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ORIGINAL PAPER

Design and synthesis of carbonyl group modified conjugated polymers for photovoltaic application

Minmin Shi · Lei Fu · Xiaolian Hu · Lijian Zuo · Dan Deng · Jian Chen · Hongzheng Chen

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Abstract In this article, a simple and common electron-withdrawing moiety, carbonyl group, is applied in the molecular design of conjugated polymers for high-performance polymer solar cells (PSCs). Two series of donor–acceptor (D–A) copolymers are synthesized through alternating copolymerization of the electron-donating (D) benzodithiophene and dithienopyrrole with various electron-accepting (A) units containing carbonyl groups. The absorption range and the band gap of copolymers can be tuned by changing the molecular structure of A unit and the number of carbonyl groups. Moreover, by introducing the carbonyl group, the highest occupied molecular orbital energy level of the copolymer is lowered efficiently, leading to the improvement of the open-circuit voltage (V_{OC}) of PSCs. The best photovoltaic performance is obtained while poly(benzodithiophene-*alt*-thiophene-3-carboxylate) is functioned as the electron donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester as electron acceptor in a bulk heterojunction solar cell with a power conversion efficiency of 4.13%, a V_{OC} of 0.80 V, a short-circuit current of 8.19 mA/cm^2, and a fill factor of 63.2%.

Keywords Carbonyl group · Conjugated polymer · Polymer solar cells

Introduction

Solar energy is considered as one of the most important ways to solve global energy crisis as a renewable resource. Polymer solar cells (PSCs) are a promising alternative for producing clean and renewable energy due to their unique

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M. Shi · L. Fu · X. Hu · L. Zuo · D. Deng · J. Chen · H. Chen (✉)
MOE Key Laboratory of Macromolecule Synthesis and Functionalization, State Key Lab of Silicon Materials & Department of Polymer Science and Engineering, Zhejiang University,
Hangzhou 310027, People's Republic of China
e-mail: hzchen@zju.edu.cn

advantages, such as low-cost, simple manufacturing process, light weight, and the capability to fabricate flexible large-area devices [1–7]. So far, the most successful PSCs are bulk heterojunction devices, where a mixture of conjugated polymer (electron donor) and fullerene (electron acceptor) is used as the photoactive layer. With many efforts over the past decade to create numerous novel conjugated polymers and better control of the nanoscale morphology of the photoactive layer, PSCs have achieved a power conversion efficiency (PCE) over 7% [8–10].

Since, the wavelength of the maximum photon flux density of the solar spectrum is located at ~700 nm, to fully exploit the endless source of solar energy, the absorption spectrum of a conjugated polymer needs to cover both the visible and the near-infrared ranges to match the greater part of the solar spectrum and hence harvest efficiently solar irradiance [7, 11]. It is highly desirable to develop new conjugated polymers with broader absorptions through narrowing their optical band gap (E_g). The most widely accepted strategy to design a low band gap conjugated polymer is to incorporate alternatingly electron-donating (D) and electron-accepting (A) segments in the polymer backbone (D–A copolymers). In recent years, several D–A copolymers have showed the promising for photovoltaic applications. For instance, electron-deficient units derived from 3,6-diaryl-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione [11] and thieno[3,4-b]-thiophene-2-carboxylate moieties [12], when conjugated with various electron-donating units, such as fluorene, carbazole, dithienosilole, and benzodithiophene (BDT), have demonstrated distinguished PCEs after systematic optimization. On the other hand, because the open-circuit voltage (V_{OC}) of PSCs is mainly determined by the difference between the highest occupied molecular orbital (HOMO) of the donor (polymer) and the lowest unoccupied molecular orbital (LUMO) of the acceptor (fullerene), it is expected that better photovoltaic performance can be obtained if the HOMO energy level of the donor is low enough while the light harvesting ability of the donor is good. The HOMO energy level of polymers can be significantly lowered by reducing the effective conjugation length to inhibit the delocalization of π-electrons in the polymer main chain. But this method often results in a wider band gap and poor charge transport properties. Another attractive method to lower the HOMO energy level of polymers is the adoption of electron-withdrawing substituents [13]. In this way, Hou and co-workers developed a series of low band gap copolymers (PBDTTTs) alternating BDT and thieno[3,4-b]thiophene (TT) units. When the electron-withdrawing functional groups, such as ester group, ketone group, and fluorine atom, were introduced into the TT unit, the HOMOs of PBDTTTs could drop obviously and hence the V_{OC} of the PSC was successfully improved to 0.76 V [10, 14].

