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Indolo[3,2-b]carbazole-based alternating donor–acceptor copolymers: synthesis, properties and photovoltaic application

Erjun Zhou,[a] Shimpei Yamakawa,[b] Yue Zhang,[b] Keisuke Tajima,[b] Chunhe Yang[a] and Kazuhito Hashimoto*[ab]

Two new donor–acceptor (D–A) type copolymers, poly{5,11-di(1-decylundecyl)-indolo[3,2-b]carbazole-3,9-diyl-alt-4,7-dithien-2-yl-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DTBT) and poly{5,11-di(1-decylundecyl)indolo[3,2-b]carbazole-3,9-diyl-alt-4,7-di(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DT2BT) were synthesized. The polymers have an alternating structure consisting of a large-size fused aromatic ring, indolo[3,2-b]carbazole (IC), as the donor segment and 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) or 4,7-di(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole (DT2BT) as the acceptor segment. The absorption spectra and the electrochemical properties of PIC-DTBT and PIC-DT2BT indicate that these copolymers have suitable energy levels for photovoltaic application. Polymer photovoltaic devices based on blends of the copolymers and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) have a high open-circuit voltage (>0.9 V) under the illumination of AM 1.5 (100 mW cm^{-2}). The higher power conversion efficiency (PCE) of PIC-DT2BT (2.07%) compared to that of PIC-DTBT (1.47%) suggests that DT2BT could be a promising building block for the efficient D–A type copolymers if the low solubility is overcome by the molecular design of the donor segment.

Introduction

In the past few years, polymer solar cells (PSCs) have attracted growing attention[1] as a potential renewable energy technology based on their simple and low-cost manufacturing processes and capability to fabricate flexible large-area devices.[2] From the early days of these studies, poly(p-phenylenevinylene)s (PPVs)[3] and polythiophenes (PTs)[4] have often been used as the electron donor materials in bulk heterojunction type PSCs. However, the upper limits of the PCEs obtained by using PPV or P3HT seem to have been reached due to their relatively high-lying HOMO energy levels, large band gaps and the limited possibilities to alter their electronic properties through structural modifications.

Therefore, the design of novel photovoltaic polymers with low-band-gaps and broader absorptions is one of the major challenges today.[5] A promising strategy for the design of low-band-gap polymers is to use the strategy of incorporating donor (electron-rich) and acceptor (electron-deficient) segments alternatively in a conjugated polymer chain.[6] For the acceptor segments, 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) is one of the most effective building blocks to date for tuning the energy levels and the absorption spectra of the resulting D–A copolymers for use in photovoltaic devices (Table 1). For the donor segments, (hetero)aromatic structures based on biphenyl or bisthiophene with a bridging atom (C, S, or N) have been extensively studied.[7–11] Recently, we synthesized dithieno[3,2-b:2′,3′-d]pyrrole (DTP) in which the bisthiophene

was bridged with an alkylamino group, and the alternating copolymer combined with DTBT as the acceptor segment (PDTP-DTBT). The PSC based on PDTP-DTBT have a moderate PCE of 2.18%,[12] which completed the synthesis and evaluation in PSCs of the possible combinations for this class of materials, as summarized in Table 1.
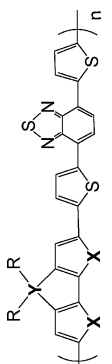
To further improve the absorption and electronic properties of the polymers used in PSCs, extension of the conjugation plane in the polymer chains would be a promising strategy. However, the solubility of the polymers in the organic solvents would decrease if the strategy was adopted without careful consideration of the molecular design. In fact, 4,7-di(2,2′-bithien-5-yl)-2,1,3-benzo-thiadiazole (DT2BT), in which two extra unsubstituted thiophene rings are attached to the ends of DTBT, has not been investigated as an acceptor segment, likely due to the poor solubility of the resulting polymers. However, the extended conjugation of the thiophene units is expected to improve the device performance. Therefore, it is necessary to explore the material designs that allow for both solubility of the polymer and extension of the conjugations of the main chain.

In this work, we synthesized a derivative of indolo[3,2-b]-carbazole (IC) and used it as the donor segment in D–A copolymers. IC has a fused ring structure of carbazole that could extend the conjugation and also promote the close packing of the molecules in the films. After their first utilization in the organic electronics reported by Ong et al.,[13] IC units have been utilized in field effect transistors (FETs)[14] and in PSCs.[15] In the present molecular design, two bulky 1-decylundecyl groups were attached to the nitrogen atoms of the IC segments to compensate for the low solubility induced by the extension of the conjugation in the main chain. This donor design enabled the use of not only DTBT but also DT2BT as the acceptor segment, resulting in the

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Table 1 Photovoltaic performance of D–A copolymers based on combinations of donors with the bridged aromatic rings and DTBT segments

|	CH=CH			S		
X =	CH=CH			S		
Y =	C	Si	N-CH	C	Si	N-CH
Name of donor segments	Fluorene (F)	Dibenzosilole (DBS)	Carbazole (C)	Cyclopenta[2,1-b:3,4-b']dithiophene (CPDT)	Dithienosilole (DTS)	dithieno[3,2-b:2',3'-d]pyrrole (DTP)
PCE	4.2%	5.4%	6.1%	2.1%	0.18%	2.18%
Ref.	7b	8b	9b	10	11	12

successful synthesis of two new soluble D–A type copolymers, poly{5,11-di(1-decylundecyl)indolo[3,2-b]carbazole-3,9-diyl-alt-4,7-dithien-2-yl-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DTBT) and poly{5,11-di(1-decylundecyl)indolo[3,2-b]carbazole-3,9-diyl-alt-4,7-di(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DT2BT), respectively. Photovoltaic devices were fabricated with the polymers as the electron donor and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) as the acceptor using the blend bulk-heterojunction approach.

