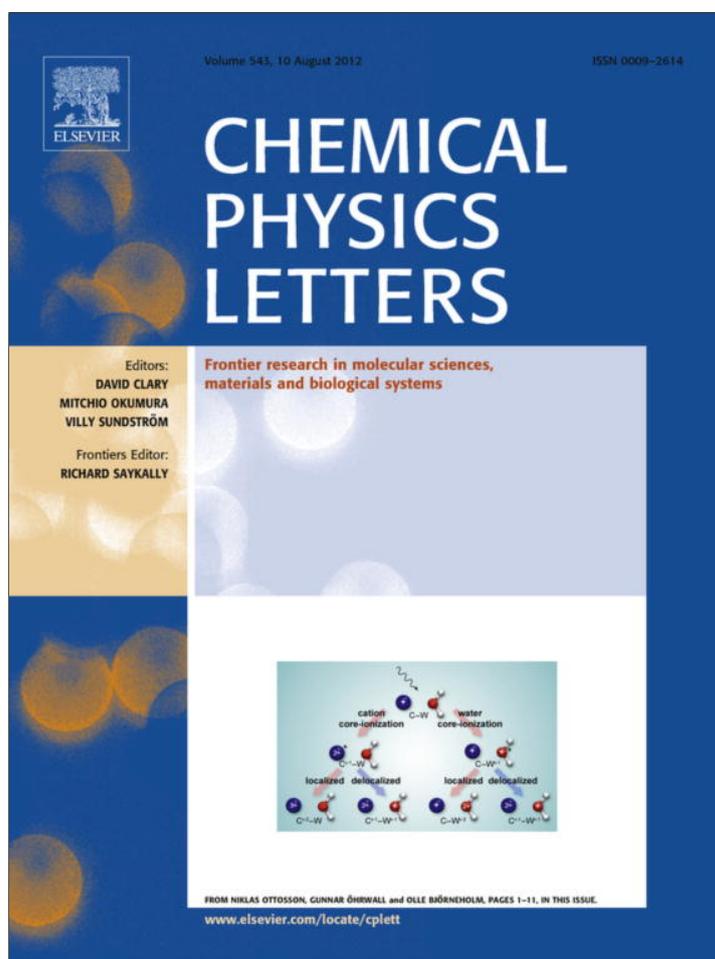


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Rational design of novel A-A-D-A-A type electron donors for small molecule organic solar cells

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ABSTRACT

We theoretically designed four new A-A-D-A-A type electron donors by side-by-side combination of strong electron-withdrawing groups. The electronic structures and optical absorption spectra of donors were calculated using density functional theory (DFT) and time-dependent DFT (TDDFT) at the 6-31G* level, respectively. The results show that the calculations are in good agreement with the experiments on electronic structures and optical spectra. The designed molecules exhibit good properties with low band gap, low LUMO energy level, and broad light absorption. Moreover, the estimated solar cell efficiency is up to ~10% when these donors are used in combination with PCBM as an acceptor.

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1. Introduction

Solution-processed organic photovoltaic (OPV) [1–6] cells have attracted increasing interest in the past decade as a potential renewable energy source [7–9]. Compared to traditional photovoltaic cells, the OPV cell has many outstanding advantages, such as low-cost, flexible, lightweight materials and large-area fabrication [4]. The performance of OPV cell was increased dramatically in the past few years, for example, the power conversion efficiency (PCE) of ~9% was achieved by using low band gap polymer in the bulk heterojunction (BHJ) structure solar cells [5]. Meanwhile, organic solar cells with small molecules as electron donors also received great attention [10–14] for the advantages of well-defined molecular structures, easier purification, and better batch-to-batch reproducibility, when compared to polymer solar cells. To date, small molecule organic solar cells (SMOSCs) based on p-type small molecules and n-type fullerene derivatives were realized with PCEs as high as 6% [13].

