



The influence of donor material on achieving high photovoltaic response for organic bulk heterojunction cells with small ratio donor component



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ABSTRACT

Authors demonstrated impact of series small ratio donors in C_{60} matrix on photovoltaic (PV) performance. A series of donor materials such as N,N' -Di-1-naphthyl- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), 4,4'-Bis(carbazol-9-yl) (CBP), 4,4',4''-tris(N -3-methylphenyl- N -phenyl-amine)triphenyl-amine (m-MTDATA), copper phthalocyanine (CuPc) and 4,4,4-tris(n -carbazolyl-triphenyl-amine) (TCTA) were blended with fullerene (C_{60}) by different ratio. It was found that although donor-acceptor (DA) interface in planar heterojunction (PHJ) structure increased charge separation probability at the near interface section, the PV response was stronger for bulk heterojunction (BHJ) with low-ratio donor doping into C_{60} matrix in which exciton dissociation can take place immediately after photon absorption without a diffusion progress. The power conversion efficiency (PCE) of BHJ-PV cell based on NPB donor reaches 2.25%, which is double of that of the PHJ cell. In terms of our series results we obtained that ΔE_{HOMO} ($\text{HOMO}_{C_{60}} - \text{HOMO}_{\text{donor}}$) between C_{60} acceptor and donors would provide a maximal influence on achievement of a maximal PCE and an optimal ΔE_{HOMO} locates around 0.8 eV, which implies that dissociation of photo-exciton at C_{60} matrix needs feasible driving force. More detail mechanism was also argued.

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1. Introduction

Organic photovoltaic (OPV) cell is a potential low-cost alternative to conventional inorganic counterpart due to their ease of processing and compatibility with flexible substrates. Since 1986 Tang [1] has introduced the first donor-

acceptor (DA) type PV cell, the PV performances were ceaselessly improved by dexterously designing cell architecture, selecting and synthesis of organic materials and so on, which all helped to lift power conversion efficiency (PCE) up to around 8% for state-of-the-art cells [2,3]. It is well known that high-efficient PV cells are mostly based on a bulk heterojunction (BHJ) structure in which mixed thin film composed of donor (D) and acceptor (A) are essentially being adopted [4]. With few exceptions [5], fullerene (C_{60} or C_{70}) [6,7] acts generally as the acceptor-component in

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BHJ-small molecule cells, whereas a large number of hole-transporting materials have been used as the D-component.

Recently, Tang group [8] has demonstrated a new BHJ OPV cells in which active blend film was C_{60} matrix with little donor, which is highly different with traditional BHJ cells with almost the same D:A ratio [9]. When 5 wt.% ratio 1,1-Bis-(4-methyl-phenyl)-aminophenyl-cyclohexane (TAPC) was used as the donor to mix with C_{60} conjunct with MoO_3 buffered ITO acting as Schottky barrier contact, a high PCE of >5% was obtained. There are still, however, some issues not be clearly understood, such as, the facts that whether such low-concentration doping structure is suitable to all the donor materials and how the carrier mobility and molecule energy level of the donor should be possessed need to be further investigated.

Here, a series BHJ OPV cells based on different donors (Fig. 1a) such as N,N' -Di-1-naphthyl- N,N' -diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), 4,4'-Bis(carbazol-9-yl)-biphenyl (CBP), 4,4',4''-tris(N -3-methylphenyl- N -phenylamine) triphenyl-amine (m-MTDATA), copper phthalocyanine (CuPc) and 4,4,4-Tris(N -carbazolyl-triphenyl amine) (TCTA) with various concentration in C_{60} matrix were constructed, respectively. The difference of the PV parameters between planar heterojunction (PHJ) and BHJ structure with identical donors were compared. The main reason affecting the PV response for different donor materials was explored. The maximal PCE of BHJ cells based on 5 wt.% NPB was 2.25% which is double of that of the PHJ cell. Our results also demonstrate that the highest occupied molecular orbital (HOMO) energy level offset (ΔE_{HOMO}) between C_{60} acceptor ($HOMO_A$) and donor ($HOMO_D$) behaves a crucial impact on extraction of a peak PCE of series donor materials based BHJ cells with C_{60} acceptor. The optimal ΔE_{HOMO} locates around 0.8 eV.