The carbonyl group is a simple and common electron-withdrawing substituent, therefore, it is also applied in the molecular design of conjugated polymers for high-performance PSCs in our group. The carbonyl group is selected due to its following advantages: (1) acylation on conjugated rings is simple; (2) carbonyl group can be easily modified to improve the solubility of polymers; (3) carbonyl group can efficiently lower the HOMO of polymers while maintaining or reducing E_g; and (4) carbonyl group is a weak electron-withdrawing substituent, thereby, assuring the electron donor characteristic of polymers. In this article, we present our study on how to tune the absorption range and the HOMO level of the resulting copolymers with carbonyl group, aiming at the improvement of the PCE of PSCs.

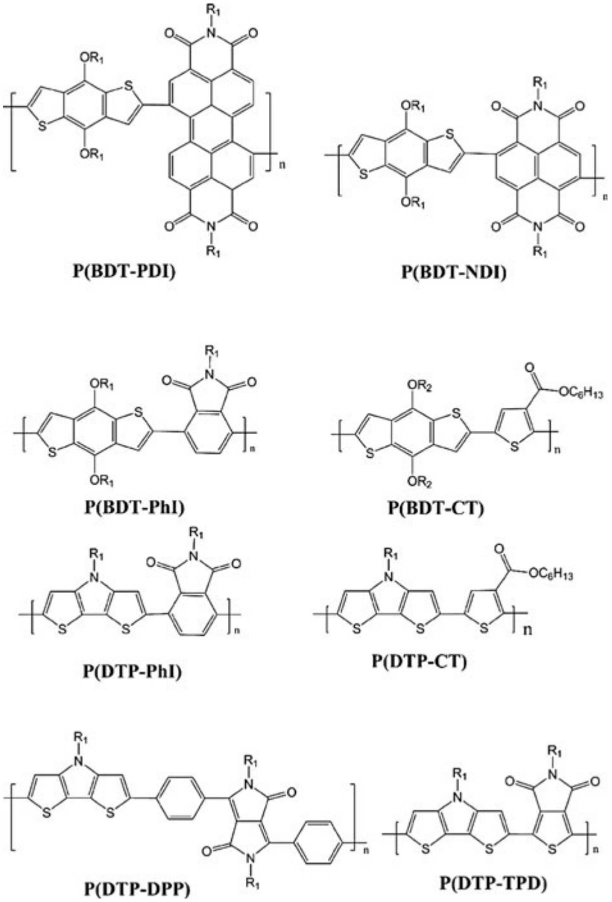
BDT-based D–A copolymers

BDT has become a "star" electron-donating (D) unit for good D–A copolymers used in PSCs due to its good planarity, high stability, and good solubility [14–16]. We also synthesize some novel copolymers based on BDT and different electron-deficient units containing carbonyl groups for photovoltaic application.

The arylene imide units have a well-conjugated structure containing double carbonyl groups, which leads to strong intermolecular π–π actions while the electron-deficient lactam parts provide an electron-withdrawing effect. Moreover, the arylene imides units are attractive candidates as electron-accepting moieties of low band gap D–A copolymers by virtue of their extremely facile synthesis and readily varied substitution at the nitrogen, allowing easy manipulation of polymer solubility, packing, and the resulting film morphology. So, three novel copolymers, P(BDT-PDI), P(BDT-NDI), and P(BDT-PhI), were synthesized by alternating copolymerization of the electron-donating BDT and three different electron-accepting monomers of perylene diimide (PDI), naphthalene diimide (NDI), and phthalimide (PhI), respectively [17]. Their chemical structures are presented in Scheme 1.

