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Preparation and characterization of alternating copolymers containing fluorene and thiophene derivatives

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A series of fluorene-based polymers with alkylsulfanyl, alkylsulfinyl and alkylsulfonyl substituted thiophene were synthesized by the palladium-catalyzed Suzuki coupling reaction and the structures were confirmed by nuclear magnetic resonance spectroscopy and mass spectrometry. The results of the absorption and emission spectra reveal that the substituents on the thiophene ring strongly affect the planarity of the polymer chains. The interruption of the effective conjugation length through the non-planar conformation results in high photoluminescence quantum yield. Cyclic voltammetry analysis of the polymers was observed that the non-planar polymers increased the band gap and decreased the highest occupied molecular orbital level. Differential scanning calorimetry trace confirmed that the less steric hindrance of substituents on the thiophene ring would increase the intermolecular interaction and the crystallinity of the polymers.

1. Introduction

Conjugated polymers have attracted much attention in recent years due to their potential in low cost and large area fabrication in electronic devices [1–3]. The materials have been widely studied for the application in optoelectronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic photovoltaics (OPVs) and sensors [4–9]. The physical, optical and electronic properties of conjugated polymers can be tailored by changing the chemical structure, the nature of the substituent, the molecular weight of the polymer and the end groups. It has been shown that alternating structure with electron donating and withdrawing groups on the polymer backbone lead to smaller band gaps and higher performance in devices [10,11]. Introduction of alternating electron donating and withdrawing groups on the polymer backbone generally decrease the photoluminescence (PL) and electroluminescence (EL) efficiencies of the resultant copolymers due to strong charge transfer effect [12]. This makes it challenging to design copolymers with balanced hole or electron transport while still retaining the high PL quantum yields. Among the variety of organic semiconductors developed, fluorene and thiophene copolymers have emerged as an important class because of their high chemical stability, their unique electronic and optical properties, the availability of regioselective methods and the possibility of introducting appropriate substitutents on the different position of the aromatic ring [13,14].

Herein, we report the preparation of the alternating copolymers with fluorene and thiophene derivatives along the backbone by palladium catalyzed coupling reaction. The different molecular weights of the copolymers can be obtained by simply changing the reaction time and solvent. The intermolecular interaction of a series of fluorene and substituted thiophene copolymers can be investigated by absorption and photoluminescence spectroscopy. The highest occupied molecular orbital and band gap of the

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copolymers are in good agreement with the absorption observed. Overall, these new polymers are interesting and will be applied to optoelectronic devices such as organic photovoltaics or light emitting diodes.

2. Experimental

2.1. Materials and measurements

Unless otherwise noted, all reagents were used as received from Alfa or Aldrich without further purification. THF was distilled under a nitrogen atmosphere over sodium/benzophenone. ^{1}H, and ^{13}C NMR spectra were recorded in deuterated chloroform on a Bruker AVIII 500 MHz spectrometer. (Abbreviations used: *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; br, broad). Electron Impact (EI) mass spectra were determined on Shimadzu LCMS-IT-TOF Mass Spectrometer. Electrospray Ionization (ESI) mass spectra were recorded on Finnigan LCQ Mass spectrometer. HRMS spectra were recorded on FINNIGAN MAT 95S Mass Spectrometer. Elemental analysis was performed on a Heraeus varioIII-NCSH elemental analyzer for NCSH, German. Gel permeation chromatography (GPC) was carried in THF solution using low polydispersity polystyrene standards for calibration with Water 2414 RI detector. UV–vis measurements were obtained on a Jasco V-670 UV–vis-NIR spectrophotometer. Photoluminescence measurements were carried out on a Jasco FP6300 fluorescence spectrophotometer. Polymer thin films were spin-coated on a glass plate from tetrahydrofuran (THF) solution at 1000 rpm for 60 s. Thermal properties were studied by Thermogravimetric Analysis on a TA TGA Q500 at a heating rate of 10 °C/min. Differential Scanning Calorimetry on a Perkin–Elmer DSC4000 thermal analyser at a heating rate of 10 °C/min. The melting point was recorded by MEL-TEMP 1001D melting point apparatus. Cyclic voltammetry (CV) was performed at 100 mV/s in a Digi-IVY DY2300 potentiostat electrochemical workstation with a three-electrode cell, Ag/AgCl as reference electrode and platinum wire as counter electrode. The polymer films onto a Pt plate is used as a working electrode with anhydrous 0.10 M tetrabutylammonium hexafluorophosphate ($[\text{n-Butyl}]_4NPF_6$) as a supporting electrolyte in nitrogen-pureged anhydrous acetonitrile (CH_3CN) solution at room temperature. In order to model the electron affinity and ionization potential, the HOMO and LUMO of oligomers with dimethyl side chains attached to fluorene and methyl side chain attached to sulfur, sulfoxide or sulfone on the thiophene ring were computed using density functional theory (DFT). Becke's three parameter exchange and the Lee–Young–Parry correlation functionals (B3LYP) were used with added polarization basis functions (6-31G*).

