Donor−Acceptor Conjugated Polymer Based on Naphtho[1,2-c:5, 6-c]bis[1,2,5]thiadiazole for High-Performance Polymer Solar Cells

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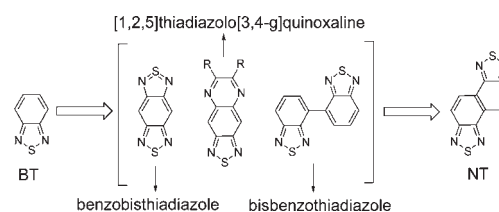
S Supporting Information

ABSTRACT: Donor−acceptor conjugated polymers PBDT-DTBT and PBDT-DTNT, based on 2,1,3-benzothiadiazole (BT) and naphtho[1,2-c:5,6-c]bis[1,2,5]thiadiazole (NT), have been designed and synthesized for polymer solar cells. NT contains two fused 1,2,5-thiadiazole rings that lower the band gap, enhance the interchain packing, and improve the charge mobility of the resulting polymer. Consequently, the NT-based polymer PBDT-DTNT exhibited considerably better photovoltaic performance with a power conversion efficiency (PCE) of 6.00% when compared with the BT-based polymer PBDT-DTBT, which gave a PCE of 2.11% under identical device configurations.

Scheme 1. Examples of Thiadiazole-Derived Acceptor Molecules

Polymer solar cells (PSCs) have received increasing attention because of the potential for fabrication of light-weight, large-area, and flexible light-harvesting devices through low-cost solution processing.[1] Considerable progress has been made in this area, as evidenced by the improvement of the power conversion efficiencies (PCEs) of PSCs from around 1% to more than 9% over the past decade.[2] PSCs usually adopt a bulk-heterojunction (BHJ) structure, where a phase-separated blend of donor and acceptor materials are used as the active layer.[3] In most cases, fullerene derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC$_{71}$BM), are used as acceptors, and conjugated polymers are used as donors.[4,5] Because most of the solar energy is harvested by donor polymers, extensive research efforts have been devoted to developing small band gap conjugated polymers for PSCs.[6−10] It is well recognized that both the band gaps and energy levels of donor polymers should be optimized simultaneously to obtain high PCEs.[11] To achieve this effect, donor−acceptor (D−A) conjugated polymers with alternating electron-rich (donor) and electron-deficient (acceptor) units along the polymer main chain have been widely developed because their band gaps and energy levels can be easily tuned by controlling the intramolecular charge transfer (ICT) from the donor to the acceptor moieties.[12]

Among the various D−A conjugated polymers, 2,1,3-benzothiadiazole (BT) has been widely used and has proven to be one of the most promising acceptor units for high-performance PSC materials (Scheme 1).[13−16] For example, by copolymerizing with various donor units, such as fluorene,[17,18] silafluorene,[19] carbazole,[20,21] and benzodithiophene derivatives,[22] the resulting BT-based, D−A conjugated polymers have shown promising performance, with PCEs ranging from 2.40% to 5.66%. Among them, Leclerc et al. systematically explored a series of 2,7-carbazole-based, D−A conjugated polymers with different acceptor units and found that the polymer using the BT acceptor exhibited the best performance, with a PCE of 3.6%.[21] Subsequently, Park et al. reported that the PCE of the PSCs based on the same polymer could reach as high as 6.1% when the devices were processed under optimized conditions and with improved device structure.[23] However, the band gaps of these BT-based, D−A conjugated polymers were approximately 1.7−1.9 eV, which were not optimal for efficient sunlight harvesting because of the relatively weak electron-withdrawing capability of the BT unit. Therefore, considerable effort has been put into modification of the BT-based acceptor units to obtain D−A conjugated materials with optimal band gaps for solar cell applications. Benzobisthiadiazole[24,25] and [1,2,5]thiadiazolo[3,4-g]quinoxaline,[26] for example, have been used as the acceptor units in D−A conjugated polymers and have exhibited much higher electron-withdrawing capability relative to BT, which could potentially reduce the resulting polymers' band gaps (Scheme 1). However, these polymers had high electron affinities because of their strong electron-withdrawing units, which affected the charge separation efficiencies between the polymers and the PC$_{61}$BM and hence reduced the corresponding PSC device performance. Moreover, bisbenzothiadiazole was also developed as an acceptor for D−A conjugated molecules, but there was found to be a large twist between the neighboring BT units in the resulting materials, which decreased the packing and effective conjugation length.[27] Thus, it still remains a challenge to develop new, ideal acceptor units in D−A conjugated polymers for high-performance PSCs.

