



Effect of substituents on electrochemical and optical properties of thienyl-derivatized polypyrenes

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ABSTRACT

A series of pyrene-based monomers that incorporate thiophene or 3,4-ethylenedioxythiophene (EDOT) units at the 1- and 1,6-positions were synthesized and electropolymerized. Through manipulating the heterocycle groups attached to pyrene unit, the electronic properties and energy levels of the polymers were effectively tuned. Substitution with alkoxy functionalized thiophene, i.e., EDOT, results in a decrease in the monomer and polymer oxidation potentials, narrowing of the electronic bandgap relative to the corresponding thiophene substituted pyrenes. With the increase of the number of substituent groups on pyrene units, the polymers show much bigger conjugated length. Moreover, the introduction of two substituent units lowers much more band gap than that of one substituent unit. These results suggested a simple and effective approach for tuning the bandgap in a conjugated polymer through modification of the pendant substituent groups.

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1. Introduction

Conjugated polymers have been the focus of intensive research activities because of their potential for applications such as photovoltaics (PVs) [1], field effect transistors (FETs) [2], light emitting diodes (LEDs) [3], electrochromic devices (ECDs) [4]. As a series of functional materials, conjugated polymers (CPs) such as thiophene-based materials or arylene derivatives have gained much attention during the past decade due to their interesting electrical and optical properties. The combination of molecules has allowed their optical and electrochemical properties to be tuned over a wide range, which can be achieved by appropriate chemical way of selecting and modifying the molecular structures. Structural modification can be obtained by changes in the planarity of the backbones as a function of steric hindrance, attachment of electron-donating and/or -withdrawing groups to the repeat unit, increase in the conjugation length by means of fused heterocycles, or copolymerization of different monomers [5–7].

Polymers derived from various functionalized aromatic derivatives, such as heterocycle-substituted polyphenylenes [8], polynaphthalenes [9], polyanthracenes [10], polypyrenes [11] and polyfluorenes [12], have been investigated extensively due to their potential applications in organic light emitting diodes, electrochromic devices and photovoltaics. Among these, pyrene and its derivatives have been the subject of investigation because the optical

and electrical properties of pyrene can be tuned by systematic substitution at the 1-, 2-, 3-, 6-, 7-, and 8-positions. Generally, fused ring aromatic molecules have more planar geometries so that the materials with fused ring moieties can be expected as promising candidates for optoelectronic device applications [13]. In recent years, there have been many reports about mono- (1-), di- (1,6- or 2,7-) and tetra- (1,3,6,8-) substituted pyrene monomers by unsubstituted or substituted thiophene, which are focused on their hole-transporting, photophysical properties and electroluminescent properties and their potential applications in photovoltaic systems and organic light-emitting diodes, organic field effect transistors (OFETs) [14–17]. Additionally, regioregular polymers such as poly(1,6-bis(2-(didecylpropylenedioxy)thienyl)pyrene) [18] and poly(2,7-bis(2-(3-dodecylthienyl)pyrene) [13], and random copolymers based on pyrene with 3,4-ethylenedioxythiophene [19] and bithiophene [20] have been synthesized and reported in the literatures, which exhibit interesting and potential useful light-emitting and electrochromic properties. Owing to the large planer conjugative structure, pyrene-containing compounds usually exhibit strong intermolecular π - π interaction. The extended π -system presents in the pyrene though considered as a weak acceptor could be exploited as a sensitizing unit by coupling with electron-rich moieties such as thiophene and/or fluorene [21]. In light of these considerations, it will be of great interest to evaluate the effects of extending the conjugation length of pyrene by electrophilic substitution at the 1- and 1,6-positions with electron-rich moieties and thus modulating the electrochemical and optical properties of the corresponding polymers.

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In this report, a series of pyrene-based monomers that incorporate thiophene and 3,4-ethylenedioxythiophene units at the 1- and 1,6-positions were synthesized and electropolymerized. And the substituents variation effect on the optical and electrochemical properties of both the monomers and their corresponding polymers was also studied in detail.

2. Experimental

2.1. Materials

1-Bromopyrene, 1,6-dibromopyrene, thiophene, 3,4-ethylenedioxythiophene (EDOT, 98%) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were all purchased from Aldrich Chemical and used as received. Commercial high-performance liquid chromatography grade acetonitrile (ACN, Tedia Company, INC., USA) and dichloromethane (DCM, Shanghai Chemical Reagent Company) were used directly without further purification. Sodium perchlorate (NaClO₄, Shanghai Chemical Reagent Company, 98%) was dried in a vacuum at 60 °C for 24 h before use. The precursors 2-(tri-*n*-butylstannyl)-thiophene and 2-(tri-*n*-butylstannyl)-3,4-ethylenedioxythiophene were prepared according to literature method [22]. Other reagents were all used as received without further treatment. Indium–tin-oxide-coated (ITO) glass (sheet resistance: <10 Ω □⁻¹, purchased from Shenzhen CSG Display Technologies, China) was successively washed with ethanol, acetone and deionized water in an ultrasonic bath and then dried by a constant stream of N₂.