Material synthesis

4,7-Di(2-bromothien-5-yl)-2,1,3-benzothiadiazole (monomer **1**) was synthesized according to reported procedures.[16] A similar route was used to obtain 4,7-di(5′-bromo-2,2′-bithien-5-yl)-2,1,3-benzothiadiazole (monomer **4**). 3,9-Dibromoindolo[3,2-b]carbazole (monomer **6**) was synthesized by following a reported method.[14a] The alkylation reaction was carried out in a mixed solvent (THF and DMSO) with the tosylate derivative (compound **5**). The long alkyl chains with a Y-shaped structure (1-decylundecyl) were used to give a high solubility to the IC segments. Compound **8** was synthesized through a double lithiation of compound **7** with n-BuLi and subsequent quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1). The alternating copolymers of PIC-DTBT and PIC-DT2BT were synthesized via a Suzuki coupling reaction. PIC-DTBT and PIC-DT2BT are readily soluble in common organic solvents such as chloroform, THF, toluene and chlorobenzene. The molecular weight and polydispersity index (PDI) of the copolymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. PIC-DTBT and PIC-DT2BT had weight-averaged molecular weights (M_w) of 33.9 kg mol^{-1} and 13.7 kg mol^{-1}, respectively, and PDIs of 1.94 and 1.65, respectively. The lower molecular weight of PIC-DT2BT compared to that of PIC-DTBT is possibly the result of the poorer solubility and lower reactivity of the monomer **4** in the Suzuki reaction compared to the monomer **1** (Scheme 2).

Optical properties

The normalized UV-vis absorption spectra of PIC-DTBT and PIC-DT2BT in CHCl$_3$ solution are shown in Fig. 1. The absorption of both PIC-DTBT and PIC-DT2BT have two absorption bands, which is in accordance with other D–A copolymers.[7–12] The peak at the longer wavelength could be attributed to the intramolecular charge-transfer (ICT) transition, and the other is possibly the result of higher energy transitions. The shapes of the absorption spectra in a film are similar to those in solutions and are shown in Fig. 2. The optical data are summarized in Table 2. The absorption peak of the ICT transition of PIC-DT2BT is at a wavelength 10 nm longer than that of PIC-DTBT both in solutions and films, indicating the extension of the conjugation by the introduction of the two additional thienyl units. The absorption peaks at the longer wavelength in the films of both polymers have a red-shift of 10 nm compared with those in solution, indicating the presence of intermolecular interactions in the solid state. The interactions seem to be not as strong as those of P3HT or other D–A type polymers, which is
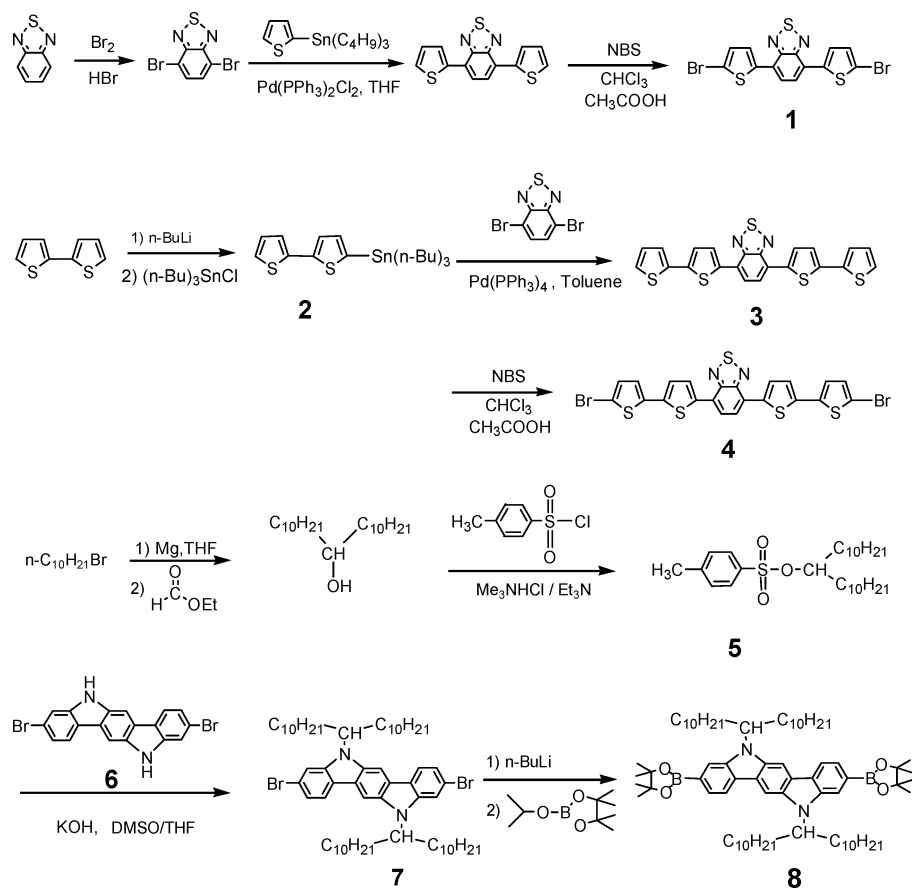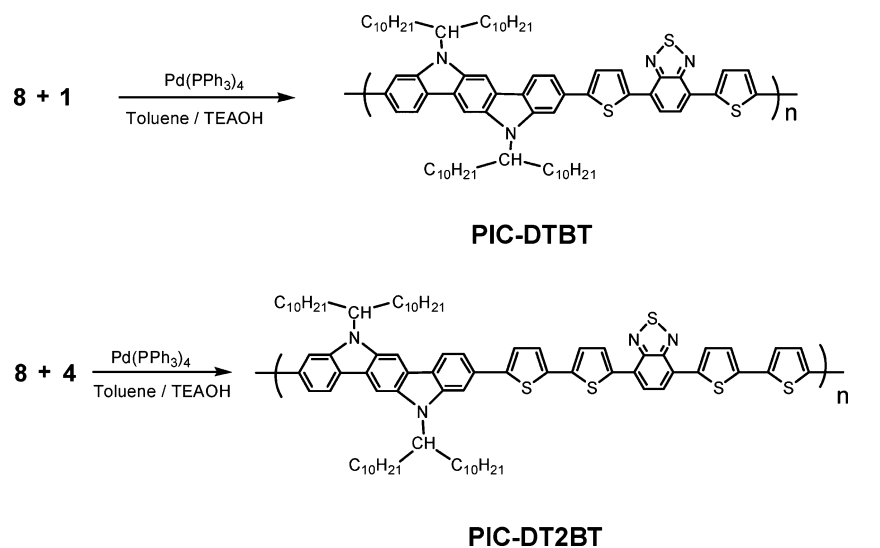
Scheme 1 Synthetic routes for acceptor and donor segments.

