Cite this: J. Mater. Chem., 2011, 21, 3768

PAPER

Triphenylamine-containing D–A–D molecules with (dicyanomethylene)pyran as an acceptor unit for bulk-heterojunction organic solar cells

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Received 12th October 2010, Accepted 22nd December 2010 DOI: 10.1039/c0jm03425h

Two new triphenylamine (TPA)-containing D–A–D molecules with TPA as the donor unit (D), (dicyanomethylene)pyran (PM) as the acceptor unit (A) and thienylenevinylene (TV) or 4-hexylthienylenevinylene (HTV) as the conjugated pi-bridge, TPA–TV–PM and TPA–HTV–PM, have been designed and synthesized for solution-processable organic solar cells (OSCs). The optical and electrochemical properties of these linear molecules were studied. The compounds exhibit broad absorption in the visible region with lower HOMO energy levels, which are desirable for application as a donor in organic solar cells. The OSC devices were fabricated by spin-coating the blend solution of the molecules as the donor and $PC_{70}BM$ as the acceptor (1 : 3, w/w). The power conversion efficiency of the OSCs based on TPA–TV–PM and TPA–HTV–PM reached 2.06% and 2.10%, respectively, under the illumination of AM.1.5, 100 mW cm⁻².

Introduction

In recent years, there has been a great deal of research on polymer solar cells (PSCs) composed of a polymer donor and a fullerene acceptor, for their advantages of low cost fabrication by a solution-processing method, flexibility of the photoactive layer and the abundant availability of the conjugated donor materials. Many efforts have been devoted to the design and synthesis of new conjugated polymer donor and fullerenederivative acceptor materials.¹⁻⁹ To date, the power conversion efficiency of the PSCs has reached over 7%,^{3,5} but the polymer materials always suffer from broad molecular weight distributions, difficult purification and batch-to-batch variations. There is still a long way to go before approaching commercial application.

In a parallel effort, organic solar cells (OSCs) based on small molecules with vacuum-evaporating multilayer structures have reached a power conversion efficiency of 5-6%.¹⁰⁻¹² It is remarkable that these small molecules have well-defined molecular structures, definite molecular weights without any distribution and high purity with easy purification methods like column chromatography or sublimation. However, fabrication of OSCs by vacuum evaporation is much more difficult and expensive than that of the polymer solar cells by a solution-processed method.

Compared with the polymers and the vacuum-deposited organic small molecules, solution-processable organic small molecules have attracted much interest recently as photovoltaic donor materials in organic solar cells^{13–26} because they combine the advantages of high purity, definite molecular weight of the organic small molecules and the low-cost solution processing of the polymers. The power conversion efficiencies (PCEs) of the OSCs based on the solution-processable organic molecules have reached 2-4%.^{18–20,25,26} However, the efficiencies are still lower than that of either the vacuum-evaporated OSCs or the solutionprocessable PSCs. So there is a lot of room for the further design and synthesis of high efficiency solution-processable organic photovoltaic materials.

Our group has synthesized a series of solution-processable triphenylamine (TPA)-containing organic molecules for application as donor materials in OSCs.²¹⁻²⁶ The donor materials include the star-shaped D-A molecules with TPA as the core and donor unit and benzothiadiazole (BT) as the acceptor unit,^{21,24-26} and the D-A-D molecules with TPA as the donor unit, (dicyanomethylene)pyran (or 2-pyran-4-ylidenemalononitrile) (PM) as the acceptor unit and styrene as the conjugated pi-bridge.^{22,23} The TPA- and PM-containing molecules (such as TPA-DCM-TPA,²² see Scheme 1) exhibit broad absorption and suitable HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) energy levels. The OSCs based on them as the donor showed a higher open circuit voltage (V_{oc}) but unsatisfactory power conversion efficiencies (PCE) due to a lower short circuit current density (J_{sc}) and smaller fill factor (FF). In fact, the styrene linkage in the molecules negatively influenced the charge transfer properties and solubility of the molecules,23,27 which could result in the lower PCE of the molecules. Roncali and co-workers used a thienvlenevinylene (TV) unit in the TPA-containing organic molecules to improve their photovoltaic performance.¹³ In order to improve

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Scheme 1 The chemical structures of TPA–DCM–TPA, TPA–TV–PM and TPA–HTV–PM.