One key to improve the performance of SMOSCs is to find small molecules with lower band gap, which can be achieved with molecules having A-A-D-A-A structure. Here, 'A' is the electron-withdrawing group, and 'D' is the electron-donating group. The presence of two adjacent strong electron-withdrawing groups ('A') in each side of 'D' group in this kind of molecule leads to lower band gap. Recently, Lin et al. [15] synthesized and characterized two new A-A-D-A-A type small molecules (BCNDTS and BDCDTS) as electron donors (Figure 1a) in SMOSCs. The combination of

two strong electron-withdrawing groups leads to much lower band gap molecules. In their results, the BDCDTS has a lower band gap than BCNDTS, but the BDCDTS/C₆₀ (C₆₀, fullerene) cell shows lower PCE (0.07%) than the BCNDTS/C₆₀ cell (2.3%) [15]. The possible reason is that BDCDTS has higher electron affinity (−3.92 eV) than that of fullerenes (−3.70 eV), this makes BDCDTS not suitable for paring up with fullerene. In the search for better small molecules for SMOSCs, it is important to get better parameters, and matching energy with the acceptors. Theoretical investigation in this regards involves designing new molecules with different functional groups, calculating the relevant parameters, and finding the best matches. This can provide a guide for further experimental studies.

Generally, the LUMO energy level of the donor is located above that of the acceptor by at least 0.3 eV to ensure efficient electron transfer from the donor to the acceptor [6,16–18]. The maximum short-circuit current (J_{sc}) is mostly determined by the band gaps of the two molecules, and open-circuit voltages (V_{oc}) is proportional to the difference between the HOMO (HOMO, the highest occupied molecular orbital) energy level of the donor and the LUMO energy level of the acceptor [4]. For example, the LUMO energy level of an ideal donor should be between −3.7 and −4.0 eV for the acceptor of PCBM (PCBM, [6,6]-phenyl-C61-butynic acid methyl ester, $E_{LUMO} = -4.3$ eV) which has been widely used as a standard and efficient acceptor material in organic solar cells [4,18,19]. Meanwhile, in order to maximally harvest the solar spectrum, the optimal band gaps of donors should be in the range of 1.2 and 1.9 eV [18,20]. Correspondingly, the HOMO energy levels of donors are in the range of −5.2 to −5.7 eV [21].

In this Letter, as the first step toward the optimal donors (assuming the PCBM is acceptor), we considered eight electron-withdrawing blocks as the potential substitutes for the corresponding block in BDCDTS in which the central dithienosilole

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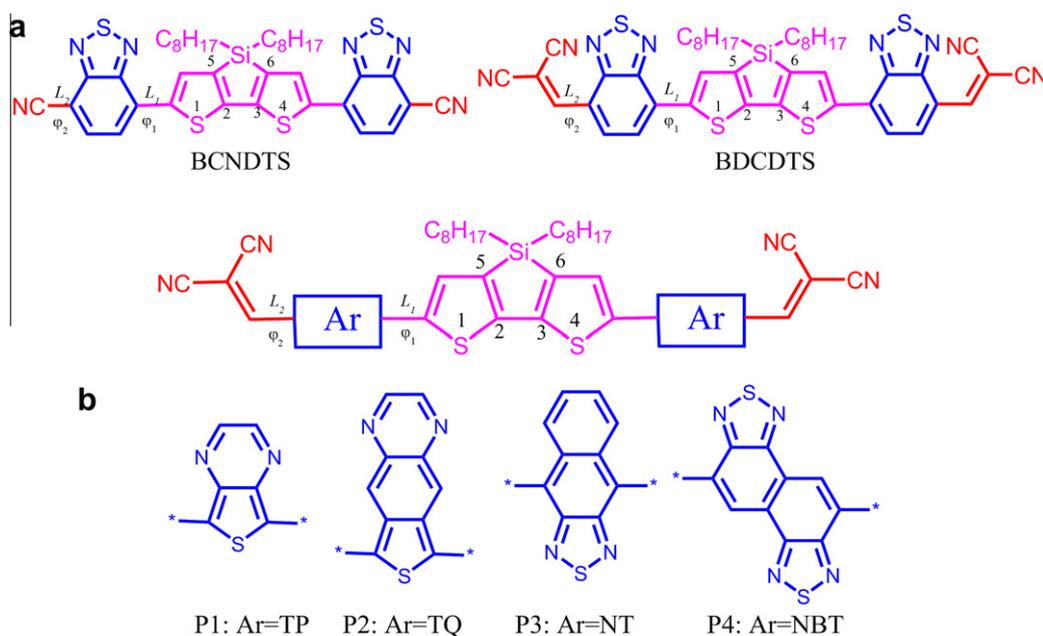


Figure 1. (a) Sketches of BCNDTS and BDCDTS, (b) calculated model and newly designed donors of P1–P4.