likely an effect of the two bulky side chains at the IC segments. The optical band gaps (E_g^{opt}) of the two polymers are estimated from the absorption onset and summarized in Table 2.

The photoluminescence (PL) spectra of the two copolymers in CHCl₃ solution are also shown in Fig. 1. The PL spectra with excitations at two different absorption maxima are almost the same for both polymers, indicating fast relaxation to stable excited states in which the electrons are localized in the IC units. The PL peak of PIC-DT2BT has a red shift of 10–12 nm relative to that of PIC-DTBT, which provides further evidence of the extended conjugation resulting from the introduction of the thiophene units.

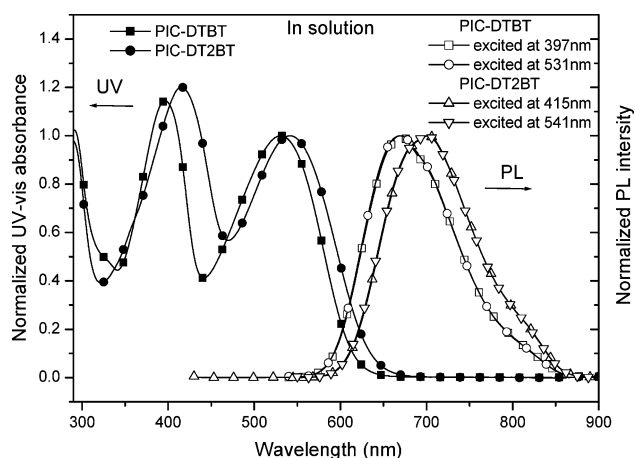**Scheme 2** Synthetic route for D–A copolymers using Suzuki reactions.

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Fig. 1 Uv-vis absorption spectra and PL spectra of two copolymers in CHCl$_3$ solution.
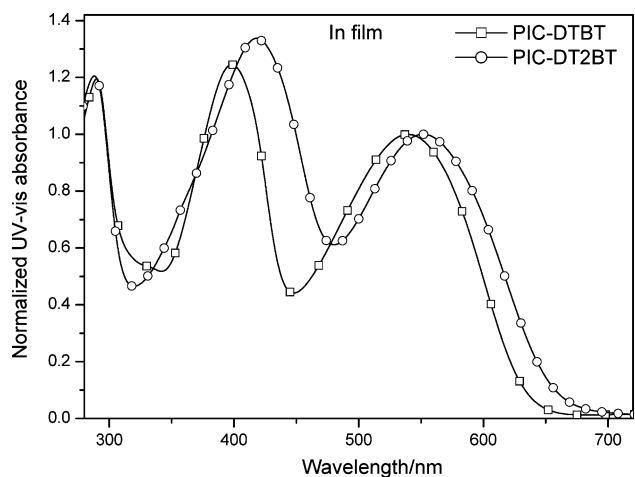
Fig. 2 Uv-vis absorption spectra of two copolymers in films.

