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Tuning Energy Levels of Low Bandgap Semi-Random Two Acceptor Copolymers

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Supporting Information

ABSTRACT: A series of low bandgap semi-random copolymers incorporating various ratios of two acceptor units—thienothiadiazole and benzothiadiazole—were synthesized by Pd-catalyzed Stille coupling. The polymer films exhibited broad and intense absorption spectra, covering the spectral range from 350 nm up to 1240 nm. The optical bandgaps and HOMO levels of the polymers were calculated from ultraviolet—visible spectroscopy and cyclic voltammetry measurements, respectively. By changing the ratio of the two acceptor monomers, the HOMO levels of the polymers were tuned from -4.42 to -5.28 eV and the optical bandgaps were varied from 1.00 to 1.14 eV. The results indicate our approach could be applied to the design and preparation of conjugated polymers with specifically desired energy levels and bandgaps for photovoltaic applications.

1. INTRODUCTION

Conjugated polymers (CPs) are promising materials for applications in sensors, field-effective transistors, organic lightemitting diodes, and organic photovoltaics (OPVs) due to their cost-effective solution processability.¹ Devices based on CPs can be easily fabricated into lightweight, large-area, and flexible panels.² The power conversion efficiency (PCE) of OPVs has reached 12% recently;³ devices with PCE that reach 15% efficiencies are expected to compete with silicon-based solar cells in the next decade.^{1a,4} New CPs that collect as much sunlight as possible are needed to meet the fundamental requirement for the photovoltaic energy conversion.⁵

The efficiency of a polymer solar cell is proportional to the short-circuit current density (J_{sc}) , the open-circuit voltage (V_{oc}) , and the fill factor (FF). These variables require optimization to reach maximum efficiencies.^{4,6} The J_{sc} is related to the product of the breadth and intensity with which polymers absorb the solar spectrum, where broader and more intense absorption theoretically leads to larger J_{sc} .^{4,7} Optimization requires the design and synthesis of low bandgap CPs extending the absorption further into red and near-infrared (NIR) spectral regions. An effective device requires CPs to have a low highest occupied molecular orbital (HOMO) to help increase the V_{oc} and high lowest unoccupied molecular orbital (LUMO) for efficient charge dissociation in the CP/PCBM bulk heterojuction device.⁵ It is clear that achieving specific HOMO and LUMO energy levels with precision and controlling the bandgaps are essential for effective material development.^{5,8}

Introducing donor (D) and acceptor (A) monomers together in the polymer backbone is a promising strategy to obtain CPs with low bandgaps that absorb light in the red to NIR spectral



regions.^{5,7,9} The D–A copolymer is also employed to rationally tune the HOMO and LUMO levels, crystallinity, and charge mobility of the CPs by changing the chemical structures of the donor and acceptor units. Recently, a series of D-A random copolymers incorporating donor or acceptor units randomly distributed in the backbone have been reported.4,10 These polymers showed compositional dependent energy levels, solubility, charge mobility, and crystallinity-all useful in photovoltaic applications. Copolymers incorporating two acceptor units are of particular interest: the properties could be manipulated by changing different acceptors structure and composition. In this contribution, we report a series of semirandom copolymers containing different ratios of two strong acceptors-benzothiadiazole and thienothiadiazolewhich have been utilized to prepare D-A low bandgap CPs.^{9c,d,11} By systematically changing the composition of the two acceptors, each with different electron-accepting abilities, the energy levels and bandgaps can be tuned stoichiometrically, thus offering a new class of CPs with bandgaps as low as 1.0 eV.

2. RESULTS AND DISCUSSION

Polymer Synthesis. Copolymerization of 5,7-bis(5-bromo-4-decanyl-2-thienyl)thieno[3,4-*b*]thiadiazole (TTD), 4,7-bis[5-bromo-4-(2-ethyhexyl)-2-thienyl]-2,1,3-benzothiadiazole (TBT), and 2,5-bis(tri-*n*-butyltin)thiophene in chlorobenzene at 120 °C with Pd(PPh₃)₄ as the catalyst yielded the desired polymers, as illustrated in Scheme 1. All the polymers show