2.2. Monomers synthesis

2.2.1. 1-(Thiophen-2-yl)pyrene (TP)

TP was synthesized via Stille cross coupling reaction. 1-Bromopyrene (1.0 g, 3.56 mmol) and 2-(tri-*n*-butylstannyl)-thiophene (2.8 g, 7.5 mmol) were dissolved in dry THF (80 ml), the solution was purged with nitrogen for 30 min and tetrakis(triphenylphosphine)palladium(0) (0.15 g, 0.13 mmol) was added at room temperature. The mixture was refluxed over night under nitrogen atmosphere. The crude mixture was chromatographed on silica gel by eluting with hexane: ethyl acetate (4:1, v/v) to give TP as white solid (0.53 g, 52%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 7.27 (dd, 1H), 7.39 (d, 1H), 7.52 (d, 1H), 8.01–8.22 (m, 8H), 8.50 (d, 1H). ¹³C NMR (CDCl₃; δ in ppm): 124.7, 125.2, 125.5, 126.4, 127.5, 127.7, 128.0, 128.1, 128.7, 129.4, 130.0, 131.2, 131.7, 142.8. Elemental analysis for: C₂₀H₁₂S, Calc. C, 84.51; H, 4.23; S, 11.26. Found: C, 84.48; H, 4.24; S, 11.28.

2.2.2. 1-(3,4-Ethylenedioxythiophen-2-yl)pyrene (EP)

EP was synthesized by a coupling of 1-bromopyrene with 2-(tri-*n*-butylstannyl)-3,4-ethylenedioxythiophene according to the method as TP. The purified product was a yellow solid (0.74 g, 61%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 4.25–4.33 (m, 4H), 6.57 (s, 1H), 8.00–8.20 (m, 8H), 8.29 (d, 1H). ¹³C NMR (CDCl₃; δ in ppm): 65.0, 99.9, 116.3, 124.9, 125.2, 125.3, 125.5, 126.0, 126.3, 127.4, 127.6, 127.9, 128.0, 129.1, 129.6, 131.2, 131.4, 131.6, 138.6, 141.8. Elemental analysis for: C₂₂H₁₄O₂S, Calc. C, 77.19; H, 4.09; S, 9.36. Found: C, 76.98; H, 4.15; S, 9.31.

2.2.3. 1,6-Bis(2-thienyl)pyrene (TPT)

TPT was also prepared by Stille coupling of 1,6-dibromopyrene with 2-(tri-*n*-butylstannyl)-thiophene in THF using Pd(PPh₃)₄ as catalyst with the same procedure described above. The purified product was a yellow solid (0.58 g, 57%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 7.27 (dd, 2H), 7.39 (d, 2H), 7.53 (d, 2H), 8.10 (t, 4H), 8.19 (d, 2H), 8.52 (d, 2H). ¹³C NMR (CDCl₃; δ in ppm):

129.8, 130.0, 130.2, 131.6, 132.7, 133.0, 133.1, 133.8, 134.2, 135.1, 135.6, 150.0. Elemental analysis for: C₂₄H₁₄S₂, Calc. C, 78.69; H, 3.83; S, 17.48. Found: C, 78.43; H, 3.89; S, 17.68.

2.2.4. 1,6-Bis(2-(3,4-ethylenedioxy)thienyl)pyrene (EPE)

EPE was synthesized by a coupling of 1,6-dibromopyrene with 2-(tri-*n*-butylstannyl)-3,4-ethylenedioxythiophene according to the method as EP. The purified product was a yellow solid (0.63 g, 47%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 4.26–4.32 (m, 8H), 6.57 (s, 2H), 8.08 (dd, 4H), 8.19 (d, 2H), 8.30 (d, 2H). Elemental analysis for: C₂₈H₁₈O₄S₂, Calc. C, 69.71; H, 3.73; S, 13.28. Found: C, 69.51; H, 3.79; S, 13.32. (The ¹³C NMR spectra of monomer EPE cannot be obtained because of its poor solubility in solvent CDCl₃, DMSO-d₆ or their mixture).

2.3. Measurements

¹H NMR and ¹³C NMR spectroscopy studies were carried out on a Varian AMX 400 spectrometer and tetramethylsilane (TMS) was used as the internal standard. Elemental analyses are determined by a Thermo Finnigan Flash EA 1112, CHNS-O elemental analyses instrument. Scanning electron microscopy (SEM) measurements were taken by using a Hitachi SU-70 thermionic field emission SEM. Electrochemical synthesis and experiments were performed in a one-compartment cell with a CHI 760 C Electrochemical Analyzer under the control of a computer, employing a platinum wire with a diameter of 0.5 mm as working electrode, a platinum ring as counter electrode, and a Ag wire (0.03 V vs. SCE. [23]) as pseudo reference electrode. In UV-vis and spectroelectrochemical measurements, solution spectra of the obtained monomers, dissolved in chloroform, as well as the solid state spectra of their thin films deposited on an ITO/glass electrode, were recorded on a Perkin-Elmer Lambda 900 UV-vis – near-infrared spectrophotometer. Moreover, the thickness of the polymer films grown potentiostatically on the ITO/glass electrode was controlled by the total charge passed through the cell.

2.4. Electrochemical polymerization

Electrochemical polymerization of the monomers was carried out in a ACN/DCM (1:1, by volume) solution of 0.005 M monomer and 0.2 M NaClO₄ by repetitive cycling at a scan rate of 100 mV s⁻¹. A platinum wire was used as a counter electrode and Ag wire as a pseudo reference. The polymers were directly coated onto platinum wire or indium–tin oxide glass (ITO/glass, <10 Ω □⁻¹, 0.9 cm × 5 cm) and then the films were rinsed with acetonitrile to remove from electrolyte salt.

3. Results and discussion

3.1. Synthesis

A series of pyrene derivatives mono or difunctionalized in the 1 or 1,6-positions with thiophene or 3,4-ethylenedioxythiophene groups have been synthesized as shown in Scheme 1. A general synthetic route was used: Stille coupling reaction between mono or dibromopyrene with the corresponding stannyl compounds, which were obtained previously by a reaction between thiophene or EDOT and tributyltin chloride in THF. The obtained monomers were initially characterized by spectral (¹H and ¹³C NMR) and elemental analyses data, which was in well agreement with the structures (see Supporting information).

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