Design, synthesis, and properties of benzobisthiadiazole-based donor- π -acceptor- π -donor type of low-band-gap chromophores and polymers

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Abstract: A novel low-band-gap chromophore (**5**, 0.86 eV) having fluorene as a donor, benzobisthiadiazole (BBTD) as an acceptor, and pyrrole as a π -spacer was successfully designed and synthesized, to probe the effect of π -spacer on the band-gap level of the donor- π -acceptor- π -donor type of chromophores. Compared with the thiophene spacer analogue (in compound **3**), the intramolecular hydrogen bonding between the pyrrole and the neighboring BBTD unit pushes the absorption maximum and fluorescence emission of chromophore **5** into the near-infrared spectral region with a red shift of 172 and 158 nm, respectively. The same red-shift phenomenon can also be realized by addition of Lewis acid (e.g., BF₃) to the BBTD-containing chromophores with other spacers. Attempt of using low-band-gap chromophore **5** in bulk heterojunction (BHJ) solar cells was made, showing a non-optimized photovoltaic device with the power conversion efficiency of 0.01%. A precursor approach to introduction of the alkaline-labile BBTD acceptor into the polymer backbone has been demonstrated by successful synthesis of low-band-gap polymer **P2**. The same strategy can be in principle applied to the synthesis of a series of low-band-gap chromophores or polymers with strong acceptors.

Key words: donor $-\pi$ -acceptor $-\pi$ -donor, chromophore, low band gap, bulk heterojunction (BHJ), precursor polymer.

Résumé : Afin de pouvoir étudier l'effet d'un espaceur π sur le niveau d'énergie interbande des chromophores de type donneur- π -accepteur- π -donneur, on a développé et synthétisé un nouveau chromophore de basse énergie interbande (**5**, 0,86 eV) comportant un fluorène comme donneur, un benzobisthiadiazole (BBTD) comme accepteur et un noyau pyrrole comme espaceur π . Par comparaison avec l'analogue comportant un espaceur thiophène (dans le composé **3**), la liaison hydrogène intramoléculaire entre le pyrrole et l'unité adjacente BBTD déplace le maximum d'absorption et l'émission de fluorescence du chromophore **5** dans la région spectrale du proche infrarouge avec des déplacements vers le rouge de respectivement 172 et 158 nm. On peut observer le même phénomène de déplacement vers le rouge par l'addition d'un acide de Lewis (tel le BF₃) à des chromophores comportant du BBTD et d'autres espaceurs. On a essayé d'utiliser le chromophore **5** à faible énergie interbande dans des cellules solaires à hétérojonction globale (HJG); on a obtenu un dispositif non voltaïque non optimisé ayant une efficacité de conversion de pouvoir de 0,01 %. On a démontré l'applicabilité d'une autre approche à l'introduction de l'accepteur BBTD labile aux produits alcalins dans le squelette d'un polymère en effectuant avec succès la synthèse du polymère **P2** de faible énergie interbande. En théorie, la même stratégie peut être appliquée à la synthèse d'une série de chromophores ou de polymères de faible énergie interbande avec des accepteurs forts.

Mots-clés : donneur– π –accepteur– π –donneur, chromophore, faible énergie interbande, hétérojonction globale (HJG), polymère précurseur.

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Introduction

Research on low-band-gap organic materials (e.g., chromophores and polymers), whose band-gap levels, defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, are typically below 1.8 eV, has been the focal point in a number of technologically important areas. Low-band-gap organic materials absorb light with wavelengths longer than 700 nm or within the near-in-frared (NIR) spectral region of 750–2000 nm.

In the area of solar-energy conversion, it is essential that the absorption of the light-harvesting material matches the spectral characteristics of the sun.¹ For the polythiophene (P3HT)-based bulk heterojunction (BHJ) solar cells, P3HT has a band gap of ~1.90 eV and a rather narrow absorption

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band (FWHM ≈ 150 nm) and can absorb only a limited fraction of the solar photons (~30%). Thus, the NIR-absorbing chromophores and polymers have the possibility to improve the efficiency of organic BHJ solar cells owing to a better overlap with the solar spectrum.²

Near-infrared fluorescent organic materials may find applications as NIR-fluorescent tags for bio-imaging³ and chemical sensing⁴ or emitters in NIR light-emitting diodes (LED) for information-secured display and background lighting. To date, most of organic materials that have been shown to emit the light around 700–1000 nm are mainly with lanthanide complexes,⁵ transition-metal complexes,⁶ ionic dyes,⁷ and low-band-gap polymers.⁸ NIR organic photovoltaic materials have recently been demonstrated for use in NIR photodetectors.⁹

