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Dithieno[*a*,*e*]pentalene Based Conjugated Polymers: Synthesis and Characterization

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The concept of introducing π-conjugated but anti-aromatic repeating units into conjugated polymers has been explored. The thermal stability, optical and electrochemical properties of dithieno[*a*,*e*]pentalenes (DTP) based polymers have been studied. The effect of introducing electron withdrawing repeating units into DTP based polymer on the physical properties of polymer has also been investigated. The new polymers showed broad absorption in visible and near-infrared region.

Keywords pentalene, conjugated polymer, low-bandgap polymer, anti-aromatic

Introduction

Ring-fused structures with extended π-conjugation have received considerable amount of attention as building blocks for organic semiconducting materials, recently.[1-16] Fused heteroaromatic units such as thieno[3,2-*b*]thiophene[7,17-22] and thieno[3,4-*b*]thiophene[23,24] have been successfully incorporated into many high performance conjugated polymers for field-effect transistor (OFET) and organic photovoltaic (OPV) applications. The five: five fused heterocyclic systems are isoelectronic with the 10-π-electron pentalene dianion and can be considered as hetero analogs of the dianion.[25] The parent pentalene is an eight-π-electron system. It is antiaromatic and highly reactive.[25-27] Some pentalene derivatives such as dibenzopentalenes have been perceived as useful building blocks for synthesis of conjugated polymers because of their rigid planar and conjugated structure.[28-32] Small molecules based on dibenzopentalenes have been synthesized and applied in organic electronic devices.[31] Substituted dithieno[*a*,*e*]pentalenes (DTPs) are stable compounds and the efficient synthetic methods for them have been developed lately.[28,29] The DTPs can be interesting building blocks for conjugated polymers. However, the application of DTP derivatives as building blocks for conjugated polymer has never been reported. Herein, we reported the first synthesis of conjugated polymers with DTP as building blocks. The optical and electrochemical properties of polymers were also investigated.

Experimental

Materials

Chemicals were purchased from Sigma-Aldrich Chemical Company, Alfa Aesar Chemical Company, Sinopharm Chemical Reagent Co. Ltd. and Darui Chemical Co. Ltd. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium wire under nitrogen prior to use. Other materials were used without further purification. All flash chromatography separations were carried out on silica gel (200－300 mesh). The 2-bromo-3-iodothiophene,[33] 4-hexylphenylacetylene,[34] and dibromo monomer **6**[35,36] were synthesized according to reported methods. Bis(trimethylstannyl) monomer **4** and **5** were reported in our previous work.[37,38]

Measurements and characterization

NMR spectra were recorded on a Mercury plus 400 MHz machine. GPC analysis was performed on a Shimadzu LC-20 A coupled with refractive index detector using THF as eluent with polystyrenes as standards. TGA was carried out on a TA instrument QS000IR at a heating rate of 20 ℃•min^{-1} under nitrogen gas flow. UV-vis spectra were recorded on a Perkin Elmer Lambda 20 UV-Vis spectrophotometer. Electrochemical measurements were conducted with a CHI 600 electrochemical analyzer under nitrogen atmosphere in a deoxygenated anhydrous solution of tetra-*n*-butylammoniumhexafluorophosphate (0.1 mol/L) in acetonitrile. A platinum electrode was used as a working electrode, a platinum wire was used as an auxiliary electrode, and an Ag/Ag$^+$ electrode was used as a reference electrode. Polymer thin films were coated on platinum electrode and ferrocene was chosen as a reference. A potential scan rate of 50 mV•s^{-1} was used for all experiments.