Scheme 2. Synthesis of PBDT-DTBT and PBDT-DTNT[a]
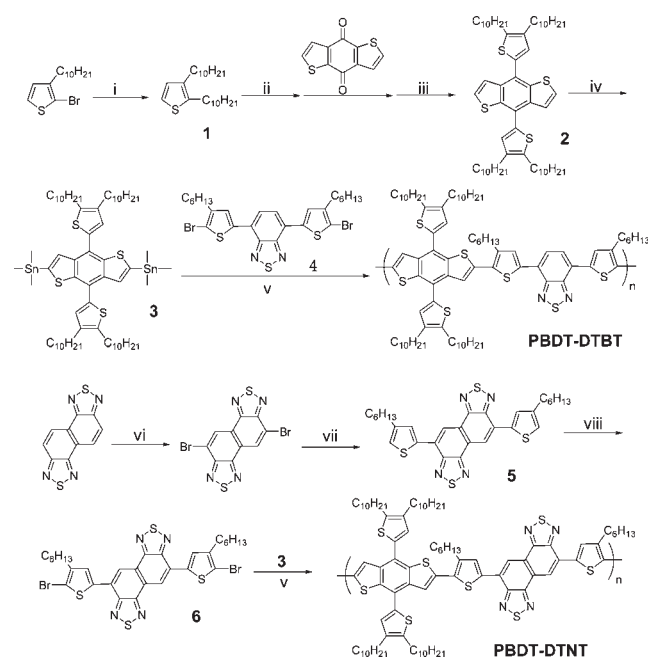
[a] Reagents and conditions: (i) $C_{10}H_{21}MgBr$, (dppp)NiCl$_2$; (ii) n-BuLi, 0 °C, then 50 °C; (iii) SnCl$_2$, 10% HCl aq; (iv) n-BuLi, 0 °C, then ambient temperature, 3 h; Me$_3$SnCl, 0 °C; (v) Pd$_2$(dba)$_3$, P(o-Tol)$_3$, toluene, reflux, 48 h. (vi) NBS, oil of vitriol, 60 °C, 24 h; (vii) (4-hexylthiophen-2-yl)-tributylstannane, Pd(PPh$_3$)$_4$, DMF, 120 °C; (viii) NBS, THF, 50 °C.

Herein, we report the use of naphtho[1,2-c:5,6-c]bis[1,2,5]-thiadiazole (NT) as a new acceptor unit in D—A conjugated polymers for high-performance PSCs (Scheme 1). Compared with BT, NT has an enlarged planar aromatic structure containing two fused 1,2,5-thiadiazole rings, which may facilitate the interchain packing of the resulting polymer and may further enhance the carrier mobility. In addition, the electron-withdrawing capability of NT is slightly stronger than that of BT, which will lower the resulting polymer band gap, resulting in more efficient solar energy harvesting while still maintaining enough driving force for the charge separation between the polymer and PC$_{61}$BM. Consequently, compared with the analogous BT-based polymer, the NT-based polymer exhibited a red-shifted absorbance, greatly enhanced hole mobility, and much improved PSC performance, with a PCE of 6.00%.

Scheme 2 shows the synthetic route for the relevant monomers and polymers; the detailed synthesis procedures are described in the Supporting Information. A recent report has shown that benzodithiophene derivatives are promising donor units in the PSC polymer materials because of their planar-conjugated structure and weak steric hindrance between adjacent units.[28] Thus, a benzodithiophene derivative 3 was chosen as the donor unit in the copolymerization. The key monomer 6 was synthesized from NT by a three-step procedure,[29] including bromination of NT, Stille coupling with (4-hexylthiophen-2-yl)-tributylstannane, and bromination of the coupling product 5. The resulting NT-based D—A copolymer PBDT-DTNT was obtained through Stille coupling polymerization of 3 and 6 in a yield of 86%. For comparison, the BT-based analogous polymer, PBDT-DTBT, was also synthesized. Both polymers were soluble in common organic solvents and exhibited good thermal stability
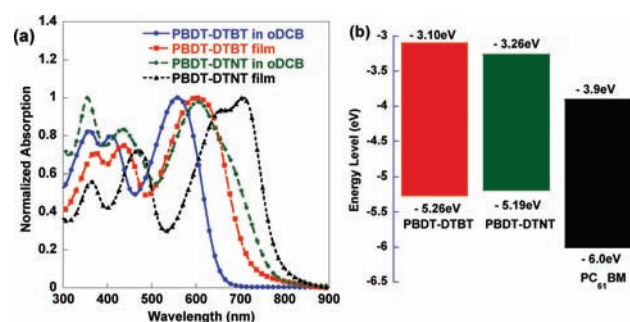