Fig. 3 Cyclic voltammogram of the polymer films on a platinum plate in an acetonitrile solution of 0.1 mol L^{-1} [Bu$_4$N]PF$_6$ (Bu = butyl) at a scan rate of 50 mV s^{-1}.

Electrochemical properties

The electrochemical properties of the two copolymers films on a Pt electrode were investigated by cyclic voltammetry (CV). The CV curves were recorded and referenced to an Ag/Ag$^+$ (0.01 M AgNO$_3$ in acetonitrile) electrode. In order to obtain accurate redox potentials, the reference electrode was calibrated by the ferrocene/ferrocenium (Fc/Fc+) redox couple (4.8 eV below the vacuum level). As shown in Fig. 3, both the copolymers underwent reversible oxidation–reduction processes. In the reduction–re-oxid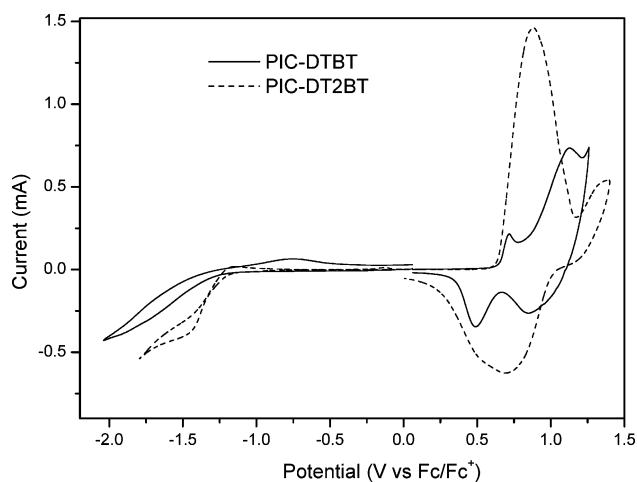ation processes, however, a reduction peak was not observed, which was different from the behavior of the poly-thiophene derivatives.[17] From the values of the onset oxidation potential (E_{on}^{ox}) and onset reduction potential (E_{on}^{red}) of the poly-mers, the HOMO and LUMO energy levels as well as the elec-trochemical band gaps (E_g^{EC}) were calculated (Table 2). E_g^{EC} coincides with the optical band gaps estimated from the UV-vis absorption onset for both copolymers.

Compared with other copolymers containing indolo[3,2-b]carbazole,[15] the HOMO energy levels of PIC-DTBT and PIC-DT2BT are quite low-lying. It is now widely accepted that the maximum V_{OC} of photovoltaic device is related to the energy difference between the LUMO of the acceptor and the HOMO of the donor,[18] therefore, PSCs based on PIC-DTBT and PIC-DT2BT are expected to have high open-circuit voltages (V_{OC}).
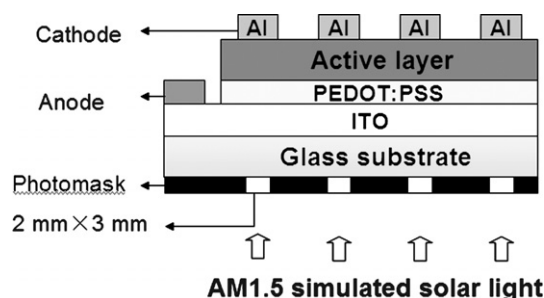
Photovoltaic properties

The bulk heterojunction PSCs were fabricated with a device structure of ITO/PEDOT:PSS/Polymer:PCBM/Al. In order to accurately evaluate the PCEs of the photovoltaic devices, it is essential to measure the device area correctly.[19] For this purpose, the effective areas of the PSCs, contributing to photocurrent, were defined using a metal photomask during irradiation with simulated solar light (Scheme 3).

It has been proposed that building an interpenetrated network of donors and acceptors inside a film is critical for obtaining high-performance photovoltaic devices.[20] Building inter-penetrated networks relates to many factors such as the ratio of

Table 2 Optical and electrochemical properties of PIC-DTBT and PIC-DT2BT

| Polymer | UV-vis absorption spectra | | | | Cyclic voltammograms | | | | |
| | In CHCl$_3$ λ_{max}/nm | In film | | | p-doping | | n-doping | | |
		λ_{max}/nm	λ_{onset}/nm	E_g^{opt}/eV	E_{on}^{ox}/V	HOMO/eV	E_{on}^{red}/V	LUMO/eV	E_g^{EC}/eV
PIC-DTBT	397, 531	398, 540	650	1.91	0.65	−5.45	−1.25	−3.55	1.90
PIC-DT2BT	415, 541	418, 551	670	1.85	0.63	−5.43	−1.18	−3.62	1.81

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Scheme 3 Schematic representation of the polymer/fullerene bulk-heterojunction PSCs.