the photovoltaic properties of the TPA- and PM-containing molecules, we designed and synthesized two new solutionprocessable TPA- and PM-containing organic molecules TPA-TV-PM and TPA-HTV-PM (Scheme 1). We changed the styrene to thienylenevinylene (TV) and 4-hexyl-thienylenevinylene (HTV) linkages in TPA-TV-PM and TPA-HTV-PM, respectively, to obtain better solubility, charge transporting and film-forming properties. The hexyl groups in TPA-HTV-PM are for further improving the solubility and film-forming properties of the molecule. The two compounds show good solubility in common organic solvents, broad absorption from 350 nm to 650 nm and lower HOMO energy levels of ca. -5.15 eV. The OSC devices based on the compounds as the donor and PC₇₀BM as the acceptor (1:3, w/w) demonstrate a PCE higher than 2%, under the illumination of AM.1.5, 100 mW cm⁻², which is significantly improved in comparison with a PCE of 1.40% for the OSCs based on TPA-DCM-TPA : PC70BM under the same experimental conditions.

Experimental section

Materials

2,6-Dimethyl-4-pyrone, 2-bromo-3-hexyl-thiophene, 5-bromo-2thiophenecarboxaldehyde, *n*-butyllithium (2.50 mol L^{-1} in hexane), pyridine, tetrabutylammonium bromide, sodium acetate, palladium acetate, acetic anhydride, acetonitrile and DMF were obtained from Acros Organics. Tetrahydrofuran (THF) was dried over Na/benzophenoneketyl and freshly distilled prior to use. Other chemicals were common commercial grade and were used as received.

Measurements

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. MALDI-TOF spectra were recorded on a Bruker BIFLEXIII. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The organic molecule films on quartz used for absorption spectral measurements were prepared by spin-coating their chloroform solutions. The electrochemical cyclic voltammogram was obtained using a Zahner IM6e electrochemical workstation in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. A Pt electrode coated with the sample film was used as the working electrode; a Pt wire and Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) were used as the counter and reference electrodes, respectively.

Fabrication and characterization of organic solar cells

Organic solar cells (OSCs) were fabricated in the traditional sandwich structure with an ITO positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of *ca.* 10 Ω sg⁻¹ was purchased from CSG Holding Co., Ltd (China). The ITO glass was cleaned in an ultrasonic bath of acetone and isopropanol, and treated by UVO (ultraviolet ozone cleaner, Jelight Company, USA). Then a thin layer (30 nm thickness) of PEDOT : PSS (poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)) (Baytron PVP A1 4083, Germany) was spin-coated on the ITO glass and baked at 150 °C for 30 min. Subsequently, the photosensitive layer was prepared by spin-coating the blend chlorobenzene solution of TPA-TV-PM : $PC_{70}BM(1:3 \text{ w/w})$ or TPA-HTV-PM : $PC_{70}BM$ (1 : 3 w/w) on the top of the PEDOT : PSS layer and baked at 80 °C for 30 min. Thickness of the active layer is ca. 60 nm measured by an Ambios Tech. XP-2 profilometer. Finally, a metal electrode layer of Al (ca. 120 nm) was vacuum evaporated on the photoactive layer under a shadow mask in a vacuum of ca. 10^{-4} Pa. The effective area of one cell is 4 mm^2 . The current–voltage (*I–V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp coupled with A.M.1.5 solar spectrum filters was used as the light source, and the optical power at the sample was *ca*. 100 mW cm⁻².

Synthesis

The synthesis routes to TPA–TV–PM and TPA–HTV–PM are shown in Scheme 2. The detailed synthetic processes are as follows.

2-Bromo-5-formyl-3-hexylthiophene (1). Lithium diisopropylamide (22 ml, 2.0 M in hexane, 44 mmol) was added dropwise to a stirred solution of 2-bromo-3-hexyl-thiophene (10 g, 40 mmol) in dry THF (100 ml), under argon at -78 °C. The reaction mixture was maintained under this condition for a further 2 h before DMF (3.39 ml, 44 mmol) was added dropwise. The mixture was stirred at room temperature for 12 h and quenched with hydrochloric acid (3%, 10 ml). The product was extracted into dichloromethane $(3 \times 150 \text{ ml})$ and the combined organic extracts were washed with brine and dried by anhydrous magnesium sulfate. The crude product was purified by column chromatography (petroleum ether (bp: 60-90 °C)/dichloromethane, 10:1) to afford 2-bromo-5-formyl-3-hexylthiophene (1) as yellow liquid. Yield 7.8 g (70%). MS: m/z = 274 (M⁺). ¹H NMR (CDCl₃, 400 MHz) δ/ppm: 9.75 (s, 1H), 7.46 (s, 1H), 2.62 (t, 2H), 1.61 (m, 2H), 1.36 (m, 6H), 0.85 (t, 3H).



