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COMMUNICATION

Synthesis of annulated thiophene perylene bisimide analogues: their applications to bulk heterojunction organic solar cells†

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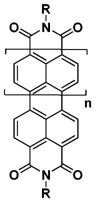
Annulated thiophene perylene bisimides and their triphenylamine based oligomers have been synthesized. One of the oligomers FPTTPA has been demonstrated to be an efficient electron donor in bulk heterojunction (BHJ) organic solar cells, giving a power conversion efficiency of 1.42%.

Perylene bisimides (PBIs) represent a class of thermally stable organic semiconductors with high extinction coefficients, high photostabilities and high quantum yields.[1] They have shown wide applications such as in field-effect transistors,[2] electron transfer cascades,[3] photovoltaic devices,[4] and dye lasers.[5] PBIs are also potential candidates as organic solar cells since they have been found to possess excellent electron affinities and mobilities.[6] Recently, the extension of the aromatic core of PBI has been intensively studied for n-type semi-conductors and NIR dyes.[7] Extension of the aromatic unit along the long molecular axis such as in **2** and **3** induced a bathochromic shift of about 100 nm per addition of naphthalene unit.[8]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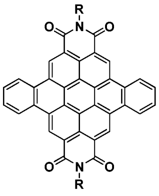
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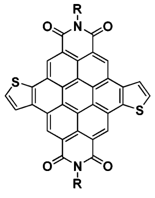
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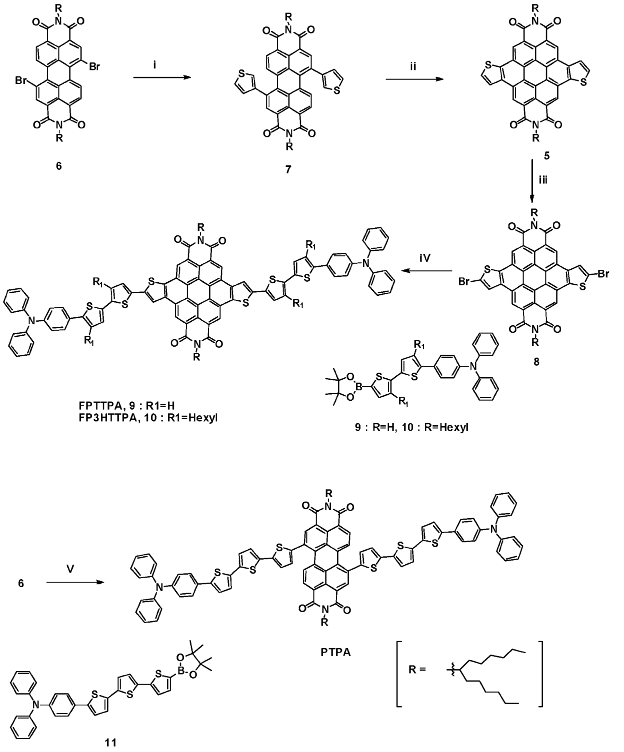
Annulation of PBIs with a variety of cyclic units in the bay region has been actively investigated.[9] Such core-expanded perylene dyes include annulated dibenzocoronenebis(dicarboximide) **4**[10] and diverse heterocycles such as pyridyl-,[11] sulfur-,[12] and *N*-heterocycles[13] substituted PBI. However, the above annulated PBIs hamper further applications because they do not have specific substitution sites for any structural modifications. Therefore, we envisioned that if from the thiophene annulations of PBI **1** compounds such as **5** could be synthesized, they could be utilized for the synthesis of electronic materials through the incorporation of numerous electron-rich or electron-deficient chromospheres to the annulated thiophene unit.

In this communication, we report the synthesis of the annulated thiophene perylene bisimide, its electron-rich derivatives and its applications for organic solar cells.

The three oligomeric molecules **FPTTPA**, **FP3HTTPA**, and **PTPA** have been efficiently synthesized by the stepwise synthetic protocol illustrated in Scheme 1. The Suzuki coupling reaction[14] of 1,7-dibromoperylenebis(dicarboximide)s with thiophene-3-ylboronic acid led to **7**. Photocyclization in the presence of I_2 yielded the thiophene annulated PBI **5**. Bromination of **5** with Br_2 gave **8**. **FPTTPA** and **FP3HTTPA** were prepared from **8** with compound **9** and compound **10** by a Suzuki reaction, respectively. For comparison, the triphenyl



Scheme 1 *Reagents*: (i) thiophene-3-ylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF; (ii) I_2, $h\nu$, dichloromethane; (iii) Br_2, CH_2Cl_2; (iv) for R = H, compound **9**; for R = hexyl, compound **10**, $Pd(PPh_3)_4$, K_2CO_3, THF; (v) compound **11**, $Pd(PPh_3)_4$, K_2CO_3, THF.