Synthesis of monomer

2-Bromo-3-(4-hexylphenyl)ethynylthiophene (1)

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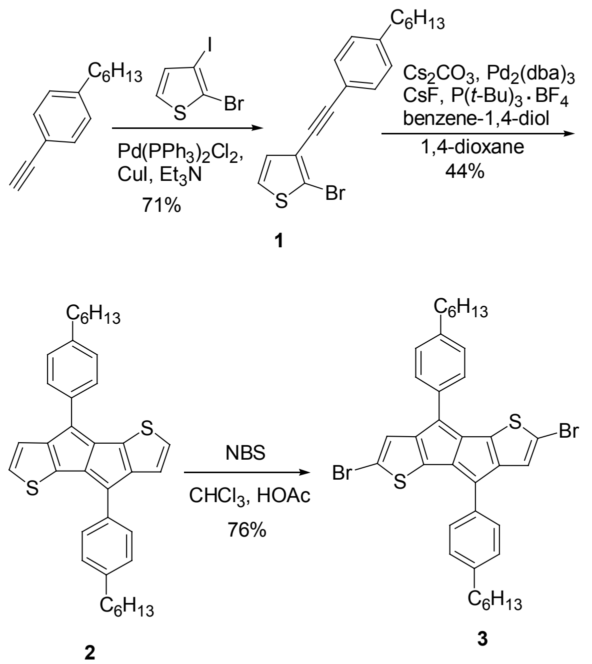
A mixture of 2-bromo-3-iodothiophene (5.07 g, 17.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.061 g, 0.087 mmol) and copper(I) iodide (0.033 g, 0.173 mmol) in triethylamine (150 mL) was degassed for 10 min. 4-Hexylphenylacetylene (3.43 g, 18.4 mmol) was added to the solution. After stirring at room temperature for 12 h, the mixture was filtered through a celite pad and the filtrate was collected. The solvent was removed under reduced pressure and residue was purified by chromatography on silica gel with petroleum ether (boiling range 60—90 ℃) as an eluent to give the product as a colorless liquid (4.31 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=8.0 Hz, 2H), 7.21 (d, J=2.4 Hz, 1H), 7.18 (d, J=8.0 Hz, 2H), 7.04 (d, J=2.4 Hz, 1H), 2.63 (t, J=8.0 Hz, 2H), 1.68—1.58 (m, 2H), 1.50—1.19 (m, 6H), 0.91 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.03, 131.82, 130.02, 128.74, 125.96, 124.97, 120.21, 116.82, 93.64, 82.69, 36.20, 31.96, 31.46, 29.18, 22.87, 14.37.

Scheme 1 Synthesis of monomers



4,8-Di(4-hexylphenyl)-2,6-dithia-dicyclopenta[*a*,*e*]pentalene (2) Hydroquinone (0.634 g, 5.76 mmol), cesium carbonate (1.88 g, 5.77 mmol), cesium fluoride (0.962 g, 6.334 mmol), tris(dibenzylideneacetone)dipalladium (0.040 g, 0.044 mmol), tri-*tert*-butylphosphoniumtetrafluoroborate (0.050, 0.173 mmol) were added into a reaction vessel under nitrogen. A degassed solution of **1** (1.0 g, 2.879 mmol) in 1,4-dioxane (20 mL) was transferred to the vessel. The vessel was sealed with a Teflon stopcock and was heated at 140 ℃ for 48 h. After cooled to room temperature, the mixture was filtered through a celite pad and was washed thoroughly with chloroform. The filtrate was collected and evaporated to dryness. The residue was purified by chromatography on silica gel with petroleum ether (boiling range 60—90 ℃) as an eluent to give the titled product as a brown solid (0.35 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, J=8.0 Hz, 4H), 7.24 (d, J=8.0 Hz, 4H), 6.80 (d, J=4.8 Hz, 2H), 6.70 (d, J=4.8 Hz, 2H), 2.64 (t, J=8.0 Hz, 4H), 1.68—1.58 (m, 4H), 1.50—1.19 (m, 12H), 0.90 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.35, 145.97, 142.77, 139.26, 137.18, 130.79, 129.02, 127.85, 127.36, 121.46, 36.22, 31.96, 31.49, 29.29, 22.85, 14.36.

