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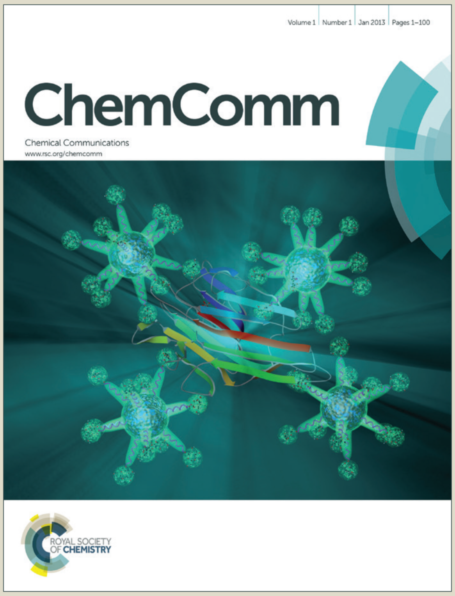

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ARTICLE TYPE

New conjugated molecular scaffold based on [2,2]paracyclophane as electron acceptors for organic photovoltaic cells

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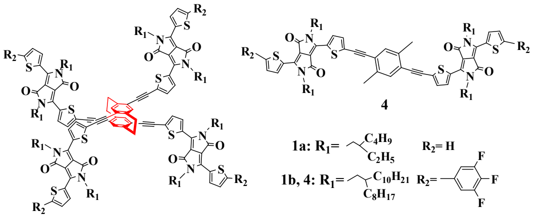
Two conjugated molecules with a [2,2]paracyclophane core were designed as non-fullerene electron acceptors for photovoltaic cells. Using P3HT as the donor, high power conversion efficiency (2.69%) is achieved for the blending thin film of 1b with P3HT, which is relatively high for solution-processed OPVs based on small molecular non-fullerene acceptors and P3HT as the electron donor.

Solution-processed bulk heterojunction organic photovoltaic cells (OPVs) that possess advantages such as low cost, light-weight and flexibility have received tremendous attentions in recent years.[1,2] The past decade has witnessed great progresses in this promising area; power conversion efficiency (PCE) of OPVs is over 9.0% for single layer devices,[2c] owing to the development of high-performance photovoltaic materials based on various small conjugated molecules and polymers as well as appropriate modification of interfacial structures.

Among these organic photovoltaic materials, fullerene-derivatives such as well-known **$PC_{61}BM$** and **$PC_{71}BM$** have played a dominant role as electron acceptors. This is particularly true for OPVs with high PCE. The merits of fullerene molecules including high electron affinity, high electron mobility and isotropic charge-transporting may explain their wide applications in OPVs.[3] However, fullerene molecules usually show weak absorptions in the visible region, and their preparation and purification are expensive. Moreover, HOMO/LUMO energies of fullerenes are not easily tuned to match the electron donors to maximize the open-circuit voltage (V_{OC}) and minimize the energy loss.[4] For this reason, non-fullerene acceptors, which absorb strongly in the visible region and can be easily functionalized to tune the energy levels, have been intensively pursued recently. A number of non-fullerene electron acceptors are designed and investigated for OPVs.[5-8] It is anticipated that these non-fullerene acceptors will provide more possibilities for the available electron donors (either conjugated small molecules or polymers) to form OPVs of high PCE by properly pairing electron donors and acceptors according to their energy levels and absorptions. To date, with **P3HT** as the donor, only a limited number of OPVs fabricated with non-fullerene small-molecule acceptors exhibit PCEs higher than 1.5%,[7] and fewer with PCEs higher than 2.5%.[8] Thus, there is plenty of room for further improvement.



Scheme 1. Chemical structures of compounds **1a, 1b** and **4**.

We herein report two conjugated molecules **1a** and **1b** (Scheme 1) entailing [2,2]paracyclophane framework as non-fullerene electron acceptors for OPVs. The molecular design rationale is based on the following considerations: i) [2,2] paracyclophane is known for the transannular through space pi-pi interaction.[9] Moreover, introduction of various functional groups to [2,2]paracyclophane framework can be achieved in different ways. In fact, [2,2]paracyclophane framework has been utilized for studying chromophore-chromophore interaction;[10] ii) Diketopyrrolopyrrole (DPP) as a dye stuff shows strong absorptions in the visible region, and its frontier energy levels can be finely tuned by incorporation of either donating or accepting moieties such as 3,4,5-triflurophenyl groups in **1b**;[11,12] iii) the [2,2]papacyclophane framework endows **1a** and **1b** with a cylindrical and rigid structure, and such molecular structure is expected to be beneficial for their dense packing and thus formation of molecular domains. The results reveal that both **1a** and **1b** can function as non-fullerene electron acceptors for OPVs after blending with **P3HT**, for which the PCE and V_{OC} can reach 2.05% and 1.06 V, 2.69% and 0.90 V, respectively, after thermal annealing.