2. Experiments methods

Patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of $20 \Omega/sq$ were routinely cleaned and treated in an ultraviolet-ozone chamber for 20 min immediately before loading into a high vacuum chamber ($\sim 5 \times 10^{-4}$ Pa). All chemicals were purchased commercially and used without further purification. Organics and metal films were sequentially deposited onto the clean

patterned ITO glass substrates via shadow masks to form devices with an area of 0.1 cm^2 . The evaporating rates were kept at $0.5\text{--}1 \text{ \AA/s}$ for organic layers and MoO_3 layer as well $10\text{--}15 \text{ \AA/s}$ for Al cathode, respectively. BHJ-cells were realized by co-deposition of two sources. The current–voltage characteristics were measured using a programmable source meter (Keithley 2400) in the dark and under illumination of 100 mW/cm^2 with AM 1.5 G simulated solar spectrum from a solar simulator. All measurements were carried out at room temperature and under ambient conditions without encapsulation.

3. Results and discussion

We have fabricated a series PV cells with structure of ITO/ MoO_3 (5 nm)/ x wt.% Donor: C_{60} (40 nm)/bathophenanthroline (Bphen) (6 nm)/Al (100 nm) in which MoO_3 functions as an anode buffer and Schottky barrier, and Bphen functions as the cathode buffer layer as shown in Fig. 1b. Various donors described in above introduction section were used as the donor components and their ratio in C_{60} matrix by weight ratio was varied. We firstly investigate the effects of blending ratios on PV response. The PV parameters of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), PCE derived from the $I\text{--}V$ traces for these cells with various donor ratio are depicted in Fig. 2. It is noticed that they behave several alike PV features: (1) the J_{sc} and FF increase with decreasing donor ratio but decreased as the donor ratio is above 5 wt.%, which is consistent with previous report [8]; (2) the V_{oc} decreases with increasing donor ratio but by a quite different rates; (3) the optimal ratio are respectively 2 wt.% and 5 wt.% for m-MTDATA donor and other four donors. PV responses of respective optimal donor ratio in C_{60} matrix of the series cells are summarized in Table 1.

From Fig. 2 we can see that as the donor ratio in C_{60} matrix is too low (below 5 wt.%) the PV responses is very similar to that of a Schottky barrier diode. Thanks to the high work function of MoO_3 , which has been estimated to be as high as 6.8 eV [10], Schottky cell of ITO/ MoO_3 / C_{60} /Bphen/Al could offer a V_{oc} as high as 1.2 V [11]. With donor ratio increasing, devices more like D–A based cell in which energy offset between HOMO of the donor and the lowest occupied molecular orbital (LUMO) of C_{60} determines the V_{oc} [12]. FF of less donor ratio based BHJ PV cells cannot

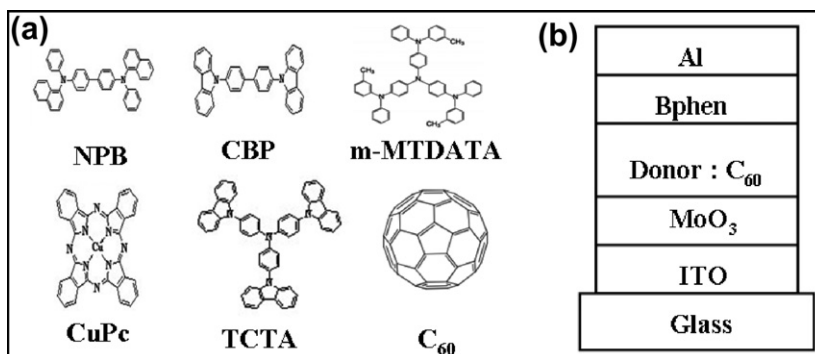


Fig. 1. (a) Chemical structures of the materials and (b) device structure of the cell.