(DTS) core is electron-donating group. Based on the calculated results of blocks, we chose four novel blocks and designed four new donors (denoted as P1–P4 hereafter) by replacing the 2,1,3-benzothiadiazole (BT) block in BDCDTS with the thieno[3,4-*b*]pyrazine (TP) [22] (P1), thieno[3,4-*g*]quinoxaline (TQ) [18,23] (P2), naphtho[2,3-*c*][1,2,5]thiadiazole (NT) [20] (P3), and naphtho[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (NBT) [24,25] (P4), respectively, and theoretically investigated electronic structures and optical properties by (TD) DFT. The results show that compared to BDCDTS, the newly designed molecules of P1–P4 have better frontier orbital energy levels and broader optical absorption spectra. When those donors are used in combination with PCBM as an acceptor, the solar cell efficiency is estimated to be up to ~10%.

2. Computational methods

The geometric and electronic structures of these small molecules were studied by DFT, and the optical absorption spectra were calculated using TDDFT [26–29]. All the calculations were carried out in the Gaussian 03 package [30]. The DFT method was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP) [31–33]. All calculations were performed without any symmetry constraints using polarized split-valence 6-31G* basis set. All calculations were carried out in the gas phase.

3. Results and discussions

To evaluate the reliability of computational method used in the molecular system, we first calculated the HOMO and LUMO energy levels of BCNDTS and BDCDTS using B3LYP/6-31G*. B3LYP is by far the most popular density functional in chemistry, representing 80% of the total of occurrences of density functionals in the literatures in the period 1990 to 2006 [34]. The method of B3LYP/6-31G* has been also widely used as a precise formalism for calculating the structural and optical properties of many molecular systems [18]. Table 1 shows the calculated HOMO energy levels (–5.54, –5.74 eV for BCNDTS and BDCDTS) and band gaps (2.17, 1.88 eV

Table 1

Theoretical and experimental FMO energy levels of BCNDTS and BDCDTS.

Compounds	Theoretical value			Experimental data ^a		
	LUMO eV	HOMO eV	E_g eV	LUMO eV	HOMO eV	E_g eV
BCNDTS	–3.37	–5.54	2.17	–3.23	–5.40	2.17
BDCDTS	–3.86	–5.74	1.88	–3.92	–5.80	1.88

^a Experimental thin film E_g (ΔE_{film}) are from Table 1 of reference [15].

for BCNDTS and BDCDTS). The predictions are in good agreement with those available experimental HOMO energy levels (–5.40, –5.80 eV [15] for BCNDTS and BDCDTS) and band gaps (2.17, 1.88 eV [15] for BCNDTS and BDCDTS), respectively. This comparison shows DFT/B3LYP/6-31G* is a reliable formalism for predicting the electronic properties of such type of molecules. Therefore, we conducted the following calculations and discussions with the same method.

According to above experiments and calculations, the LUMO energy level of –3.92 eV for BDCDTS is in the optimal range of –3.7 to –4.0 eV, whereas the band gap of 1.88 eV is close to the upper limit of 1.9 eV. In order to search for the stronger electron-withdrawing blocks for BDCDTS, we considered eight functional groups, as shown in Figure 2. The calculated LUMO energy levels (E_{LUMO} : –2.44, –3.28, –1.92, –2.38, –2.26, –2.51, –2.72, –2.85 and –2.35 eV for benzo[*c*][1,2,5]oxadiazole (BO) [6], [1,2,5]thiadiazolo[3,4-*d*]pyridazine (TDP) [35], quinoxaline (Qx) [36], pyrido[3,4-*b*]pyrazine (PP) [37], TP, TQ, NT, NBT and BT) are from the B3LYP eigenvalues, the band gaps (E_g : 4.42, 3.71, 4.77, 4.61, 3.98, 2.84, 2.97, 3.60 and 4.26 eV for BO, TDP, Qx, PP, TP, TQ, NT, NBT and BT) are the differences of energy level of HOMOs and LUMOs ($E_g = E_{LUMO} - E_{HOMO}$). Although TDP has a lower band gap (3.71 eV) than BT (4.26 eV), the LUMO energy level of TDP (–3.28 eV) is much deeper than BT (–2.35 eV). The band gaps of BO (4.42 eV), Qx (4.77 eV) and PP (4.61 eV) are all larger than that of BT (4.26 eV). Therefore, we chose other four groups of TP, TQ, NT and NBT, which all gave appropriate LUMO energy levels and band gaps as compared with BT, as the candidates to replace BT, and designed four small new molecules (P1–P4).