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Scheme 1. Synthesis and Structures of the Copolymers with Different Compositions of TTD and TBT



good solubility at room temperature in organic solvents such as chloroform, chlorobenzene, and *o*-dichlorobenzene (ODCB). The comonomer feed ratios are 85:15, 70:30, 50:50, 30:70, and 15:85, and the corresponding polymers are named as PTTDTBT8515, PTTDTBT7030, PTTDTBT5050, PTTDTBT3070, and PTTDTBT1585, respectively. Polymers containing only one acceptor unit were also synthesized for comparison, named as PTTD and PTBT. Table 1 summarizes

Table 1. Polymerization Results and Thermal Properties of Polymers

polymer	$M_{\rm n}^{\ a}$ (kDa)	${M_{ m w}}^b$ (kDa)	PDI ^c	T_{d}^{d} (°C)	ratio in the polymer ^e
PTTD	1.6	4.0	2.4	305	
PTTDTBT8515	6.4	16.3	2.5	269	92:8
PTTDTBT7030	3.2	12.1	3.7	314	79:21
PTTDTBT5050	3.7	14.2	3.8	350	56:44
PTTDTBT3070	5.0	17.0	3.4	369	32:68
PTTDTBT1585	9.3	24.3	2.6	360	13:87
PTBT	13.2	18.6	1.4	417	
			1.		

^aNumber-average molecular weight. ^bWeight-average molecular weight. ${}^{c}M_{\rm w}/M_{\rm n}$. ^dDecomposition temperature (5% weight loss) determined by thermal gravimetric analysis (TGA) under N₂. ^eTTD:TBT in the polymer estimated from absorption spectra.

the polymerization results including molecular weight, molecular weight distribution (PDI), thermal stability, and estimated compositions of the copolymers. The polymers containing two acceptor units have relatively low molecular weights (M_n) ; this could probably be increased further by optimization of polymerization conditions such as monomer concentration in solution, reaction time, catalyst, and temperature.^{9h} The polymers have good thermal stability with an increasing decomposition temperature (5% weight loss) when the TBT content is increasing.

Optical Properties. The UV–vis–NIR absorption spectra of the copolymers in thin film formats are shown in Figure 1. PTTD, in which only thienothiadiazole was incorporated as the acceptor unit, displayed two absorption bands: the first one at 358–620 nm, which was assigned to localized π – π * transitions, and the second broader band at 620–1266 nm, in the long wavelength region, which corresponds to intramolecular charge transfer (ICT) between D–A–D charge transfer states.^{9d} Incorporating benzothiadiazole as the only acceptor unit, PTBT



Figure 1. UV-vis absorption spectra of polymers in thin films.

exhibited localized $\pi - \pi^*$ transitions at 350–480 nm, while the absorption band resulted from ICT was between 480 and 800 nm. It has been shown that 4,6-di(2-thienyl)thieno[3,4c][1,2,5]thiadiazole has a coplanar structure which generally leads to better π -electron delocalization in conjugated polymers and hence lower bandgap between the HOMO and the LUMO.¹² As illustrated in Figure 1, PTTD has absorption that extends to the NIR region with an optical bandgap as low as 0.98 eV, while PTBT has an optical bandgap of 1.84 eV. The optical bandgap was calculated from the onset wavelength of absorption by $E_g^{opt} = 1240 \text{ nm}/\lambda_{onset}$ where E_g^{opt} is the optical bandgap and λ_{onset} is the onset wavelength of absorption. It is clear that D-A polymer with a structure containing TTD as the acceptor units has a longer conjugation length and better π electron delocalization and hence a lower bandgap than that incorporating TBT as the acceptor units.

By introducing these two acceptor units in one D–A conjugated polymer and systematically changing the ratios of the two components from 85:15 to 15:85, we were able to tune the absorption properties and bandgaps of the resulting copolymers. As shown in Figure 1, all of the polymers contain two absorption bands that correspond to the two different ICT states originated from the two individual acceptor units. The absorption band at 440–800 nm was attributed to ICT of the TBT containing D–A structure, while the absorption band around 800-1240 nm comes from the ICT of TTD containing D–A structure. The relative intensity of the absorption band increases as the content of the corresponding acceptor unit

increases. As two different acceptor units with different electron-accepting abilities are incorporated in the polymer, by systematically changing the composition of the acceptor units, the relative planarity and π -electron delocalization of the resulting polymer can be tuned. As a result, the bandgaps and the energy levels can be engineered. Figure 1 shows that the absorption onset wavelength of the CPs changed from 1237 to 1091 nm as the ratio of TTD to TBT changed from 85:15 to 15:85. This variation resulted in a bandgap change from 1.00 to 1.14 eV (Table 2). A lower bandgap is obtained when the TTD

