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Journal:	<i>ChemComm</i>
Manuscript ID:	CC-COM-05-2014-004020.R1
Article Type:	Communication
Date Submitted by the Author:	06-Jul-2014
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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/chemcomm

ARTICLE TYPE

High performance asymmetrical push-pull small molecules end-capped cyanophenyl with narrow band gap for solution-processed solar cells

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth -XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Two novel asymmetrical push-pull small molecules have been synthesized successfully, consisting of triphenylamine and diketopyrrolopyrrole as a fundamental dipolar D- π -A structure with ethynylbenzene as π -bridge. TPATDPPCNCN end-capped cyanophenyl exhibits a low optical band gap of 1.65 eV, and an impressive PCE of 5.94% has been achieved.

Solution-processed bulk heterojunction (BHJ) organic solar cells (OSCs) have experienced rapid development during the past two decades because they represent one of the most promising technologies for environmentally friendly solar energy conversion¹. So far, fullerene derivatives such as PC₆₁BM and PC₇₁BM have been widely used as representative *n*-type acceptor materials for BHJ OSCs². Much work has been done to develop novel *p*-type donors in order to maximize photovoltaic (PV) efficiency for commercialization. Nowadays small molecular donors (SMDs) have attracted considerable attention for preparing BHJ OSCs due to the advantages over their polymer counterparts, including well-defined molecular structure, easier purification and better batch-to-batch reproducibility³. To date, SMDs based BHJ single cells exhibit an encouraging power conversion efficiency (PCE) of 9.02%⁴, which is comparable with the best PCE of 9.2% in polymers⁵, making solution-processed SMDs-based OSCs a fast growing field. However, the overall performance of SMDs-based BHJ devices are still behind those of their polymer counterparts. Hence, solution-processed SMDs-based OSCs still require better material design toward 10-15% efficiency for future applications.

To design ideal SMDs, alternating electron-donating (D) and electron-accepting (A) units in the conjugated backbone are commonly applied to improve PV performance⁶, because such architecture can not only easily reduce the energy band gap (*E_g*), but also effectively control the PV properties of materials. In general, the molecular configurations of most SMDs can be classified into two main categories: symmetrical D-A-D and A-D-A systems. In contrast, the solution-processed asymmetric dipolar D-A or D-A-A systems are relatively less explored, and their PV performance far lags behind those of symmetrical SMDs-based OSCs⁷. From the study of dye-sensitized solar cells, we learned that excellent organic dyes with D-A molecular architectures exhibited remarkably high PCEs over 10%⁸. In addition, important progress has been made on vacuum-deposited SMDs-based OSCs with a PCE of 6.8%⁹. Consequently, we

believe that these asymmetrical push-pull small molecules possess attractive potential for BHJ OSCs. However, such type of molecules generally suffers from insufficient light-absorption range, which may be one of the main impediments to further improvement of their performance¹⁰. Therefore, it is highly desired to design new asymmetrical push-pull small molecules with narrow *E_g* for BHJ OSCs.

In this communication, two new asymmetrical push-pull small molecules TPATDPP and TPATDPPCNCN have been designed and synthesized, consisting of triphenylamine (TPA) and diketopyrrolopyrrole (DPP) as a fundamental dipolar D- π -A structure with ethynylbenzene as π -linkage, as shown in Fig. 1(a). In these molecules, TPA unit behaves as D building block due to its good hole-transporting capability and excellent electron-donating property¹¹. On the other hand, DPP has been regarded as a promising A group owing to its prominent electron-deficient property and strong light-harvesting capacity, as well as excellent photochemical stability¹². Moreover, ethynylbenzene-linkage could not only improve the molecular planarity but also facilitate the intramolecular charge transfer (ICT) process because of the coplanar and rigid nature of C \equiv C¹³. In order to further extend the spectral regions, cyano-group was introduced into the molecule as A unit, which could effectively reduce *E_g*¹⁴. Accordingly, an asymmetrical D-A-A-type TPATDPPCNCN end-capped with cyanophenyl (CP) was synthesized and studied, resulting a low optical *E_g* of 1.65 eV in film. Finally, their PV properties were investigated using simple spin-coating device. Among them, TPATDPPCNCN-based device showed an impressive PCE of 5.94%, which is the highest efficiency reported to date for solution-processed D-A-A-type small molecule OSCs. The result indicates the great potential of such asymmetrical push-pull SMDs in creating high performance for solution-processed OSCs.