Scheme 2 Synthesis routes to the compounds: (I) CNCH₂CN, acetic anhydride, N₂, reflux at 140 °C for 24 h; (II) and (III) CH₃CH₂CN, piperidine, N₂, reflux at 80 °C for 24 h; (IV) POCl₃, DMF, N₂, 45 °C for 2 h; (V) MePh₃PBr, *n*-butyllithium, THF, N₂, -78 °C; (VI) Pd(OAc)₂, NaOAc, *n*-Bu₄NBr, DMF, N₂, 100 °C for 24 h.

2-(2,6-Bis(2-(4-bromothienyl)vinyl)pyran-4-ylidene)-malononi-

trile (2). A mixture of 2-(2,6-dimethylpyran-4-ylidene)-malononitrile (2.44 g, 14 mmol), 5-bromo-2-thiophenecarboxaldehyde (5.8 g, 30.5 mmol), piperidine (2 ml) and freshly distilled acetonitrile (60 ml) were refluxed at 80 °C under argon for 24 h. After cooling the reaction mixture to room temperature, the dark red precipitate was purified by recrystallization from methanol to get compound **2** as a brown solid. Yield 6.7 g (84.8%). MS: m/z = 516 (M⁺). ¹H NMR (CDCl₃, 400 MHz) δ /ppm: 7.44 (q, 2H), 7.09 (d, 2H), 7.06 (s, 2H), 6.92 (d, 2H), 6.41 (q, 2H).

2-(2,6-Bis(2-(4-bromo-3-hexylthienyl)vinyl)pyran-4-ylidene)-

malononitrile (3). 2-(2,6-dimethylpyran-4-ylidene)-malononitrile (2.44 g, 14 mmol), compound **1** (7.8 g, 28.4 mmol), piperidine (2 ml) and freshly distilled acetonitrile (28.4 ml) were mixed under argon and refluxed at 80 °C under argon for 24 h. The reaction mixture was cooled to room temperature, dissolved in dichloromethane, washed with brine, and dried by anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (petroleum/dichloromethane, 5 : 1) to produce compound **3** as a red solid. Yield 5 g (55.56%). MALDI-TOF MS: 686.6, calcd for $C_{32}H_{34}Br_2N_2OS_2$ 686.56. ¹H NMR (CDCl₃, 400 MHz) δ /ppm: 7.41 (d, 2H), 7.00 (s, 2H), 6.61 (s, 2H), 6.40 (d, 2H), 2.56 (t, 4H), 1.6 (t, 4H), 1.33 (m, 12H), 0.90 (t, 6H).

4-Formyltriphenylamine (4). Phosphorus oxychloride (14.7 ml) was added dropwise into a stirred solution of triphenylamine (5 g, 20 mmol) in DMF (4 ml), under argon at 0 °C. Then, the reaction mixture was stirred at 45 °C for 2 h, poured into ice water, and neutralized with sodium hydroxide (2 M). The crude product was filtered and recrystallized from ethyl acetate to afford 4-formyltriphenylamine (4) as the white solid. Yield 3 g (54%). MS: m/z = 273 (M⁺). ¹H NMR (CDCl₃, 400 MHz) δ /ppm: 9.80 (s, 1H), 7.68 (d, 2H), 7.34 (m, 4H), 7.17 (m, 6H), 6.90 (d, 2H).