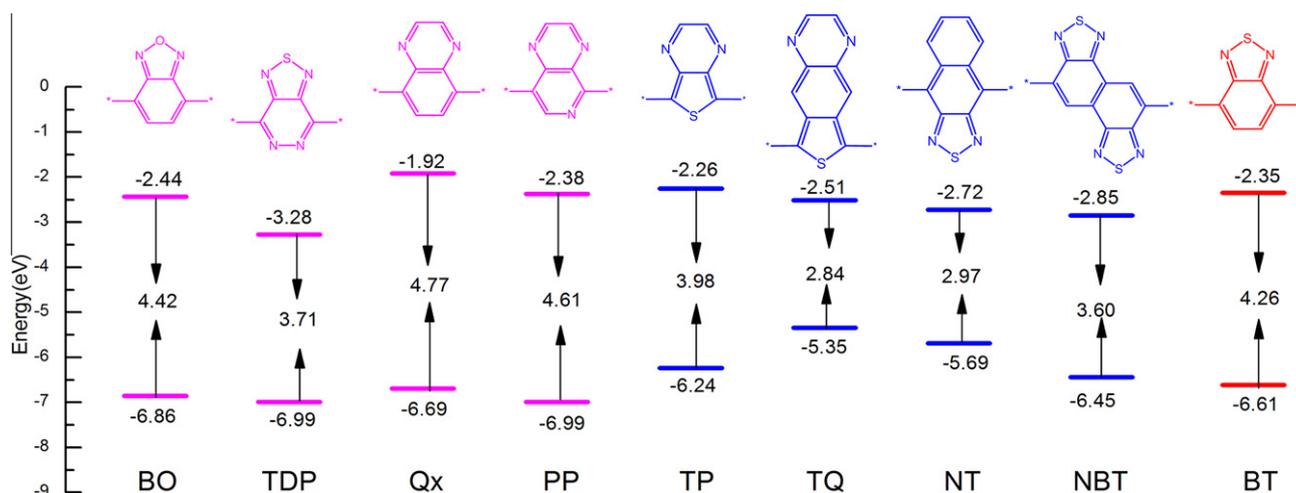


Figure 2. The block structures and calculated FMO diagrams for separate unit candidates of electron-withdrawing blocks and BT.

