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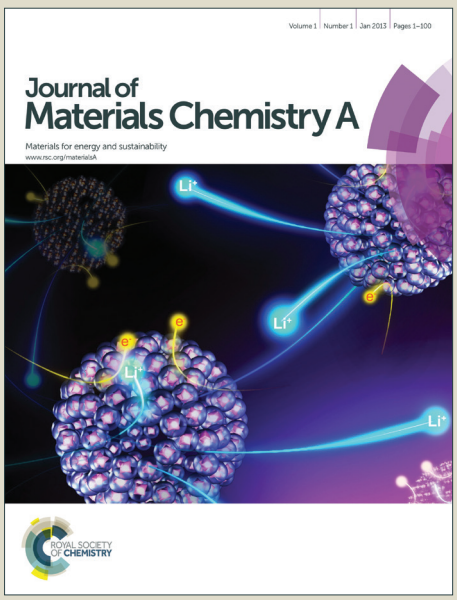

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ARTICLE TYPE

Molecular Engineering of Small Molecules Donor Materials Based on Phenoxazine Core Unit for Solution-Processed Organic Solar Cells

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A D–π–A type small molecule **POZ4** and a A–π–D–π–A type small molecule **POZ6**, in which phenoxazine was used as the central building block and dicyanovinyl was employed as the electron-withdrawing end-group, have been designed and synthesized. Compared with D–π–A type donor material **POZ4**, the donor material **POZ6** with A–π–D–π–A configuration shows much wider response to solar light. An efficiency of 5.60% was obtained for the **POZ6**:**PC71BM** based solar cells and the device fabricated with **POZ6**:**PC71BM** (1:1) shows a much better balanced hole and electron mobility of 2.24×10^{-4} $cm^2\cdot V^{-1}\cdot s^{-1}$ and 3.17×10^{-4} $cm^2\cdot V^{-1}\cdot s^{-1}$, respectively.

Introduction

With the rapid development of economy all over the world, energy demand increases a lot, and traditional fossil energy crisis is becoming serious. Thus, make full use of renewable energy becomes more necessary and important. Solar energy attracts wide attention due to the merits of abundant, clean and easy to use. As a powerful photovoltaic device, organic solar cells (OSCs) have attracted significant attention in the past few years due to light-weight, flexible and their potential for low cost.[1-3] According to the types of donor materials, the OSCs can be divided into polymer organic solar cells (P-OSCs) and small molecule organic solar cells (SM-OSCs). [2, 3] To data, the photoelectric conversion efficiency (PCE) of the solution-processed SM-OSCs has been improved to higher than 8%,[4-8] with a recent best PCE of 9.02%.[4] However, the efficiency needs to be further improved for future application. To achieve this goal, better material design is required and there is still much work needs to be done to optimize the energy levels and band gap of donor materials.

As reported, many high efficient small molecule donor materials used in SM-OSCs have linear conjugated structures, and the extension of conjugation can efficiently intensify and broaden the absorption spectra.[6-18] For conjugated small molecules with acceptor–π-bridge–donor–π-bridge–acceptor (A–π–D–π–A) and donor–π-bridge–acceptor (D–π–A) structure, many promising end-group acceptors have been reported, including dicyanovinyl,[18-23] alkyl cyanoacetate[7, 11, 16, 18] and 3-alkyl-rodanine[6-8] and so on. Recently, Chen et al. reported a series of A–π–D–π–A featured small molecules comprised of a 3-ethylrodanine end-group, yielding a certified PCE of 7.6%. [8] By employing 3-octylrodanine as the electron-withdrawing end-group, Liu et al. reported a similar small molecule **SMPV1**. [6] Applied to SM-OSCs, an efficiency of 8.1% was achieved. [6] Thus, promising and higher OSC performance for SM-OSCs can indeed be achieved through rational molecule design.