N,*N*-diphenyl-*N*-(4-vinylphenyl)amine (5). To a solution of methyltriphenylphosphonium bromide (7.19 g, 20 mmol) in dry THF (250 ml) under argon at -78 °C was added *n*-butyllithium (8 ml, 2.5 M, 20 mmol) by syringe. The mixture was warmed to room temperature slowly. Compound **4** (5 g, 18 mmol) in dry THF (50 ml) was added dropwise to the mixture and the resultant mixture was kept at room temperature for 12 h. The mixture was poured into water and extracted into dichloromethane (3 × 150 ml). The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (hexane) to get compound **5** as a white solid. Yield 4.33 g (87%). MS: m/z = 271 (M⁺). ¹H NMR (CDCl₃, 400 MHz) δ /ppm: 7.25 (m, 6H), 7.08 (d, 4H), 6.99 (d, 4H), 6.67 (q, 1H), 5.62 (d, 1H), 5.14 (d, 1H).

TPA-TV-PM. A mixture of compound 2 (1 g, 1.9 mmol), 5 (1.13 g, 4.18 mmol), palladium (II) acetate (15 mg), tetra-nbutylammonium bromide (198 mg, 0.6 mmol), and anhydrous sodium acetate (3.2 g, 38 mmol) were dissolved and kept in degassed anhydrous DMF (30 ml) under argon at 100 °C for 24 h. The mixture was poured into water (30 ml). The precipitate was filtered, washed with water, dissolved in dichloromethane and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (petroleum/dichloromethane, 1:1) to get TPA-TV-PM. Yield 500 mg (29%). MALDI-TOF MS: 898.5, Calcd for C₆₀H₄₂N₄OS₂ 899.13. ¹H NMR (CDCl₃, 400 MHz) δ/ppm: 7.36 (d, 4H), 7.29 (m, 18H), 7.21 (s, 2H), 7.13 (d, 10H), 7.06 (d, 4H), 7.00 (d, 2H), 6.79 (d, 2H).¹³C NMR (CDCl₃, 400 MHz): δ/ppm 158.04, 148.18, 147.28, 140.14, 138.20, 132.14, 130.78, 130.52, 130.00, 129.39, 129.04, 128.48, 128.23, 127.63, 126.81, 125.30, 124.88, 123.48, 122.92, 119.18, 117.54, 116.68, 115.43, 106.74, 58.49.

TPA-HTV-PM. A mixture of compound 3 (1 g, 1.45 mmol), 5 (0.869 g, 3.2 mmol), palladium (II) acetate (10 mg), tetra-nbutylammonium bromide (150 mg, 0.46 mmol), and anhydrous sodium acetate (2.39 g, 29 mmol) was dissolved and kept in degassed anhydrous N,N-dimethyl formamide (30 ml) under argon at 100 °C for 24 h. The mixture was poured into water (30 ml). The precipitate was filtered, washed with water, dissolved in dichloromethane and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (petroleum/dichloromethane, 2:1) to get TPA-HTV-PM. Yield 650 mg (42%). MALDI-TOF MS: 1066.7, calcd for C72H66N4OS2 1067.45. ¹H NMR (CDCl₃, 400 MHz) δ/ppm: 7.37 (d, 4H), 7.29 (s, 2H), 7.27 (d, 8H), 7.13 (d, 8H), 7.09 (d, 4H), 7.05 (d, 8H), 6.93 (d, 2H), 6.58 (s, 2H), 6.45 (d, 2H), 2.67 (t, 4H), 1.64 (m, 4H), 1.45 (m, 12H), 0.91 (t, 6H). ¹³C NMR (CDCl₃, 400 MHz): δ/ppm 158.14, 155.47, 148.11, 147.45, 142.11, 141.48, 136.70, 134.30, 130.65, 130.45, 130.25, 129.52, 127.68, 124.93, 123.55, 123.22, 117.67, 116.69, 115.71, 106.81, 58.88, 31.84, 30.91, 29.21, 28.52, 22.77, 14.27.

Results and discussion

Synthesis and thermal stability of the compounds

TPA-TV-PM and TPA-HTV-PM were synthesized by the routes shown in Scheme 2. First, 2-(2,6-bis(2-(4-bromothienyl)-vinyl)pyran-4-ylidene)-malononitrile (2) and 2-(2,6-bis(2-(4-bis(2-bis(2-(4-bis(2-(4-bis(2-bis(2-(4-bis(2-bis(2-(4-bis(2-bis(2-bis(2-(4-bis(2-bis(2-bis(2-bis(2-(4-bis(2-b



Fig. 1 A TGA plot of TPA-TV-PM and TPA-HTV-PM.

bromo-3-hexylthienyl)vinyl)pyran-4-ylidene)-malononitrile (3) were synthesized according to the method reported in the literature.²⁸ Compound **5** was prepared by Wittig reaction. Then, TPA–TV–PM and TPA–HTV–PM were synthesized from compound **2** and **5**, and **3** and **5**, respectively by a palladiumcatalyzed Heck reaction.²⁴ TPA–TV–PM and TPA–HTV–PM are soluble in common organic solvents, such as CHCl₃, THF, chlorobenzene and toluene.