The synthesis of compounds **1a**, **1b** is outlined in Scheme S1 (see ESI†). The chemical structures and purities of **1a** and **1b** were established and confirmed by spectroscopic data and elemental analysis. **1a** and **1b** show good solubilities in common organic solvents such as chloroform, tetrahydrofuran, toluene and *o*-DCB at room temperature. Thermogravimetric analysis (TGA) reveals that **1a** and **1b** are thermally stable below 350 °C (see Fig. S1).

In order to determine HOMO/LUMO energies of **1a** and **1b**, their cyclic voltammograms were measured as depicted in Fig. S2. **1a** exhibits three reversible oxidation waves and one reduction wave, while **1b** shows three reversible oxidation waves and one irreversible reduction wave. Based on the respective onset oxidation and reduction potentials, LUMO/HOMO energies of **1a** and **1b** were estimated to be -3.47 eV/-5.24 eV and -3.53 eV/-5.29 eV, respectively (see Table S1). Accordingly, bandgaps of **1a** and **1b** were calculated to be 1.77 eV and 1.76 eV, respectively. Obviously, LUMO level of **1b** is lower than that of **1a**. This is owing to the electron withdrawing effect of 3,4,5-triflurophenyl groups in **1b**. As shown in Fig. S2c, the respective HOMO and LUMO energy differences between both **1a**/**1b** and **P3HT** are large enough to guarantee efficient exciton dissociation. Judging from the energy levels, both **1a** and **1b** can be utilized as electron acceptor in OPVs. Moreover, the energy differences between the HOMO level of **P3HT** and the LUMO levels of **1a** or **1b** are higher than 1.2 eV, thus high open-circuit voltages (V_{OC}) are expected for OPVs with **1a** or **1b** as acceptors after combining with **P3HT**.

Fig. S3a depicts the absorption spectra of **1a** and **1b** in solutions and their thin films. The solutions of **1a** and **1b** absorb strongly at 598 nm with ε_{max}=196300 (extending to 650 nm) and at 631 nm with ε_{max}=154900 (extending to 700 nm), respectively. Compared to those in solutions, the absorption spectra of the thin-films of **1a** and **1b** are red-shifted. For instance, the absorption band at 598 nm in solution is shifted to 631 nm for the thin-film of **1a**. Such absorption spectral shifts are likely owing to the intermolecular pi-pi interactions within thin films. The absorption spectra of **1b** in both solution and thin film are red-shifted in comparison with those of **1a**. This is understandable by considering the presence of 3,4,5-triflurophenyl groups in **1b** which may elongate the conjugation length. Based on the respective onset absorptions of thin-films of **1a** and **1b**, the optical bandgaps of **1a** and **1b** were estimated to be 1.80 eV and 1.70 eV. These are in good agreement with those obtained based on their cyclic voltammetric data (see Table S1).

OPVs with the conventional ITO/PEDOT:PSS/active layer/Ca/Al structure were fabricated with the blending thin films of **1a** or **1b** with **P3HT** in different weight ratios. Fig. 1 depicts the respective *J-V* curves before and after thermal annealing. Table 1 lists V_{OC}, J_{SC}, FF and PCE of these OPVs with the respective blending thin films before and after thermal annealing. The pairing of **1a** with **P3HT** yielded OPVs with V_{OC} of 1.05-1.08 V, thanks to the large energy level difference between the HOMO of **P3HT** and LUMO of **1a**. Among the blending thin films, the one of **P3HT** with **1a** at weight ratio of 2:1 led to the best performance with V_{OC} = 1.07 V, J_{SC} = 2.71 mA cm^{-2}, FF =0.41 and PCE= 1.17%. After thermal annealing of the blending thin films at 150 °C for 10 min, J_{SC} increased to 4.18 mA cm^{-2} and FF was also slightly enhanced (see Table 1), thus leading to PCE of 2.05%. Similarly, the blending thin films of **P3HT** and **1b** gave the highest photovoltaic performance at weight ratio of 2:1 (see Table 1). The PCE was measured to be 1.60% for OPV with the thin films of **P3HT** and **1b** before thermal annealing; to our delight it increased to 2.69% because of the enhancement of J_{SC} (from 4.22 to 5.88 mA cm^{-2}), FF (from 0.46 to 0.51) and V_{OC} (from 0.82 V to 0.90 V) after thermal annealing of the photoactive thin film at 150 °C for 10 min.

