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Solar Cells

Enhanced Photovoltaic Performance of Low-Bandgap Polymers with Deep LUMO Levels**

*Huaxing Zhou, Liqiang Yang, Samuel C. Price, Kelly Jane Knight, and Wei You**

As a potential low-cost alternative to mainstream silicon solar cells, bulk heterojunction (BHJ) polymer solar cells have attracted a significant amount of attention in the research community.[1] Fullerene derivatives (such as [6,6]-phenyl-C_{61}-butyric acid methyl ester, $PC_{61}BM$) have been extensively used as the n-type semiconductor in BHJ solar cells because of their superior electron-accepting and transport behavior. However, these fullerene derivatives are usually poor light absorbers, thereby leaving the task of light absorbing to the conjugated polymers. Moreover, fullerene derivatives usually have fixed energy levels (e.g., a lowest unoccupied molecular orbital (LUMO) of 4.3 eV), which dictate that the proposed "ideal" conjugated polymer should exhibit a low highest occupied molecular orbital (HOMO) energy level of −5.4 eV and a small bandgap of 1.5 eV.[2] Therefore, a significant amount of effort has been devoted to engineering the bandgap and energy levels of conjugated polymers. As a result, a few highly efficient polymers have been reported with the record high efficiency surpassing 7 %.[3]

To simultaneously lower the HOMO energy level and the bandgap as required by the ideal polymer, a "weak donor–strong acceptor" strategy was proposed.[2c] A few such materials, by incorporating weak donor moieties based on fused aromatic systems and a strong acceptor based on 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT), have been successfully demonstrated with high efficiency in typical BHJ devices.[4] In these conjugated polymers, close to ideal HOMO energy levels were achieved (e.g., −5.33 eV), which led to an observed open circuit voltage (V_{oc}) as high as 0.83 V.[4a] However, the bandgaps of these materials were still larger than the proposed 1.5 eV of ideal polymers, which explains why mediocre short-circuit currents (J_{sc}) were obtained. Logically, to further improve the efficiency, a smaller bandgap is needed to achieve a higher short-circuit current (J_{sc}), while the low HOMO energy level should still be maintained. Fortunately, our previous study indicated that the LUMO of donor–acceptor copolymers largely resides on the acceptor moiety.[5] Therefore, we envisioned that incorporating a more electron deficient acceptor to lower the LUMO would lead to a smaller bandgap and maintain the low HOMO energy level in the newly designed materials.

Compared with benzene, pyridine is π-electron deficient. Therefore, if we replaced the benzene in the 2,1,3-benzothiadiazole (BT) unit with pyridine, the new acceptor, thiadiazolo[3,4-*c*]pyridine (PyT), would be one such stronger acceptor. A similar strategy has been demonstrated recently by Leclerc et al.[6] The copolymer of a carbazole unit with a thienyl-flanked PyT unit (PCDTPT) did show a much lower LUMO level compared with that of the copolymer with a BT unit. However, a low efficiency was obtained, presumably because of the low molecular weight and low solubility of PCDTPT. To solve these issues, we employed the strategy of a "soluble" acceptor[4a,5a] by flanking the PyT moiety with two alkylated thienyl units, which converted the PyT into the new, soluble, stronger acceptor DTPyT. As demonstrated in our previous study,[5a] anchoring of alkyl chains to the 4-position of the thienyl units of DTPyT would only significantly improve the molecular weight and solubility of the resulting polymers without introducing much steric hindrance.

Herein, we report the synthesis of a series of weak donor–strong acceptor polymers, PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT, by copolymerizing various donor moieties, namely naphtho[2,1-*b*:3,4-*b*′]dithiophene (NDT), dithieno[3,2-*f*:2′,3′-*h*]quinoxaline (QDT), and benzo[1,2-*b*:4,5-*b*′]dithiophene (BnDT), with the newly conceived soluble DTPyT acceptor moiety (Scheme 1). Our preliminary investigation on the photovoltaic properties of these polymers in typical BHJ devices using $PC_{61}BM$ as the electron acceptor showed highly respectable power conversion efficiencies (PCEs) of over 5.5 % for PQDT–DTPyT, and over 6 % for PBnDT–DTPyT and PNDT–DTPyT.