Table 2. Optical and Electrochemical Properties of Polymers

polymers	$E_{\text{ox,onset}}^{a}$ (V)	${E_{\rm HOMO}}^{b}_{\rm (eV)}$	$E_{\rm LUMO}^{c}$ (eV)	$\lambda_{ m onset}^{d}$ $(m nm)$	$E_{\rm g}^{\rm opt e}$ (eV)					
PTTD	0.05	-4.45	-3.47	1266	0.98					
PTTDTBT8515	-0.02	-4.42	-3.42	1237	1.00					
PTTDTBT7030	-0.02	-4.42	-3.39	1199	1.03					
PTTDTBT5050	0.37	-4.77	-3.69	1145	1.08					
PTTDTBT3070	0.65	-5.05	-3.93	1106	1.12					
PTTDTBT1585	0.88	-5.28	-4.14	1091	1.14					
PTBT	0.87	-5.27	-3.72	800	1.55					
^a Onset potential of oxidation scan (vs Ag/AgCl). ${}^{b}E_{HOMO} = -(4.4 +$										
$E_{\text{ox,onset}}$) (eV). $^{c}E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}^{\text{opt}}$. ^d Onset of absoption of thin										
films. ${}^{e}E_{g}^{opt} = 1240 \text{ nm}/\lambda_{onset}$.										

acceptor unit has a higher mole fraction in the polymer, since increased TTD leads to a structure with higher planarity and π -electron delocalization.

As has been reported, a main weakness of the D–A copolymers is the frequently observed red-shifting of the absorption profile to the long wavelength region instead of a true broadening across both the visible and NIR regions. This red-shift could hinder the desired increase in $J_{\rm sc}$ and ultimately the efficiency.^{10d,13} Interestingly, the copolymers reported here have relatively strong absorption in the entire visible to NIR region when the TTD to TBT ratios are between 70:30 and 50:50 (Figure 1). The absorption profile comes from two complementary ICT absorption bands generated by the two different acceptor units in the copolymers. Furthermore, the specific compositions results in a balanced absorption of those bands. This unique feature of absorption may lead to better performance of the polymers in photovoltaic applications.

Electrochemical Properties. The electrochemical properties of the copolymers were investigated by using cyclic voltammetry (CV) to determine the energy levels of the HOMO and the LUMO. Tetrabutylamonium perchlorate (Bu_4NClO_4) in acetonitrile (0.1 M) was used as the electrolyte system. The HOMO level of each polymer was calculated from the onset of electrochemical oxidation (Figure 2). The Ag/ AgCl reference electrode was calibrated by ferrocene. By assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be -4.8 eV below the vacuum level, the HOMO level of polymer was determined by $E_{\text{HOMO}} = -(4.4 + E_{\text{ox,onset}}) \text{ (eV).}^{14}$ The LUMO levels were estimated as $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$, where E_g^{opt} is the optical bandgap (Table 2).^{1c} The HOMO level positions were -4.42, -4.42, -4.77, -5.05, and -5.28 eV for the polymers as the ratio of TTD to TBT changed from 85:15 to 15:85 (Table 2). The HOMO level decreased (860 meV range) and the E_{g}^{opt} increased (140 meV range) almost monotonically with increasing TBT content in the copolymers. These results further demonstrated the ability of tuning the energy levels and bandgaps of this kind of copolymer.



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Figure 2. Oxidation scans of cyclic voltammograms of polymer thin films in 0.1 M Bu_4NClO_4 solution in acetonitrile at a scan rate of 100 mV/s.

3. CONCLUSION

In conclusion, we have synthesized a family of low bandgap D– A copolymers containing two different acceptor units (TTD and TBT) with well-defined compositions. The copolymer with a specific composition (TTD to TBT ratios between 70:30 and 50:50) has relatively strong absorption covering the entire visible to NIR region. As illustrated above, systematically changing the ratio of the two acceptors affords the ability to designate the HOMO/LUMO levels and bandgaps of the copolymers. The integration of these polymers into organic photovoltaic devices and the application of this approach to other D–A systems are currently underway.