Fig. 5 I–V curves of the PSC based on PIC-DTBT and PCBM with different mixing ratios under the illumination of AM 1.5, 100 mW cm^{-2}.

the polymer to PCBM in the blend and post-annealing treatment at suitable temperatures. In this system, the ratio of PIC-DTBT (or PIC-DT2BT) to PCBM was varied between 1 : 1 and 1 : 4 (wt/wt). The devices that were post-annealed at 110 °C for 10 min produced the best results in each case. This post-annealing treatment has been reported to induce moderate phase separation between the polymers and PCBM, which results in the construction of better pathways for both holes and electrons in the case of the P3HT:PCBM system. Fig. 4 shows atomic force microscopy (AFM) phase images of PIC-DTBT/PCBM (1 : 3, wt/wt) composite films with post-annealing at 110 °C and 130 °C. The film had low roughness (R_a = 0.29 nm) and no significant aggregation after post-annealing at 110 °C. However, post-annealing temperatures higher than 110 °C promoted the aggregation of PCBM and the formation of large PCBM crystals that possibly degraded device performance. Similar phenomena were also observed in the PIC-DT2BT/PCBM system.

Fig. 5 shows the I–V curve of the best devices based on PIC-DTBT:PCBM (1 : 3, wt/wt) and PIC-DT2BT:PCBM (1 : 3, wt/wt) under the illumination of AM 1.5 (100 mW cm^{-2}). The thicknesses of the active layers were 60 and 70 nm, respectively, measured by surface profilometry. The photovoltaic performance as measured by the open-circuit voltage (V_{OC}), short-circuit current ($I_{S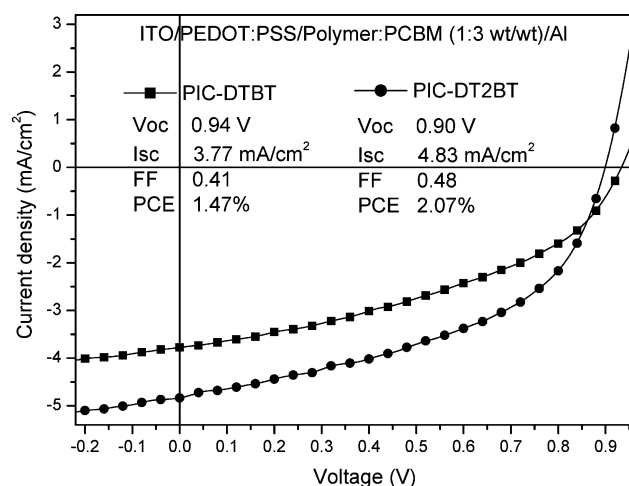C}$), fill factor (FF) and power conversion efficiency (PCE) for different ratios of polymers and PCBM is summarized in Table 3.

The PCEs of photovoltaic devices based on PIC-DT2BT:PCBM were higher than those of the PIC-DTBT:PCBM system for all mixing ratios: this can be attributed to the higher values of I_{SC} and FF. These results suggest that increasing the number of unsubstituted thienyl units in D–A copolymers could be simple and effective method for improving the photovoltaic performance of PSCs, especially for DTBT-based polymers.

The V_{OC} values of the devices based on PIC-DTBT:PCBM and PIC-DT2BT:PCBM are around 0.9 V, which is almost the maximum value deduced from the difference between the HOMO levels of the copolymers (PIC-DTBT: −5.45 eV; PIC-DT2BT: −5.43 eV) and the LUMO level of PCBM (-4.3 eV).[1e] The values of V_{OC} are similar with those of some D–A derivatives, such as DTBT copolymerized with fluorene (∼1.0 V),[7] dibenzosilole (0.9–0.97 V)[8] or carbazole (0.88 V),[9] but higher than those of other D–A derivatives, such as DTBT copolymerized with cyclopenta[2,1-b:3,4-b']dithiophene (0.6 V),[10] dithienosilole (0.44 V)[11] or dithieno[3,2-b:2′,3′-d]pyrrole (0.52 V)[12] The comparison between these analogs suggests that the V_{OC} values of photovoltaic devices are also related to the fused structure of the donor in the copolymers with DTBT. It seems that bridged biphenyl segments give higher V_{OC} than the bridged bisthiophene segments. This result will help us to design new photovoltaic polymers with higher V_{OC}. Interestingly, the V_{OC} of the cells with PIC-DT2BT (0.88–0.96 V) is higher than that with P(InCzTh$_2$BTD) (0.69 V) that has the same conjugated polymer backbone with different alkyl chains[15a] This result suggests not only the main chain but also the side chain of the polymer can affect the V_{OC}, possibly through the main chain distortion or the change of the mixing morphology in the films. Similar phenomena can be also found in the PSCs with polythiophene derivatives that showed the variations of V_{OC} by modifying the side chains.[5a,17,21] Considering the high PCEs of copolymers of DTBT in combination with fluorene, dibenzosilole or carbazole (Table 1), copolymers of these donors segments in combination with DT2BT are expected to be promising if the problem of solubility can be solved by material design.
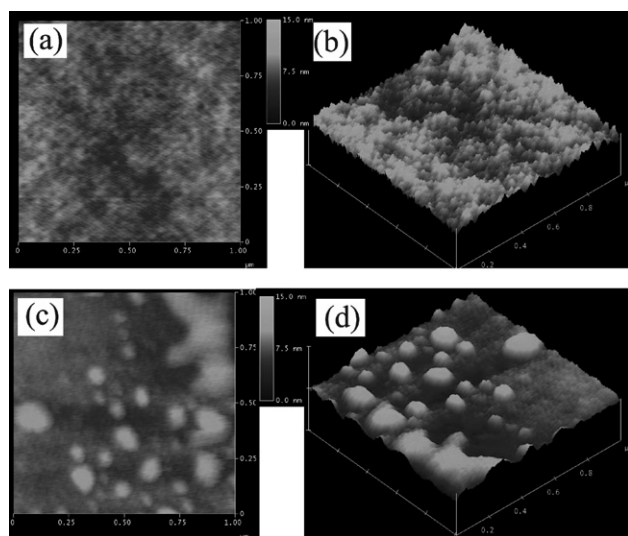