Among various types of low-band-gap organic materials, much effort has been focused on the design and synthesis of the chromophores and polymers consisting of powerful electron donor (D) and acceptor (A) units. Some of the best-performing BHJ organic solar cells are fabricated with the D-A type of conjugated polymers.¹⁰ Some of these D-A polymers contain benzo-2,1,3-thiadiazole (BT) as the acceptor unit.¹¹ Recently, we have shown that the D- π -A- π -D type of chromophores, where π is a spacer or linking unit, can absorb light with the wavelength around 1000 nm and fluoresce above 1000 nm, such as compounds 1-3 in Fig. 1.¹² The band-gap levels of this class of chromophores depend on the strength of the donor and acceptor. Those containing a strong electron-withdrawing heterocyclic quinoid, namely, benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole)(BBTD), tend to have a lower band gap than other acceptor-containing chromophores, since the BBTD unit is known to posses a substantial quinoidal character within a conjugated backbone, allowing for greater electron delocalization, and thus lowering the band gap.¹³ However, the scope and limitations of the acceptor strength and the role of the spacer in tuning the band gap are still not fully understood. For example, a recent work shows that the band gap of the D-A type of benzothiadiazole (BT)-containing chromophores can be significantly lowered by the introduction of Lewis acids as a result of changing the electronic properties of the BT fragment via interactions with Lewis acids that bind nitrogen.14

Considering the D– π –A– π –D system such as compounds 1-3, by diminishing the electron density on the nitrogen of the BBTD unit, a further decrease in band gap or red shift in absorption and emission spectra of the chromophores should be expected. Conceivably, the BBTD acceptor strength can be increased through either the intermolecular or intramolecular interaction by addition of Lewis acid or other electron-accepting species. In this work, we intend to show that by the introduction of pyrrole as a spacer, the band gap of the D- π -A- π -D chromophores can be further lowered due to the intramolecular hydrogen bonding with the neighboring BBTD unit, which is similar to the effect of adding a Lewis acid to the chromophores having other spacers. Accordingly, a new $D-\pi-A-\pi-D$ chromophore (5, Fig. 1) is designed, synthesized, and characterized. Furthermore, for potential applications in thin-film devices, such as polymer BHJ solar cells, a new general approach to lowband-gap polymers having the $D-\pi-A-\pi-D$ unit in the backbone is demonstrated.

Experimental section

Materials

All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon atmosphere. 2-Bromo-9,9-dioctylfluorene (**6**),¹⁵ *N*-(*tert*-butoxycarbonyl)-2-(trimethylstannyl) pyrrole (**7**),¹⁶ 4,8-dibromobenzo[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole) (**10**),^{13d} 4,7-bis[4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl]-5,6-diamino-2,1,3-benzo-thiadiazole (**11**),^{12b} and 9,9-dioctyl-2,7-bis(trimethyleneboronate)fluorene (**13**)¹⁷ were prepared according to literature methods.

Methods

¹H NMR spectra were recorded using a Bruker Avance 300 NMR spectrometer. The high-temperature NMR experiments were performed on a Varian Unity-400 MHz spectrometer. High-resolution mass spectrometry (HRMS) was obtained from 7.0 T Actively Shielded Fourier Transform Ion Cyclotron Resonance Mass Spectrometers. The numberand weight-average molecular weights of the polymers were determined by gel-permeation chromatography (GPC) with a Waters 410 instrument and polystyrene as a standard and THF as eluent. Absorption and fluorescence spectra were recorded with a Shimadzu UV-3600 or Lambda 900 Perkin-Elmer spectrophotometer and a PTI fluorescence spectrophotometer, respectively. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI660b electrochemical workstation, in dry dichloromethane containing $n-Bu_4NPF_6$ (0.1 mol/L) with a scan rate of 50 mV/s at room temperature under argon, using a Pt disk (2 mm diameter) as the working electrode, a Pt wire as the counter electrode and a Ag/AgCl electrode as the reference electrode.

