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ARTICLE TYPE

Selenophenyl Bridged Perylene Diimide Dimer as Efficient Solution-Processable Small Molecule Acceptor

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We report herein a new solution-processable small molecule acceptor, a selenophenyl bridged perylene diimide dimer, that gives 4.0% efficiency when employed PBDTTT-C-T as the polymer donor and a conventional cell structure.

Finding efficient solution-processed small molecule acceptor is an important issue for the fabrication of high-performance non-fullerene solar cells (NF-SCs), in which N-type organic acceptor (small molecule or polymer) is applied to replace the fullerene one that is currently the dominant acceptor material in organic solar cells.¹⁻⁵ Among the reported small molecule acceptors such as those based on 9,9'-bifluorenylidene,⁶ benzothiadiazole,⁷ naphthalene diimide,⁸ quinacridone,⁹ fluoranthene-fused imide,¹⁰ and decacycene triimide,¹¹ perylene diimide (PDI) based ones are highly efficient. PDIs are a typical kind of N-type organic semiconductors. They usually have a strong absorption band in the visible wavelength region (400 – 600 nm), a relatively high extinction coefficient ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$),¹² a good electron mobility (up to $10^1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)¹³ and a low-lying lowest unoccupied molecular orbit (LUMO) (typically, -4.0 eV).¹⁴ Additionally, PDIs are normally stable to light, heating, and chemicals.¹⁴ Recently, a power conversion efficiency (PCE) of 3 – 4% has been reported from the PDI based small molecule acceptors¹⁵⁻²¹ as their aggregation tendency is reduced, for example, by the formation of the twisted dimeric^{15-20,22} or trimeric^{21,23} backbone, or by imidization using branched alkyl amine such as 1-ethylpropylamine²⁴⁻²⁷ or by incorporation of large conjugated π -systems, for example, on the bay region.²⁸ With respect to the conventional cell configuration, an inverted cell structure takes advantages of the carrier-extraction favourable donor/acceptor (D/A) distribution in the top and buried surface of the active layer, which leads to a higher PCE value (4.34 vs. 3.28%).¹⁶ Very recently, a PCE of 5.9% has been achieved from a PDI dimer by using an inverted cell structure with a fullerene self-assembled monolayer (C₆₀-SAM) on the ZnO electron selective layer.²⁹ In this communication, we present a new efficient PDI dimer based solution-processable small molecule acceptor, namely 1,1'-bis(2-methoxyethoxy)-(7,7'-(2,5-selenophenyl) bis-PDI (**bis-PDI-Se-EG**, Figure 1A), in which a selenophenyl moiety is selected as

the aromatic bridge since it has been reported that replacement of the thienyl with the selenophenyl unit may enhance charge transport and performance of all polymer solar cells.³⁰

This dimer was synthesized by the palladium-catalyzed Stille cross-coupling reaction between 1-(2-methoxyethoxy)-7-brominated PDI and 2,5-bis(trimethylstannyl)selenophene in a yield of 85%. The final product was successfully characterized with ¹H-NMR, ¹³C-NMR, TOF-MS and elemental analysis (ESI).

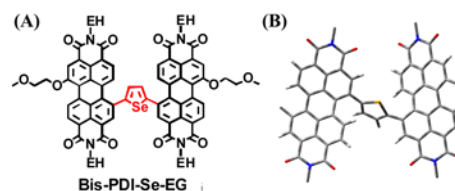


Figure 1. (A) Chemical structure of the PDI dimer. (B) Optimal conformation of the dimeric backbone.

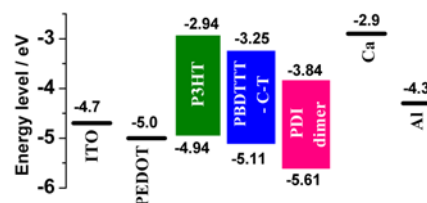


Figure 2. Energy diagram of the PDI dimer, polymer donors and other components used in a normal solar cell.