Compound 3

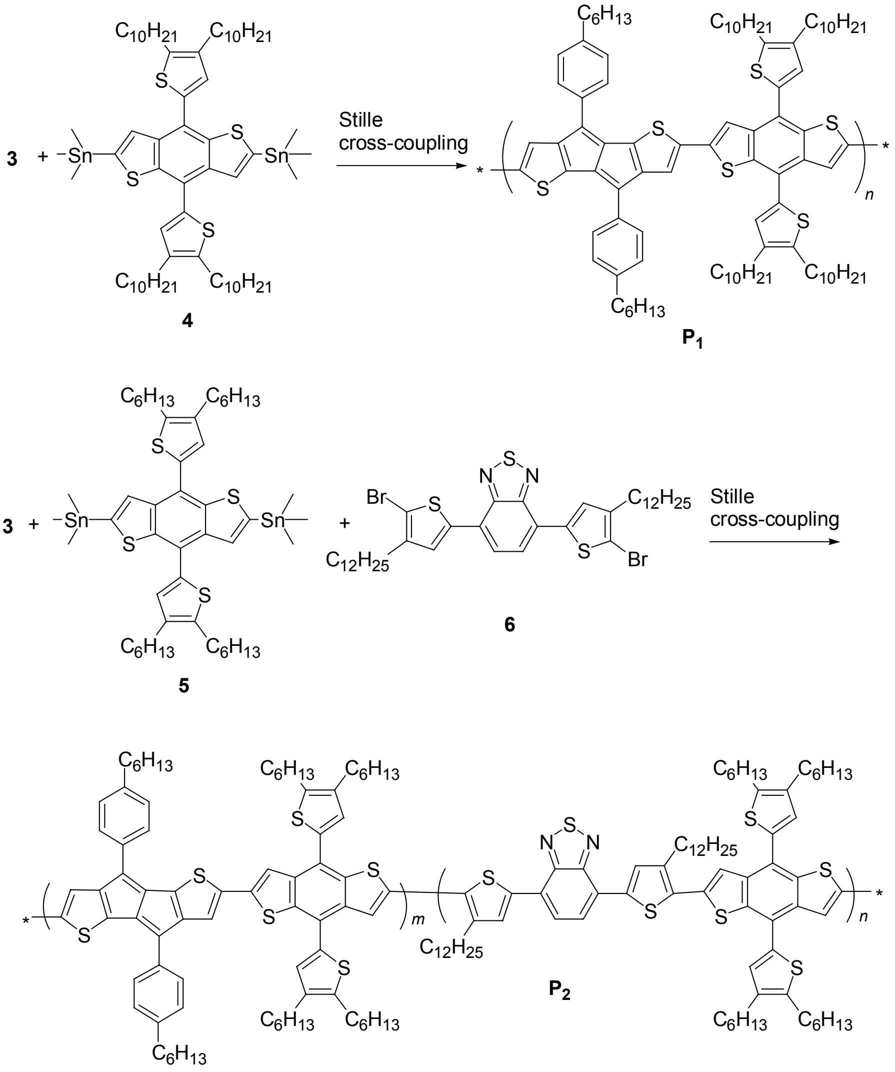
N-Bromosuccinimide (0.210 g, 1.18 mmol) was added to the solution of **2** (0.30 g, 0.561 mmol) in chloroform (45.0 mL) and acetic acid (45.0 mL) at 0 ℃. The mixture was stirred for 1 h at 0 ℃ and then was quenched with water. The mixture was extracted with diethyl ether (100 mL) for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and the residue was purified by recrystalization in acetone to afford a dark orange solid (0.30 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J=8.0 Hz, 4H), 7.18 (d, J=8.0 Hz, 4H), 6.56 (s, 2H), 2.63 (t, J=8.0 Hz, 4H), 1.68—1.58 (m, 4H), 1.50—1.19 (m, 12H), 0.90 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.10, 145.65, 142.06, 138.31, 138.28, 130.05, 129.22, 127.67, 124.42, 113.76, 36.21, 31.92, 31.43, 29.26, 22.82, 14.33. Anal. calcd for $C_{36}H_{36}Br_2S_2$: C 62.43, H 5.24; found C 62.11, H 5.18.

