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Synthesis and Characterization of Thieno[3,4-*b*]thiophene-Based Copolymers Bearing 4-Substituted Phenyl Ester Pendants: Facile Fine-Tuning of HOMO Energy Levels

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Supporting Information

Polymer solar cells (PSCs) have been attracting much interest because of their advantages; they are low cost, lightweight, and flexible and have the potential for the production of large-area devices.[1] Bulk heterojunction (BHJ) PSCs have become the most successful device configurations. In such devices, conjugated polymers, as an electron donor, and fullerene derivatives, as an electron acceptor, form an interpenetrating network on the nanometer scale.[2] For BHJ PSCs, regioregular poly(3-hexylthiophene) (P3HT) has been extensively used as the electron-donor material because of its solubility, stability, and compatibility with the typical electron acceptor [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$).[1,3] However, P3HT can only harvest less than ca. 23% of the available solar photons because its absorption band is located at wavelengths of less than 650 nm.[4] Extensive research efforts have therefore been devoted to developing novel conjugated polymers with low bandgaps to better harvest the solar energy and improve the power-conversion efficiencies (PCEs) of PSCs.[4,5]

Recently, Yu et al. reported π-conjugated polymers consisting of alternating thieno[3,4-*b*]thiophene (TT) and benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) units (PTB-based polymers), promising donor materials for PSCs, whose absorption region reached ca. 800 nm as a result of the stabilization of the quinoidal resonance structure in the polymer main chain by the thieno[3,4-*b*]thiophene unit.[6] The extended absorption of sunlight directly contributed to increasing the short-circuit current density (J_{sc}), and these PSCs exhibited high PCEs of over 5%, while the open-circuit voltages (V_{oc}) of the PSCs were relatively low, at ~0.6 V. It is known that the V_{oc} of a PSC is closely related to the difference between the highest occupied molecular orbital (HOMO) of the donor component and the lowest unoccupied molecular orbital (LUMO) of the acceptor, and deepening the HOMO energy level of the donor polymer is a potential way of developing highly efficient PSCs with a high V_{oc}.[7] The following two strategies have been used to deepen the HOMO energy level of PTB-based polymers: the introduction of a fluorine atom, which is the atom with the highest electronegativity, in the TT ring[6b] and the replacement of the alkyl ester pendants of the TT unit with alkyl ketone pendants.[8] These modifications reduced the HOMO energy levels of the polymers from −5.01 to −5.12 eV, and the PCEs were effectively improved from 5.15 to 6.10 and 6.58, respectively. An excellent PCE of 7.73% was achieved by combining the two strategies.[9] However, the synthesis of PTB-based polymers bearing a fluorine atom on the polymer main-chains is very time-consuming, and further structural modifications are quite limited.

In the present study, we designed and synthesized PTB-based polymers bearing 4-substituted phenyl esters instead of the previously reported alkyl esters as the pendants of the TT unit and found that their HOMO energy levels could be readily fine-tuned by changing the substituents on the phenyl groups.

The synthetic routes to the monomers and polymers are shown in Scheme 1. Four novel TT monomers bearing various phenyl ester groups (**TT1**−**TT4**) were easily prepared in one pot from commercially available phenol derivatives and the key precursor compound, 4,6-dibromothieno[3,4-*b*]thiophene-2-carboxylic acid (**1**), which was synthesized by modified literature procedures.[6b,10] These TT monomers were obtained in good yields (>70%). Initially, copolymerization of **TT1** and bis(trimethylstannyl) BDT comonomer **BDTa** with 2-ethylhexyloxy substituents, by Stille cross-coupling, was carried out using $Pd(PPh_3)_4$ as a catalyst in a toluene/*N*,*N*-dimethylformamide (DMF) mixture (4/1, v/v) to yield **PTT1BDTa**.[6] However, the resulting **PTT1BDTa** exhibited very low solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, and chlorobenzene, even at high temperatures. To improve the solubility of the polymer, a novel bis(trimethylstannyl) BDT bearing longer branched alkyl side chains, 2-octyldodecyloxy groups (**BDTb**), was synthesized and used as the comonomer instead of **BDTa**.