Photovoltaic device fabrication and characterization

The solar-cell devices were fabricated with the device structure of [indium tin oxide (ITO)/poly(3,4-ethylene diox-ythiophene):poly(styrenesulfonate) (PEDOT:PSS)/Compound 5:PCBM/AI]. The ITO glass was pre-cleaned and coated with PEDOT:PSS. Then, the active layer was spin-coated from the chlorobenzene solution of compound 5 and PCBM (1:1, w/w) on the substrate. Finally, the Al cathode was deposited at a vacuum level of 4×10^{-4} Pa. The effective area of the unit cell is 16 mm². The current–voltage (*I–V*) measurement of devices was conducted on a computer controlled Keithley 236 Source meter. A xenon lamp (500 W) with AM 1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm².

N-(*tert*-Butoxycarbonyl)-2-(9,9-dioctylfluoren-2-yl)pyrrole (8)

2-Bromo-9,9-dioctylfluorene (6) (4.7 g, 10 mmol), *N*-(*tert*-butoxycarbonyl)-2- (trimethylstannyl)pyrrole (7) (6.6 g, 12 mmol), and tetrakis(triphenylphosphane) palladium(0) (115.5 mg, 0.1 mmol) were dissolved in a mixture of tol-

Fig. 1. Chemical structures of $D-\pi-A-\pi-D$ chromophores 1–5.



uene (20 mL) and a 1 mol/L aqueous solution of sodium carbonate (20 mL). The mixture was stirred at 110 °C for 60 h. After cooling, the resulting solution was extracted with dichloromethane. The combined organic layers were washed with water and dried with anhydrous MgSO₄. Evap-

oration of the solvent and subsequent column chromatography (silica gel, dichloromethane/petroleum ether = 1/5) afforded the product as pale yellow oil (1.1 g, 20%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.74–7.68 (m, 2H), 7.40–7.26 (m, 6H), 6.30–6.24 (m, 2H), 1.98 (t, 4H, J =

8.37 Hz), 1.41 (s, 9H), 1.40–1.10 (m, 20H), 0.89–0.87 (m, 6H), 0.73–0.61 (m, 4H).

Tributyl[*N*-(*tert*-butoxycarbonyl)-5-(9,9-dioctylfluoren-2yl)pyrrole-2-yl]stannane (9)

A 100 mL three-necked flask was charged with dry THF (20 mL) and 2,2,6,6-tetramethylpiperidine (1.85 mL, 11 mmol). The mixture was cooled to -78 °C and *n*-BuLi (2.5 mol/L in hexane, 4.8 mL, 12 mmol) was added dropwise. The mixture was stirred at -78 °C for 10 min, then warmed to 0 °C and stirred for additional 10 min. At this point, the mixture was cooled again to -78 °C, a solution of *N*-(*tert*-butoxycarbonyl)-2-(9,9-dioctylfluoren-2-yl)pyrrole

(8) (5.5 g, 10 mmol) in dry THF (10 mL) was added, and the mixture was stirred for 1.5 h while keeping the temperature below -65 °C. Bu₃SnCl (3.7 mL, 13 mmol) was added dropwise. The mixture was stirred for 40 min at -75 °C and for additional 40 min at 0 °C, and then for 12 h at room temperature. The mixture was poured into water and extracted with diethyl ether. The organic extracts were dried over anhydrous MgSO₄. Upon evaporation of the solvent, the crude product was obtained as pale yellow oil and used for the next step without further purification. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.75-7.67 (m, 2H), 7.40-7.24 (m, 5H), 6.44 (d, 1H, J = 3.75 Hz), 6.33 (d, 1H, J =3.00 Hz), 1.99 (t, 4H, J = 8.10 Hz), 1.65-1.62 (m, 6H), 1.40-1.37 (m, 6H), 1.24 (s, 9H), 1.18-1.08 (m, 26H), 0.97-0.92 (m, 9H), 0.89-0.83 (m, 6H), 0.73-0.61 (m, 4H).

4,8-Bis[*N*-(*tert*-butoxycarbonyl)-5-(9,9-dioctylfluoren-2yl)-2-pyrrolyl]benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (4)

To a solution of compound 9 (1.0 g, 1.2 mmol) and 4,8dibromobenzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (10)(0.18 g, 0.5 mmol) in toluene (40 mL) was added Pd(PPh₃)₄ (71 mg, 0.061 mmol). The mixture was stirred for 36 h at 110 °C. After cooling, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with saturated aqueous potassium fluoride and brine before being dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1:1) as the eluent to afford the product (0.13 g, 20%)as black solid. ¹H NMR (400 MHz, o-C₆D₄Cl₂, 403 K) & (ppm): 7.78–7.72 (m, 4H), 7.54–7.46 (m, 4H), 7.41–7.35 (m, 6H), 7.05 (d, 2H, J = 3.5 Hz), 6.56 (d, 2H, J = 3.5 Hz), 2.05-2.00 (m, 8H), 1.59 (s, 18H), 1.29-1.00 (m, 40H), 0.86 (t, 12H, J = 6.7 Hz), 0.70 (br, 8H).