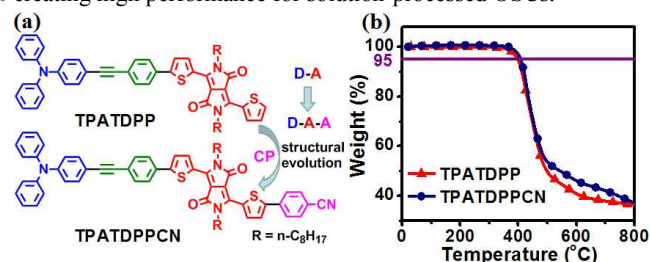
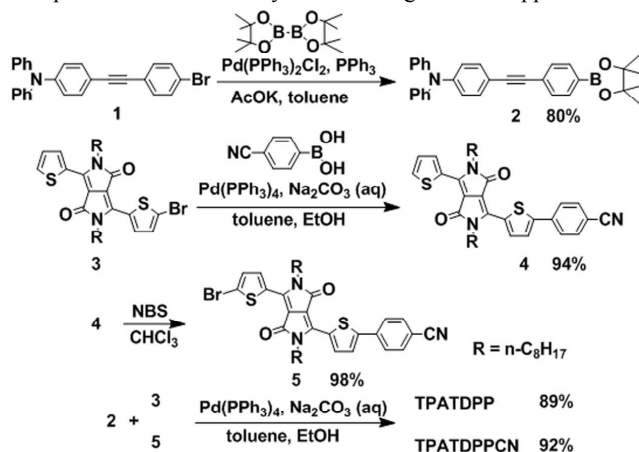


Fig. 1 Molecular structures (a) and TGA plots at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere (b) of TPATDPP and TPATDPPCNCN.

The synthesis of **TPATDPP** and **TPATDPPCN** is described in Scheme 1. Starting from TPA, compound **1** was obtained by Pd-catalyzed Sonogashira reaction^{11b, 12c, 15}. By Miyaura borylation of compound **1** using Pd(PPh₃)₂Cl₂ as catalyst, borate ester **2** was obtained in a yield of 80%. Compound **4** was prepared by Suzuki coupling of bromide **3** in a high yield of 94%. Bromide **5** was obtained by the NBS bromination of **4** in a mild condition with a high yield of 98%. Finally, **TPATDPP** and **TPATDPPCN** were facily synthesized by Pd-assisted Suzuki coupling in high yields of 89% and 92%, respectively. Detailed synthetic procedures and characterization are given in ESI.† Their thermal stability was studied by thermogravimetric-analysis (TGA, see Fig. 1(b)). The onset decomposition temperatures of them with 5% weight-loss are 397 °C and 408 °C, respectively, which demonstrate the exceptional thermal stability for their long-term PV applications.



Scheme 1 Synthetic route for **TPATDPP** and **TPATDPPCN**.

The density functional theory (DFT) calculations were carried out to preliminarily investigate the influence of molecular structure on their electronic property (calculation method is given in ESI.†). The calculated energy levels and electronic-density distribution are shown in Fig. 2(a). The electronic density of the highest occupied molecular orbital (HOMO) are distributed on the entire molecules whereas that of the lowest unoccupied molecular orbital (LUMO) are located on A units, showing an apparent ICT process existed in the push-pull molecules. In addition, both HOMO and LUMO of **TPATDPPCN** are lower than those of **TPATDPP**, which are attributed to the introduction of CP unit. Moreover, the end-capped CP provoked a greater decrease of LUMO, resulting in a large decrease of E_g from 2.22 eV of **TPATDPP** to 2.04 eV of **TPATDPPCN**.

The UV-vis absorption spectra of two SMDs in chloroform and in thin film are depicted in Fig. 2(b), and the corresponding optical data are summarized in Table 1. Both molecules exhibit a strong absorption in the long-wavelength region due to the ICT transition. It is worth mentioning that **TPATDPPCN** exhibits higher molar extinction coefficient (ϵ) than those of **TPATDPP** (see Fig. S10 in ESI.†). The solution of **TPATDPP** shows an absorption peak at 582 nm, and the spectrum of its film is broadened and red-shifted by 37 nm due to solid-state packing. In comparison with **TPATDPP**, both spectra of **TPATDPPCN** in solution and in film are greatly broadened and red-shifted to 614 and 671 nm, respectively, probably due to the stronger ICT transition and the stronger intermolecular interaction in solid-