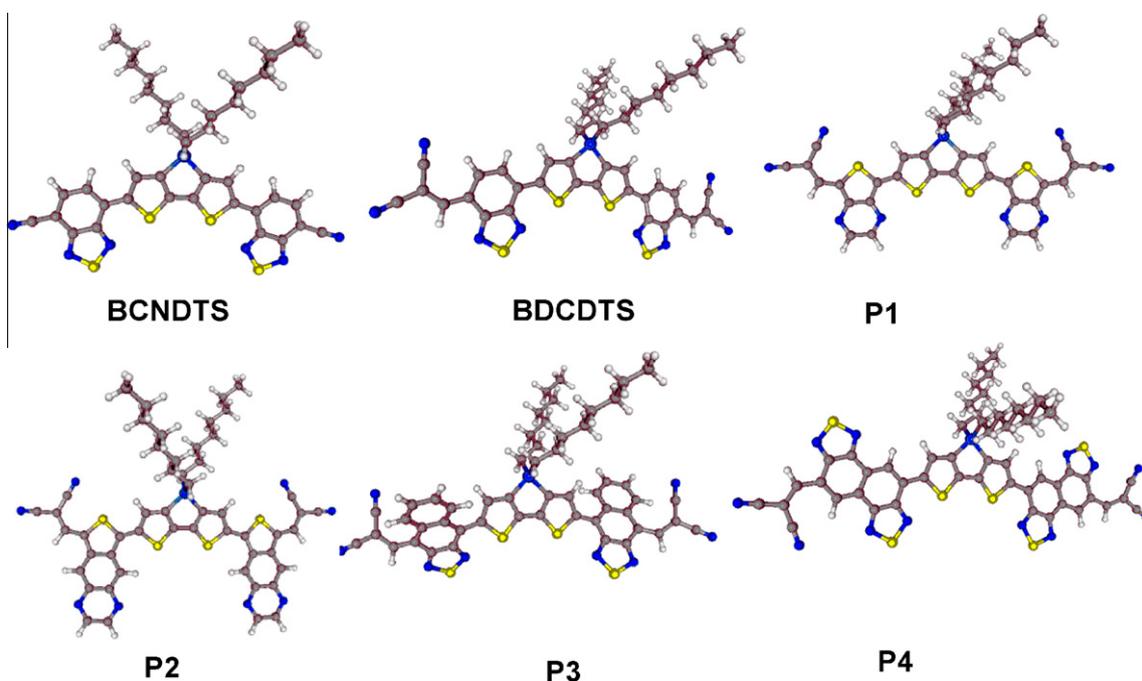


Figure 3. The optimized geometries of BCNDTS, BDCDTS and P1–P4. Color code: yellow (S), blue (N), green (Si), black (C) and grey (H). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The calculated structures of BCNDTS, BDCDTS and P1–P4 are shown in Figure 1a and b. Figure 1b also shows calculated model and newly designed donors of P1–P4. The optimized geometries of BCNDTS, BDCDTS, and P1–P4 are shown in Figure 3. The calculated bond lengths (L), bond angles and dihedral angles (φ) are listed in Table 2. In Table 2, the bond lengths of C–C for P1–P4 are all within 1.41–1.45 Å, which are shorter by ~ 0.1 Å than that of ethane (1.54 Å). This is partly caused by the π -bonding interaction and results in partial double-bond character on the bridge bond, thereby strengthening and shortening the bridge bond. The results demonstrate that the π -electrons are delocalized over the entire molecular framework rather than partially distributed on the donor or acceptor unit. The bridge bond (L_1 and L_2) lengths of BCNDTS, BDCDTS, P3 and P4 are approximately equal to each other. This may be due to the fact that both the NT and NBT units contain BT unit and lead to the same effect on the bridge band. Similarly,

the bridge bond lengths of P1 and P2 have no obvious differences. The dihedral angles (φ) in BCNDTS, BDCDTS, P1 and P4 are all close to zero, which suggests that those molecules have good coplanar configurations. For P2 and P3, there is a slight twist between the central dithienosilole (DTS) core [15] (the donor unit) and electron-withdrawing groups (19.06° in P2 and 35.82° in P3). In addition, the parameters of the central DTS cores have no significant difference for all these molecules, for example, the S(1)–C(2)–C(3) values of BCNDTS, BDCDTS, P1, P2, P3 and P4 are 90.6, 90.4, 90.2, 90.3, 90.5 and 90.5 degree, respectively, also the C(2)–C(3) values of the all molecules are equal to 1.44 Å, which means the presence of electron-withdrawing groups has no effect on the configurations of the central DTS cores.

For a certain molecule, the frontier molecular orbitals (FMOs) and E_g are directly related to the electronic and optical properties. Figure 4 shows the FMOs energy diagrams of P1–P4 and PCBM.

Table 2
Calculated bond lengths (L), bond angles and dihedral angles (φ) of BCNTDS, BDCDTS and P1–P4.

Donors	Interring distance (Å)			Dihedral angle (°)		Bond angles (°)		
	L_1	L_2	C(2)–C(3)	φ_1	φ_2	S(1)–C(2)–C(3)	C(2)–C(3)–S(4)	C(5)–Si–C(6)
BCNTDS	1.45	1.44	1.44	1.47	0.01	90.6	130.3	130.3
BDCDTS	1.45	1.44	1.44	0.16	0.02	90.4	130.2	130.3
P1	1.42	1.41	1.44	0.24	0.01	90.2	130.2	130.6
P2	1.43	1.41	1.44	19.06	1.48	90.3	130.4	130.5
P3	1.45	1.44	1.44	35.82	31.01	90.5	130.4	130.3
P4	1.45	1.44	1.44	0.10	0.12	90.5	130.3	130.3