The photophysical characteristics of the copolymers were investigated by UV–Vis absorption spectroscopy in dilute chloroform solutions and spin-coated films on quartz substrates. It can be seen from Fig. 1 that both P(BDT-PDI) and P(BDT-NDI) show broader and more red-shifted absorption bands than P(BDT-PhI). This phenomenon can be attributed to the larger electron affinity and bigger π-extended systems of PDI and NDI than those of PhI [18]. Therefore, P(BDT-PDI) and P(BDT-NDI) own stronger D–A interactions with more delocalized π-electrons along the polymer backbones, thus, the narrowed E_g. From the absorption band-edge of the copolymer films, the optical band gaps (E_g^{opt}) are calculated as 1.74, 1.63, and 2.15 eV for P(BDT-PDI), P(BDT-NDI), and P(BDT-PhI), respectively.

Figure 2 shows the cyclic voltammograms (CV) of P(BDT-PDI), P(BDT-NDI), and P(BDT-PhI). The electrochemical data are calculated in Table 1. For P(BDT-PDI) and P(BDT-NDI), there are quasi-reversible reduction and oxidation peaks only at the negative potential range, suggesting that these two copolymers are typical n-type materials, mainly because of the strong electron-withdrawing ability of PDI and NDI units with four carbonyl groups. On the contrary, P(BDT-PhI) shows quasi-reversible reduction and oxidation peaks only at the positive potential range, suggesting that it is an intrinsic p-type semiconductor due to the weak electron-withdrawing ability of PhI. The LUMO energy levels of P(BDT-PDI) and P(BDT-NDI) (−4.18 and −3.99 eV) are close to that of the commonly used fullerene derivative, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) (−4.0 eV), suggesting that they can be used as electron acceptor in PSCs. And the HOMO energy level of P(BDT-PhI) is −5.51 eV, 0.4 eV lower lying than that of the most important polymer electron donor, poly(3-hexylthiophene) (P3HT), indicating that a larger V_{OC} can be obtained while applied in PSCs. However, the band gap of P(BDT-PhI) is too large to harvest solar irradiance sufficiently.



Scheme 1 The molecular structures of conjugated polymers. R_1 stands for 2-ethylhexyl, R_2 stands for *n*-octyl

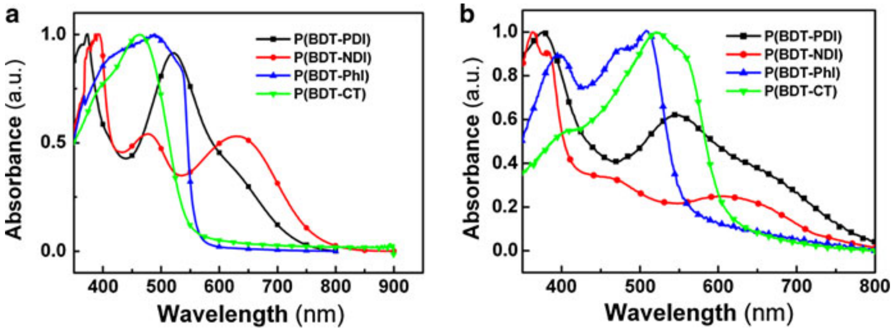


Fig. 1 Normalized UV–Vis absorption spectra of P(BDT-PDI), P(BDT-NDI), P(BDT-PhI), and P(BDT-CT) in $CHCl_3$ solutions (**a**) and in thin films (**b**)