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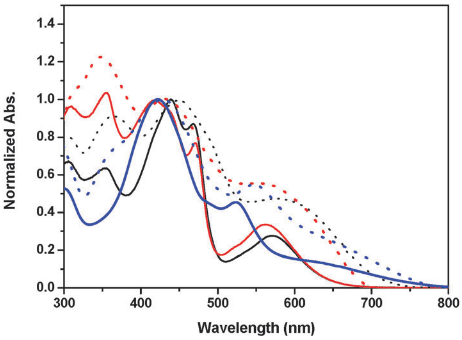

Fig. 1 Absorption spectra of **FPTTPA** (black line), **FP3HTTPA** (red line), and **PTPA** (blue line) in CH_2Cl_2 (solid line) and thin film (dotted line).

amine moiety was connected at 1, 7 bay positions of perylene bisimide to give **PTPA**.

Optical absorption spectra of **FPTTPA**, **FP3HTTPA**, and **PTPA** in CH_2Cl_2 and in films are shown in Fig. 1. The absorption spectrum of **PTPA** showed two broad maxima at 420 and 523 nm. The short wavelength absorption at 420 nm is associated with the characteristic perylene transition, while the long wavelength absorption at 523 nm corresponds to an intramolecular charge transfer between the TPA-thiophene donor part and the acceptor perylene group. Comparison of the spectra of the three compounds shows that the absorption maximum of **FPTTPA** and **FP3HTTPA** in the long wavelength is bathochromically shifted by 50 and 40 nm compared with that of **PTPA**, respectively, as a result of the more planar conformation. The **FPTTPA**/C_{61}-**PCBM** film has three broad absorption bands, which span a wide range of the UV and visible spectrum from 300 to 680 nm (see S1 in the ESI†). Such a broad spectrum makes **FPTTPA** a potential compound for organic solar cells.

Electrochemical properties of the three compounds **FPTTPA**, **FP3HTTPA**, and **PTPA** were investigated by cyclovoltammetry. All three compounds exhibited two reversible oxidation potentials. The oxidation potentials of **PTPA** are lower by about 250 mV than those of **FPTTPA** and **FP3HTTPA**, indicating a significant HOMO-raising effect. **FPTTPA** showed a large positive shift in its redox potential, rendering oxidation more difficult due to the electron delocalization on a relative planar configuration. Compounds **FPTTPA** and **PTPA** exhibited two reversible reduction potentials, whereas **FP3HTTPA** exhibited one irreversible reduction potential at −1.38 V. The first reduction potential of **FPTTPA** is 0.21 eV lower than that of **FP3HTTPA**, indicating stronger electron accepting power, which makes it a potential p-type material for organic solar cells (see S2 in the ESI†).

The HOMO and LUMO levels of the three compounds were calculated to be −4.98 to −5.27 and −3.33 to −3.55 eV, respectively. In comparison with the HOMO level of −6.1 eV and LUMO level of −3.7 eV of **PCBM**, the three compounds are suitable for use as donor materials blended with **PCBM** as the acceptor in organic solar cells.

Solution processable small molecule semiconductors as alternatives to conjugated polymers in bulk heterojunction (BHJ) organic solar cells are subject to a considerable current interest.[15] Therefore, we adopted the triphenylamine-based oligomers incorporating an annulated perylene unit as donor materials for organic solar cells because the compounds have broad absorptions and high extinction coefficients as well as the proper energy difference in the LUMO of the donor and acceptor used as the active layer.

Bulk heterojunction (BHJ) organic solar cells were fabricated by spin-coating perylene : **PCBM** (weight ratio = 1 : 2, perylene = **FPTTPA**, **FP3HTTPA**, and **PTPA**) blends in chlorobenzene onto cleaned indium tin oxide (ITO), deposited by first spin-coating with PEDOT : PSS [poly(3,4-ethylene-dioxythiophene) : polystyrenesulfonate] (layer thickness: 40 nm). The thickness of an active layer was 40 nm. After the cells were completely dried, vacuum deposition of Al (∼ 100 nm) as the cathode was conducted.