4,8-Bis[5-(9,9-dioctylfluoren-2-yl)-2-pyrrolyl]benzo[1,2*c*:**4**,5-*c*']bis([1,2,5]thiadiazole) (5)

Thermolysis of compound **4** (98 mg) at 200 °C under reduced pressure (10^{-5} torr, 30 min) (1 torr = 133.322 Pa) afforded 92 mg (94% yield) of product as black solid. ¹H NMR (400 MHz, *o*-C₆D₄Cl₂, 403 K) δ (ppm): 11.72 (br, 2H), 8.04 (br, 2H), 7.78–7.67 (m, 8H), 7.55–7.37 (m, 6H), 6.96 (br, 2H), 2.15–2.11 (m, 8H), 1.23–1.15 (m, 40H), 0.85–0.80 (m, 20H). HRMS (for [M]⁺) calcd.: 1100.65119; found: 1100.64015.

4,7-Bis[4-(*N*-(4-bromophenyl)-*N*-(4methylphenyl)amino)phenyl]-5,6-diamino-2,1,3benzothiadiazole (12)

A solution of tetrabutylammonium tribromide (0.96 g, 2.0 mmol) and 4,7-bis[4-(*N*-phenyl-*N*-(4-methylphenyl)amino)phenyl]-5,6-diamino-2,1,3-benzothiadiazole (**11**) (0.61 g, 9.0 mmol) in freshly distilled dichloromethane (45 mL) was stirred at room temperature for 3 h. The precipitates were filtrated and washed with dichloromethane. The solid was dried under vacuum to give the product as orange solid (0.55 g, 73%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.43 (d, 4H, *J* = 8.3 Hz), 7.34 (d, 4H, *J* = 8.7 Hz), 7.19 (d, 4H, *J* = 8.1 Hz), 7.04 (d, 4H, *J* = 8.7 Hz), 2.33 (s, 6H).

Polymer P1

To a mixture of 9,9-dioctyl-2,7-bis(trimethyleneboronate)fluorene (13) (0.279 g, 0.500 mmol) and 4,7-bis[4-(N-(4bromophenyl)-N-(4-methylphenyl)amino)phenyl]- 5,6-diamino-2,1,3-benzothiadiazole (12) (0.419 g, 0.500 mmol) was added Aliquat 336 (0.120 g), Pd(PPh₃)₄ (7.9 mg, 0.007 mmol), degassed toluene (7 mL), and aqueous 2 mol/L potassium carbonate (3 mL) under a dry argon atmosphere. The mixture was heated to 95 °C and stirred in the dark for 48 h. After cooling, the mixture was poured into methanol. The precipitate was collected by filtration and then dissolved in dichloromethane. The solution was washed with water, dried with anhydrous MgSO₄, and then concentrated to an appropriate volume. The fiber-like brown polymer (0.500 g, 94%) was obtained by pouring the concentrated solution into methanol. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.74 (d, 2H, J = 7.9 Hz), 7.61–7.55 (m, 8H), 7.47 (d, 4H, J = 8.7 Hz), 7.29–7.25 (m, 8H), 7.20-7.13 (m, 8H), 2.36 (s, 6H), 2.00 (br, 4H), 1.20-1.00 (m, 20H), 0.80-0.75 (m, 10H).

Polymer P2

To a solution of polymer **P1** (0.107 g, 0.1 mmol) in dry pyridine (10 mL) was added *N*-sulfinylaniline (0.5 mL, 4 mmol) and chlorotrimethylsilane (0.5 mL, 3.6 mmol) in argon atmosphere. The mixture was heated to 80 °C and stirred overnight. After workup, excess chlorotrimethylsilane was distilled off. The solution was concentrated to 5 mL and poured into methanol. The fiber-like dark blue polymer **P2** (98.0 mg, 89%) was collected by filtration, washed with ethanol, and dried under vacuum. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.20 (d, 4H, *J* = 8.5 Hz), 7.75 (d, 2H, *J* = 7.4 Hz), 7.63–7.56 (m, 8H), 7.34–7.16 (m, 16H), 2.37 (s, 6H), 2.06 (br, 4H), 1.06 (br, 20H), 0.80–0.75 (m, 10H).