For comparison, the reference molecule **4** (see Scheme 1) was synthesized (ESI) and its HOMO/LUMO energies were estimated to be -5.22 eV and -3.52 eV, being close to those of **1b**. OPVs with thin films of **P3HT**:**PC$_{61}$BM** and **P3HT**:**4** were also fabricated under the same conditions. After optimization, [13] the **P3HT**:**PC$_{61}$BM** blending thin film at weight ratio of 1:1 yielded PCE of 3.98%, whereas the **P3HT**:**4** at weight ratio of 1:1 led to poor photovoltaic performance with PCE of 0.90%. Thus, the OPV with **1b** as a non-fullerene acceptor can reach 68% of PCE of that with **P3HT**:**PC$_{61}$BM** as the active layer. By comparing the photovoltaic performance of the blending thin films of **P3HT** with **1b** or **1a** with that of **P3HT**:**4**, it can be concluded that the cylindrical scaffold structure of **1b** or **1a** is more favorable for better photovoltaic performance after blending with **P3HT**.[14] Notably, PCEs of 2.05% and 2.69% are relatively high for solution-processed OPVs based on small molecular non-fullerene acceptors in pairing with **P3HT** with the conventional OPV configuration. The relatively high PCE for the blending thin films of **P3HT**:**1b** is owing to the higher carrier mobilities in comparison with those of **P3HT**:**1a**.[15]

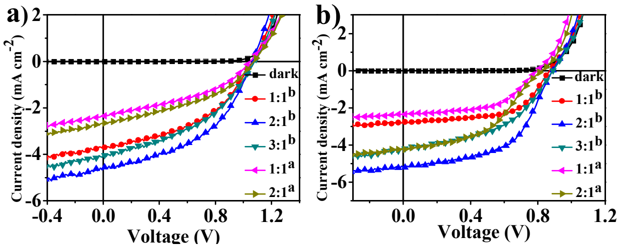


Fig. 1. *J-V* curves of OPVs based on **P3HT**:**1a** (a) and **P3HT**:**1b** (b) with different weight ratios under the illumination of AM 1.5G, 100 mW cm^{-2}.

Table 1. The device data of OPVs based on **P3HT**:**1a** and **P3HT**:**1b** as well as **P3HT**:**4** under the illumination of AM 1.5G, 100 mW cm^{-2}.

donor: acceptor	w/w	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	PCE [%]
P3HT:**1a**	1:1$^{a)}$	1.05	2.38	0.39	1.00
	2:1$^{a)}$	1.07	2.71	0.41	1.17
	1:1$^{b)}$	1.06	3.67	0.46	1.78
	2:1$^{b)}$	1.06	4.18	0.46	2.05
	3:1$^{b)}$	1.08	4.03	0.43	1.85
P3HT:**1b**	1:1$^{a)}$	0.80	2.43	0.52	1.03
	2:1$^{a)}$	0.82	4.22	0.46	1.60
	1:1$^{b)}$	0.87	2.79	0.58	1.42
	2:1$^{b)}$	0.90	5.88	0.51	2.69
	3:1$^{b)}$	0.89	4.26	0.47	1.76
P3HT:**4**	1:1$^{b)}$	0.97	1.91	0.48	0.90

$^{a)}$ Without thermal annealing; $^{b)}$ after thermal annealing at 150 °C for 10 min.

Fig. S4 shows the absorption spectra of the blending thin films of **P3HT**:**1a** and **P3HT**:**1b** at weight ratios of 2:1 and their IPCE (incident photon to converted current efficiency) spectra after thermal annealing. **P3HT**:**1a** thin film absorbs in the range of 300-700 nm with absorption maximum at 561 nm, whereas **P3HT**:**1b** thin film shows a broad absorption around 554 nm with shoulders at 601 nm and 666 nm. The absorption shoulders in IPCE spectra have similar profiles to the absorption peaks of the neat films of **1a** and **1b**, implying that **1a** and **1b** within the blending thin films make considerable contribution to IPCE and J_{SC}. As a whole, the IPCE spectra correspond well to the respective absorption spectra of **P3HT**:**1a** and **P3HT**:**1b** thin films. Relatively high IPCE was observed in the range of 350-500 nm with respect to the corresponding absorptions, in particular for the **P3HT**:**1b** blending thin film. **P3HT**:**1a** and **P3HT**:**1b** thin films exhibit maxima IPCEs of 27% (at 522 nm) and 33% (at 516 nm), respectively.[16]