Fig. 4 AFM phase images of PIC-DTBT/PCBM (1 : 3, wt/wt) composite film with post-annealing (a, b) at 110 °C and (c, d) at 130 °C.

Table 3 Device characteristics of PSCs based on PIC-DTBT:PCBM and PIC-DT2BT:PCBM

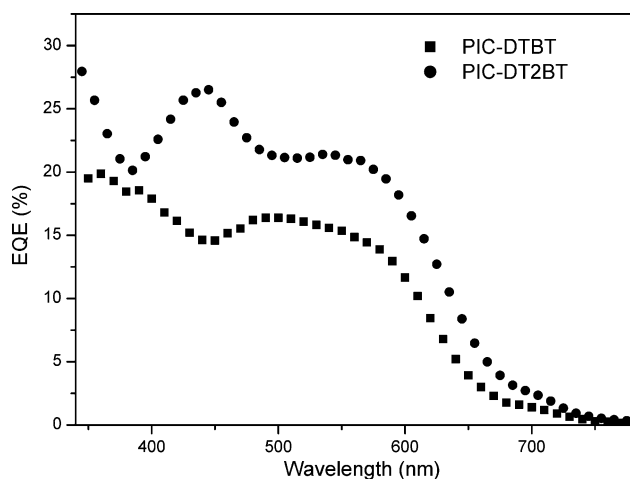| Active layer (wt/wt)	V_{SC}/V	I_{SC}/mA cm^{-2}	FF	PCE (%)
PIC-DTBT:PCBM (1 : 1)	0.98	1.24	0.26	0.32
PIC-DTBT:PCBM (1 : 2)	0.90	3.33	0.43	1.29
PIC-DTBT:PCBM (1 : 3)	0.94	3.77	0.41	1.47
PIC-DTBT:PCBM (1 : 4)	0.92	2.75	0.40	1.01
PIC-DT2BT:PCBM (1 : 1)	0.96	2.83	0.30	0.82
PIC-DT2BT:PCBM (1 : 2)	0.88	4.21	0.45	1.68
PIC-DT2BT:PCBM (1 : 3)	0.90	4.83	0.48	2.07
PIC-DT2BT:PCBM (1 : 4)	0.88	3.59	0.47	1.48

Fig. 6 EQEs of PSCs based on PIC-DTBT:PCBM (1 : 3, wt/wt) and PIC-DT2BT:PCBM (1 : 3, wt/wt).

Fig. 6 shows the external quantum efficiency (EQE) plots of the devices under the illumination of monochromatic light. The shapes of the EQE curves of the devices are similar to the absorption spectra, indicating that all the absorption wavelengths of the polymers contributed to the photovoltaic conversion. The EQE value of PIC-DT2BT was higher than that of PIC-DTBT for all wavelengths from 350 nm to 700 nm, reflecting the higher I_{SC} of PIC-DT2BT. However, the EQEs of both PIC-DT2BT and PIC-DTBT were still lower than that of the P3HT:PCBM system. Although the reason for this is not yet clear, it is possibly due to the low hole mobility of the polymers. We attempted to measure the FET mobility of the pristine polymer films but failed, probably due to the hole mobility being too low or poor hole-injection efficiency to the low-lying HOMO levels. Further attempts to investigate the charge-transport properties in both the pristine polymer film and blend film are in progress.

Conclusion

The combinations of IC with DTBT or DT2BT resulted in two D–A-type conjugated polymers. The polymers had good solubility in organic solvents and compatibility with PCBM in blend films. Both optical and electrochemical measurements showed that the band gap of PIC-DT2BT was smaller than that of PIC-DTBT. The photovoltaic device based on a PIC-DT2BT:PCBM bulk heterojunction had a power conversion efficiency of 2.07%,

which is 40% higher than that of PIC-DTBT (1.47%). Both polymers had high V_{OC} values of 0.9 V, which can be attributed to the large difference between the HOMO level of the polymers and the LUMO level of PCBM. These results suggest that the DT2BT acceptor segment could be a promising building block for the design of efficient D–A-type photovoltaic polymers.