4. EXPERIMENTAL SECTION

Materials and Methods. All reagents purchased from Sigma-Aldrich or Fisher were used without further purification, unless otherwise noted. 5,7-Bis(4-decanyl-2-thienyl)thieno[3,4-b]thiadiazole (1) and 4,7-bis[4-(2-ethyhexyl)-2-thienyl]-2,1,3-benzothiadiazole (2) were synthesized by the reported procedures.^{9d,11d,e} Detailed synthesis and purification procedures for the chemicals and characterization details are given in the Supporting Information.

Synthesis of 5,7-Bis(5-bromo-4-decanyl-2-thienyl)thieno-[3,4-b]thiadiazole (TTD). 1 (0.645 g, 1.1 mmol) was dissolved in pyridine (20 mL) under argon, and *N*-bromosuccinimide (NBS) (0.411 g, 2.34 mmol) was added in several portions during 30 min in the absence of light. The reaction mixture was stirred for another 30 min, pyridine was evaporated in vacuo, and a dark blue solid (0.69 g, 84%) was obtained with column chromatography on silica gel in hexane/dichloromethane (11:1 by volume). ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 0.89 (t, *J* = 6.73 Hz, 6H), 1.24–1.44 (m, 28H), 1.54–1.71 (m, 4H), 2.57 (t, *J* = 7.61 Hz, 4H), 7.17 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 156.04, 143.42, 134.33, 124.65, 111.58, 109.79, 31.92, 29.66, 29.63, 29.60, 29.54, 29.42, 29.35, 29.28, 22.70, 14.14. ESI-MS: $M_{\rm calcd}$ = 742.08, $M_{\rm found}$ = 741.9.

Synthesis of 4,7-Bis[5-Bromo-4-(2-ethyhexyl)-2-thienyl]-2,1,3-benzothiadiazole (TBT). 2 (1.43 g, 2.73 mmol) was dissolved in anhydrous THF (40 mL) under argon, and N-bromosuccinimide (NBS) (1.02 g, 5.74 mmol) was added in several portions at 0 °C for 30 min in the absence of light. Stirred for another 30 min, the reaction mixture was warmed up to room temperature and stirred overnight. Saturated ammonium chloride solution (80 mL) was added and stirred, extracted with ethyl acetate (3 × 100 mL), washed with H₂O (3 × 300 mL) and brine (300 mL), and dried over Na₂SO₄. A brown solid (1.71 g, 92%) was obtained with column chromatography on silica gel in hexane. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 0.89–0.98 (m, 12H), 1.29–1.44 (m, 16H), 1.72 (dt, *J* = 12.29, 6.21 Hz, 2H), 2.58 (d, *J* = 7.34 Hz, 4H), 7.70 (s, 2H), 7.73 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ (ppm) = 152.19, 142.22, 138.30, 128.58, 125.25,

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124.75, 112.25, 40.01, 33.92, 32.53, 28.80, 25.75, 23.08, 14.13, 10.87. ESI-MS: $M_{calcd} = 680.06$, $M_{found} = 680.1$.

Representative Procedure for Stille Coupling Polymerization: Polymerization of TTD and TBT in Mole Ratio of 1:1 To Afford Polymer PTTDTBT5050. A 50 mL Schlenk tube was heated under reduced pressure and then allowed to cool to room temperature under argon. In this tube, TTD (122.5 mg, 0.165 mmol), TBT (112.6 mg, 0.165 mmol), and 2,5-bis(tri-n-butyltin)thiophene (218.1 mg, 0.329 mmol) were dissolved in dry chlorobenzene (7 mL) and degassed (argon) for at least 30 min. A catalytic amount of $Pd(PPh_3)_4$ (15.2 mg, 0.0132 mmol) was then added to the reaction mixture under argon and degassed and filled with argon three times. The reaction mixture was stirred vigorously at 120 °C for 24 h under argon. After it was cooled to room temperature, the polymerization mixture was poured and stirred into 200 mL of methanol and 5 mL of hydrochloric acid solution for 5 h. The polymer precipitated out as a dark solid and filtered using a filter paper. The polymer was purified by Soxhlet extraction with methanol (24 h) and hexane (24 h). The final polymers were dried under vacuum for at least 24 h and then subjected for the required analysis, yielding 183 mg (87%) black solid. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) = 0.92 (s, br, 18H), 1.11–1.52 (m, 44H), 1.58-1.84 (m, 6H), 2.50-2.91 (m, 8H), 7.01-8.03 (m, 10H).

ASSOCIATED CONTENT

S Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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