Results and discussion

Design and synthesis of low-band-gap chromophores

Design concept and synthesis

The concept for designing low-band-gap chromophores is based on the use of a strong electron acceptor, namely, benzobisthiadiazole, and electron donors that are linked through a π -conjugated spacer. In particular, the D- π -A- π -D type of chromophores, such as compounds **1**-**3** (Fig. 1), previously reported by our group,^{12a} is the focal point of design

Scheme 1. Synthetic route to intermediates and chromophores **4** and **5**. Reagents and conditions: (i) Pd(PPh₃)₄, Na₂CO₃ (aq., 1 mol/L), toluene, 110 °C, 60 h; (ii) *N*-lithium-2,2,6,6-tetramethylpiperidine, -70 °C, (Bu)₃SnCl, THF, -70 °C to room temperature; (iii) Pd(PPh₃)₄, toluene, 110 °C, 36 h; (iv) 200 °C, 30 min, 10⁻⁵ torr.



and study. With the same acceptor, the absorption wavelength of chromophores 1-3 varies according to the strength of donors and the nature of spacer. Between compounds 2 and 3, the difference in band-gap levels is attributed to the different donors. However, a larger difference in the bandgap levels or absorption ($\Delta \lambda_{max} = 157$ nm) between chromophores 1 and 2 is clearly due to the presence of different π -spacers (thiophene vs. benzene or nil). Therefore, the π -spacer or linking moiety in the D- π -A- π -D type of chromophores can play an important role in band-gap tuning, which may lead to further band-gap lowering or spectral red shift relative to chromophores 1-3. Accordingly, in this work, pyrrole was introduced as π -spacer in a new chromophore 5 (Fig. 1) to study the scope and limitations of the π -spacer regarding the band-gap tuning. Any additional contribution to a better D-A interaction or lowering the LUMO level of the acceptor unit that may be brought by the use of a new π -spacer is likely to result in a further red shift in absorption in reference to the structurally analogous chromophore **3** ($\lambda_{max} = 848$ nm).

Scheme 1 outlines the synthetic route to compounds 4 and 5. Compound 4 was readily synthesized by the Stille coupling reaction of dibromo-BBTD 10 with tributyltin compounds 9 derived from the donor. It should be noted that aqueous sodium carbonate solution was not added, as required to suppress the C–Sn bond cleavage in the Stille coupling reaction,¹⁸ due to instability of the BBTD group in alkaline solution, which caused a rather poor yield (20%) for compound 4. Removal of the *tert*-butoxycarbonyl (*t*-Boc) protecting group in 4 by heating under reduced pressure afforded the target compound 5 with high yield.

Optical and electrochemical properties

The absorption and photoluminescence of compounds 4 and 5 in toluene are shown in Fig. 2, and the data are presented in Table 1. As for compounds 1–3, compound 5 has mainly two absorption bands. The peaks from 300 to 500 nm are attributed to the π – π * transition and the possible n– π * transition of the conjugated aromatic segments, and those at longer wavelengths are due to the intramolecular charge transfer (ICT) transitions between the donor and acceptor. Compared with compound 3, the maximum absorption of compound 4 is blue-shifted. Since pyrrole is more electron-donating than thiophene, the observed blue

Fig. 2. Normalized absorption (10^{-5} mol/L) and fluorescence emission (10^{-4} mol/L) spectra of compounds **4** and **5** in toluene.



shift is mainly due to non-planarity between the BBTD and the pyrrole induced by t-Boc group. After removal of the t-Boc group, both the maximum absorption and emission wavelengths were red-shifted dramatically (about 183 and 121 nm, respectively; Fig. 2) relative to its precursor 4. The pyrrole spacer and the neighboring BBTD core in compound 5 are expected to be completely coplanar by virtue of hydrogen bonding (Fig. 3), which should facilitate the charge transfer from donor to acceptor, and thus lowers the bandgap level. This intramolecular hydrogen bonding also contributes to altering the energy level of the BBTD acceptor by sharing or removing partial electrons on the nitrogen in BBTD. In the ¹H NMR spectra of compound 5, the pyrrole N-H signal is found at the low field ($\delta = 11.68$, Fig. 4), which is an indication for strong intramolecular hydrogen bonding.¹⁹