Phenoxazine (POZ) is a good conjugated heterocyclic compound with electron-rich oxygen and nitrogen heteroatoms. Due to the strong electron donating ability and facile structure modification, POZ have also been successfully utilized for the application of dye-sensitized solar cells (DSSCs). [24-28] Herein, by employing POZ as core unit and dicyanovinyl as the electron-withdrawing end-group, we developed a novel D–π–A type photon-active small molecule **POZ4** and a novel A–π–D–π–A type photon-active small molecule **POZ6** (molecular structures shown in Fig. 1). The photophysical and photochemical properties of these two donor materials are detailed studied. Applied to SM-OSCs, a morphology–performance relationship is discussed.

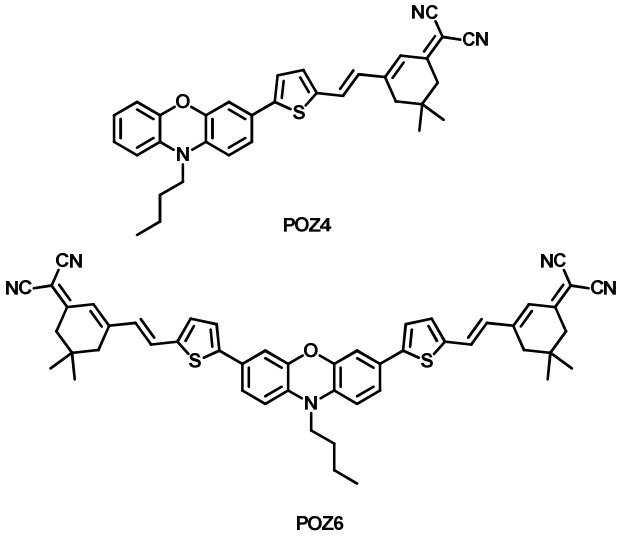

Fig. 1 The structures of small molecule donor materials

Results and Discussion

The detailed synthetic routes (see Fig. S1 and Fig. S2) and characterization of donor materials **POZ4** and **POZ6** are shown in supporting information.

Optical and Electronic Properties

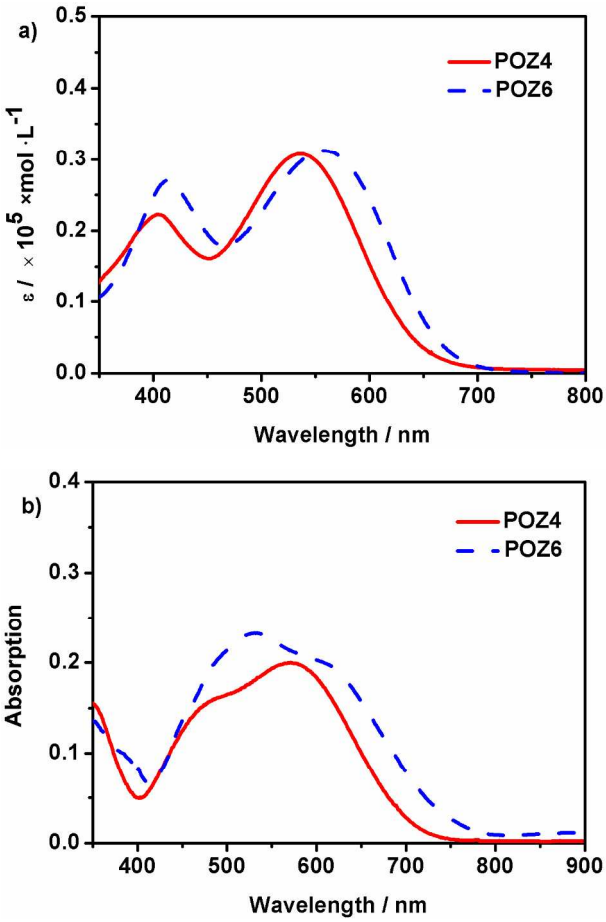

Fig. 2 Absorption spectra of **POZ4** and **POZ6** in chloroform and in solid film

POZ4 and **POZ6** are both dissolve well in chloroform and *o*-dichlorobenzene. Dissolve in chloroform, for D–π–A typed photon-active small molecule **POZ4**, two well-defined absorption peaks at 404 nm (ε = 2.23×10^4 M^{-1} cm^{-1}) and 535 nm (ε = 3.08×10^4 M^{-1} cm^{-1}) was detected, respectively. Compared to **POZ4**, A–π–D–π–A structured donor material **POZ6** displays similar peak shape while the absorption peaks slightly red-shift about 24 nm. Cast as thin films by spin coating, the spectra of these two donor materials are broadened. This is mainly due to effective solid-state packing between the molecule backbones. Determined from the absorption onsets in the film state, the optical band gaps (E_{0-0}) are approximately 1.72 eV and 1.65 eV for **POZ4** and **POZ6**, respectively. The E_{0-0} is efficiently reduced by constructing A–π–D–π–A structured donor material.

