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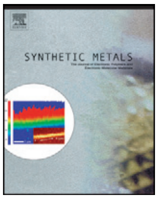

Polymerization of fluorene-based monomers modified with thiavinylidene structure at 9-position and their optical properties

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ABSTRACT

Two iodo-functionalized fluorene-based monomers having a thiavinylidene moiety at 9-position [2,7-diiodo-9-(*n*-hexylthiavinylidene)fluorene and 2,7-diiodo-9-((2-(2-methoxyethoxy)ethyl)thiavinylidene) fluorene] were synthesized. Suzuki coupling reactions with thienylboronic acids bearing a *n*-hexyl chain were subsequently conducted to obtain two thiophene-functionalized monomers [2,7-bis(4-hexylthienyl)-9-(*n*-hexylthiavinylidene)fluorene and 2,7-bis(3-hexylthienyl)-9-(*n*-hexylthiavinylidene)fluorene]. The dehalogenative polycondensation using Ni(cod)$_2$/cod/bpy system and the oxidation coupling polymerization using FeCl$_3$ gave three homopolymers (**HP1**, **HP2**, and **HP3**). The polymerization under Suzuki coupling condition gave three copolymers (**CP1**, **CP2**, and **CP3**). The number-averaged molecular weights ranged from 2500 to 23,000. The optical properties of polymer were dependent upon the character of arylene unit. Namely, **HP1** solely consisting of a 9-(*n*-hexylthiavinylidene)fluorene segment demonstrated the short absorption maximum wavelength but the large red-shift (13 nm) from the solution state to film state. **CP3** having a hydrophilic side chain showed the larger red-shift (13 nm) as compared with **CP2** bearing the similar backbone and a hydrophobic side chain.

1. Introduction

Since the pioneering work by Shirakawa, MacDiarmid, and Heeger [1], many conjugated polymers have been developed from academic and industrial viewpoints. Conjugated polymers are potentially applicable as optoelectronic materials such as light-emitting diode, plastic laser, solar cell, field-effect transistor, and so forth. Although the polymer materials have a merit over low molecular weight counterparts because the large area flexible devices can be fabricated in a low cost process such as spin coating and inkjet printing, the device performance is often lower than those using low molecular weight materials as an active layer. Understanding factors limiting charge carrier mobility is thus the current topic to make conjugated polymers useful as the optoelectronic devices in the next generation [2–5]. The device performance based on these kinds of material is strongly dependent upon the macromolecular morphology constituted by polymer chains, which is deeply related to non-covalent π–π stacking, hydrogen bonding, hydrophobic, and electrostatic interactions in the solid state. Among conjugated polymers, poly(3-hexylthiophene) having a precisely controlled head-to-tail regioregularity demonstrated the quite high charge carrier mobility. This polymer is known to form a densely packed crystalline lamella structure due to the strong π–π interaction [6]. Recently, the synthesis and device fabrication of alkylidene fluorene liquid crystalline semiconducting polymers have been reported by McCulloch and co-workers [7]. The introduction of sp^2-hybridized carbon at 9-position of fluorene forced the alkyl chain to adopt coplanar conformation relative to the polymer backbone, and resulted in the efficient intermolecular π–π stacking and the smooth charge carrier hopping between polymer chains. On the other hand, not only the π–π interaction but also the S–S and S–π interactions play important roles to modify the packing arrangement of the material as confirmed with 6,13-bis(alkylthio)pentacene derivatives [8]. The intermolecular crystal packing of pentacene derivatives could be changed from the typical herringbone structure to the slipped cofacial π–π stacking one by introducing small methylthio functionality at 6,13-positions of pentacene. With these backgrounds in our mind, we started the synthesis of conjugated polymers containing fluorene modified with a thiavinylidene structure at 9-position in order to tune the stacking of polymer chains.

2. Experimental

2.1. Materials

All reactions were performed under nitrogen unless otherwise noted. Dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide

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(DMF), $CHCl_3$, toluene, 1,5-cyclooctadiene (cod) were dried following to standard methods and distilled under nitrogen prior to use. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Triphenylphosphine (PPh_3) and 2,2′-bipyridine (bpy) were recrystallized from *n*-hexane. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$] were purchased from Aldrich Chemical Co. and iron(III) chloride ($FeCl_3$) was purchased from Kishida Chemical Co. 9,9-Dihexylfluorene-2,7-diboronic acid was purchased from Aldrich Chemical Co. 2,7-Diiodofluorene [9], sodium 4-hexyl-2-thienylboronate [10,11], 3-hexyl-2-thienylboronic acid pinacol ester [12], 2,5-didecyloxybenzene-1,4-diboronic acid [13] were synthesized according to previous reports.