Both of the HOMO energy levels (-5.56 , -5.44 , -5.54 , -5.63 eV for P1–P4) and the LUMO energy levels (-3.92 , -3.94 , -3.86 , -3.84 eV, for P1–P4) are from the B3LYP eigenvalues. The HOMO and LUMO energy levels of PCBM are from reference [19]. Figure 4 also shows the visualized HOMOs and LUMOs of P1–P4. For all configurations of molecular orbitals, the HOMOs are spread over the whole conjugated molecules, while the LUMOs are mainly localized on the electron-withdrawing blocks and seldom localized on the central dithienosilole (DTS) cores. This clearly shows that these molecules possess strong intra-molecular charge transfer from DTSs to the electron-withdrawing blocks.

In Figure 4, the E_{HOMO} , E_{LUMO} and E_g are in the order of $P2 > P3 > P1 > P4$, $P4 > P3 > P1 > P2$ and $P4 > P3 > P1 > P2$, respectively. A different trend between the planarity and band gap for P1–P4 is observed in Figure 3, Table 2 and Figure 4. The listed dihedral angles show P1 and P4 are more planar than P2 and P3, which means, compared to P2 and P3, P1 and P4 have higher degree of hybridization and π conjugation between the DTS cores and electron-withdrawing groups, whereas E_g presents the order of $P4 > P3 > P1 > P2$. The contradiction in planarity and band gap shows the structural planarity is not the only parameter for band gap level, the other parameters, such as the electronic inductive effect of the functional group also have contribution to the changes on HOMO levels and band gaps.

According to the energy level diagram in Figure 4, the LUMO energy levels of P1–P4 are all in the range of -3.8 and -4.0 eV, within the optimal LUMO energy range [18,19]. Most importantly, the band gaps of the designed molecules of P1–P4 are reduced by 0.24, 0.38, 0.20 and 0.09 eV, respectively, as compared to that of BDCDTS. The results indicate that the substituting of BT by four new electron-withdrawing blocks has significant effect on the band gaps and LUMO energy levels, and potentially improves performance of solar cell. It is worth mentioning that the LUMO energy levels of P1 (-3.92 eV) and P2 (-3.94 eV) are both close to -4.0 eV, and the band gaps are only 1.64 eV and 1.50 eV, respectively. Among these four newly designed molecules, both P1 and P2 possess the best MO energy, which potentially are the best candidates for electron donors.

In organic solar cells, typical ITO (ITO, indium tin oxide)/PEDOT:PSS or ITO/MoO₃ and LiF/Al or Ca/Al are considered to be suitable electrodes and are the most commonly used [5,38,39]. In order to evaluate the consistency of energy levels between the active layer (designed donors and the acceptor of PCBM) and electrodes, we assume the ITO/MoO₃ and LiF/Al are anode and cathode respectively in this Letter. Mihailetchi et al. [40] also reported that there was no barrier energy for electron extraction between LiF/Al electrode with PCBM as an acceptor material. According to the energy diagram of P1–P4, the HOMOs of these