Cyclic voltammetry (CV) was employed to estimate the energy levels of **POZ4** and **POZ6**. The highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecylar orbital (LUMO) level of **POZ4** are –5.22 eV and –3.50 eV *vs.* vacuum level, respectively. Compared with **POZ4**, with the introduction of π-bridge (thiophene and isophorone) and electron-withdrawing end-group (dicyanovinyl) on the other side of POZ unit, the HOMO level and the LUMO level of **POZ6** negatively shift in different extent. The HOMO level locate at –5.31 eV, which negative shifts about 0.09 V and the LUMO level negative shift to –3.66 eV. The HOMO level of donor materials **POZ6** is lower and higher open circuit voltage (V_{oc}) can be expected when applied to SM-OSCs. The energy surplus between the LUMO levels of donor materials (–3.50 eV for **POZ4** and –3.66 eV for **POZ6**) and **PC71BM** (–4.0 eV) is around 0.50–0.34 eV (see Fig. 3), which shall be enough for exciton dissociation.

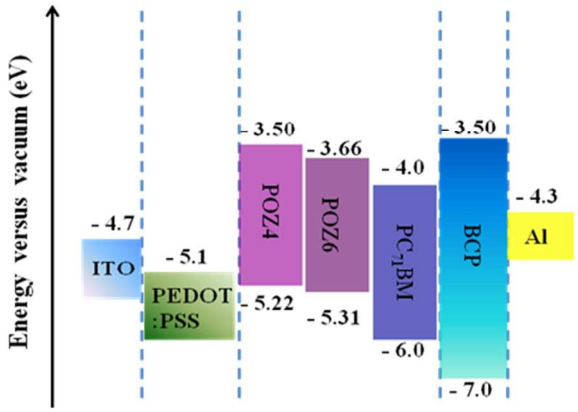

Fig. 3 Energy levels of **POZ4** and **POZ6** based single junction device

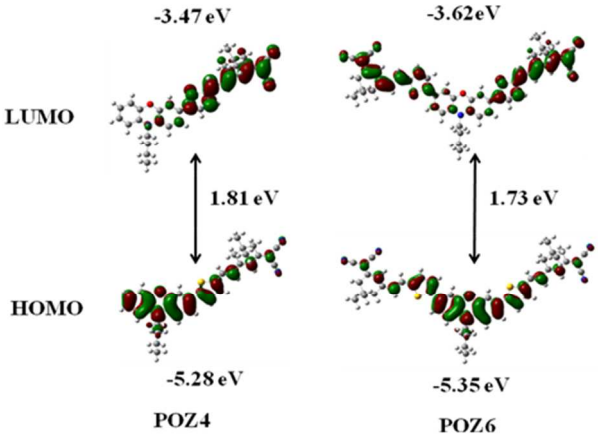

Fig. 4 HOMO and LUMO orbitals of **POZ4** and **POZ6**

In order to gain insight into the difference of the geometrical configuration and electron distribution of D–π–A typed small molecule **POZ4** and A–π–D–π–A typed small molecule **POZ6**, quantum chemical calculations based on density functional theory (DFT) method was performed employing Gaussian 09 software. From the calculate results (see Fig. 4) we can see that the A–π–D–π–A typed **POZ6** displays lower energy gap, with the HOMO level negative shifts 0.07 eV and LUMO level negative shifts 0.15 eV compared with that of **POZ4**. The calculated values of the HOMO and LUMO level for these two donors are consistent with experimental data considering the error. Both of these two donor materials can realize effective charge separation at HOMO and LUMO, which facilitates to the separation of strongly bound Frenkel excitons on donor-acceptor interface.