Similar to the effect of hydrogen-bonding interaction, addition of Lewis acids should also alter the band gap as a result of binding with the nitrogen in BBTD. Figure 5 shows the absorption spectra of compound **3** and a mixture of **3** with excess BF₃. The spectrum of compound **3** exhibits an absorption maximum (λ_{max}) at 834 nm with an onset (λ_{onset}) at 958 nm. Upon addition of an excess of BF₃, a color change took place immediately, going from yellowish green

Compound	$\lambda_{max}^{abs} \ (nm)^a$	Log ε^a	$\lambda_{max}^{PL} (nm)^b$	Stokes shift (nm)	$\Phi_{\mathrm{f}} (\%)^{c}$	HOMO $(eV)^d$	LUMO (eV) ^d	Energy gap (eV)
1^e	763	4.38	1065	302	7.1	4.95	3.76	1.19
2^e	920	4.86	1125	205	5.3	4.77	3.94	0.83
3 ^e	848	4.71	1055	207	18.5	5.14	3.99	1.15
4	837	4.53	1092	255	NA	4.96	3.85	1.11
5	1020	4.57	1213	193	0.3	4.75	3.89	0.86

Table 1. Optical and electrochemical data of chromophores.

^{*a*}Measured in toluene with a concentration of 10^{-5} mol/L.

^bMeasured in toluene with a concentration of 10^{-4} mol/L. Excitation wavelengths for 1–4 are at their maximum absorption wavelengths, and at 980 nm for 5.

^cFluorescence quantum yield measured relative to IR-125 ($\Phi_f = 0.13$ in DMSO).

^dCalculated from the formula, $E_{(HOMO)} = -(E_{ox} + 4.34)$ (eV), $E_{(LUMO)} = -(E_{red} + 4.34)$ (eV).

^eSee ref. 12a.

Fig. 3. Hydrogen bonding in compound 5 and the 3-BF3 adduct.



Fig. 4. ¹H NMR spectra (400 MHz, o-C₆D₄Cl₂, 403 K) of compounds 4 and 5.



to dark blue visually. Consequently, the λ_{max} and λ_{onset} of compound **3**-BF₃ adduct appeared at 1260 nm and 1580 nm, being red-shifted by 426 nm and 622 nm, respectively. According to the confirmed structure of the complex of benzothiadiazole derivatives with Lewis acid,¹⁴ in the **3**-BF₃ adduct, BF₃ should bind to the nitrogen of each thia-

Fig. 5. Normalized absorption spectra of compound 3 (10^{-4} mol/L in THF) and a mixture of 3 with excess BF₃.



diazole rings (Fig. 3), effectively pulling the electron density away from the BBTD unit, enhancing the ICT transition between peripheral donor and acceptor core, and thus leading to a significant bathochromic shift in absorption. Additionally, there is a synergistic lowering of the absolute energies of the two frontier molecular orbitals, thereby giving rise to the narrower band gap.

Considering the potential application of the D $-\pi$ -A $-\pi$ -D type of low-band-gap chromophores in photovoltaic cells, compound **5** was blended with PCBM and cast into films. Figure 6 shows the absorption spectrum of the blend film (1:1, *w/w*; solid line) and displays mainly three peaks centered at 333, 428, and 1046 nm, respectively. Compared with the absorption spectrum of **5**, the peak at 333 nm increases, which was due to the absorption of PCBM. Additionally, the ICT transition peak becomes broad and is red-shifted (about 26 nm). Thus, there is additional charge transfer interaction in the blend, which is likely due to the one between the acceptor and PCBM and similar to the effect of adding a Lewis acid to the chromophores.

The electrochemical properties of compounds **4** and **5** were investigated by CV (Fig. 7), and the data are summarized in Table 1. They are all electrochemically active, having two reversible oxidation and two reduction waves in the cyclic voltammogram, respectively. The first reduction potential is from the reduction of the BBTD core, and the first

Fig. 6. Absorption spectra of the blend film of compound **5** with PCBM (1:1, *w/w*; solid line) and compound **5**.



Fig. 7. Cyclic voltammograms of compounds 4 and 5 (1 mmol/L concentration).



oxidation wave is attributed to the oxidation of the donors and π -spacers. For chromophore **5**, the first oxidation potential increases significantly (about 0.2 eV); however, the reduction potentials keep nearly unchanged. The HOMO and LUMO levels of compounds **4** and **5** were calculated according to empirical equations of $E_{(HOMO)} = -(E_{ox} + 4.34)$ (eV) and $E_{(LUMO)} = -(E_{red} + 4.34)$ (eV), respectively. As shown, compound **5** has the band gap of 0.86 eV and absorbs at the longest wavelength (1020 nm) among chromophores **1–5**.