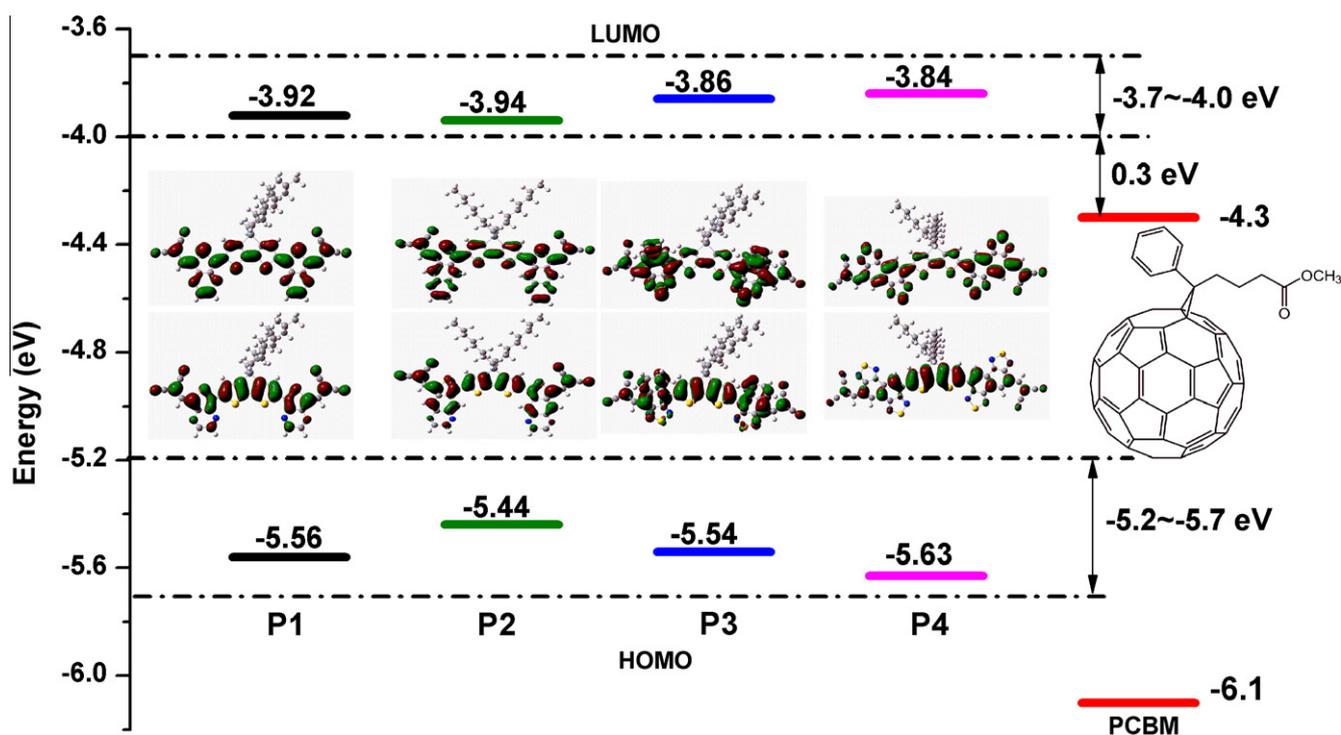


Figure 4. Calculated energy level diagrams and visualized FMOs of P1–P4, and energy level of PCBM.

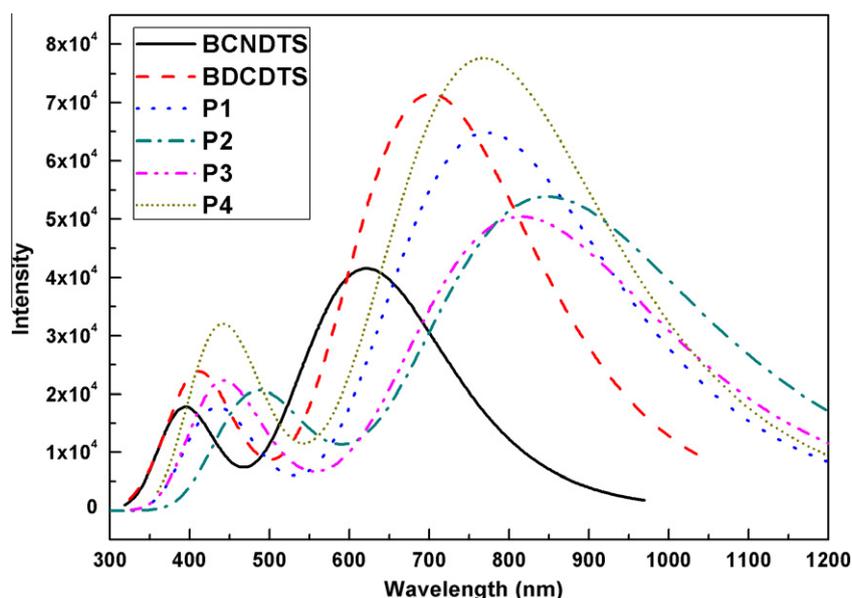


Figure 5. Calculated optical absorption spectra of BCNDTS, BDCDTS and P1–P4.

molecules (-5.56 , -5.44 , -5.54 and -5.56 eV) are deeper than the Fermi energy levels of ITO/MoO₃ (-4.8 – -5.4 eV), and the LUMO of PCBM (-4.3 eV) is equal to the Fermi energy level of LiF/Al (-4.3 eV) [41], which means the energy levels of designed donors and acceptor match the corresponding Fermi energies of electrodes of ITO/MoO₃ and LiF/Al.