The blending thin films of **P3HT**:**1a** and **P3HT**:**1b** at weight ratios of 2:1 were also investigated with XRD and AFM techniques. Fig. S5 shows the out-of-plane and in-plane XRD patterns before and after thermal annealing. In the out-of-plane patterns, XRD signals at 5.50^{o} and 10.85^{o} were detected for both blending thin films, and the intensity at 5.50^{o} was slightly enhanced after thermal annealing. Besides a weak diffraction peak around 5.20^{o} and a broad weak signal around 22^{o} (perhaps due to inter-chain pi-pi interactions) were observed in the in-plane XRD patterns. These XRD signals are probably owing to the formation of crystalline domains of **P3HT** within the blending thin films.[17]

The root-mean-square (rms) roughness of the **P3HT**:**1a** blend film decreases slightly from 3.13 nm to 3.01 nm before and after thermal annealing, whereas that of the **P3HT**:**1b** blend film decreases from 4.16 nm to 3.64 nm on the basis of height AFM images shown in Fig. S6. Thus, the **P3HT:1b** thin film becomes smoother after thermal annealing. The bright and dark domains in the phase AFM images are more clearly separated for the **P3HT:1b** thin film than those for the **P3HT:1a** thin film. Moreover, sizes of bright domains are varied from 40-90 nm to 25-60 nm for **P3HT:1a** thin film, whereas those of **P3HT:1b** thin film are reduced from 35-60 nm to 20-40 nm after thermal annealing. These AFM images are consistent with the observation that thermal annealing led to the improvement of PCEs for both thin films according to the previous studies.[7c]

In summary, two conjugated molecules **1a** and **1b** (Scheme 1) entailing [2,2]paracyclophane framework were designed and synthesized as non-fullerene electron acceptors for OPVs. Both **1a** and **1b** exhibit good solubility in common organic solvents and good thermal stability as well as high molar extinction coefficients. The HOMO/LUMO levels of **1a** and **1b** indicate that they can function as appropriate non-fullerene acceptors for OPVs. The blending thin film of **1b** with **P3HT** at weight ratio of 1:2 yielded the highest PCE (2.69%), whereas the thin film of **1a** with **P3HT** at weight ratio of 1:2 gave PCE of 2.05%. The relatively high PCE for the blending thin film of **P3HT**:**1b** is owing to the higher carrier mobilities in comparison with those of **P3HT**:**1a**. Notably, PCEs of 2.05% and 2.69% are relatively high for solution-processed OPVs based on small molecular non-fullerene acceptors and **P3HT** as the electron donor. These results demonstrate that new conjugated molecules can be constructed from [2,2]paracyclophane framework and such molecular scaffolds with appropriate electron accepting moieties are potential non-fullerene acceptors for OPVs.

Notes and references

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13. This included variation donor/acceptor weight ratios and thermal annealing. But, addition of additives led to no PCE improvement.
14. Other state-of-the-art high performance donor polymers or oligomers were also considered for blending with **1a** or **1b** for OPVs with high PCEs. Unfortunately, the corresponding HOMO/LUMO energy differences are too small to drive exciton dissociation as depicted in Fig. S7.
15. As shown in Table S2, the blending thin film of **P3HT**/**1b** exhibit higher hole and electron mobilities than **P3HT**/**1a** thin film, in particular after thermal annealing, and the ratio of μ_h/μ_e becomes lower after thermal annealing.
16. According to the IPCE spectra, the integral current densities for OPVs based on **P3HT**:**1a** and **P3HT**:**1b** thin films were calculated to be 3.88 mA cm^{-2} and 5.41 mA cm^{-2}, respectively. The difference between the integral current densities and the JSC data obtained from *J-V* curves is within 8%, indicating that the *J-V* measurements in this work are reliable.
17. Similar XRD patterns were reported for **P3HT**:**$PC_{61}BM$** thin film on PEDOT:PSS (see: S. Shao, J. Liu, J. Zhang, B. Zhang, Z. Xie, Y. Geng, L. Wang, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5704.). The appearance of *out-of-plane* diffractions at 5.50^{o} and 10.85^{o} as well as the weak in-plane one around 22^{o} may indicate that **P3HT** predominately adopts *edge-on* arrangement on the surface. However, the rather weak *in-plane* diffraction around 5.20^{o} implies the *face-on* packing for the small fraction of **P3HT**.