Photovoltaic property

Organic BHJ photovoltaic cells were fabricated using compound **5** as electron donor and PCBM as electron acceptor, with a structure configuration of ITO/PEDOT:PSS/ **5**:PCBM/A1. Typical performance data of the devices are listed in Table 2, and the corresponding current–voltage curves are illustrated in Fig. 8. Without optimization, the device gave power conversion efficiency (PCE) of 0.01% with an open-circuit voltage (V_{oc}) of 0.27 V and a short-circuit

 Table 2. Performance of photovoltaic device under illumination of 100 mW/cm² white light.

Material	$V_{\rm oc}~({ m V})$	$J_{\rm sc}~({\rm mA/cm}^2)$	FF	PCE (%)
5 :PCBM (1:1, <i>w/w</i>)	0.27	0.13	0.28	0.01

Fig. 8. Current density–voltage curves of solar-cell devices in dark and under illumination of 100 mW/cm² white light. Inset: Proposed energy-level scheme of compound **5** and PCBM.



current (J_{sc}) of 0.13 mA/cm² under AM 1.5 solar simulator (100 mW/cm²). Accordingly, a fill factor (FF) was calculated to be 0.28. For BHJ devices, V_{oc} is linearly correlated with the energy difference of the HOMO of the donor and the LUMO of the acceptor. Our result (0.27 V) coincides well with the empirical calculation.²⁰ The relatively low V_{oc} is likely due to the high HOMO level of the donor (Fig. 8, inset). The J_{sc} is determined by the amount of absorbed light and the internal conversion.²¹ The absorption profile of the active layer shows a quiet mismatch to the solar photon flux, thus leading to the quite low J_{sc} . Nevertheless, the device based on low-band-gap chromophore **5** is still comparable well to some other solution-processed molecular BHJ solar cells.

Design and synthesis of low-band-gap polymer

The band gap of polymers can be reduced by incorporating alternating donor and acceptor moieties in the polymer main chain. BBTD is a strong electron acceptor and can be used by design to construct many different kinds of lowband-gap polymers. However, because the BBTD unit is unstable in alkaline solution and readily attacked by nucleophiles (e.g., OH?), the polymers containing the BBTD moiety are often difficult to be synthesized by the Suzuki coupling reaction or other methods that need to use a base. Up to now, several polymers containing BBTD have been reported,²² and are mainly synthesized by the Stille coupling reaction or electrochemical polymerization. However, the required tributylstannane monomers for the Stille polymerization are toxic and difficult to purify, and electrochemical polymerization is difficult to produce high-molecular-weight soluble polymers. Therefore, it remains a challenge to synthesize high-molecular-weight low-band-gap polymers containing BBTD unit.

Scheme 2. Synthetic routes to polymers P1 and P2. Reagents and conditions: (i) Bu₄NBr₃, CH₂Cl₂, 25 °C, 3 h; (ii) Pd(PPh₃)₄, K₂CO₃ (aq., 2 mol/L), toluene, Aliquat 336, 95 °C, 24 h; (iii) PhNSO, TMSCl, pyridine, 80 °C, overnight.



Fig. 9. ¹H NMR spectra (300 MHz, CDCl₃) of polymers P1 and P2.



In this work, we intend to explore a precursor approach to introduction of the BBTD unit in polymers. The feasibility of such a precursor approach is based on the fact that the monomers containing the 1,2-diaminophenylene group can be utilized in the Suzuki coupling reaction to produce high-molecular-weight polymers,²³ and the 1,2-diaminophenylene group can be converted into various electron-deficient groups (e.g., quinoxaline and benzothiadiazole).²⁴ Therefore, we demonstrated this precursor strategy by making the precursor polymer **P1** and subsequently converting to the BBTD-containing polymer **P2** (Scheme 2). The monomer **12** was prepared by bromination of compound **11** with tetrabutylammonium tribromide. Because of the presence of the

Fig. 10. IR spectra of polymers P1 and P2.



methyl group on one of the two phenyl groups, bromination only takes place at one of the phenyl rings of the diphenylamino moiety in **11**. Using the Suzuki cross-coupling reaction, polymerization of monomers **12** and **13** gave the precursor polymer **P1**. By simple treatment of **P1** with *N*-sulfinylaniline and chlorotrimethylsilane in dry pyridine, the target low-band-gap polymer **P2** was readily obtained with high yield (89%).