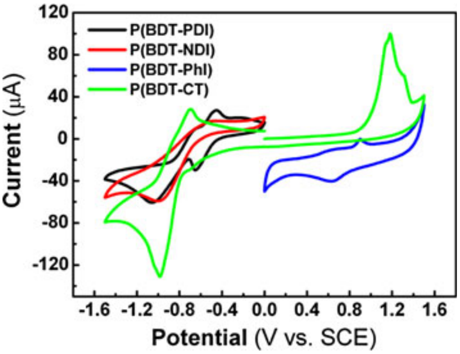


Fig. 2 CV traces of P(BDT-PDI), P(BDT-NDI), P(BDT-PhI), and P(BDT-CT)

Delocalization of the flowing π-electrons along the conjugated chain converts double bonds into single bonds and synchronously transforms single bonds into double bonds, leading to a resonance structure as the quinoid form [19]. In general, thiophene ring owns lower aromaticity than benzene, which causes that thiophene-based copolymers is even more likely to adopt a quinoid form. To decrease the band gap of BDT-based copolymers while maintaining their *p*-type characteristic and low HOMO energy level, thiophene-3-carboxylate (CT) [20] was used as the electron-accepting unit to copolymerize with BDT moiety, thus, the copolymer of poly(benzodithiophene-*alt*-thiophene-3-carboxylate) [P(BDT-CT)] is obtained [21], whose structure is shown in Scheme 1.

As predicted, the band gap of P(BDT-CT) (1.98 eV) becomes narrower than that of P(BDT-PhI) although CT owns only a carbonyl group. It is also observed that the absorptions of P(BDT-CT) in film show significant red-shift while compared to that in solution, implying that the planarity of P(BDT-CT) is excellent because of the quinoid structures in the polymer main chains, providing strong π–π stacking in the solid state (Fig. 1). From its CV curve (Fig. 2), it is found that P(BDT-CT) also exhibits a relatively deep HOMO energy level (−5.36 eV), due to the introduction of ester group onto polymer side chain, which is in accordance with the results reported by Hou et al. [14].

To explore the potentials of BDT-based copolymers in photovoltaics, bulk heterojunction PSCs are fabricated by blending the *n*-type materials of P(BDT-PDI) and P(BDT-NDI) with P3HT, and the *p*-type materials of P(BDT-PhI) and P(BDT-CT) with PCBM. Figure 3 shows *I*–*V* characteristics of the devices under the illumination of AM 1.5 simulated solar light. From Fig. 3, their corresponding V_{OC}, short-circuit current (I_{SC}), fill factor (FF), and PCE are obtained and summarized in Table 1. It is found that the all-polymer devices based on P(BDT-PDI) and P(BDT-NDI) show bad photovoltaic performances (PCEs are both less than 0.005%). It is notable that the I_{SC} of this kind of device is much weaker than that of the device based on the blend of P3HT and PCBM, indicating that the mobility of P(BDT-PDI) and P(BDT-NDI) can not be comparable to that of PCBM, or bad phase separation forms in the blended films. For the *p*-type materials, it is found that PCE of the device based on P(BDT-PhI) was 0.53%, with a V_{OC} of 0.93 V, an I_{SC} of 1.35 mA/cm^2, and a FF of 0.42. It is noted that the V_{OC} of the device is one of the

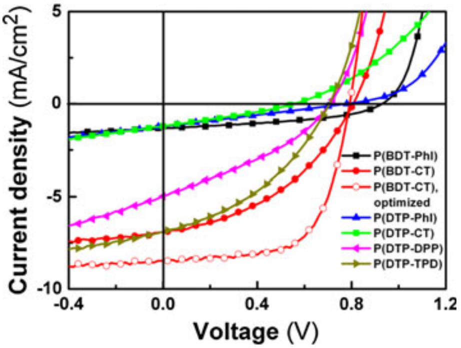


Fig. 3 *I*–*V* curves of the photovoltaic devices made from the blends of copolymers and PCBM

Table 1 Optical and electrochemical properties of the copolymers, and the photovoltaic parameters of the corresponding PSCs