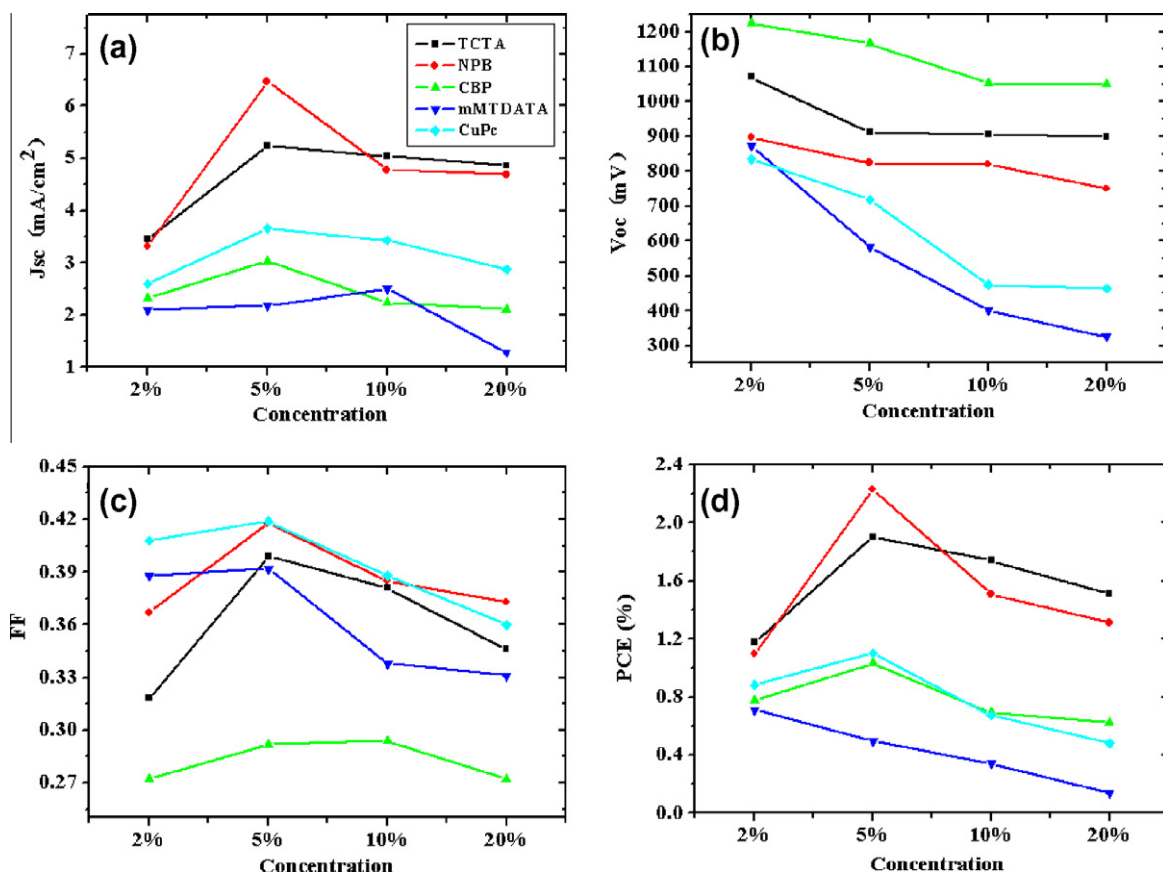


Fig. 2. Photovoltaic characteristics of (a) J_{sc} , (b) V_{oc} , (c) FF and (d) PCE versus donors concentration for Donor:C₆₀ cells under AM1.5 at 100 mW cm² illumination.

Table 1

The PV parameters of ITO/MoO₃ (5 nm)/x wt.% Donor: C60 (40 nm)/Bphen (6 nm)/Al (100 nm) devices for five donors at respective optimal concentration.

Donor (optimal ratio)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	PCE (%)
NPB (5%)	6.5 ± 0.1	825 ± 5	0.42 ± 0.01	2.25 ± 0.05
CBP (5%)	3.0 ± 0.1	1167 ± 5	0.29 ± 0.01	1.01 ± 0.05
m-MTDATA (2%)	2.1 ± 0.1	873 ± 5	0.39 ± 0.01	0.71 ± 0.05
CuPc (5%)	3.7 ± 0.1	718 ± 5	0.42 ± 0.01	1.11 ± 0.05
TCTA (5%)	5.2 ± 0.1	912 ± 5	0.40 ± 0.01	1.91 ± 0.05

be satisfied, which can be considered as a Schottky cell like behavior and strong bias dependent charge recombination is serious as free electron and hole exist in the whole active layer instead of the planar case where free electrons and holes are restricted in acceptor layer and donor layer, respectively. The device reaches a maximal J_{sc} when donor concentration is at around 5 wt.%. As suggested by a previous study, moderate carrier mobility is sufficient for obtaining high PCE [13]. A high donor ratio in BHJ cells increases in hole mobility but inevitably would decrease in electron mobility, while more disparity in the mobilities between the two carriers in such a cell would increase in the escape probability of the carrier from D:A mixture with BHJ structure [14]. On the other hand increase in hole mobility may induce serious bimolecular recombination