The optimal conformation of this dimer was calculated on Gaussian 09 at the B3LYP/6-31G level of theory in the gas phase (Figure S3). The dihedral angle between two PDI planes is of 21.89° and that between the PDI and the selenophenyl plane is of 55.98° . This dimer forms highly twisted dimeric backbone.

The electrochemical properties of the dimer were analyzed by using cyclic voltammetry (CV) with Ag/AgCl as the reference electrode (Figure S4). Energy levels of the LUMO and the highest occupied molecular orbit (HOMO) were determined to be -3.84 and -5.61 eV , respectively, from the onset of oxidation and reduction waves by using an offset of 4.40 eV for the Ag/AgCl electrode versus the vacuum level. Both the LUMO and HOMO levels are close to those of our previously reported thienyl bridged dimer, bis-PDI-T-EG.¹⁵ Figure 2 depicts the energy diagrams of the PDI dimer and the selected polymer donors of P3HT and PBDTTT-C-T.³¹ The HOMO and LUMO energy of the PDI dimer match well with those of P3HT and PBDTTT-C-T,

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respectively.

Figure 3 is the UV-Vis absorption spectra of the dimer, P3HT and PBDTTT-C-T. In a dilute solution (Figure 3A), the dimer has an absorption peak around 562 nm with a maximum extinction coefficient of $\epsilon_{\max} = 56800 \text{ M}^{-1}\cdot\text{cm}^{-1}$. The absorption properties are also similar to those of bis-PDI-T-EG.¹⁵ In thin film (Figure 3B), the dimer shows an absorption band extending from 440 to 700 nm, which closely overlaps with that of the pure P3HT film, while it is complementary to that of the pure PBDTTT-C-T film. In the absorption spectra of the 1:1 (w/w) blend films (Figure 3C). The blend of PBDTTT-C-T:PDI dimer has a much wider spectral coverage than that of P3HT:PDI dimer (300 – 800 vs. 300 – 650 nm), benefiting for the solar energy utilization.

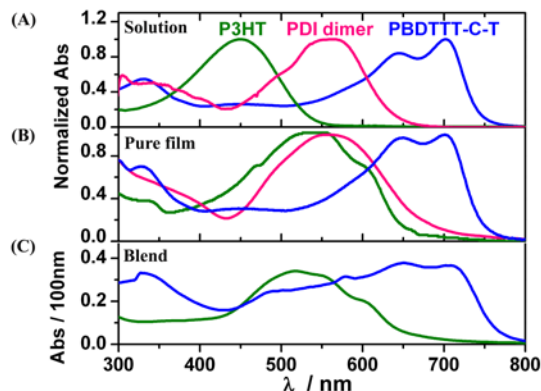


Figure 3. UV-vis absorption spectra of the PDI dimer, P3HT and PBDTTT-C-T in the dilute solution (A, $1 \times 10^{-6} \text{ M}$ for PDI dimer, 2.5 mg/L for P3HT and 10 mg/L for PBDTTT-C-T) and in pure (B) and 1:1 (w/w) blend (C) film, respectively.

The photovoltaic properties of the PDI dimer were characterized by selecting the commercial P3HT and the conjugated polymer of PBDTTT-C-T as the blend donor, respectively. The solution-processed bulk-heterojunction solar cell devices were fabricated with a conventional configuration of ITO glass/PEDOT:PSS/donor:acceptor/Ca/Al and were tested under an AM 1.5G simulated solar light at 100 mW cm^{-2} (AAA grade). Here, PEDOT:PSS is poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate). The cells were optimized by changing the host solvent, the donor:acceptor (D:A) weight ratio, the additive content,³² and the thermal annealing temperature and time, respectively. Table S1 and S2 collect the photovoltaic data optimized under these conditions. The best D:A weight ratio is of 1:1 for both donors.