2.2. Synthesis of monomers and polymers

2.2.1. Synthesis of 2,2′-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**)

To a solution of 2,7-dibromo-9,9-dioctylfluorene (4.0 g, 7.3 mmol) in dry THF (80 mL) was added n-butyllithium (12 mL, 19.2 mmol, 1.6 M) dropwise over ten minutes and the mixture was stirred at −78 °C for 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (4.6 mL, 19.8 mmol) was then added and the resulting mixture was stirred for a further 1.5 h at −78 °C, allowed to warm to room temperature and stirred for a further 18 h. The reaction mixture was poured into water (200 mL), extracted with diethyl ether (100 mL), washed with water (2 × 50 mL) and dried with magnesium sulfate. The solvent was evaporated and then the crude product was purified by recrystallization from the solvent system of DCM and methanol and column chromatography using 5% ethyl acetate in hexane as eluent to give white crystals in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 7.5 Hz, 2H), 7.75 (s, 2H), 7.72 (d, J = 7.5 Hz, 2H), 2.00 (m, 4H), 1.39 (s, 24H), 1.23–0.97 (m, 20H), 0.81 (t, J = 7.2 Hz, 6H), 0.56 (m, 4H) ppm. ^{13}C NMR (167 MHz, $CDCl_3$): δ 150.30, 143.74, 133.21, 128.48, 118.92, 83.27, 54.73, 39.64, 31.33, 29.48, 28.74, 28.70, 24.49, 23.15, 22.14, 13.61 ppm. Mass spectrum (EI+, *m*/*z*) 643 (M^+). m.p 127–128 °C.

2.2.2. Synthesis of 2,5-dibromo-3-hexylsulfanylthiophene (**2**)

To a mixture of dichloromethane (20 mL) and 3-hexylsulfanylthiophene (3.0 g, 15 mmol), *N*-bromosuccinimide (5.3 g, 30 mmol) was added slowly. The mixture was then stirred at 40 °C for 14 h. After the reaction was cooled to room temperature, the solution was poured into dilute potassium hydrate to adjust the pH to 7 and then the solution mixture was extracted with chloroform. The combined organic fractions were washed with water and dried over $MgSO_4$. The solvent was then completely removed and the remains were purified by column chromatography (eluent:hexane). A light yellow oil was obtained in a yield of 59%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90 (s, 1H), 2.82 (t, J = 7.3 Hz, 2H), 1.57 (m, 2H), 1.40 (m, 2H), 1.29 (m, 4H), 0.89(t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (167 MHz, $CDCl_3$): δ = 134.05, 132.32, 112.79, 110.91, 35.29, 31.28, 29.47, 28.2, 22.49, 13.98 ppm. Mass spectrum (EI+, *m*/*z*) 358 (M^+).

2.2.3. Synthesis of 2,5-dibromo-3-hexylsulfinylthiophene (**3**)

To hydrogen peroxide (0.1 mL, 1 mmol, 30%, $d = 1.1\ \text{g cm}^{-3}$) was added to 2,5-dibromo-3-hexylsulfanylthiophene (0.36 g, 1 mmol) in toluene (7.5 mL) and glacial acetic acid (2.5 mL) under argon. The mixture was stir at 100 °C for 4 h. After the reaction was cooled to room temperature, the solution was extracted with dichloromethane and water. The organic layer was dried over $MgSO_4$ and removed by evaporator. The crude compound was purified by silica gel column chromatography (eluent: hexane: ethyl acetate = 4:1) to give a brown liquid (0.29 g, yield 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28(s, 1H), 2.85–3.00(m, 2H), 1.62–1.78(m, 2H), 1.39–1.58(m, 2H), 1.30(m, 4H), 0.88(t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (167 MHz, $CDCl_3$): δ = 143.8, 127.4, 113.6, 110.55, 55.59, 31.27, 28.24, 22.33, 22.2, 13.91 ppm. Mass spectrum (EI+, *m*/*z*) 375 (M^+). HRMS (EI+, *m*/*z*) 374.8898 (calculated for M^+: 374.8905).

2.2.4. Synthesis of 2,5-dibromo-3-hexylsulfonylthiophene (**4**)

To hydrogen peroxide (0.1 mL, 2.5 mmol, 30%, $d = 1.1\ \text{g cm}^{-3}$) was added to 2,5-dibromo-3-hexylsulfanylthiophene (0.36 g, 1 mmol) in toluene (7.5 mL) and glacial