[15,16]. When the donor ratio is less than 5 wt.%, two factors could limit J_{sc} , i.e., no enough-larger hole mobility for guaranteeing hole collection and no enough mutual contact sites between donor and acceptor for the exciton dissociation.

To confirm the superiority of the BHJ cells with low ratio donor, we constructed a series PHJ cells with above five donor components in the structure of ITO/MoO₃ (5 nm)/Donor (5 nm)/C₆₀ (40 nm)/Bphen (6 nm)/Al (100 nm). The select on the donor thickness is based on the following considerations: (1) uniform film must be formed so that the film could cover full on the surface of MoO₃ layer; (2) donor layer should be as thin as possible to assure small light absorption, and hole transport exhibits little influence on cell performance and can therefore be ignored in this

Table 2

The PV parameters of the PHJ cells with the structure of ITO/MoO₃ (5 nm)/Donor (5 nm)/C₆₀ (40 nm)/Bphen (6 nm)/Al (100 nm).

Donor	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	PCE (%)
NPB	3.1 ± 0.1	812 ± 5	0.43 ± 0.01	1.06 ± 0.05
CBP	1.4 ± 0.1	1050 ± 5	0.33 ± 0.01	0.47 ± 0.05
m-MTDATA	1.1 ± 0.1	320 ± 5	0.40 ± 0.01	0.14 ± 0.05
CuPc	3.2 ± 0.1	358 ± 5	0.50 ± 0.01	0.56 ± 0.05
TCTA	2.9 ± 0.1	897 ± 5	0.36 ± 0.01	0.96 ± 0.05

work. Table 2 lists PV parameters for PHJ cells derived from the I - V traces of Fig. 3b. By comparing Table 2 with Table 1 we observed that all the PV responses are markedly larger for BHJ cells than for PHJ cells and structure of low-ratio donor bulk cells has advantages on obtaining high V_{oc} and J_{sc} . For PHJ-cells V_{oc} is limited by the offset between HOMO_D - LUMO_A, but for BHJ-cells based on low-ratio donor, V_{oc} is largely determined by the MoO₃/BHJ Schottky barrier so that a large V_{oc} is easily obtained. J_{sc} of the BHJ-PV cells far exceeds the planar case. Except that J_{sc} of the CuPc cell was enhanced by only 16% due to its larger absorption at visible waveband, J_{sc} of other donor based cells increase by more than 100%. Considering almost the same light absorption for the the PHJ and BHJ cells and the probability for geminate charge separation at a planar D/A interface is expected to be substantially enhanced over the bulk case since (1) the volume available for electron-hole recombination is reduced to a thin section near the DA interface; (2) the D/A interface orients the electron-hole pair, favoring carrier separation in the direction normal to the interface plane [14], the photocurrent improvement can be taken into account as bellow. Although DA interface of PHJ structure increased in charge separation probability at section that is near to the interface, more excitons located far away from the interface may be wasted by recombination during the exciton diffusion since the exciton diffusion length is often much shorter than the device thickness. For low-ratio donor BHJ cells exciton dissociation takes place immediately after photon absorption without an exciton diffusion progress; so much

more exciton can be dissociated to free charge and consequently collected by electrode even if a considerable amount of free charge may loss in the transport process. As J_{sc} or V_{oc} are improved, PCE increases by 95%, 98%, 110%, 117% and 407% for CuPc, TCTA, NPB, CBP and m-MTDATA donor cells, respectively.