The results of the copolymerizations of **TT1**−**TT4** with **BDTb** are summarized in Table 1 (runs 1−4). The resulting polymers were purified by successive Soxhlet extractions with methanol (MeOH) and hexane to remove byproducts and oligomers and subsequent filtration through Celite to remove the metal catalyst. The four polymers, **PTT1BDTb**, **PTT2BDTb**, **PTT3BDTb**, and **PTT4BDTb**, were obtained in relatively good yields (60−85%). The introduction of 2-octyldodecyloxy substituents on the BDT unit enhanced the solubility of the resulting polymers, and the obtained polymers exhibited good solubility in THF, chloroform, and chlorinated benzene. For comparison, we also prepared the corresponding alkyl ester type polymer **PTT5BDTb** (run 5 in Table 1) and the reported PTB-based polymer **PTT5BDTa** (run 6 in Table 1).[6b] The molecular weights (M_n) of the obtained polymers were determined by size-exclusion chromatography (SEC) in THF. All the polymers have a similar molecular weight, so the structural modification of the ester groups in the TT units seems to have little effect on the polymerizability of these

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Scheme 1. Synthesis and Structures of Monomers and Polymers

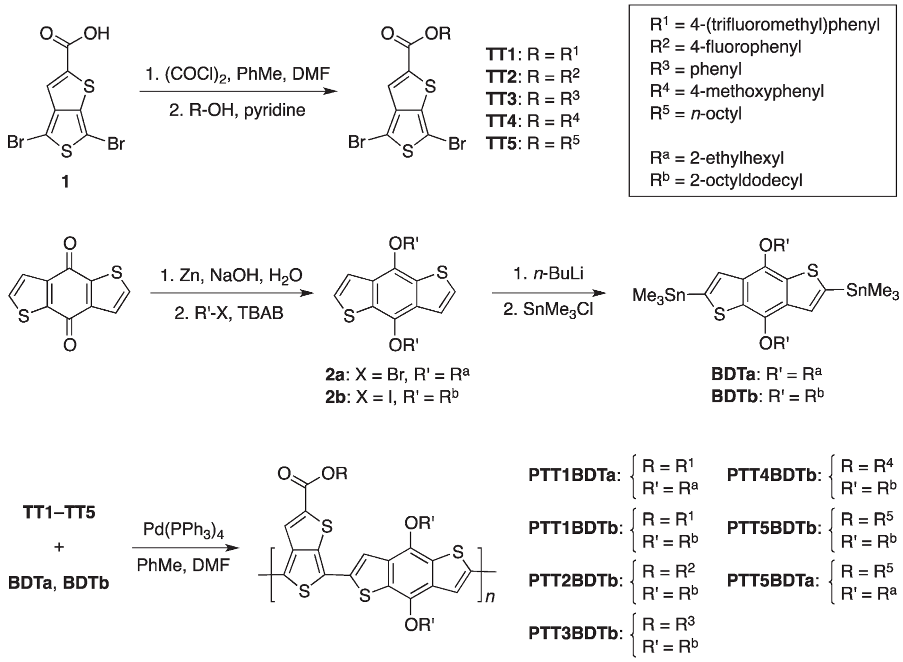

Table 1. Polymerization Results and Thermal and Optical Properties of the Polymers

run	polymer	yield (%)[a]	M_n (10^4)[b]	PDI[b]	T_d (°C)[c]	λ_{max} (nm)	λ_{onset} (nm)	E_g (eV)[d]	HOMO (eV)[e]	LUMO (eV)[f]
1	**PTT1BDTb**	62	5.9	3.0	313	692	761	1.63	−5.60	−3.97
2	**PTT2BDTb**	60	6.1	3.6	316	686	755	1.64	−5.39	−3.75
3	**PTT3BDTb**	85	7.1	3.3	315	682	748	1.66	−5.23	−3.57
4	**PTT4BDTb**	82	6.7	2.3	313	684	751	1.65	−5.12	−3.47
5	**PTT5BDTb**	77	6.1	2.4	316	671	736	1.68	−5.13	−3.45
6	**PTT5BDTa**	71	4.7	2.7	326	675	758	1.63	−5.01	−3.38

[a] MeOH and hexane-insoluble part. [b] Determined by SEC (eluent: THF, PSt standard). [c] The 5% weight-loss temperatures with a heating rate of 10 °C/min in N_2. [d] Calculated from $E_g = 1240/\lambda_{onset}$. [e] Measured by photoelectron spectroscopy in air. [f] Calculated from LUMO = E_g + HOMO.