The synthesis of the alkylated DTPyT is modified from the reported procedure[6] (see the Supporting Information for experimental details). The other comonomers—alkylated NDT, QDT, and BnDT—were prepared by established literature procedures.[4a,7] Three polymers, PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT, were synthesized by the microwave-assisted Stille polycondensation[1e] between alkylated dibrominated DTPyT and the corresponding distannylated monomers. Crude polymers were purified by

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[*] H. Zhou, S. C. Price, K. J. Knight, Prof. Dr. W. You
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290 (USA)
Fax: (+1) 919-962-2388
E-mail: wyou@email.unc.edu
Homepage: http://www.chem.unc.edu/people/faculty/you/group/index.html

L. Yang, Prof. Dr. W. You
Curriculum in Applied Sciences and Engineering
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3287 (USA)

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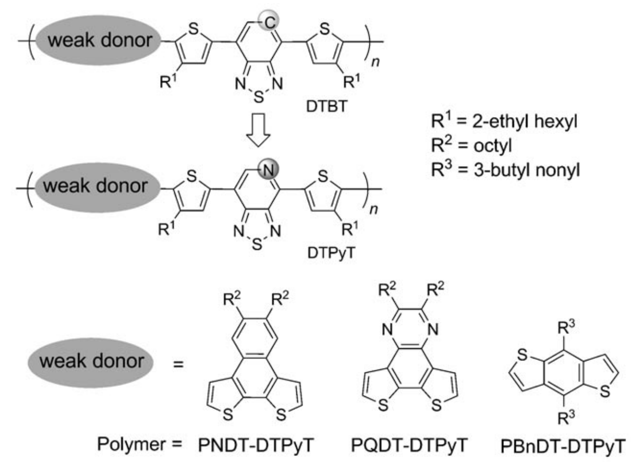

Scheme 1. Molecular structures of PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT.

Soxhlet extraction with methanol, ethyl acetate, hexane, and chloroform. The chloroform fraction was concentrated and reprecipitated in methanol to afford the purified polymers. All three polymers showed high molecular weights, especially in the case of PBnDT–DTPyT (Table 1), thus underscoring the importance of introducing the "soluble" acceptor.

Table 1: Polymerization results and energy levels of PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT.

Polymer	Yield [%]	Molecular weight [kg mol^{-1}][a]	PDI[b]	HOMO [eV][c]	LUMO [eV][c]
PNDT–DTPyT	92	17.1	2.14	5.36	3.42
PQDT–DTPyT	88	21.7	2.27	5.50	3.44
PBnDT–DTPyT	53	104.4	3.64	5.47	3.44

[a] Determined by GPC in 1,2,4-trichlorobenzene at 135 °C using polystyrene standards. [b] Polydispersity index. [c] HOMO and LUMO levels were calculated from the onsets of oxidation peaks and reduction peaks, respectively.

The UV/Vis absorption spectra of the three polymers in chlorobenzene solution at elevated temperature (100 °C) and in the solid state are shown in Figure 1. The solution absorption spectra of the three polymers at high temperature are almost identical and contain two absorption maxima, as typically observed for donor–acceptor low-bandgap materials. However, these polymers tend to aggregate, indicated by a large bathochromic shift (ca. 25–90 nm) in the solution spectra at room temperature.[8] The absorption spectra in the solid state are quite different for these three polymers, which indicates different polymer-chain organization and interaction in thin films.[1e] For example, the absorption of PBnDT–DTPyT has the largest redshift when transitioning from solution to the film, presumably because of the symmetric molecular structure of the BnDT unit which helps molecular stacking in the solid state. A larger redshift of the absorption spectrum of PNDT–DTPyT than that of PQDT–DTPyT was observed, which suggests that PNDT–DTPyT adopts a more planar polymer-chain conformation and more effective chain–chain stacking in the solid state. The estimated optical bandgaps of PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT are 1.53, 1.56, and 1.51 eV, respectively, noticeably reduced (ca. 0.09–0.19 eV) compared with the bandgaps of their BT counterparts.[4]

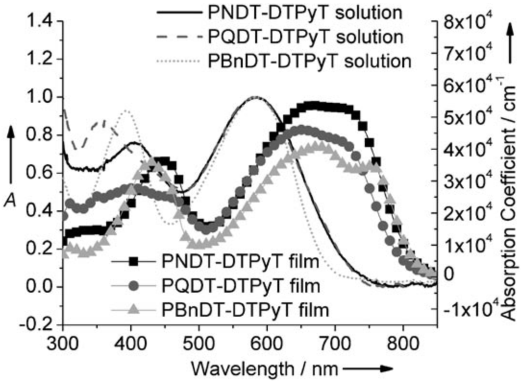

Figure 1. UV/Vis absorption spectra of PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT in chlorobenzene solution at 100 °C and in solid films.