Structural characterization

The chemical structures of polymers **P1** and **P2** were fully characterized by NMR and IR spectroscopic methods. Fig-

Table 3. Characterization of Polymers P1 and P2.

Polymer	$M_{\rm n}^{\ a} \ (\times 10^3)$	$M_{\rm w}^{\ a} (\times 10^3)$	PDI	$\lambda_{\max}^{abs} (nm)^b$	Log ε	$\lambda_{\max}^{\text{PL}} (\text{nm})^b$	Stokes shifts (nm) ^b	Band gap (eV) ^c
P1	56	179	3.2	371, 440 (sh) ^d	NA	558	187	2.67
P2	28	75	2.7	749	4.39	980	231	1.41

^aDetermined by GPC.

^bMeasured in chlorobenzene, excitation wavelengths for P1 and P2 are at their maximum absorption wavelengths.

^cOptical band gap, estimated from the onset wavelength of optical absorption spectra.

^dShoulder peak.

ure 9a shows the ¹H NMR spectrum of polymer **P1**. A peak at δ 4.18 ppm is assigned to the amine hydrogen and the aliphatic and aromatic hydrogens are observed at δ 0.6–2.5 and δ 7.1–7.7 ppm, respectively. After conversion of the diamine into the thiadiazole group, the peak at δ 4.18 disappeared (Fig. 9b), indicating that the transformation reaction was successful and the amino group was converted completely. A new peak at δ 8.20 is assigned to the hydrogens in the phenylene that is adjacent to the BBTD core (Ha shown in Scheme 2). Because of the strong electron-withdrawing BBTD unit, the signal of Ha shifted to a lower field. The observed chemical shift (δ 8.20) coincides well with that of a small compound with similar structure (δ 8.18),^{12b} further demonstrating the formation of the BBTD unit in P2. The IR spectrum of polymer P1 (Fig. 10) shows two distinct v(NH) bands at 3442 and 3357 cm⁻¹, which, as expected, are absent in the spectrum of P2 (Fig. 10).

The molecular weights were estimated by gel-permeation chromatography (THF as eluent) relative to polystyrene standards. Polymer **P1** shows high molecular weight with the number-average molecular weight (M_n) of 56 000 g/mol and a polydispersity index of 3.2 (Table 3). The apparent M_n of **P2** was found to be only 28 000 g/mol, although it should be the same or similar to that of **P1**, which was mainly due to poor solubility of the high-molecular-weight fraction of **P2** in THF.

Optical property

The absorption and photoluminescence of polymers P1 and P2 were recorded in chlorobenzene. Without a strong acceptor or strong intramolecular charge transfer, P1 absorbs in the visible spectral region with a maximum (λ_{max}) at 440 nm and emits at 558 nm. In comparison, owing to the presence of the BBTD acceptor, the absorption and emission maxima of P2 were red-shifted dramatically to 749 and 980 nm, respectively (Table 3 and Fig. 11). Similar to chromophores 1–5, the absorption bands of polymer P2 mainly have two parts. The peaks in the higher energy region are attributed to the $\pi - \pi^*$ and also possible $n - \pi^*$ transitions of the conjugated aromatic segments. The high molar extinction coefficient (Log $\varepsilon = 4.39$) of the ICT band of P2 is ideal for photovoltaic application. The optical band-gap levels of P1 and P2 were estimated from the onset wavelength (λ_{onset}) of the optical absorption spectra to be 2.7 and 1.4 eV, respectively.

Conclusions

A novel $D-\pi-A-\pi-D$ type of low-band-gap (0.86 eV) chromophore **5** has been successfully designed and synthesized. The use of pyrrole as π -spacer is proven to be effec-

Fig. 11. Absorption and fluorescence emission of polymer P2 in chlorobenzene.

tive and beneficial in further lowering the band-gap level of the D– π –A– π –D chromophores. Compared with the thiophene spacer (in compound **3**), the pyrrole spacer provides the intramolecular hydrogen bonding to the BBTD acceptor, which pushes the absorption maximum and fluorescence emission of chromophore **5** into the near-infrared spectral region with a red shift of 172 and 158 nm, respectively. A precursor approach to the introduction of the alkaline-labile BBTD acceptor into the polymer backbone has been demonstrated by successful synthesis of low-band-gap polymer **P2**. The same strategy can be in principle applied to the synthesis of a series of low-band-gap polymers with the structures and properties similar to chromophores **1–5**.

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