2.2. Instruments

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance200 FT-NMR spectrometer using tetramethylsilane (^1H NMR, δ 0.00) or $CDCl_3$ (^{13}C NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Jasco FT-IR 460plus spectrophotometer. Melting points (Mp) were determined on a Yanagimoto micro melting point apparatus MP-J3. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh DP-8020 using tandem TSK Multipore H_{XL}-M columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with the refractive index detector (RI-8012). The average molecular weights were calculated from calibration curve made from standard polystyrene samples. Ultraviolet (UV) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using a 1 cm quartz cell. Quantum yields in the solution state were determined relative to quinine sulfate in 0.1 N H_2SO_4 with a quantum yield of 0.55.

2.3. Monomer synthesis

2.3.1. 2,7-Diiodo-9-(n-hexylthiavinylidene)fluorene (*DIHTF*)

In a two-necked round bottom flask, 2,7-diiodofluorene (2.0 g, 4.8 mmol) was dissolved in DMSO (50 mL) and NaH (0.52 g, 13 mmol) was added to the solution. After the solution color changed to dark-red, CS_2 (0.40 mL, 5.4 mmol) was added and the mixture was stirred at room temperature for 1 h. 1-Bromohexane (2.0 mL, 13.3 mmol) was added and the reaction was conducted for further 4 h. The mixture was poured into water and extracted with CH_2Cl_2, which was dried over $MgSO_4$, and the solvent was evaporated. The crude product was recrystallized from *n*-hexane to give a yellow crystal in 2.9 g (93% yield). Mp. 74–76 °C. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 4H), 1.70 (m, 4H), 1.47–1.28 (12H), 0.87 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 145.3, 139.6, 138.1, 136.1, 135.7, 135.2, 120.6, 92.6, 36.4, 31.3, 30.0, 28.6, 22.5, 14.0. IR (ATR) (cm^{-1}) 2924.5, 2850.3, 1519.6, 1438.6, 1384.6, 1263.2, 1113.7, 1060.7, 961.3, 805.1, 719.3, 656.6. Found: C, 47.12; H, 4.83 %. Calcd for $C_{26}H_{32}I_2S_2$: C, 47.14; H, 4.87 %.

2.3.2. 2,7-Diiodo-9-((2-(2-methoxyethoxy)ethyl)thiavinylidene) fluorene (*DIMEETF*)

This material was prepared by the procedure similar to **DIHTF** from 2,7-diiodofluorene (0.20 g, 0.48 mmol) and diethylene glycol monomethyl ether mono(*p*-toluenesulfonate) (0.36 g, 1.3 mmol). The product was purified by column chromatography (SiO_2, CH_2Cl_2:acetone = 12:1) to give a yellow solid in 0.05 g (13 % yield). Mp. 41–43 °C. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.33 (d, *J* = 1.3 Hz, 2H), 7.65 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 4H), 3.62–3.58 (m, 4H), 3.55–3.51 (m, 4H), 3.35 (s, 6H), 3.27 (t, *J* = 6.2 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 142.6, 139.5, 138.3, 137.3, 136.5, 135.4, 120.6, 92.6, 71.8, 70.4, 69.9, 59.0, 35.2. IR (ATR) (cm^{-1}) 2872.5, 1515.8, 1438.6, 1386.6, 1351.9, 1194.7, 1094.4, 1059.7, 970.0, 814.8, 805.1. Found: C, 41.19; H, 3.70%. Calcd for $C_{24}H_{28}I_2O_4S_2$: C, 41.27; H, 4.04%.