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Table 1 Optical and electrochemical data of donor materials **POZ4** and **POZ6**

donor material	λ_{max} solution / nm	ε / $M^{-1}\cdot cm^{-1}$	λ_{max} film / nm	$E_{0\text{-}0}$ / eV	HOMO / eV	LUMO / eV
POZ4	535	3.08×10^4	578	1.72	–5.22	–3.50
POZ6	559	3.14×10^4	615	1.65	–5.31	–3.66

Device Properties

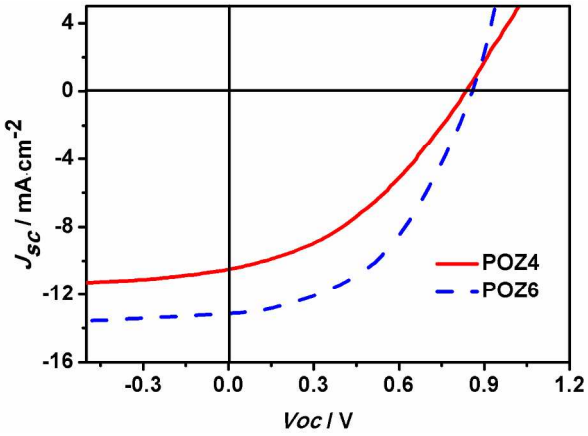

Fig. 5 *J*–*V* curves of solar cells with an active layer composed of **POZ4**:**PC71BM** (1:1.2, w/w) and **POZ6**:**PC71BM** (1:1.0, w/w)

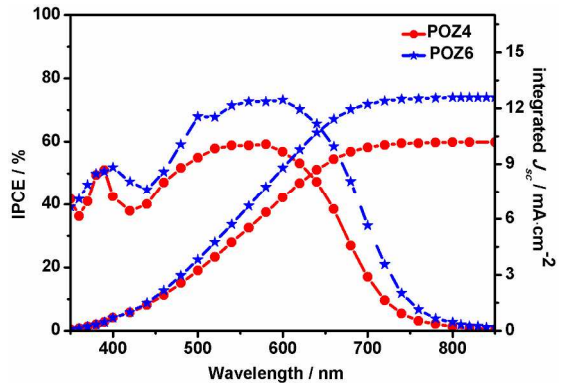

Fig. 6 EQE plots of solar cells with an active layer composed of **POZ4**:**PC71BM** (1:1.2, w/w) and **POZ6**:**PC71BM** (1:1.0, w/w)

SM-OSC devices based on these two small molecules were fabricated with a conventional structure of glass/ITO/PEDOT-PSS/active layer/BCP/LiF/Al and tested under the illumination of AM 1.5G, 100 mW·cm^{-2}. The detailed manufacturing processes are shown in supporting information. The current-voltage (*J*–*V*) curves are reported in Fig. 5, Fig. S3 and Fig. S4. The corresponding parameters are collected in Table 2, Table S1 and Table S2. With the optimized weight ratio (w/w) of **POZ4**:**PC71BM** at 1:1.2, the best but moderate PCE of 3.58% was obtained, with a short-circuit current (J_{sc}) of 10.5 mA·cm^{-2}, a V_{oc} of 0.847 V, and a fill factor (*FF*) of 40.3%. In contrast, the devices fabricated with **POZ6**:**PC71BM** (1:1.0, w/w) received much higher PCE of 5.60%, with a J_{sc} of 13.1 mA·cm^{-2}, a V_{oc} of 0.862 V and a *FF* of 49.6%. It is worth noting that for **POZ6** based devices, the V_{oc}, J_{sc} and *FF* are improved in different degree. The increase of V_{oc} can mainly attribute to the lower HOMO level of **POZ6**. The improvement of J_{sc} is maily due to better light absorption of **POZ6**. However, for all **POZ4** or **POZ6** based devices, the *FF* values are relatively low, which can mainly attributed to large resistance at open-circuit (R at V_{oc}, see Table S1 and Table S2).