Synthesis of polymers

Polymer P1 Tris(dibenzylideneacetone)dipalladium (0.0040 g, 0.0044 mmol) and tri-*o*-tolylphosphine (0.0050 g, 0.0160 mmol) were added to a solution of **3** (0.140 g, 0.202 mmol) and **4** (0.251 g, 0.202 mmol) in toluene (12.0 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was heated to 110 ℃ for 24 h. After cooled to room temperature, the mixture was poured into methanol (100 mL) and was stirred for 2 h. The precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 24 h each time. It was extracted with hot chloroform in a Soxhlet extractor for 24 h. After removing solvent, a black solid was collected (0.25 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.2—7.9 (br, 14H), 2.4—3.2 (br, 12H), 0.4—2.1 (br, 98H). Anal. calcd for $C_{94}H_{124}S_6$: C 78.06, H 8.64; found C 78.32, H 8.66; GPC: M_n=20.1 kDa; PDI=4.52.

Polymer P2 Tris(dibenzylideneacetone)dipalladium (0.0040 g, 0.0044 mmol) and tri-*o*-tolylphosphine (0.0050 g, 0.0160 mmol) were added to a solution of **3** (0.065 g, 0.094 mmol), **6** (0.075 g, 0.094 mmol), and **5** (0.191 g, 0.188 mmol) in toluene (12.0 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was heated to 110 ℃ for 8 h. After cooled to room temperature, the mixture was poured into methanol (100

Scheme 2 Synthesis of polymers



mL) and was stirred for 2 h. The precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 24 h each time. It was extracted with hot chloroform in a Soxhlet extractor for 24 h. After removing solvent, a black solid was collected (0.21 g, 88%). ^1H NMR ($CDCl_3$, 400 MHz) δ: 6.8—8.1 (b, 22H), 2.5—3.0 (b, 24H), 1.0—2.0 (b, 120H), 0.6—1.0 (b, 36H). Anal. calcd for $C_{158}H_{202}N_2S_{13}$: C 74.53, H 8.00, N 1.10; found C 74.62, H 8.74, N 1.01; GPC: M_n=14.5 kDa; PDI=2.32.

Results and Discussion

Synthesis and characterization

The synthetic routes for monomer and polymers are shown in Schemes 1 and 2. The precursor, 2-bromo-3-(4-hexylphenyl)ethynylthiophene (**1**) was synthesized through Sonogashira cross-coupling reaction between 2-bromo-3-iodothiophene and 4-hexylphenylacetylene at room temperature in 71% yield. The dithieno[*a*,*e*]pentalenes (**2**) was synthesized according to Tilley's method with slight modification. The Pd-catalyzed reductive homocoupling of haloenynes was carried out with tris(dibenzylideneacetone)dipalladiumas catalyst and tri-*tert*-butylphosphoniumtetrafluoroborate as ligand, hydroquinone as reducing agent, cesium carbonate as base and cesium fluoride as additive. The bromination of **2** with NBS at 0 ℃ gave the monomer **3** in 77% yield. Benzodithiophene (BDT) was chosen as co-monomer for **P1**. The BDT and 4,7-bis(4-dodecylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (DTBTz**)** were chosen as co-monomers for **P2**. The BDT is a rigid planar structure with extended π-conjugation. This structure facilitates π-electron delocalization within the polymer chain and improves π-π interactions between polymer chains in solid states.[24] The DTBTz was a repeating unit for enhancing the donor/acceptor interaction of polymers, therefore, reducing the bandgap of polymer.[36]