The HOMO and LUMO energy levels of each polymer were estimated by cyclic voltammetry and are presented in Table 1. The LUMO levels of all three polymers, calculated from the onset of the reduction potential,[8] are almost identical within experimental error, indicative of the identical acceptor unit (DTPyT). This agrees well with the previous discovery that the LUMO of a donor–acceptor polymer is primarily located in the acceptor unit.[2c,5a,6] More importantly, incorporating the stronger acceptor DTPyT in these three polymers lowers the LUMO energy levels by approximately 0.2 eV compared with their DTBT analogues.[4] The lowered LUMO energy level explains the observed bandgap reduction in these polymers. It is also worth noting that all three weak donors—NDT, QDT, and BnDT—are able to maintain low HOMO energy levels around the ideal HOMO energy level of −5.4 eV.

BHJ photovoltaic devices were fabricated with a typical configuration of ITO/PEDOT:PSS(40 nm)/polymer:$PC_{61}BM$/Ca(40 nm)/Al(70 nm) (ITO = indium tin oxide, PEDOT = poly(3,4-ethylenedioxythiophene), PSS = polystyrene sulfonic acid). All photovoltaic devices were tested under simulated air mass coefficient AM1.5G illumination (100 mW cm^{-2}). Typical current density–voltage (J–V) characteristics are shown in Figure 2a and summarized in Table 2. In initial trials, all devices showed promising efficiency of over 5.5 % with one of these three polymers as the donor material and $PC_{61}BM$ as the electron acceptor. The highest current of 14.2 mA cm^{-2} was obtained for PNDT–DTPyT-based devices, which is among the highest J_{sc} values obtained for a BHJ device consisting of a donor polymer and $PC_{61}BM$ as the acceptor.[9] The high J_{sc} value, along with a V_{oc} value of 0.71 V and a high fill factor (FF) of 0.61, yields an impressive PCE of 6.20 % for PNDT–DTPyT:$PC_{61}BM$-based BHJ solar cells.

When PQDT–DTPyT or PBnDT–DTPyT with deeper HOMO levels is used in BHJ solar cells, we observe a higher

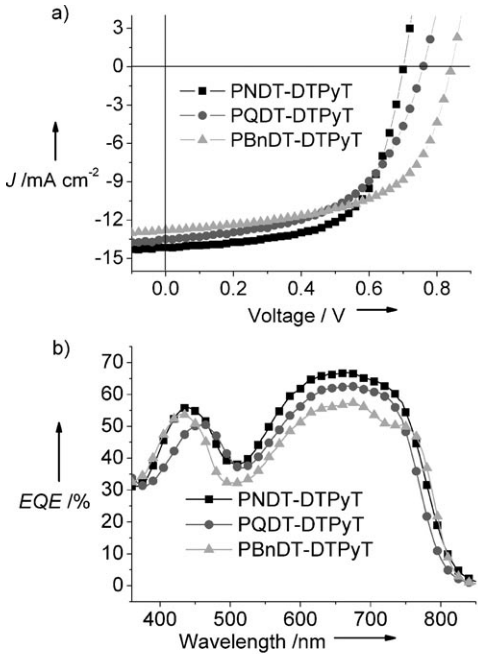

Figure 2. a) Current density–voltage (*J*–*V*) curves of polymer/PCBM-based solar cell devices under AM1.5G illumination (100 mW cm^{-2}). b) EQE curves of polymer/PCBM-based solar cell devices.

Table 2: Photovoltaic properties of PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT-based BHJ solar cells processed with polymer/PC$_{61}$BM (1:1, w/w) blend in dichlorobenzene.