The thermal stability of TPA–TV–PM and TPA–HTV–PM was investigated by thermogravimetric analysis (TGA). The temperatures with 5% weight loss are 398 °C for TPA–TV–PM and 355 °C for TPA–HTV–PM, as shown in Fig. 1. The stability of TPA–TV–PM and TPA–HTV–PM is good enough for applications in optoelectronic devices.

Absorption spectra

Fig. 2 shows the UV-vis absorption spectra of TPA-TV-PM and TPA-HTV-PM in chloroform solution and the film state. The optical absorption maxima (λ) are summarized in Table 1. Fig. 2a shows the UV-vis absorption spectra of TPA-DCM-TPA, TPA-TV-PM and TPA-HTV-PM in dilute chloroform solution with a concentration of 10^{-5} mol L⁻¹. Benefiting from their D-A molecular structure connected with a conjugated pi-bridge, the absorption spectra of TPA-TV-PM and TPA-HTV-PM solutions (see Fig. 2a) exhibit two absorption peaks in the wavelength range 350-650 nm. The absorption peak with a maximum at 420 nm for TPA-TV-PM and at 422 nm for TPA-HTV-PM corresponds to the π - π * absorption of the molecules, and the absorption band at longer wavelength with a peak at 530 nm for TPA-TV-PM and at 538 nm for TPA-HTV-PM could be assigned to the intramolecular charge transfer transition between the TPA moiety and the PM unit.13,22 Compared with the absorption peak at 466 nm of TPA-DCM-TPA solution for the intramolecular charge transfer absorption, TPA-TV-PM (530 nm) and TPA-HTV-PM (538 nm) red shifted ca. 60-70 nm, which implies that the thienvlenevinylene and 4-hexyl-thienvlenevinylene groups are better conjugated pi-bridges than styrene in the molecules, from the view point of broadening the absorption. The molar absorptivity of TPA-DCM-TPA, TPA-TV-PM and TPA-HTV-PM at their peak wavelength is 9.13 \times 10^4 , 8.19×10^4 and 8.09×10^4 , respectively, which demonstrates that all three of the molecules exhibit strong absorbance in the visible region. In comparison with the solution, the film



Fig. 2 (a) Absorption spectra of TPA–DCM–TPA, TPA–TV–PM and TPA–HTV–PM in chloroform solution at a concentration of 10^{-5} mol L⁻¹; (b) absorption spectra of TPA–TV–PM and TPA–HTV–PM films.

absorption peaks (see Fig. 2b) red shifted a little for both of the molecules, indicating that some aggregation of the molecules in the film state exists. The absorption edge of TPA-TV-PM and TPA-HTV-PM films are at *ca*. 681 nm and *ca*. 707 nm, corresponding to band gaps of 1.82 eV and 1.75 eV, respectively (Table 1).

Electrochemical properties and electronic energy levels

Electrochemical cyclic voltammetry was carried out for TPA-TV-PM and TPA-HTV-PM films on Pt electrode, in order to measure the HOMO and LUMO energy levels of the compounds. Fig. 3 shows the cyclic voltammograms of TPA-TV-PM and TPA-HTV-PM films in the positive potential range, showing the p-doping/dedoping processes of the compounds. The onset oxidation potentials (Eox onset) of TPA-TV-PM and TPA-HTV-PM are 0.45 V and 0.44 V vs. Ag/Ag⁺ respectively, obtained from the cyclic voltammograms. Then the HOMO energy levels were estimated to be -5.16 eV for TPA-TV-PM and -5.15 eV for TPA-HTV-PM, according to the following equation: $E_{HOMO} =$ $-e(E_{ox}^{ox} + 4.71)$ (eV).²⁹ The LUMO energy levels of the compounds were estimated from LUMO = HOMO + E_g . The values of the onset oxidation potential, HOMO and LUMO energy levels of the two compounds were also listed in Table 1. The two compounds of TPA-TV-PM and TPA-HTV-PM exhibit slightly lower-lying HOMO energy levels than that (-5.14 eV) of TPA-DCM-TPA,²² although their band gap is lowered. The