The polymer **P1** was synthesized by Stille cross-coupling reaction in the presence of tris(dibenzylideneacetone)dipalladium as catalyst and tri-*o*-tolylphosphine as ligand. The **P1** was purified by washing with methanol and hexane successively in a Soxhlet extractor for 24 h each time, then were extracted with hot chloroform in a Soxhlet extractor for 24 h. The copolymer **P2** consisting of 2,4,7-bis(4-dodecylthiophen-2-yl)benzo[*c*]-[1,2,5]thiadiazole (**6**), **3** and **5** at 1∶1∶2 ratio was also synthesized by Stille cross-coupling reaction. The polymer was purified by the similar method as that for **P1**. Both of the two polymers are black solid and readily soluble in common solvent such as chloroform, toluene and chlolobenzene.

Thermal stability

Thermogravimetric analyses of **P1** and **P2** are shown in Figure 1. Both polymers showed good thermal stabilities with decomposition temperatures over 250 ℃.

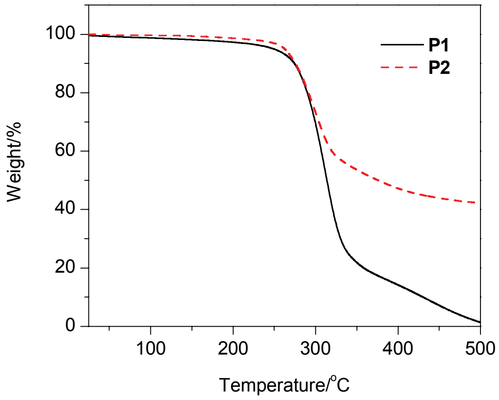


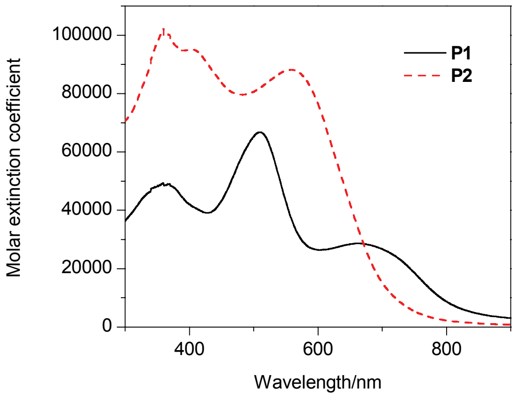
Figure 1 The TGA plots of **P1** and **P2**.

Optical properties

The UV-vis absorption spectra of **P1** and **P2** in chloroform solution and the spectra of thin films are shown in Figure 2. The optical properties of polymers are summarized in Table 1. The absorption peak positions were at 376, 513 and 691 nm for **P1** and 376, 418 and 589 nm for **P2** in chloroform soltion, respectively; and the absorption peak positions were at 376, 513 and 693 nm for **P1** and 383, 441 and 589 nm for **P2** in thin film, respectively. In chloroform solution, the absorption onsets were 812 and 707 nm for **P1** and **P2**; in thin flim, the absorption onsets were 832 and 773 nm for **P1** and **P2**. The optical bandgaps were calculated to be 1.49 and 1.60 eV for **P1** and **P2** (Table 1). The thin-film absorption onsets of polymers were red-shifted by about 20 nm for **P1** and 66 nm for **P2** compared to their solution absorption onsets. The thin-film absorption spectrum of **P2** became broad in the 300 to 700 nm region. The absorption of **P2** covered the whole visible region and it might be used as effective material for harvesting solar energy.