Polymer	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE$_{max}$ (PCE$_{average}$) [%]
PNDT–DTPyT	85	14.16	0.71	61.7	6.20 (6.07)
PQDT–DTPyT	90	13.49	0.75	55.1	5.57 (5.32)
PBnDT–DTPyT	90	12.78	0.85	58.2	6.32 (6.11)

V_{oc} value than that of PNDT–DTPyT-based devices. Although PQDT–DTPyT-based devices generate smaller J_{sc} values than those of PNDT–DTPyT devices, presumably as a result of the slightly larger bandgap of PQDT–DTPyT, a PCE of 5.57 % was still achieved because the increased V_{oc} partially compensates for the decreased J_{sc} value. Interestingly, the J_{sc} of the PBnDT–DTPyT-based device is smaller than those of the other two polymer devices, despite PBnDT–DTPyT having the smallest bandgap. One possible reason is that PBnDT–DTPyT has the longest solubilizing chains among all three polymers studied. Therefore, the effective chromophore density in the solid state is the lowest in the case of PBnDT–DTPyT, as corroborated by its relatively low absorption coefficient. However, a noticeably high V_{oc} value of 0.85 V was obtained, which helps a respectable PCE of 6.32 % to be reached in PBnDT–DTPyT-based BHJ devices.

To further confirm the accuracy of the measurements, the external quantum efficiency (EQE) curves of the devices based on these three polymers were acquired and are shown in Figure 2b. All devices showed a very high incident photoconversion efficiency, with maxima around 670 nm. The calculated J_{sc} values obtained by integrating the EQE data with an AM1.5G reference spectrum match the experimental values within 5 % error. Further increase of the J_{sc} is still possible when PC$_{71}$BM is employed to replace PC$_{61}$BM, since PC$_{71}$BM[1a,10] shows significantly more absorption in the visible region than PC$_{61}$BM.

In summary, a soluble strong acceptor, DTPyT, which is stronger than the commonly used DTBT acceptors, has been synthesized and incorporated into a "weak donor–strong acceptor" copolymer strategy. Three new polymers (PNDT–DTPyT, PQDT–DTPyT, and PBnDT–DTPyT) showed noticeably reduced LUMO levels, slightly decreased HOMO levels, and thus smaller bandgaps than their DTBT counterparts. The smaller bandgap significantly improves the observed J_{sc} values of the related BHJ devices, while the low HOMO energy level maintains the high V_{oc} values. Therefore, all three polymers achieved high efficiency numbers in the BHJ devices, thus demonstrating the great utility of the DTPyT acceptor moiety in designing high-performance solar cell materials.

Experimental Section

Reagents and instrumentation: All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, Matrix Scientific) and used without further purification unless stated otherwise. Reagent-grade solvents were dried when necessary and purified by distillation. Microwave-assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument (at the University of Chicago) using 1,2,4-trichlorobenzene as the eluent (stabilized with 125 ppm butylhydroxytoluene) at 135 °C. The obtained molecular weight is relative to the polystyrene standard. ^{1}H and ^{13}C NMR measurements were recorded with either a Bruker Avance 300 MHz AMX or a Bruker 400 MHz DRX spectrometer. UV–visible absorption spectra were obtained by a Shimadzu UV-2401PC spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Cyclic voltammetry measurements were carried out using a Bioanalytical Systems (BAS) Epsilon potentiostat.

Polymer solar cell fabrication and testing: Glass substrates coated with patterned ITO were purchased from Thin Film Devices, Inc. The 150 nm sputtered ITO pattern had a resistivity (sheet resistance) of 15 $\Omega\,\square^{-1}$. Prior to use, the substrates were ultrasonicated for 20 min in acetone followed by deionized water and 2-propanol. The substrates were dried under a stream of nitrogen and subjected to UV–ozone treatment over 30 min. A filtered dispersion of PEDOT:PSS in water (Baytron PH500) was then spun-cast onto clean ITO substrates and baked at 140 °C for 15 min. A blend of polymer and PCBM was dissolved in chlorinated solvent with heating at 110 °C for 8 h. All the solutions were then spun-cast onto a PEDOT:PSS layer and dried at room temperature in a glove box under a nitrogen atmosphere for 12 h. Then a 40 nm film of calcium and a 70 nm aluminum film were thermally deposited at a pressure of about 1×10^{-6} mbar. There were eight devices per substrate, with an active area of 0.12 cm^2 per device. Device characterization was carried out under AM1.5G irradiation with an intensity of 100 mW cm^{-2} (Oriel 91160, 300 W) calibrated by a NREL-certified standard silicon cell. Current density versus voltage (*J*–*V*) curves were recorded with a Keithley 2400 digital source meter. EQEs were detected under monochromatic illumination (Oriel Cornerstone 260 $^1/_4$ m monochromator equipped with an Oriel 70613NS QTH lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. All fabrication steps, after adding the

PEDOT:PSS layer onto the ITO substrate, and characterizations were performed in glove boxes under a nitrogen atmosphere.

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