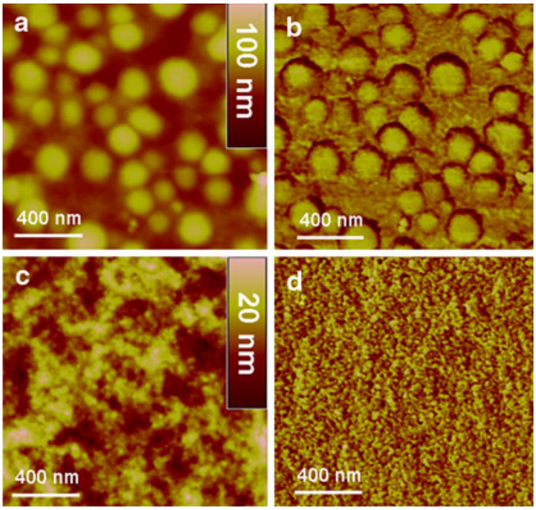
Polymer	E_{ox} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{opt} (eV)	V_{OC} (V)	I_{SC} (mA/cm^2)	PCE
P(BDT-PDI)	–	−0.55	−5.92	−4.18	1.74	0.62	0.014	0.002
P(BDT-NDI)	–	−0.75	−5.62	−3.99	1.63	0.70	0.024	0.004
P(BDT-PhI)	0.77	–	−5.51	−3.36	2.15	0.93	1.35	0.53
P(BDT-CT)	0.96	−1.02	−5.36	−3.38	1.98	0.80	6.94	2.32
						0.80[a]	8.19[a]	4.13[a]
P(DTP-PhI)	0.98	−0.98	−5.38	−3.42	1.96	0.78	1.22	0.25
P(DTP-DPP)	0.87	−0.78	−5.27	−3.62	1.65	0.70	5.02	1.22
P(DTP-CT)	0.70	−0.99	−5.10	−3.41	1.69	0.56	1.21	0.19
P(DTP-TPD)	0.69	−0.98	−5.09	−3.42	1.67	0.70	6.97	1.90

[a] The active layer's morphology is optimized by the addictive

largest values among all reported PSCs due to the deep HOMO energy level of P(BDT-PhI). However, the final PCE is limited by the poor I_{SC} which probably originates from its large band gap (2.15 eV). With the narrowed band gap and better planarity of polymer conformation, the P(BDT-CT)-based device exhibits a much bigger I_{SC} of 6.94 mA/cm^2, and a relatively higher PCE of 2.32%. Moreover, It is impressive that the V_{OC} of PSCs made from P(BDT-CT) (0.80 V) is obviously larger than that of the PSCs made from P3HT (0.52 V), owing to its lower HOMO energy level [21]. The PCE of PSC made from P(BDT-CT):PCBM blend has been elevated to 4.13%, with a V_{OC} of 0.80 V, an I_{SC} of 8.19 mA/cm^2, and a FF of 0.63 by optimization of the active layer's morphology recently.

Figure 4 shows the morphology of P(BDT-CT):PCBM blended film with a weight ratio of 1:1. It can be easily judged that the darker phase represents the polymer while the brighter for PCBM. From Fig. 4, it is found that, with 3 wt% addictive of naphthalene chloride, a much finer phase separation structure forms, with domain sizes of 10–20 nm (It is close to exciton diffusion length), so that excitons can be separated effectively to enhance I_{SC}. Furthermore, a bicontinuous

Fig. 4 Height (**a**, **c**) and phase (**b**, **d**) images of P(BDT-CT):PCBM (1:1, by wt.) blended films spin-coated from toluene (**a**, **b**) and toluene containing 3 wt% naphthalene chloride (**c**, **d**), respectively



structure is also observed, which is favorable for efficient charge transport and high FF, hence, the photovoltaic performance improves significantly.