Experimental

Materials and characterization

All chemicals were purchased from Alfa, Aldrich or Wako and used without further purification. 4,7-Di(2-bromothien-5-yl)-2,1,3-benzothiadiazole (monomer **1**),[16] toluene-4-sulfonic acid 1-decylundecyl ester (monomer **5**)[22] and 3,9-dibromoindolo[3,2-b]-carbazole (monomer **6**)[14a] were synthesized according to similar procedures in the literature.

^{1}H NMR (400 MHz) spectra were measured using a JEOL Alpha FT-NMR spectrometer equipped with an Oxford superconducting magnet system. Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence system equipped with a UV detector using CHCl$_3$ as the eluent. The sample solutions were filtered with a PTFE filter (pore size: 0.2 μm) before injection. Absorption spectra were measured using a SHIMADZU spectrophotometer MPC-3100. Cyclic voltammograms (CVs) were recorded on an HSV-100 (Hokuto Denkou) potentiostat. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag$^+$ (0.01 M of AgNO$_3$ in acetonitrile) electrode were used as the counter and reference electrodes (calibrated by Fc/Fc$^+$), respectively. AFM measurements were carried out using a Digital Instrumental Nanoscope 31 operated in tapping mode.

Fabrication and characterization of polymer solar cells

ITO-coated glass substrates were cleaned by ultrasonication in detergent, water, acetone, and 2-propanol, sequentially. After drying, the substrate was further cleaned with ozone for 15 min before PEDOT:PSS (Baytron P) was spin-coated (4000 rpm for 30 s) onto it. The film was dried at 150 °C under an N$_2$ atmosphere for 10 min. After cooling the substrate, a chlorobenzene solution of polymer and PCBM mixture (1 : 1 to 1 : 4, wt/wt) was spin-coated. Al electrodes were then evaporated under high vacuum (approximately 2 × 10^{-4} Pa) in a ULVAC UPC-260F vacuum evaporation system. The thickness of the Al electrode was approximately 40 nm. Post-annealing was carried out at 110 °C for 10 min inside a nitrogen-filled glove box. The current–voltage characteristics of the photovoltaic cells were measured

using the Keithley 2400 *I–V* measurement system. The measurements were conducted under the irradiation of AM 1.5 simulated solar light (100 mW cm^{-2}, Peccell Technologies PCE-L11). Light intensity was adjusted by a standard silicon solar cell with an optical filter (Bunkou Keiki BS520). The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight System (Bunkoh-Keiki SM-250F).

Synthesis of 5-tri-*n*-butylstannyl-2,2′-bithiophene (2)

n-Butyllithium (12.5 mL, 20 mmol, 1.6 M in hexane) was added *via* a syringe to a solution of 2,2′-bithiophene (3.32 g, 20 mmol) in anhydrous THF (80 mL) at −78 °C under an N$_2$ atmosphere. After the reaction was stirred for 2 h at −78 °C, tri-*n*-butyl-stannyl chloride (6.0 mL, 22 mmol) was added dropwise. After one additional hour at −78 °C, the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with CHCl$_3$. The combined organic layers were dried over MgSO$_4$, and the solvents were removed by rotary evaporation. The product was dried under high vacuum, and the resulting 8.40 g of greenish viscous oil were used for subsequent preparation of 4,7-di(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole without purification.

Synthesis of 4,7-di(2,2′-bithien-5-yl)- 2,1,3-benzothiadiazole (3)

5-Tri-*n*-butylstannyl-2,2′-bithiophene (8.4 g), 4,7-dibromo-2,1,3-benzothiadiazole (1.47g, 5 mmol) and toluene (100 mL) were added to a 200 mL double-neck round-bottom flask. The reaction container was purged with N$_2$ for 30 min to remove O$_2$. Pd(PPh$_3$)$_4$ (5%, 290 mg) was added, and the reaction mixture was heated to 110 °C and stirred overnight. After cooling, methanol (100 ml) was added, and the mixture was filtered and washed with water, methanol and hexane. The crude product was recrystallized in CHCl$_3$ to afford compound **3** as a golden brown solid. Yield: 1.84 g (79%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ(ppm) 8.07 (br, 2H), 7.88 (br, 2H), 7.4–7.3 (m, 4H), 7.07 (br, 2H). MALDI-TOF MS (*m/z*) 464.1 (M$^+$).

Synthesis of 4,7-di(5′-bromo-2,2′-bithien-5-yl)-2,1,3-benzothiadiazole (4)

In a 1 L round-bottom flask, compound **3** (465 mg, 1.0 mmol) was dissolved in a mixed solvent of CHCl$_3$ (500 mL) and acetic acid (100 mL), and the flask was covered with aluminium foil. *N*-Bromosuccinimide (374 mg, 2.1 mmol) was added in portions, and the reaction mixture was stirred overnight at room temperature. Then, methanol (100 mL) was added, and the mixture was filtered and washed with water, methanol, hexane and CH$_2$Cl$_2$. The precipitate was collected as a dark blue solid. Yield: 0.48 g (77%). MALDI-TOF MS (*m/z*) 621.8 (M$^+$).

