU, 23 μL , 1.52 mmol) in toluene (100 mL). The mixture was stirred at 70 °C for 40 h. During the polymer reaction, 6TTF-C₆₀ polymer (**10**) was precipitated from the mixture as a dark brown power (0.05 g, 46%). The obtained compound **10** was washed with methanol several times and dried in a vacuum oven. The dark brown powder was not soluble in any of common organic solvents.

Measurements. $^1\text{H NMR}$ spectra were recorded with a Jeol JNM-EX 400 spectrometer using CDCl_3 . Here, Me_4Si was used as the internal standard. Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence system equipped with a UV detector using CHCl_3 as the eluent at 40 °C. The sample solutions were filtered with a PTFE filter (pore size: 0.2 μm) before injection. UV-vis absorption spectra were measured in dichloromethane with a Hewlett-Packard 8452A diode array spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. Cyclic voltammetry (CV) experiment was performed utilizing the Autolab PGSTAT 30 workstation. The electrolyte solution (0.1 M) was prepared from tetrabutylammonium perchlorate (Bu_4ClO_4). Platinum wire (2 mm in a diameter) was employed as the counter electrode. Here, an aqueous Ag/AgCl electrode was used as the reference and ferrocene (Fc) was added as an internal reference. A glassy carbon electrode was also used as the working electrode. The HOMO level (E_{HOMO}) of the 6TTF-polymer was obtained from the equation, $E_{\text{HOMO}} = - (E_{\text{onset}}^{\text{ox}} + 4.4 \text{ eV})$, where $E_{\text{onset}}^{\text{ox}}$ are the onset potentials for

the oxidation in CV.¹⁴ The band-gap energy (E_g) of the 6TTF-polymer was calculated from the equation, $E_g = hc/\lambda_{0.1max}$, where h , c and $\lambda_{0.1max}$ stand for the Planck constant, the speed of light and the wavelength (the absorption coefficient drops to 10% of the peak value in UV spectrum), respectively.¹⁴ For the measurement of the photo-conversion efficiency, PEDOT:PSS (Baytron PH 500) was first spin-coated to get the thin film (thickness = 30 nm) on the ITO surface. The film was baked at 120 °C for 20 min in a nitrogen-filled glovebox. Then, 6TTF-polymer/PCBM composites layer (*ca.* 100 nm thick) was applied on the top of PEDOT:PSS film. Finally, as an electrode Al layer was deposited with the thickness of 80 nm. The active area of all devices was 6 mm². All current-voltage (I - V) characteristics of the devices were measured utilizing Keithley 2400 sourcemeter under the AM 1.5G-filtered irradiation (100 mW cm⁻²).

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