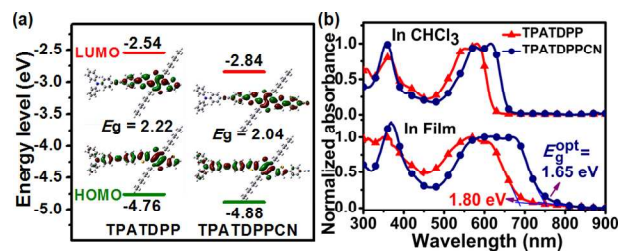


Fig. 2 (a) Theoretically calculated energy levels and electronic-density distribution; (b) Normalized UV-vis absorption spectra of **TPATDPP** and **TPATDPPCN** in CHCl₃ and in thin film.

state. As a result, the optical E_g of **TPATDPP** and **TPATDPPCN** corresponding to their absorption onsets are 1.80 eV and 1.65 eV, respectively.

The cyclic voltammogram (CV) measurements in dichloromethane were carried out to evaluate approximately the energy levels of the two molecules^{12c, 16}. The CV curves are shown in Fig. 3(a), and the pertinent electrochemical data are summarized in Table 1 (experimental details and calculation are given in ESI.†). **TPATDPP** exhibits the onset reduction potential at -1.37 V, corresponding to the reduction of the DPP fragment. On the other hand, two reduction waves are observed in the cathodic potential regime for **TPATDPPCN**. The first onset reduction potential at -1.27 V can be ascribed to the reduction of DPP fragment and the second one is assigned to the reduction of CP group. In contrast to the reduction behaviors, the oxidation potentials of the two molecules are relatively insensitive, and the first onset oxidation potentials are observed at 0.53 V and 0.50 V for **TPATDPP** and **TPATDPPCN**, respectively, corresponding to oxidation of the TPA. As a result, less-negative reduction potential and slightly less-positive oxidation potential of **TPATDPPCN** relative to **TPATDPP** can be rationally ascribed to the presence of the electron-withdrawing CP block, resulting in a relatively lower E_g of 1.77 eV. The energy level diagram of the components for PV device is schematically depicted in Fig. 3(b). Both **TPATDPP** and **TPATDPPCN** in principle can behave as donors in BHJ OSCs, and the fairly low-lying HOMO would ensure relatively large open-circuit voltage (V_{oc}). Notably, the narrow E_g of **TPATDPPCN** would result an increased short-circuit current density (J_{sc}).

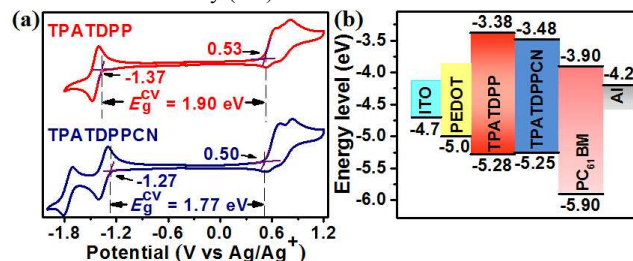


Fig. 3 (a) CV curves of compounds in 0.1 M Nbu₄BF₄/CH₂Cl₂ at a scan rate of 100 mV s⁻¹; (b) Energy levels of the components for PV device.

To investigate the PV properties of two SMDs, BHJ devices based on SMDs:PC₆₁BM active layer with area of 0.05 cm² were fabricated and characterized. The related current density-voltage (J - V) curves of the devices are described in Fig. 4(a) and the PV parameters are summarized in Table 1. The device based on **TPATDPP** with a lower HOMO level gave a relatively higher V_{oc} of 0.97 V, a J_{sc} of 7.07 mA cm⁻², a fill factor (FF) of 0.30

Table 1 Photophysical, electrochemical, hole mobility and PV performance data of **TPATDPP** and **TPATDPPCN**

Compound	$\lambda_{\max}^{\text{sol}}$ nm	$\lambda_{\max}^{\text{film}}$ nm	E_g^{opt} eV	HOMO ^{CV} eV	LUMO ^{CV} eV	E_g^{CV} eV	μ_h cm ² V ⁻¹ s ⁻¹	R_s Ω cm ²	R_{sh} Ω cm ²	V_{oc} V	J_{sc} mA cm ⁻²	FF	PCE %
TPATDPP	582	619	1.80	-5.28	-3.38	1.90	7.49×10^{-5}	56.00	156	0.97	7.07	0.30	2.06
TPATDPPCN	614	671	1.65	-5.25	-3.48	1.77	1.51×10^{-4}	11.40	251	0.93	14.86	0.43	5.94