Table 1 Absorption and electrochemical properties and electronic energy levels of TPA-DCM-TPA, TPA-TV-PM and TPA-HTV-PM

Compounds	$\lambda_{solution} (nm)$	$\varepsilon (L \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{\mathrm{film}} \left(\mathrm{nm} \right)$	$(E_{g}^{opt})_{\text{film}} (\text{eV})$	$E^{\text{ox}}_{\text{onset}}$ (V ^a)/HOMO(eV)	$LUMO^{b}$ (eV)
TPA-DCM-TPA ^c	393, 466	9.13×10^4	411, 498	1.88	0.75/-5.14	-2.76
TPA-TV-PM	420, 530	8.19×10^4	432, 536	1.79	0.45/-5.16	-3.37
TPA-HTV-PM	422, 538	8.09×10^4	433, 540	1.71	0.44/-5.15	-3.44

^{*a*} The reference electrode is Ag/Ag⁺. ^{*b*} LUMO energy level was calculated from the HOMO level and optical energy gap: LUMO = HOMO + E_g^{opt} . ^{*c*} The data were taken from Ref. 22.

lower HOMO energy level of the organic molecules is very important for the higher $V_{\rm oc}$ of the OSCs based on the molecules as donor materials, because the $V_{\rm oc}$ of the OSCs is proportional to the difference between the LUMO level of acceptor and the HOMO level of the donor.³⁰

Morphology of the compound : PC₇₀BM films

The morphology of the photoactive layer is very important for the photovoltaic performance of OSCs.^{31,32} We used atomic force microscopy (AFM) to investigate the morphology of the two organic molecules : $PC_{70}BM$ (1 : 3, w/w) blend films. TPA–TV– PM : $PC_{70}BM$ and TPA–HTV–PM : $PC_{70}BM$ blend films were prepared by spin-coating their chlorobenzene solution on the top of the PEDOT : PSS layer, which was spin-coated on the ITO glass. Both of the AFM images of the blend films exhibit typical amorphous morphology without any crystalline domains, as shown in Fig. 4. We can see intuitively that the surfaces of the blend films of TPA–TV–PM and TPA–HTV–PM are smooth and uniform, which is beneficial for application in OSCs.

Photovoltaic properties

Bulk-heterojunction OSCs were fabricated by using the two linear organic molecules as the donor materials, $PC_{70}BM$ as the acceptor material^{33–35} and Al as the negative electrode. For comparison, we also fabricated bulk-heterojunction OSCs based on the TPA–DCM–TPA : $PC_{70}BM$ (1 : 3, w/w) blend. The device structure is ITO/PEDOT : PSS/photoactive layer/Al. Fig. 5 shows the typical current density–voltage (*J–V*) curves of



Fig. 3 Cyclic voltammograms of TPA–TV–PM and TPA–HTV–PM films on Pt electrode in an acetonitrile solution of 0.1 mol L^{-1} Bu₄NPF₆ (Bu = butyl) with a scan rate of 100 mV s⁻¹.

the OSCs in the dark and under the illumination of AM.1.5, 100 mW cm⁻². The photovoltaic performance data of the OSCs, including open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) values, are summarized in Table 2. For TPA–DCM–TPA, the device with PC₆₀BM as acceptor material, Ba/Al as cathode and a donor : acceptor weight ratio of 1 : 3 showed a V_{oc} of 0.9 V, a J_{sc} of 2.14 mA cm⁻², a FF of 29%, corresponding to a PCE of 0.79%.²² In comparison, the OSC devices based on TPA–DCM–TPA : PC₇₀BM (1 : 3, w/w) exhibited a V_{oc} of 0.71 V, J_{sc} of 5.07 mA cm⁻², a FF of 38% and a PCE of 1.4%, which implied that PC₇₀BM is a better acceptor than PC₆₀BM in the OSCs for its stronger absorption in the wavelength range 350–550 nm.