Just as above introduced that compared with PHJ cells, low-ratio donor based BHJ cells behave advantages for extraction of V_{oc} and J_{sc} , however, PCEs of the BHJ cells with the different donors are in a big difference. The PCE with NPB as the donor are larger than 2%, but PCEs of m-MTDATA cells are even below 1%. The difference between the PV responses was considered to be two possible reasons in which one is the mobility difference between the donors (Table 3), and the other one is the HOMO difference between the donors which is related to exciton dissociation [25]. We prefer the latter to be the main reason for affecting PCE extraction. As well accepted that in most PHJ or BHJ photovoltaic cells exciton dissociation is presumably controlled by level offset between the HOMO_A-HOMO_D (ΔE_{HOMO}) [26], which is the energy gap between the HOMO energy levels of the donor and acceptor, or equivalently LUMO energy level offset (ΔE_{LUMO}). Note that for our series cells, most light absorption and exciton generation arise from acceptor C₆₀, so exciton dissociation energy is presumably controlled by ΔE_{HOMO} as shown in Fig. 4a. Fig. 4b sketches the J_{sc} and PCE as a function of ΔE_{HOMO} , it can be seen that both J_{sc} and PCE vary with the rising energy offset, and peak ΔE_{HOMO} lies at 0.8 eV which is a central value at maximal J_{sc} and PCE then J_{sc} and PCE decreased after a ΔE_{HOMO} of above 0.8 eV. It is interesting to point out that the donor materials Tang group have used, such as TAPC, Rubrene and TiOPc which have achieved a high PCE all have a ΔE_{HOMO} around 0.8 eV, and is in accordance with our result. The presence of an optimal ΔE_{HOMO} was attributed to following reasons. At donor/C60 interfaces, there is a minimal energy offset, (i.e., ΔE_{HOMO}) for exciton dissociation, in other words, there needs such an energy which is larger than the binding energy of the exciton in the acceptor C₆₀ matrix. Quantum mechanically, the aptly excess over the binding energy would be in favor of the formation of charge

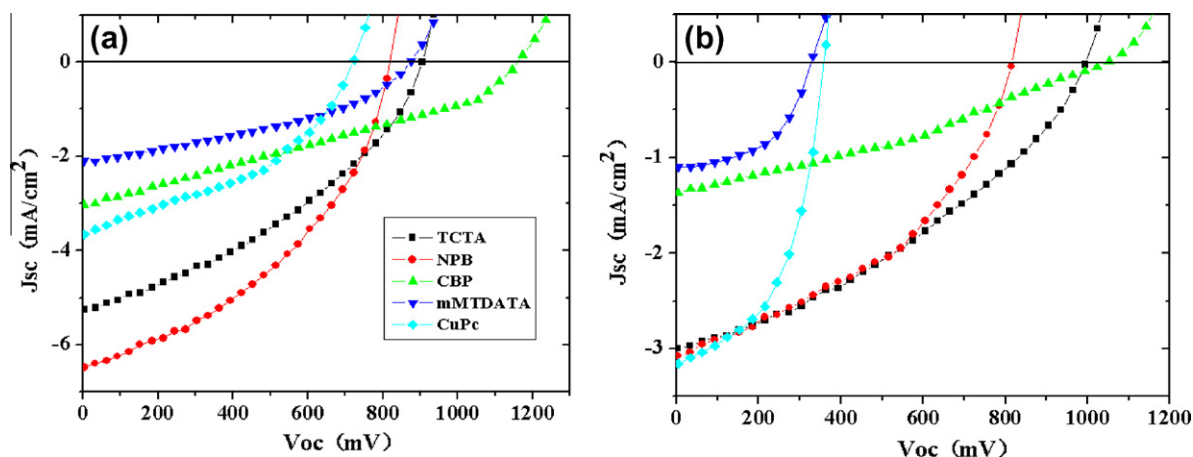


Fig. 3. I - V characteristics under 1 sun, AM 1.5G illumination for (a) optimized BHJ cells and (b) PHJ cells.

Table 3

The hole mobility and molecule energy level of donors.