Figure 1. (a) Normalized absorption spectra of PBDT-DTNT and PBDT-DTBT in oDCB solutions and in films. (b) HOMO and LUMO energy levels of the polymers and PC$_{61}$BM.

up to 400 °C. According to size-exclusion chromatography (SEC) experiments, PBDT-DTNT has a number-average molecular weight (M_n) of 40.5 kDa, with a polydispersity index (PDI) of 3.20, while PBDT-DTBT has an M_n of 24.1 kDa, with a PDI of 2.46.

The absorption spectra of both polymers in solution and as thin-films are shown in Figure 1a. In comparison with PBDT-DTBT, PBDT-DTNT clearly exhibited more obvious red-shifted absorbance spectra both in o-dichlorobenzne (oDCB) solution and as a thin film, which was likely a result of the more electron-deficient nature of the NT acceptor. Both PBDT-DTBT and PBDT-DTNT exhibited considerably more significant red-shifted absorbance in films when compared with solution data, which is a common feature of linear D—A conjugated polymers; this phenomenon is caused by the increased polymer chain aggregation in the solid state. By changing the acceptor from BT to NT, the optical band gaps of the polymers (calculated from the onset of the film absorption) were decreased from 1.73 eV for PBDT-DTBT to 1.58 eV for PBDT-DTNT, the latter being much closer to the ideal band gap for PSC donor materials.[11] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of the polymers were obtained by cyclic voltammetry (CV) (Figure 1b). It was found that the use of NT units simultaneously changed the HOMO and LUMO levels of the polymer, resulting in a much narrower band gap of PBDT-DTNT with respect to that of PBDT-DTBT.

Notably, compared to its absorption in oDCB solution, PBDT-DTNT showed a distinctively different absorption spectrum as a thin film, with a large shoulder at 705 nm, while PBDT-DTBT exhibited similar absorption shapes both in solution and as a thin film. This particular enhanced shoulder absorption in films has been observed for many high-performance PSC materials, generally indicating a strong intermolecular packing in the solid state caused by their planar and rigid backbones.[30,31] Obviously, compared to PBDT-DTBT, PBDT-DTNT exhibited more pronounced aggregation in the solid state because of its more rigid NT acceptor unit, which might further enhance its mobility. To verify this observation, the mobilities of both polymers were measured using the space charge limited current (SCLC) model. Indeed, PBDT-DTNT had a much higher hole mobility than PBDT-DTBT. The hole mobilities were $\sim 10^{-5}$ cm^2 V^{-1} s^{-1} for PBDT-DTNT and $\sim 10^{-6}$ cm^2 V^{-1} s^{-1} for PBDT-DTBT (see Supporting Information).

The photovoltaic properties of both polymers were studied in a device structure of ITO/PEDOT:PSS/polymer:PCBM/Ca/Al

Table 1. Performance of Polymer Solar Cells[a]

active layer[b]	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
PBDT-DTBT/PC$_{61}$BM	4.00	1.05	35.3	1.56
PBDT-DTBT/PC$_{71}$BM	5.80	1.00	34.6	2.11
PBDT-DTNT/PC$_{61}$BM	10.15	0.80	62.2	5.32
PBDT-DTNT/PC$_{71}$BM	11.71	0.80	61.0	6.00