Electrochemichal properties

The cyclic voltammograms of the polymers **P1** and **P2** are displayed in Figure 3, and the electrochemical properties are summarized in Table 2. Both **P1** and **P2** showed irreversible oxidizing cycles and quasi-reversible reducing cycles. The HOMO levels were estimated from the onset oxidation. The HOMO energy levels of **P1** and **P2** were calculatd to be −5.19 and −5.40 eV, respectively (Table 2). The LUMO energy levels of **P1** and **P2** were estimated from the onset reduction. The LUMO energy levels of **P1** and **P2** were calculatd to be −3.39 and −3.76 eV, respectively. The electrochemical bandgaps were calculated to be 1.80 and 1.64 eV for **P1** and **P2**, respectively. After addition of benzothiadiazole repeating units, the HOMO and LUMO energy levels of copolymer **P2** were both reduced. However, the benzothiadiazole units which were electron-accepting units had larger effect on the LUMO level than on the HOMO level of the copolymer. This resulted in overall decreasing of electrochemical bandgap of **P2**.



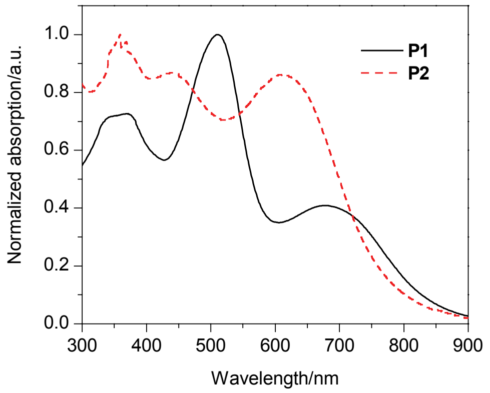


Figure 2 UV-Vis absorption spectra of **P1** and **P2** in chloroform solution (top) and as thin films (bottom).

Table 1 Optical properties of **P1** and **P2**

Polymer	Solution $\lambda_{\text{onset}}^{\text{abs}}$ ^{a}/nm	Film $\lambda_{\text{onset}}^{\text{abs}}$ /nm	E_g ^{b}/eV
P1	812	832	1.49
P2	707	773	1.60

^{a} Chloroform solution (2×10^{-5} and 1×10^{-5} mol/L for **P1** and **P2**, respectively); ^{b} E_g=1240/ $\lambda_{\text{onset}}^{\text{abs}}$.

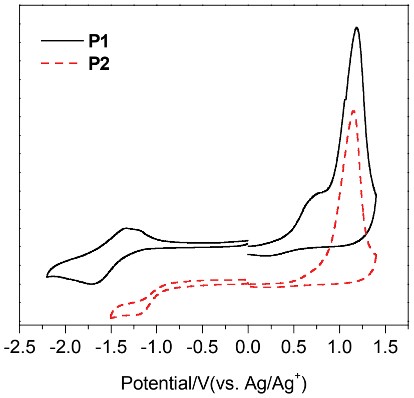


Figure 3 Cyclic voltammograms for **P1** and **P2** polymer films.

Table 2 Electrochemical properties of **P1** and **P2**

Polymer	$E_{\text{onset}}^{\text{red}}$ /V	$E_{\text{onset}}^{\text{ox}}$ /V	LUMO^a /eV	HOMO^b /eV	$E_g^{electrochem\ c}$/V
P1	−1.32	0.48	−3.39	−5.19	1.80
P2	−0.95	0.69	−3.76	−5.40	1.64

[a] LUMO = $-(4.71 + E_{\text{onset}}^{\text{red}})$; [b] HOMO = $-(4.71 + E_{\text{onset}}^{\text{ox}})$; [c] $E_{\text{g}}^{\text{electrochem}}$ =LUMO−HOMO.

Conclusions

Two new polymers with dithieno[*a*,*e*]pentalenes as repeating units have been synthesized. The conjugated but anti-aromatic repeating unit can be used as building block for low bandgap polymer. They can provide π-orbital overlap in the conjugated main-chain. The fused heterocyclic structures provide stability for the polymers. The thermal stability, optical and electrochemical properties of dithieno[*a*,*e*]pentalenes based polymer were characterized for the first time. The new polymers showed broad absorption in visible and near-infrared region and they might be used as material for harvesting solar energy.

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