	C ₆₀	NPB	CBP	m-MTDATA	CuPc	TCTA
Hole mobility (cm ² V ⁻¹ s ⁻¹)	–	2.6 × 10 ⁻⁴ [18]	2 × 10 ⁻³ [19]	3 × 10 ⁻⁵ [21]	1.8 × 10 ⁻⁴ [23]	3 × 10 ⁻⁴ [19]
HOMO (eV)	6.2 [17]	5.4 [18]	5.9 [20]	5.0 [22]	5.2 [24]	5.7 [20]
ΔE _{HOMO} (eV)	–	0.8	0.3	1.2	1.0	0.5

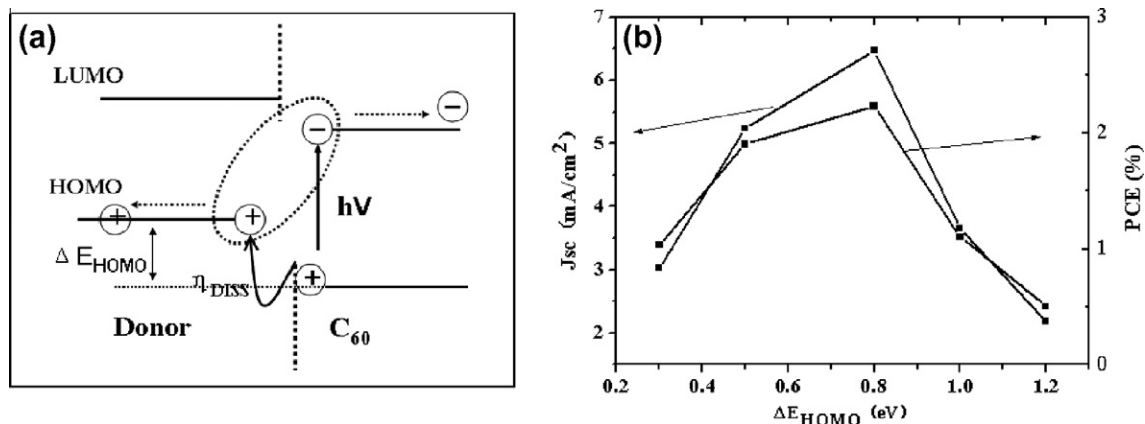


Fig. 4. (a) The schematic of exciton formation, dissociation and charge transfer progress for smaller ratio donor in C₆₀ matrix under illumination. (b) J_{sc} (left) and PCE (right) as a function of ΔE_{HOMO} , respectively. ΔE_{HOMO} is the difference between HOMO_{C₆₀} and HOMO_{Donor}.

transfer states with high internal quantum numbers [27]. When ΔE_{HOMO} is below maximal ΔE_{HOMO} zone, the energy region is the “normal” region, corresponding to increasing hole transfer rate (k_{ET}) [28]. To further increases ΔE_{HOMO} , decreasing k_{ET} occurs in the Marcus “inverted” region [29] and could lead to decrease in J_{sc} and PCE because as k_{ET} decreases, decay rate from charge-transfer states to the ground states could be increased. On the other hand, small HOMO offsets may be desirable for high overall PCE [30]. For a large ΔE_{HOMO} , more exciton energy is expended in the charge separation process, such as the m-MTDATA donor case, $\Delta E_{HOMO} = 1.2$ eV means that more than two-thirds of energy of the C₆₀ exciton is wasted in the charge separation progress. It is noticed that the relation between PCE and ΔE_{HOMO} would indicate a direction for donor material select and molecular structure design for achieving high PCE using such a BHJ structure with near 5 wt.% donor component, while other properties for example carrier mobility, LUMO level and so on of the donors could be ignored, although their light absorption is aptly considered.

4. Conclusion

Authors demonstrated impact of low concentration different donors in C₆₀ matrix on PV PCE of the cells and compared with corresponding PHJ-cells. It was observed that low-concentration donor based BHJ cells behave advantages for extracting higher V_{oc} and J_{sc} over the PHJ-cells. The PCE of BHJ-PV cells based on 5 wt.% NPB in C₆₀ acceptor reaches up to 2.2%, which is double of that of the PHJ cell. We also find that ΔE_{HOMO} plays a crucial role in harvesting high PCE and the optimal ΔE_{HOMO} is found to be around 0.8 eV. This rule could guide us to design and select

more appropriate donor material for achieving high efficient PV cells by a low-concentration donor doping structure, but other properties, for example, carrier mobility, LUMO level, etc. of the donors could be ignored.

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