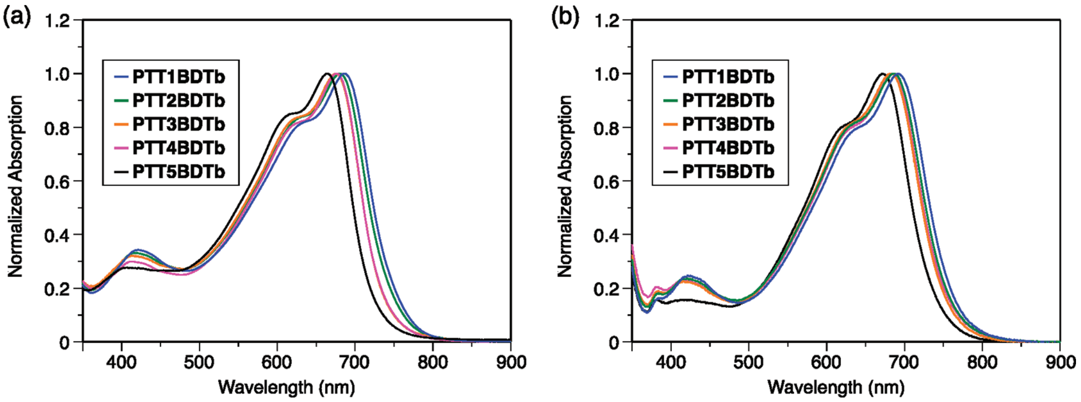

Figure 1. Absorption spectra of the polymers in chlorobenzene (a) and in the film state (b).

TT-based monomers. The thermal stability of these polymers was investigated by thermal gravimetric analysis (TGA) under a nitrogen atmosphere (Supporting Information, Figure S1). All polymers showed good thermal stability with 5% weight loss temperatures (T_d) above 300 °C, which is adequate for application in PSC devices.

Figure 1 shows the absorption spectra of the polymers in chlorobenzene and in the film state. The absorption spectra of the polymers in solution are very similar to those in the solid state, suggesting that the polymers possess a similar rigid-rod conformation in both states. The absorption bands of the polymers with phenyl

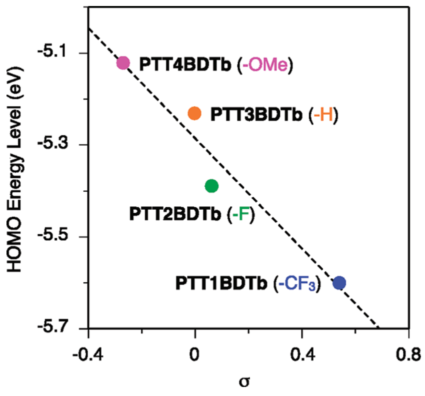

Figure 2. Plots of HOMO energy levels of the polymers against the Hammett constants σ of the substituents.

ester groups and those of **PTT5BDTb** were located at around 500–800 nm; this was consistent with the spectra of previously reported PTB-based polymers with alkyl ester groups, such as **PTT5BDTa**.[6b] The optical bandgaps ($E_g^{opt} = 1240/\lambda_{onset}$) were estimated based on the absorption onset wavelength (λ_{onset}) of the polymer films and are summarized in Table 1. Compared with **PTT5BDTb** bearing an alkyl ester group, the polymers bearing phenyl ester groups exhibited somewhat narrower E_g^{opt} values, depending on the type of substituent. As the electron-withdrawing ability of the substituent increases, the optical bandgaps tend to be slightly narrower. These results mean that the phenyl ester groups can contribute to elongation of the π-conjugation length of the polymer main chains.