The external quantum efficiencies (EQE) of the optimized devices are illustrated in Fig. 6. The **POZ6**:**PC71BM** (w/w, 1:1.0) SM-OSCs exhibit a broad and high photo response from 500 to 700 nm, with EQE value exceeding 70%. In comparison, the EQE values of the device fabricated with **POZ4**:**PC71BM** (w/w, 1:1.2) are much lower and response range is relatively narrower than that of the device based on **POZ6**:**PC71BM** (w/w, 1:1.0). According to the EQE spectra, the integral current densities are 10.2 mA·cm^{-2} and 12.6 mA·cm^{-2}, respectively (see Fig. 6), for **POZ4**:**PC71BM** (w/w, 1:1.2) and **POZ6**:**PC71BM** (w/w, 1:1.0) based devices, which is in good agreement with the measured photocurrent density, considering the error. These EQE spectra are consistent with the UV absorption and prove that the A–π–D–π–A typed donor material indeed can broaden the response range and improve the photoconversion efficiency.

Film Morphologies

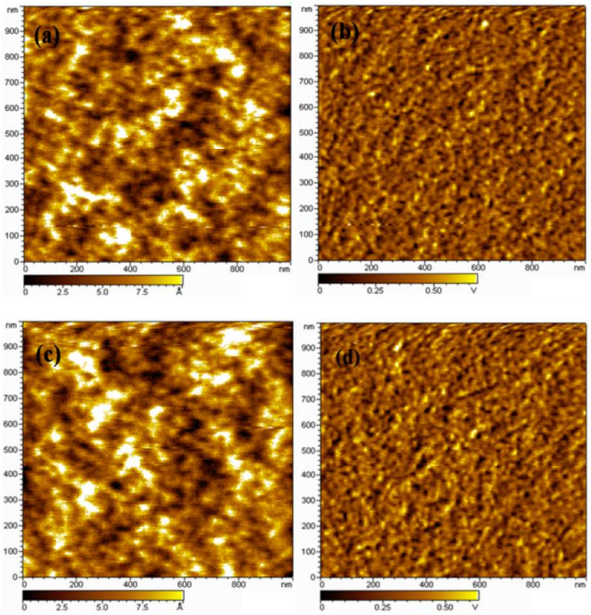

Fig. 7 Tapping-mode AFM images of the active layers: (a) height image of **POZ4**:**PC71BM** (1:1.2, w:w), (b) phase image of **POZ4**:**PC71BM** (1:1.2, w/w), (c) height image of **POZ6**:**PC71BM** (1:1, w:w), (d) phase image of **POZ6**/ **PC71BM** (1:1.2, w:w)

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Table 2 Device performance parameters for SM-OSCs based on **POZ4** and **POZ6**

Donor Material(P)	P:N(**PC71BM**)	J_{sc} / mA·cm^{-2}	Integrated J_{sc} / mA·cm^{-2}	V_{oc} / V	*FF* / %	η / %	R at V_{oc}
POZ4	1:1.2	10.5	10.2	0.847	40.3	3.58	97.6
POZ6	1:1.0	13.1	12.6	0.862	49.6	5.60	86.2

The morphology of the active layer has great effects on solar cell performance, thus atomic force microscopy (AFM) was employed to investigate the morphology of the blend films **POZ4**:**PC71BM** (1:1.2, w:w) and **POZ6**:**PC71BM** (1:1.0, w:w). As shown in Fig. 7, the AFM images of both two blend films exhibit a similar smooth surface without large aggregated domains. The interpenetrating network can be observed on the surface of the blend films of these small molecules and **PC71BM**, which should be beneficial to charge separation and transportation in the OSC devices. Compared with blend film **POZ4**:**PC71BM** (1:1.2, w/w), the root-mean-square (RMS) roughness of the **POZ6**:**PC71BM** blend film decreases slightly from 6.40 to 4.67 nm. The slight decreases of roughness of the blend film indicates that A–π–D–π–A typed small molecule led to more evenly distributed morphological features.