Fig. 2a shows the J–V curves of devices based on the three compounds. A summary of photovoltaic properties is listed in Table 1. The device with a 1 : 2 weight ratio of **FPTTPA** to **PCBM** gave the best performance with a power conversion efficiency (η) of 1.42% which is significantly higher than the other two devices based on **FP3HTTPA** and **PTPA**. The devices based on **FPTTPA** and **FP3HTTPA** exhibited a higher V_{oc} of 0.78–0.96 V compared to the device based on **PTPA**, which is in agreement with the higher HOMO level of both compounds. The J_{sc} enhancement of the **FPTTPA** : **PCBM** blend relative to the other two blends can be related to the charge carrier mobility. In order to confirm our results, space charge current limited measurements in dark were carried out on the three blend layer. The hole and electron mobilities of the **FPTTPA** : **PCBM** device were calculated to be $\mu_h = 364 \times 10^{-6}$ and $\mu_e = 6.42 \times 10^{-4}$, whereas those of **PTPA** : **PCBM** were sharply decreased to $\mu_h = 1.28 \times 10^{-6}$ and $\mu_e = 2.74 \times 10^{-6}$ (see S4 in the ESI†). The increased mobility of charge carriers and balanced charge transport in

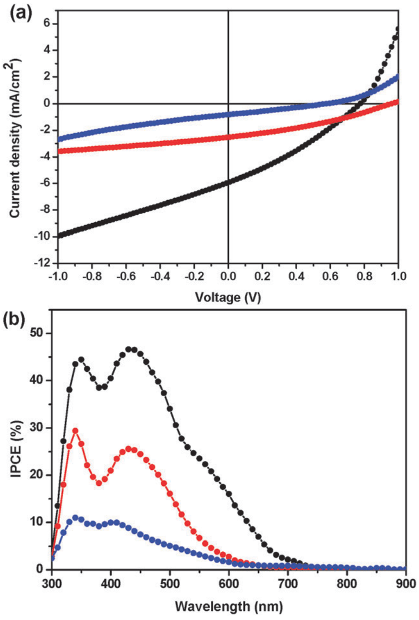

Fig. 2 J–V curves (a) and IPCE (b) spectra of BHJ solar cells based on the **FPTPA** : C_{61}-**PCBM** (black line), **FP3HTTPA** : C_{61}-**PCBM** (red line), and **PTPA** : C_{61}-**PCBM** (blue line).

Table 1 Photovoltaic performances of the BHJ oligomer solar cells composed of perylenes/**C_{61}-PCBM** (1 : 2) blends

Components	J_{sc}/mA cm^{-2}	V_{oc}/V	FF (%)	η (%)
FPTTPA	5.94	0.776	30.80	1.42
FP3HTTPA	2.53	0.960	33.31	0.81
PTPA	0.83	0.575	27.24	0.13

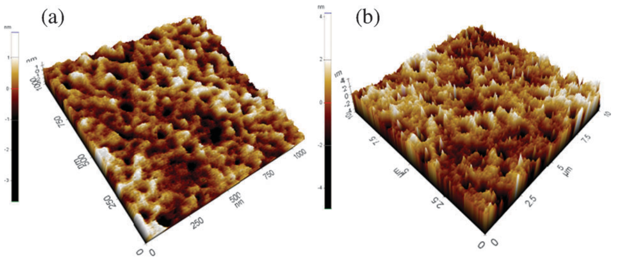

Fig. 3 AFM surface topography of the film cast from the (a) **FPTTPA : C_{61}-PCBM** composite and (b) **PTPA : C_{61}-PCBM** composite.

the **FPTPA : PCBM** device led to the large enhancement in the power conversion efficiency.

Fig. 2b shows the IPCE curves based on the three devices. The shape of the curves is quite similar to the corresponding absorption spectra of three blend films (see ESI†), which indicates that the visible spectrum of the blend contributed to the power conversion efficiency.

The maximum quantum efficiency of the device based on the **FPTTPA : PCBM** blend reached 47% at 435 nm.

Fig. 3 shows AFM images of the blend films of **FPTTPA** and **PTPA** with **PCBM**. In the image of **FPTTPA : PCBM** blends, randomly distributed islands are connected to each other and demonstrate interpenetrating networks. In contrast, the **PTPA : PCBM** blend shows large segregation of each phase. The good photovoltaic performance obtained with **FPTTPA** as the donor should be ascribed to the synergistic effects of its enhanced absorption and good quality uniform film due to a planar configuration.

In summary, three types of novel perylene-based oligomers were synthesized and used as the electron donors in bulk heterojunction (BHJ) organic solar cells. The overall power conversion efficiency of the ITO/PEDOT : PSS/**FPTTPA : PCBM** (1 : 2 wt% ratio)/Al device is 1.42%. The high efficiency of the device is attributed to the improved light harvesting, balanced charge transport, and good morphology. These results provide a potential design strategy for developing novel electron donor oligomers or polymers with high photovoltaic performance through sophisticated structural modifications.

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