Synthesis of 3,9-dibromo-5,11-di(1-decylundecyl)indolo[3,2-*b*]carbazole (7)

In a flame-dried 100 mL double-neck round-bottom flask, 3,9-dibromoindolo[3,2-*b*]carbazole (1.656 g, 4.0 mmol) and 2.24 g (40 mmol) freshly powdered potassium hydroxide was dissolved in anhydrous dimethyl sulfoxide (DMSO, 30 mL), and a solution of 5.60 g (12 mmol) of monomer **6** in DMSO and THF (40 mL,

1 : 1 v/v) was added dropwise through an addition funnel over 2 h at room temperature. After stirring at room temperature over-night, the reaction mixture was poured into water and the aqueous layer was extracted three times with hexane. The combined organic layers were dried over MgSO$_4$, and the solvents were removed by rotary evaporation. The crude compound was purified by column chromatography (silica gel; eluent: hexane), and compound **7** was isolated as a yellow powder. Yield: 3.40 g (85%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ(ppm) 8.12–7.31 (m, 8H), 4.65–4.50 (m, 2H), 2.40–2.27 (m, 4H), 1.99 (br, 4H), 1.4–0.8 (m, 76H). MALDI-TOF MS (*m/z*) 1001.43 (M$^+$). Anal. calcd for C$_{60}$H$_{94}$Br$_2$N$_2$: C, 71.83; H, 9.44; N, 2.79; found: C, 72.06; H, 9.63; N, 2.74.

Synthesis of 3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-di(1-decylundecyl)indolo[3,2-*b*]carbazole (8)

n-BuLi (4.1 mL, 6.56 mmol, 1.6 M in hexane) was added *via* a syringe to a solution of 3,9-dibromo-5,11-di(1-decylundecyl)indolo[3,2-*b*]carbazole (3.009 g, 3 mmol) in anhydrous THF (80 mL) at −78 °C under an N$_2$ atmosphere. After the reaction was stirred for 2 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.8 mL, 8.82 mmol) was added rapidly *via* a syringe. After one additional hour at −78 °C, the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with CHCl$_3$. The combined organic layers were dried over MgSO$_4$, and the solvents were removed by rotary evaporation. Lastly, the crude compound was purified by column chromatography (silica gel; eluent: chloroform–hexane 10 : 90 v/v) and isolated as a pale-yellow sticky solid. Yield: 2.0 g (61%).

^{1}H NMR (CDCl$_3$, 400 MHz): δ(ppm) 8.23–7.63 (m, 8H), 4.74 (br, 2H), 2.39(m, 4H), 2.01 (m, 4H), 1.4–1.0 (m, 70H), 0.82 (m, 30H). MALDI-TOF MS (*m/z*) 1096.06 (M$^+$).

Synthesis of poly{5,11-di(1-decylundecyl)indolo[3,2-*b*]carbazole -3,9-diyl-*alt*-4,7-dithien-2-yl-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DTBT)

Monomer **1** (117 mg, 0.255 mmol), monomer **8** (280mg, 0.255 mmol) and toluene (10 mL) were added to a 50 mL double-neck round-bottom flask. The reaction container was purged with N$_2$ for 30 min to remove O$_2$. Pd(PPh$_3$)$_4$ (3%, 9 mg) was added, and the reaction mixture was heated to 110 °C for 10 min. Tetrae-thylammonium hydroxide (0.9 mL, 20% by weight in H$_2$O) was added, and the mixture was heated under reflux overnight. Phenylboronic acid (100 mg in 1 mL THF) was added, and after 2 h, bromobenzene (1 mL) was added. The mixture was allowed to reflux for 2 h and cooled to room temperature. The polymer was precipitated by slowly adding the mixture into MeOH, filtered and Soxhlet extracted with ether and CHCl$_3$. The CHCl$_3$ solution was passed through a column packed with alumina, celite and silica gel. The column was eluted with CHCl$_3$. The combined polymer solution was concentrated to 30 mL and poured into methanol (300 mL). The precipitate was then collected and dried under vacuum overnight. Yield: 0.23 g (79%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ(ppm) 8.42–7.30 (m, 14H), 4.74 (br, 2H), 2.50 (br, 4H), 2.06 (br, 4H), 1.4–1.0 (br, 64H),

0.85 (m, 12H). Anal. calcd. for $C_{74}H_{100}N_4S_3$: C 77.84, H 8.83, N 4.91; found: C 77.60, H 8.77, N 4.90.

Synthesis of poly{5,11-di(1-decylundecyl)indolo[3,2-*b*]carbazole-3,9-diyl-*alt*-4,7-di(2,2′-bithien-5-yl)-2,1,3-benzothiadiazole-5′,5″-diyl} (PIC-DT2BT)

A procedure similar to the synthesis of PIC-DTBT was used starting from monomer **4** (127 mg, 0.204 mmol) and monomer **8** (224 mg, 0.204 mmol). Yield: 0.22 g (82%). ^{1}H NMR (CDCl₃, 400 MHz): δ(ppm) 8.40–7.22 (m, 18H), 4.71 (br, 2H), 2.48 (br, 4H), 2.04 (br, 4H), 1.4–1.0 (br, 64H), 0.82 (m, 12H). Anal. calcd. for $C_{82}H_{104}N_4S_5$: C 75.41, H 8.03, N 4.29; found: C 75.20, H 8.12, N 4.27.

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