The OSC device based on the TPA–TV–PM : $PC_{70}BM$ (1 : 3, w/w) blend showed a V_{oc} of 0.79 V, a J_{sc} of 5.94 mA cm⁻², a FF of 44% and a PCE of 2.06%, and the OSC device based on the



Fig. 4 AFM images of the molecule : $PC_{70}BM$ films spin-coated from their solution at a weight ratio of 1 : 3: (a) TPA–TV–PM : $PC_{70}BM$ film, (b) TPA–HTV–PM : $PC_{70}BM$ film, the scan size of the images is 5 μ m × 5 μ m.



Fig. 5 Current density-voltage characteristics of the OSC devices based on the blend of TPA–DCM–TPA, TPA–TV–PM or TPA–HTV–PM/ PC₇₀BM (1 : 3, w/w) with Al as the negative electrode at dark and under the illumination of AM.1.5, 100 mW/cm².

Table 2 The photovoltaic performance of ITO/PEDOT : PSS/TPA– DCM–TPA, TPA–TV–PM or TPA–HTV–PM : $PC_{70}BM$ (1 : 3, w/w)/Al under the illumination of AM.1.5, 100 mW cm⁻²

Active layer	V _{oc} (V)	$J_{ m sc} \ (m mA\ cm^{-2})$	FF (%)	PCE (%)
TPA–DCM–TPA : PC ₇₀ BM	0.71	5.07	38	1.40
TPA–TV–PM : PC ₇₀ BM	0.79	5.94	44	2.06
TPA–HTV–PM : PC ₇₀ BM	0.78	6.78	39	2.10

TPA-HTV-PM : $PC_{70}BM$ (1 : 3, w/w) blend displayed a V_{oc} of 0.78 V, a $J_{\rm sc}$ of 6.78 mA cm⁻², a FF of 39% and a PCE of 2.10%. In comparison with the photovoltaic performance of the OSC devices based on TPA-DCM-TPA : PC₇₀BM (1 : 3, w/w), TPA-TV-PM and TPA-HTV-PM exhibited better photovoltaic performance, especially the J_{sc} and PCE values, which benefited from their broad absorption (the absorption edge of the TPA-TV-PM and TPA-HTV-PM films is red-shifted by more than 40 nm compared to that of the TPA-DCM-TPA film) and good film-forming properties. In addition, the lower band gap of the two new molecules resulted from the significant decrease of their LUMO energy levels. Interestingly, their HOMO energy levels also decreased a little in comparison with that of TPA-DCM-TPA. The lower HOMO energy level is beneficial to the higher $V_{\rm oc}$ of the OSCs based on the two new molecules.³⁰ The results indicate that thienylenevinylene and 4-hexyl-thienylenevinylene as conjugated pi-bridges in TPA-TV-PM and TPA-HTV-PM are superior to styrene in TPA-DCM-TPA for application as donor materials in solution-processed OSCs.

Conclusions

Two new solution-processable D–A structured organic molecules TPA–TV–PM and TPA–HTV–PM, with TPA as the donor unit, PM as the acceptor unit, thienylenevinylene (TV) or 4hexyl-thienylenevinylene (HTV) as the conjugated pi-bridge, were designed and synthesized for application as donor materials in OSCs. The compounds demonstrate broad absorption from 350 nm to 650 nm along with lower HOMO energy levels at *ca.* -5.15 eV. The OSC devices were fabricated by spin-coating the blend solution of the organic molecules as the donor and PC₇₀BM as the acceptor (1 : 3, w/w). The OSCs based on TPA–TV–PM and TPA–HTV–PM showed power conversion efficiencies (PCE) of 2.06% and 2.10%, respectively, under the illumination of AM.1.5, 100 mW cm⁻², which are much higher than the 1.40% PCE for the OSC based on a TPA–DCM–TPA : PC₇₀BM (1 : 3, w/w) blend. The results indicate that in the TPA- and PM-containing D–A molecules, thienylenevinylene and 4-hexyl-thienylenevinylene as conjugated pi-bridges in TPA–TV–PM and TPA–HTV–PM are superior to styrene in TPA–DCM–TV–PA for the application as donor materials in the solution-processed OSCs. Moreover, the D–A structured molecules could be promising organic photovoltaic materials by careful molecular design.

Acknowledgements

This work was supported by NSFC (Nos. 50633050, 50803071, 20874106 and 20721061).

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