The HOMO energy levels of the polymers were estimated with a photoelectron spectrometer by measuring the ionic potential of the polymer films in air (Supporting Information, Figure S2), and the LUMO energy levels were calculated from the values of the HOMO energy level and the E_g^{opt} (LUMO = E_g^{opt} + HOMO); the values are listed in Table 1. When electron-withdrawing groups such as trifluoromethyl and fluoro groups were introduced on the phenyl groups, the HOMO energy levels became deeper compared with those for the nonsubstituted **PTT3BDTb** (−5.23 eV). In contrast, electron-donating substituents such as a methoxy group raised the HOMO energy level to −5.12 eV. To visualize the substituent effect, the HOMO energy levels of the polymers are plotted against the Hammett constants (σ)[11] of the substituents in Figure 2. A relatively good linear relationship is observed between the HOMO energy levels and the σ values. Computational studies using density functional theory (DFT) at the B3LYP/6-31G(d,p) level[12] were additionally performed for the corresponding model compounds to evaluate the influence of these substituents on the HOMO energy levels of the polymers (Supporting Information, Figure S15). The calculated HOMO energy levels for the model compounds also showed a similar tendency to the experimental values for the polymers, although the calculated values were rather higher than the experimental ones (Supporting Information, Figure S16). These results suggest that the substituents on the phenyl groups can perturb the electron density of the main chain through an ester linkage, and one can finely tune the HOMO energy levels of the polymers by selecting the substituents on the phenyl groups.

The hole mobilities of these polymers were measured by a method based on the space-charge-limited current (SCLC) model using the corresponding hole-only devices.[13] The hole mobilities of **PTT1BDTb**, **PTT2BDTb**, **PTT3BDTb**, and **PTT4BDTb** bearing phenyl ester groups were estimated to be 1.4×10^{-5}, 2.8×10^{-5}, 2.0×10^{-5}, and 2.7×10^{-5} cm^2 V^{-1} s^{-1}, respectively, which are comparable to that of **PTT5BDTb** bearing alkyl ester groups (3.9×10^{-5} cm^2 V^{-1} s^{-1}). Replacement of the alkyl esters with phenyl esters therefore seems to bring about only slight changes in the hole mobility for this type of polymer. However, the hole mobilities of these polymers were relatively low compared with that of **PTT5BDTa** with 2-ethylhexyloxy side chains on the BDT unit (8.4×10^{-5} cm^2 V^{-1} s^{-1}) measured with our hole-only device.[14] The bulkier branched side chains, 2-octyldodecyloxy groups, on the BDT unit may increase the steric hindrance and make it difficult to form efficient intermolecular π–π-stacking, which is very important in transporting the holes inside the polymer films. It is therefore necessary to optimize the side-chain structures in consideration of both the solubility and the charge transport properties.

In conclusion, a series of PTB-based polymers consisting of alternating thieno[3,4-*b*]thiophene units bearing 4-substituted phenyl ester pendants and benzo[1,2-*b*:4,5-*b*′]dithiophene units were synthesized, and their thermal and optical properties were investigated. We found that the HOMO energy levels of the polymers could be finely tuned in the range −5.12 to −5.60 eV by changing the substituents on the phenyl ring, and there was a relatively good linear correlation between the HOMO energy levels and the Hammett substituent constants. Since **PTT1BDTb** and **PTT2BDTb** with electron-withdrawing substituents possess deeper HOMO energy levels, at −5.60 and −5.39 eV, respectively, compared with those of previously reported PTB-based polymers,[6b,8,9,15] the PSCs based on these polymers are expected to show higher V_{oc} values. Further improvements in hole mobility by optimizing the side-chain structures on the benzodithiophene units should therefore yield promising results for realizing high-efficiency PSCs. Detailed investigations of the photovoltaic properties of the PSCs produced using these PTB-based polymers are currently in progress and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, NMR spectra of all TT monomers and polymers, TGA curves, photoelectron spectra, DFT-calculated frontier molecular orbitals, plots of calculated HOMO energy levels against the Hammett constants, and *I*–*V* curves for the hole-only devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The hole mobility of **PTT5BDTa** has been reported to be 4.0×10^{-4} cm^2/(V s),[6b] which is rather higher than that estimated in this work. The difference may be ascribed to the different configurations of the hole-only devices (see Supporting Information).

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