Figure 4 gives the current density – voltage ($J - V$) curves of the best cells obtained with P3HT and PBDTTT-C-T as the blend donor, respectively. Table 1 lists the relative photovoltaic data. With the blend donor from P3HT to PBDTTT-C-T, the short-circuit current-density (J_{sc}) from the best cells increases from 3.30 to 10.60 mA/cm^2 , enhancing by a factor of 3.2, and the open-circuit voltage (V_{oc}) rises from 0.59 to 0.79 V . The enhancement of the J_{sc} is in line with the wider spectral coverage from the PBDTTT-C-T blend than from the P3HT one (Figure 3C). Also, it may be contributed from the smaller energy offset between the LUMOs (HOMOs) of PBDTTT-C-T and PDI dimer (Figure 2). The increase of the V_{oc} is due to the low-lying HOMO energy of PBDTTT-C-T with respect to that of P3HT. The fill factor (FF) is of 67.21% and 47.93% and the PCE is of 1.31%

and 4.01% when using P3HT and PBDTTT-C-T as the donor, respectively. The relatively higher FF is consistent with that values from the PC71BM based cells: P3HT gives a FF of $\sim 70\%$,³³ while PBDTTT-C-T has a FF of $\sim 60\%$ when using the normal cell structure.³¹

When using PBDTTT-C-T as the blend donor, **bis-PDI-Se-EG** gives a slightly higher V_{oc} (0.79 vs. 0.73 V) and a much higher J_{sc} (10.60 vs. 3.39 mA/cm^2), FF (47.93 vs. 31.1%), and, hence PCE (4.01 vs. 0.77%) than bis-PDI-T-EG,¹⁵ both solar cell blends are free of use of the additive of 1,8-diiodooctane (DIO). Use of DIO leads to a deterioration of the performance for the former dimer (Table S2 and Figure S5), whereas significantly improves all the four cell parameters of J_{sc} , V_{oc} , FF and PCE for the latter one.¹⁵ When blended with P3HT and without use of additive, **bis-PDI-Se-EG** also yields a higher J_{sc} (3.30 vs. 1.63 mA/cm^2), FF (67.21 vs. 41.6%), and PCE (1.31 vs. 0.39%) than bis-PDI-T-EG, while both dimers have a comparable V_{oc} (0.59 vs. 0.58 V).³⁴ Also, the performance is deteriorated for the selenophenyl bridged dimer, while it is improved for the thienyl bridged one after use of additive, for example, 1-chloronaphthalene. These comparisons indicate that a subtle difference in the structure of the aromatic bridge can lead to a large distinction in the cell performance.

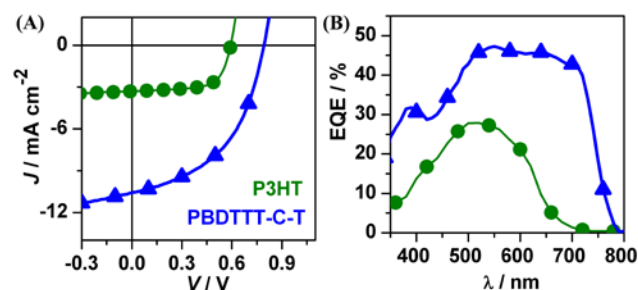


Figure 4. (A) $J - V$ and (B) EQE spectra of the best devices.

Table 1. Photovoltaic properties of the PDI dimer based best cells.

Donor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)		μ_e / μ_h $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
				Best	av. ^a	
P3HT	0.59	3.30	67.21	1.31 ^b	1.24	$0.61/7.2 \times 10^{-3}$
PBDTTT-C-T	0.79	10.60	47.93	4.01 ^c	3.93	$4.7/9.3 \times 10^{-3}$

^a av. = average value, estimated from 10 devices; ^b *o*-DCB as the host solvent, solvent annealing for 4h and subsequent thermal annealing at $110 \text{ }^\circ\text{C}$ for 10 min; ^c *o*-DCB as the host solvent, solvent annealing for 6h.