The vertical singlet–singlet electronic transition energies and optical absorption spectra of BDCDTS, BCNDTS and P1–P4 were calculated by TD-B3LYP/6–31G*. Figure 5 shows the calculated optical absorption spectra. The detailed computational absorption wavelength, oscillator strength (f), and the major MO (MO, molecular orbital) involved in the transition are listed in Table 3. The main transitions of all donors in the visible range correspond to the transitions from HOMO to LUMO and HOMO to LUMO + 2. The intramolecular charge transfer between electron-withdrawing groups and DTS units results in the lowest-energy transitions (HOMO to LUMO). The calculated maximum absorption peaks (BDCDTS: 703 nm and BCNDTS: 624 nm) are approximately consistent with the experiments (BDCDTS: 659 nm and BCNDTS: 572 nm) [15] with a small offset of ~ 50 nm. We further calculated the electronic transition energies and optical absorption spectra of four mole-

cules P1–P4 by the same method as shown in Table 3 and Figure 5. The most intense absorption peaks for donors P1–P4 are about 772, 849, 817 and 768 nm, respectively, corresponding to the optical band gaps of 1.61, 1.46, 1.52 and 1.61 eV. Compared to BDCDTS and BCNDTS, the absorption peaks of P1–P4 become much broader and more intense within visible and infrared region, which will facilitate more efficient sunlight absorption.

In order to estimate the properties of the designed molecules, we used the Scharber diagrams [19] to predict PCEs (%) of the solar cells combining P1–P4 and PCBM. Using the design rules proposed by Scharber et al. [19], which assuming a charge carrier mobility of 10^{-3} cm² V⁻¹ S⁻¹, a fill factor of 0.65 (We cannot predict the fill factor of 65% from the first principles. In real organic solar cells, the assumed FF is so large that usually difficult to achieve), one can predict the overall PCEs from the band gaps and the LUMO energy levels of the donors. The predictions by the diagram show that the PCEs of four novel designed solar cell devices made by P1–P4 and PCBM are $\sim 9\%$, $\sim 10\%$, $\sim 9\%$ and $\sim 8\%$, respectively. The predictions also show P2 with the smallest band gap and lowest LUMO energy level among the four molecules, exhibits the highest solar cell efficiency of $\sim 10\%$ when used in combination with PCBM.

Table 3

Calculated electronic transitions, oscillator strength, and major MO involved in the transition of BCNDTS, BDCDTS and P1–P4, along with the experimental optical absorption spectra of BCNDTS, BDCDTS.

		Transition energy		Oscillator strength	Major MO involved in the transition
		eV	nm		
BCNDTS	ex1	1.99	624 (572) ^a	0.99	HO → LU (71%)
	ex4	3.15	394 (~ 375) ^b	0.39	HO → LU + 2 (69%)
BDCDTS	ex1	1.76	703 (659) ^a	1.75	HO → LU (71%)
	ex5	2.99	415 (~ 375) ^b	0.41	HO → LU + 2 (48%)
P1	ex1	1.61	772	1.60	HO → LU (71%)
	ex5	2.84	437	0.40	HO → LU + 2 (68%)
P2	ex1	1.46	848	1.33	HO → LU (71%)
	ex5	2.46	505	0.27	HO → LU + 2 (67%)
P3	ex1	1.52	817	1.23	HO → LU (71%)
	ex6	2.80	443	0.68	HO → LU + 2 (68%)
P4	ex1	1.61	768	1.91	HO → LU (71%)
	ex6	2.76	449	0.42	HO-1 → LU + 1 (56%)

^a Experimental thin film absorption spectrum are from Table 1 of reference [15].

^b Experimental thin film absorption spectrum are estimated from Figure 2 of reference [15].

4. Conclusion

We rationally chose four novel blocks for substitution of BT in BDCDTS, and designed four new donors of P1–P4. The electronic structures and optical absorption spectra of these molecules have been investigated by DFT and TDDFT methods, respectively. The calculations show the novel molecules possess lower band gaps, lower LUMO energy levels, and broader optical absorptions in visible and infrared light range than BCNDTS and BDCDTS. When the newly designed donors are used in combination with PCBM, the solar cell efficiency is estimated to be up to ~10%.

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