Dithieno[3,2-b:2′,3′-d]pyrrole (DTP)-based D–A copolymers

Considering the band gap of donor polymers based on benzodithiphene is still too large for PSC application, another unit with higher electron-donating ability is needed to replace BDT to obtain low band gap polymers. DTP has good molecular planarity and strong electron-donating ability of nitrogen atoms, which can lead to the development of a low band gap polymer when it is used as electron-donating unit [22, 23]. On the other hand, diketopyrrolopyrrole (DPP) unit has a well-conjugated structure, which leads to strong π–π interaction, and its two fused electron-deficient lactam parts provide a strong electron-withdrawing effect, leading to a high electron affinity for DPP unit [24].

Thus, DTP was chosen to copolymerize with three electron-deficient units containing carbonyl groups, PhI, CT, and DPP. Three conjugated polymers P(DTP-PhI), P(DTP-DPP), and P(DTP-CT) were synthesized [25] (see Scheme 1). From the absorption spectra (Fig. 5), it is observed that all DTP-based polymers exhibit broader absorption bands than BDT-based polymers because of stronger electron-donating ability of DTP unit. Among the three polymers, P(DTP-DPP) possesses the lowest band gap (1.65 eV).

As shown in CV curves (Fig. 6), DTP-based polymers exhibit quasi-reversible oxidation/reduction processes, indicating that three polymers are potentially good semiconductive materials. It is found that HOMO energy levels of P(DTP-PhI) and P(DTP-CT) (−5.38 and −5.10 eV) are both higher than those of the corresponding BDT-based copolymers P(BDT-PhI) and P(BDT-CT), which is due to the stronger electron-donating ability of DTP unit, too. Interestingly, it is found that P(DTP-DPP) also possesses relatively low HOMO energy level (−5.27 eV) although it

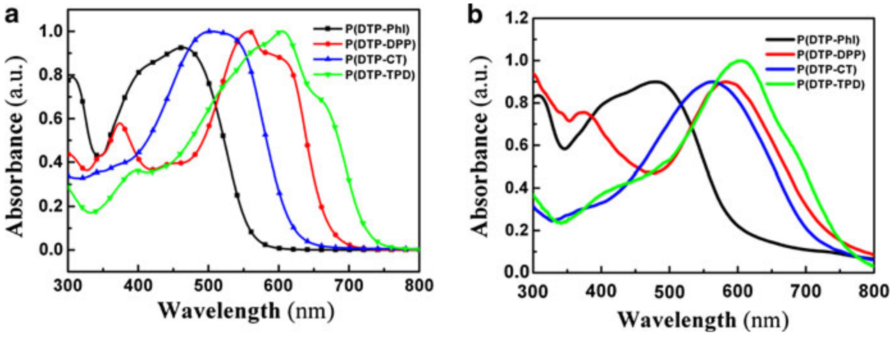
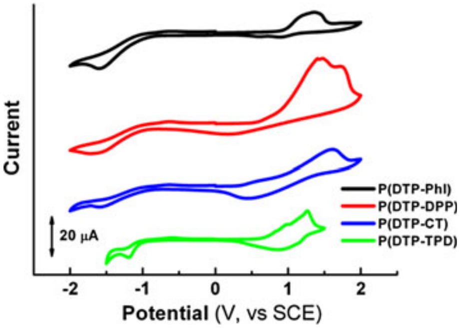


Fig. 5 Normalized UV–Vis absorption spectra of P(DTP-PhI), P(DTP-DPP), P(DTP-CT), and P(DTP-TPD) in $CHCl_3$ solutions (**a**) and in thin films (**b**)

Fig. 6 CV traces of P(DTP-PhI), P(DTP-DPP), P(DTP-CT), and P(DTP-TPD)



owns the lowest band gap among the three polymers. This phenomenon may be ascribed to phenyl rings in the main chain of P(DTP-DPP), which results in the disruption of quinoid state to some extent, and holds back excessive narrowing of band gap and unfavorable elevating of HOMO level [25]. This hypothesis is proved by density functional theory (DFT) calculations of P(DTP-DPP)'s frontier orbits (Fig. 7).