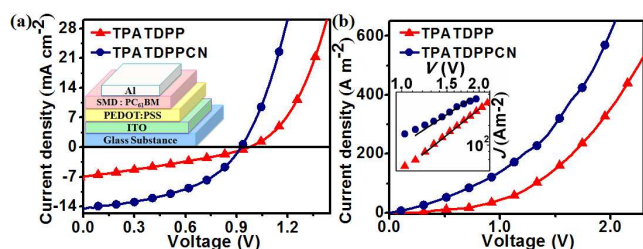


Fig. 4 (a) J - V curves of BHI devices with a configuration of ITO/PEDOT:PSS/SMDs:PC₆₁BM/Al under an illumination of AM 1.5G at 100 mW cm⁻². Inset: device structure; (b) J - V curves of the hole-only devices with a structure of ITO/PEDOT:PSS/SMDs:PC₆₁BM/Au in the dark. Inset: the J - V curves in a double logarithmic scale and the solid lines are fits of the data points to a SCLC model.

and a PCE of 2.06%. Remarkably, **TPATDPPCN** based device exhibits higher performance, with a V_{oc} of 0.93 V, a J_{sc} of 14.86 mA cm⁻², a FF of 0.43 and a PCE of 5.94%, in agreement with its higher photon-to-current responses (see Fig. S11 in ESI†). The high PV performance of **TPATDPPCN**-based device can be attributed to both the narrow E_g induced by CP group and the better carrier transporting capacity as evidenced by hole mobility (μ_h) measurement. Moreover, **TPATDPPCN** shows the stronger intermolecular interaction as evidenced by more red-shifted absorption in film, contributing to its carrier transporting property. Bearing in mind that the charge mobility of active layer might be closely related to the charge stability, and the film morphology as well as the intermolecular interaction. In order to investigate the μ_h of the synthesized SMDs, J - V characteristics of the hole-only devices were measured in the dark (details are given in ESI†), as depicted in Fig. 4(b). By fitting the J - V curves in a space-charge-limited currents (SCLC) model, as shown in inset of Fig. 4(b), the μ_h can be derived. The μ_h values of **TPATDPP** and **TPATDPPCN** are 7.49×10^{-5} and 1.51×10^{-4} cm² V⁻¹ s⁻¹, respectively, and the data are summarized in Table 1. It is interesting to note that **TPATDPPCN** exhibits about 2 times higher μ_h than those of **TPATDPP**, which is consistent with its high PV performance. Further experimental proofs of better PV performance for **TPATDPPCN** are supported by its higher crystallinity (XRD patterns in Fig. S12) and its better bicontinuous interpenetrating network (AFM images in Fig. S13). In addition, the resistance change are shown in Table 1. In contrast, the optimized D-A-A-typed **TPATDPPCN** reduces the series resistance (R_s) from 56 Ω cm² to 11.40 Ω cm² and increases the shunt resistance (R_{sh}) from 156 Ω cm² to 251 Ω cm², which leads to the increase of FF, J_{sc} and PCE. Further experiments on device optimization are underway in our laboratory.

In conclusion, two novel asymmetrical push-pull SMDs, **TPATDPP** and **TPATDPPCN**, have been synthesized and applied in the investigation of solution-processed BHI OSCs. The dipolar D-A-A structural design end-capped with CP unit enables **TPATDPPCN** to exhibit a narrow E_g , resulting in a high J_{sc} of

14.86 mA cm⁻² with a high PCE of 5.94%. The efficiency is among the highest ever reported for solution-processed D-A-A-type small-molecule-based BHI OSCs. The high performance is primarily attributed to the narrow E_g and the reasonably low-lying HOMO level as well as the high hole-mobility. The results gave an important guide for developing novel asymmetrical push-pull small molecule PV materials.

This work was supported by the NSFC (No. 21102013, 51173065), the Dalian Committee of Science and Technology (2011J21DW001), the SRF for ROCS-SEM (No. 201001438, 201001439), the Fundamental Funds for the Central Universities (DUT11LK20) and the RFDP (No. 20090041120017).

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Electronic Supplementary Information (ESI) available: measurement, characterization and calculation, synthesis and characterization, as well as PV device fabrication and hole-mobility measurement details. See DOI: 10.1039/b000000x/