[a] All the devices were measured under the illumination of AM1.5G at 95 mW/cm^2. [b] All the weight ratios of polymer and PCBM were 1:1 and annealed at 130 °C for 7 min.
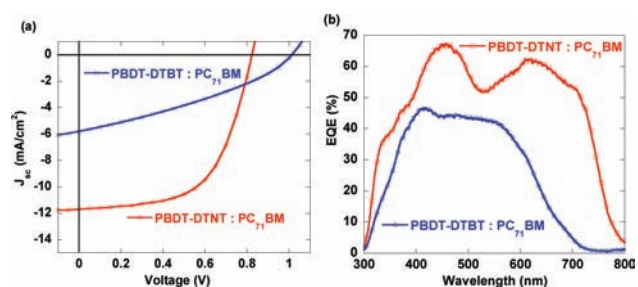

Figure 2. (a) $J-V$ curves of the PBDT-DTBT/PC71BM and PBDT-DTNT/PC71BM devices. (b) External quantum efficiency curves of the PBDT-DTBT/PC71BM and PBDT-DTNT/PC71BM devices.

(ITO, indium tin oxide; PEDOT:PSS, poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene); PCBM, PC$_{61}$BM or PC$_{71}$BM). A thin film (40 nm) of PEDOT:PSS was deposited on a pre-cleaned ITO substrate. The polymer:PCBM (1:1, w/w) solution in 1,2-dichlorobenzene was then spin-coated, and the substrate was subsequently annealed at 130 °C for 7 min. Finally, the process was completed by evaporating Ca/Al metal electrodes under high vacuum with an area of 0.16 cm^2, as defined by masks. A more detailed description of the device fabrication process is available in the Supporting Information.

The device performance data are presented in Table 1. Both PBDT-DTNT and PBDT-DTBT showed much better performance when using PC$_{71}$BM as the acceptor than with devices fabricated using PC$_{61}$BM, which can be explained by PC$_{71}$BM having a considerably stronger absorption in the visible region, complementing the absorption valley of the polymers.[32] The best cell was obtained from PBDT-DTNT:PC$_{71}$BM and showed a short-circuit current density (J_{sc}) of 11.71 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.80 V, and a fill factor (FF) of 61.0%, resulting in a PCE of 6.00%. This behavior stands in opposition to the device based on PBDT-DTBT:PC$_{71}$BM, which only showed a PCE of 2.11%, with a J_{sc} of 5.80 mA/cm^2, a V_{oc} of 1.00 V, and a FF of 34.6%. Notably, Yang et al.[22] reported a similar BT-based polymer PBDTTBT with a PCE of 5.66%. Unlike PBDTTBT, hexyl chains were introduced onto the thiophene units of PBDT-DTBT to improve their solubility. However, PBDT-DTBT exhibited a much lower PCE of 2.11%, which might be because of the strong steric hindrance of the substituted hexyl chains. Interestingly, this strong steric hindrance effect was greatly suppressed by using NT as the acceptor, which was confirmed by the X-ray diffraction measurements (see Supporting Information). Further, PBDT-DTNT exhibited pronounced red-shifted absorption spectra (solution and solid state), higher hole mobility, and improved device performance. Figure 2 shows the current density—voltage ($J-V$) curves and

external quantum efficiency (EQE) curves of the polymer: PC$_{71}$BM blends. The PBDT-DTNT:PC$_{71}$BM device exhibited a broad and high response range, covering 300—800 nm, whereas the PBDT-DTBT:PC$_{71}$BM device exhibited a relatively narrow and low response range, covering 300—700 nm. These results have shown clearly that the more effective solar energy harvesting capability and the high charge transport mobility are the main reasons for the improved PSC performance of PBDT-DTNT compared to PBDT-DTBT.

In conclusion, two D—A conjugated polymers using NT and BT as acceptor units, PBDT-DTNT and PBDT-DTBT, were developed for PSC applications. Compared with the BT-based polymer, the NT-based polymer showed more pronounced red-shifted absorption spectra and higher hole mobilities while maintaining suitable energy levels for effecting reasonable V_{oc} and efficient charge separation between the polymer and PCBM. Consequently, the NT-based polymer exhibited a much more promising photovoltaic performance, with a PCE of 6.00% when compared with the analogous PBDT-DTBT, based on the previously widely used BT acceptor.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Complete ref 25; experimental details for the synthesis, instruments, measurements, and fabrication procedures; and characterization details of the PSC devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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