2.3.3. 2,7-Bis(4-hexylthienyl)-9-(n-hexylthiavinylidene)fluorene (*B4HThHTF*)

In a two-necked round bottom flask equipped with a reflux condenser, the mixture of **DIHTF** (0.16 g, 0.24 mmol) and sodium 4-hexyl-2-thienylboronate (0.12 g, 0.48 mmol) in THF (5 mL) and saturated aq. $NaHCO_3$ (2 mL) was refluxed overnight in the presence of $Pd(PPh_3)_4$ (3.0 mg, 2.6 μmol). The mixture was extracted with CH_2Cl_2, washed with H_2O, and dried over $MgSO_4$. The crude product was recrystallized from *n*-hexane to give a yellow crystal in 0.10 g (56 % yield). Mp. 61–62 °C. ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.23 (d, *J* = 1.2 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.56 (dd, *J* = 7.9 Hz, 1.5 Hz, 2H), 7.20 (d, *J* = 1.2 Hz, 2H), 6.87 (d, *J* = 0.8 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 4H), 2.64 (t, *J* = 7.3 Hz, 4H), 1.81–1.60 (8H), 1.49–1.21 (24H), 0.93–0.79 (12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 145.1, 144.5, 142.5, 139.3, 138.8, 138.1, 133.6, 125.2, 124.3, 124.2, 119.5, 119.2, 36.5, 31.9, 31.5, 30.9, 30.6, 30.3, 29.2, 28.8, 22.8, 22.6, 14.3, 14.1. IR (ATR) (cm^{-1}) 2922.6, 2854.1, 1780.9, 1596.8, 1520.6, 1465.6, 1284.4, 1004.7, 907.3, 816.7, 728.9, 647.9. Found: C, 73.95; H, 8.27%. Calcd for $C_{46}H_{62}I_2S_4$: C, 74.34; H, 8.41%.

2.3.4. 2,7-Bis(3-hexylthienyl)-9-(n-hexylthiavinylidene)fluorene (*B3HThHTF*)

This material was prepared by the procedure similar to **B4HThHTF** from **DIHTF** (0.16 g, 0.24 mmol) and 3-hexyl-2-thienylboronic acid pinacol ester (0.15 g, 0.50 mmol). The product was purified by column chromatography (SiO_2, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.06 (d, *J* = 0.6 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.41 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.23 (s, 2H), 7.01 (d, *J* = 5.08 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 4H), 2.75 (t, *J* = 7.7 Hz, 4H), 1.80–1.56 (8H), 1.49–1.10 (24H), 1.00–0.70 (12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 142.2, 139.0, 138.9, 138.7, 138.5, 133.6, 129.7, 128.9, 127.8, 123.5, 119.2, 36.3, 31.9, 31.5, 31.2, 30.4, 29.5, 29.1, 28.8, 22.8, 22.6, 14.2, 14.1. IR (ATR) (cm^{-1}) 2953.5, 2923.6, 2854.1, 2360.4, 1518.7, 1464.7, 951.7, 906.4, 819.6, 729.9. Found: C, 73.85; H, 8.18%. Calcd for $C_{46}H_{62}I_2S_4$: C, 74.34; H, 8.41%.

2.4. Polymerization

2.4.1. *HP1*

The mixture of $Ni(cod)_2$ (0.12 g, 0.42 mmol), bpy (0.06 g, 0.36 mmol), and cod (40 μL, 0.30 mmol) in DMF (1.2 mL) was stirred at 60 °C for 30 min in a two-necked test tube. To this solution was added **DIHTF** (0.20 g, 0.30 mmol) in toluene (2.4 mL) via syringe and the polymerization was conducted overnight at 80 °C. The cooled solution was then poured into CH_3OH to collect a brownish yellow powder in 0.11 g (89 % yield). ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.45–8.95 (2H), 7.90–7.45 (4H), 3.14–2.80 (4H), 1.80–0.60 (22H). IR (ATR) (cm^{-1}) 2953.5, 2923.6, 2852.2, 1516.7, 1449.2, 1403.0, 1259.3, 1018.2, 809.0. Found: C, 63.62; H, 6.84%. Calcd for $C_{26}H_{32}S_2$: C, 76.41; H, 7.89%.

2.4.2. *HP2*

In a two-necked round bottom flask, **B4HThHTF** (0.10 g, 0.13 mmol) was dissolved in $CHCl_3$ (2.0 mL). To this solution was added $FeCl_3$ (0.09 g, 0.54 mmol) in $CHCl_3$ (10 mL) via syringe at 0 °C and the reaction temperature was gradually increased to room temperature under stirring. The polymerization was continued for