Figure 4B is the external quantum efficiency (EQE) spectra of the optimal cells. The EQE responses cover a wavelength range from 350 to 700 nm for the P3HT based cell and from 350 to 800 nm for the PBDTTT-C-T based cell, and each is in accordance with the absorption spectrum of the corresponding 1:1 (w/w) blend film (Figure 3C), indicating that both the polymer donor and the dimer acceptor contribute to the photon-to-electron conversion. The integrated current density from the EQE spectrum is of 3.02 and 9.82 mA cm^{-2} , respectively, which is in agreement with the J_{sc} value from the relative cell.

Both the electron and hole mobilities were measured using space-charge-limited current (SCLC) method. The electron-only and hole-only devices are ITO/TIPD/donor:acceptor/Al and ITO/PEDOT:PSS/donor:acceptor/Au, respectively. The extracted value of the electron and hole mobility is $0.61/7.2$ and $4.7/9.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the blend from P3HT and PBDTTT-C-T,

respectively. For both solar cell blends, the electron mobility is lower than the hole one. The relatively lower electron mobility for the P3HT blend than that for the PBDTTT-C-T one is likely responsible for its lower J_{sc} value.

Figure 5 displays the transmission electron microscopy (TEM) images of the two solar cell blends. The white/black domains are of 35/60 nm for the P3HT blend, a slightly larger than that from the bis-PDI-T-EG:P3HT blend.³⁴ The size from the PBDTTT-C-T blend is of 15/15 nm, which is close to that from the bis-PDI-T-EG:PBDTTT-C-T blend without use of DIO as the additive, suggesting that the selenophenyl and the thienyl bridged dimer shows similar compatibility with that polymer.¹⁵ Apparently, the P3HT blend gives a much larger phase domains³⁵ than the PBDTTT-C-T one. As a result, lower charge dissociation efficiency may be expected for the P3HT blend to contribute to its lower J_{sc} owing to the lower volume density of the donor-acceptor interfaces.

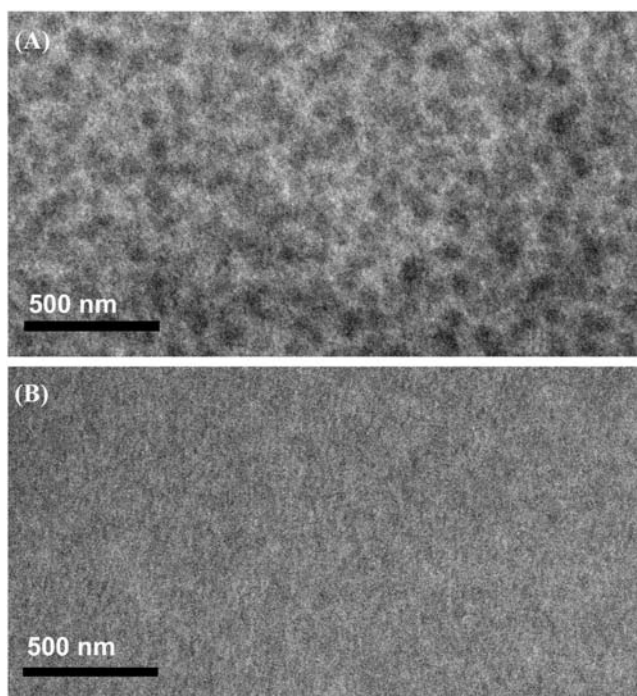


Figure 5. TEM images of the 1:1 (w/w) blend films from P3HT (A) and PBDTTT-C-T (B), respectively, both fabricated under the optimal conditions of the best cells.

Conclusions

In summary, a new selenophenyl bridged PDI dimer based solution-processable small molecule acceptor is reported. When blended with the conjugated polymer donor of PBDTTT-C-T, a PCE of 4% was obtained. The high efficiency is relative to the wide spectral coverage, matched frontier energy, improved carrier mobility and reduced phase size.

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- † Electronic Supplementary Information (ESI) available: Synthesis and characterizations, quantum chemical calculations and device fabrication and procedures. See DOI: 10.1039/b000000x/
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