Hole and Electron Mobilities

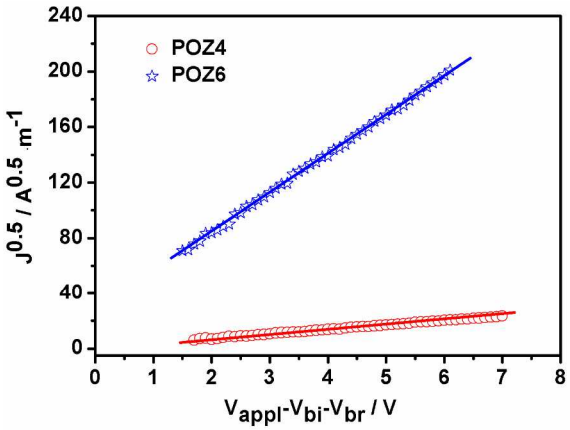

Fig. 8 $J^{0.5}$ *vs* V plots for the the hole-only diode fabricated from **POZ4**: **PC71BM** (w:w = 1:1.2) and **POZ6**: **PC71BM** (w:w = 1:1.0).The solid line is fits of the data points

The mobilities of the optimized blend of **POZ4**:**PC71BM** and **POZ6**:**PC71BM** were measured by the charge-only space charge limited current (SCLC) method. [15, 29, 30] The **POZ4**:**PC71BM** based device presents a hole and electron mobility of 2.36×10^{-5} cm$^2\cdot$V$^{-1}\cdot$s^{-1} and 3.17×10^{-4} cm$^2\cdot$V$^{-1}\cdot$s^{-1}, respectively. The device fabricated with **POZ6**:**PC71BM** shows a much better balanced hole and electron mobility of 2.24×10^{-4} cm$^2\cdot$V$^{-1}\cdot$s^{-1} and 3.17×10^{-4} cm$^2\cdot$V$^{-1}\cdot$s^{-1}, which is consistent with the better performance of devices. The test results indicate that an evener continuous interpenetrating network in the active film is formed with A–π–D–π–A typed small molecule donor materials, which is beneficial to the exciton separation and charge transport.

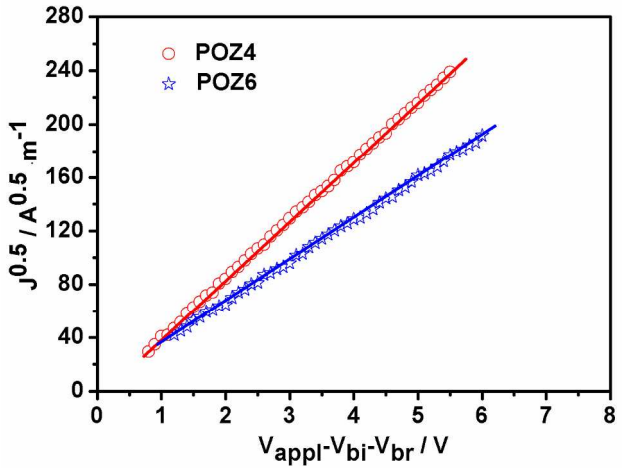

Fig. 9 $J^{0.5}$ *vs* V plots for the the electron-only diode fabricated from **POZ4**: **PC71BM** (w:w = 1:1.2) and **POZ6**: **PC71BM** (w:w = 1:1.0).The solid line is fits of the data points

Conclusions

In summary, by employing POZ as the central building block and dicyanovinyl as the electron-withdrawing end-group, a D–π–A type small molecule **POZ4** and a A–π–D–π–A type small molecule **POZ6** were designed and synthesized. The A–π–D–π–A configuration improves solar light absorption, and the SM-OSCs based on the A–π–D–π–A type small molecule **POZ6** exhibit much higher J_{sc} compared to that of the devices based on **POZ4**. An efficiency of 5.60% was obtained for the **POZ6**:**PC71BM** based solar cells. The device fabricated with **POZ6**:**PC71BM** shows a much better balanced hole and electron mobility. The results indicate that higher efficiency for SM-OSCs can be achieved through rational molecule design and the A–π–D–π–A configuration seems more promising.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of synthetic routes and characterization of donor materials, solar sell fabrication and measurement]. See DOI:10.1039/b000000x/

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