Since, the electron-withdrawing ability of CT is not enough to achieve a low band gap due to only one carbonyl group, thieno[3,4-c]pyrrole-4,6-dione (TPD) was applied as the electron-accepting unit to copolymerize with DTP [26]. The electron-deficient TPD moiety exhibits a symmetric, rigidly fused, coplanar structure, and strong electron-withdrawing properties due to the imide group and it maintains a symmetrical structure after the attachment of a solubilizing side chain, which make it a potential system for increasing intramolecular and intermolecular D–A interactions, reducing optical band gaps, and lowering HOMO energy levels when incorporated into polymeric backbones [27–29].

Both P(DTP-TPD) solution and film have broad and intense absorption covering the whole visible region, which is the broadest absorption among these two series of *p*-type copolymers. This phenomenon indicates that polymers based on TPD can efficiently decrease bond-length alternation between donor units and acceptor units. Furthermore, TPD's geometry should present decreased steric repulsion to

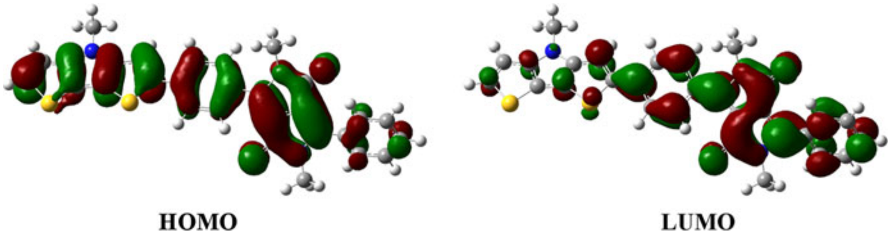


Fig. 7 HOMO and LUMO of P(DTP-DPP) obtained by DFT calculations

neighboring backbone units, and potentially attractive sulfur–oxygen interactions can assist backbone planarization [30]. TPD-based D–A copolymers should, therefore, have smaller band gaps than the corresponding PhI-based copolymer P(DTP-PhI).

Their photovoltaic properties are obtained and summarized in Table 1. Photovoltaic study of solar cells based on the blends of polymers and PCBM demonstrated that P(DTP-DPP) shows better performance than P(BDT-PhI) and P(BDT-CT): a PCE of 1.22%, with a high V_{OC} of 0.70 V and a large I_{SC} of 5.02 mA/cm^2, is achieved. This phenomenon can be attributed mainly to the more appropriate energy levels of P(DTP-DPP) (both the low band gap and the enough low HOMO energy level). Among four devices, the bulk heterojunction PSC based on P(DTP-TPD):PCBM blend exhibits the best PCE of 1.9%, with V_{OC} of 0.70 V, I_{SC} of 6.97 mA/cm^2, and FF of 39%. It's impressive that the I_{SC} of the P(DTP-TPD)-based device is obviously larger than those of the PSCs made from other DTP-based polymers in this series, because the closer intermolecular π–π interactions of P(DTP-TPD) is in favor of efficient charge transport.

Conclusions

Several kinds of electron-accepting units containing carbonyl group (PhI, CT, DPP, TPD, etc.) were used to copolymerize with electron-donating units (BDT and DTP), to obtain low band gap polymers with low-lying HOMO energy level for photovoltaic application. We can tune the band gap and the electron-withdrawing ability of copolymers by the modification of the molecular structure of A units and the number of carbonyl groups. Among all polymers, P(BDT-CT), P(DTP-DPP), and P(DTP-TPD) show promising photovoltaic performances. The best performance of the PSC device was obtained by using P(BDT-CT) as the electron donor, and a PCE of 4.13% with a V_{OC} of 0.80 V, an I_{SC} of 8.19 mA/cm^2, and a FF of 63.2% was achieved. Despite the enhanced V_{OC} had been achieved by most of the copolymers containing carbonyl group, the device performance is still limited by the low I_{SC}, which probably comes from the low carrier mobility and unoptimized morphology. The further study should focus on the molecular engineering for more planar polymer structure with a high hole mobility.

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