

Solution-Processable Star-Shaped Molecules with Triphenylamine Core and Dicyanovinyl Endgroups for Organic Solar Cells[†]

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Two new star-shaped D $-\pi$ -A molecules with triphenylamine (TPA) as core and donor unit, dicyanovinyl (DCN) as end group and acceptor unit, and 4,4'-dihexyl-2,2'-bithiophene (bT) or 4, 4'-dihexyl-2,2'-bithiophene vinylene (bTV) as π bridge, S(TPA-bT-DCN) and S(TPA-bTV-DCN), were synthesized for the application as donor materials in solution-processed bulk-heterojunction organic solar cells (OSCs). The two compounds are soluble in common organic solvents, because of the three-dimensional structure of the TPA unit and the two hexyl side chains on the bithiophene unit. S(TPA-bTV-DCN) film shows a broad absorption band from 360 to 750 nm. Absorption edge of S(TPA-bTV-DCN) film is red-shifted by ca. 78 nm than that of S(TPA-bT-DCN) film, benefitted from the vinylene bridges between TPA and bithiophene units in S(TPA-bTV-DCN). Power conversion efficiency (PCE) of the solution-processed bulk-heterojunction OSC based on a blend of S(TPA-bTV-DCN) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (1:2, w/w) reached 3.0% with a short circuit current density of 7.76 mA/cm² and an open circuit voltage of 0.88 V, under the illumination of AM.1.5, 100 mW/cm². In comparison, PCE of the OSC based on S(TPA-bT-DCN) as donor is 1.4% under the same experimental conditions. The PCE of 3.0% for S(TPA-bTV-DCN) is among the top values for the solution-processed molecule-based OSCs reported so far.

1. Introduction

Bulk heterojunction organic solar cells (OSCs)¹ are composed of a photoactive blend layer of a conjugated polymer or organic molecule donor and a soluble fullerene derivative acceptor sandwiched between an indium-tin oxide (ITO) positive electrode and a low workfunction metal negative electrode. In comparison with the traditional solar cells based on inorganic semiconductors, the OSCs possess the advantages of easy fabrication, low cost, light weight,

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and capability to fabricate flexible devices. For the donor materials in OSCs, solution-processable conjugated organic molecules have drawn much attention in recent years $^{2-16}$ because of the advantages of high purity and definite molecular weight of the organic small molecules in comparison with the lower purity and molecular weight distribution of the polymers. Among the soluble organic photovoltaic molecules, the donor- π conjugated bridge-acceptor $(D-\pi-A)$ structured organic compounds have attracted considerable research interests for their broad absorption in visible region resulted from the intramolecular charge transfer (ICT) and for their lower HOMO levels tuned by the acceptor units.^{6,8–16} For example, Nguyen et al.¹⁰ synthesized a D-A organic molecule containing benzofunanthiophene as donor unit and diketopyrrolopyrrole (DPP)

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as acceptor unit. The molecule film possesses a broad absorption covering from 380 to 700 nm and lower HOMO level of -5.2 eV. The power conversion efficiency (PCE) of the bulk heterojunction OSC (device area of 17 mm²)^{9b} based on the molecule as donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC70BM) as acceptor reached 4.4% with a high open circuit voltage (V_{oc}) of 0.92 V,¹⁰ which indicates that the organic D $-\pi$ -A molecules are promising as highefficiency photovoltaic materials for the application as donor in the bulk heterojunction OSCs.

The triphenylamine (TPA) unit possesses a threedimensional propeller structure that makes the TPAcontaining molecules exhibit good solubility. In addition, the TPA-containing molecules have high hole mobility and are widely used as hole-transporting materials in organic light-emitting diodes.¹⁷ Many D $-\pi$ -A structured molecules containing TPA as donor unit have been designed and synthesized for the applications as solution-processable organic photovoltaic donor materials, in considering its good solubility and high hole mobility.^{3,8,11-16} At present, benzothiadiazole (BT)^{15,16} and 2-{2,6-bis-[2-(4-styryl)vinyl]-pyran-4-ylidene}malononitrile (DCM)^{8,11,13} have been used as acceptor units in the solution-processable TPA-containing D- π -A molecules. The highest PCE reached 2.39% for the bulk heterojunction OSC based on a star-shaped organic molecule with TPA as core and benzothiodiazole -4-hexylthiophene as arms.¹⁵

Dicyanovinyl (DCN) is a well-known acceptor group in the organic optoelectronic materials. Roncali et al.² synthesized the star-shaped D- π -A molecules with TPA as core and donor unit, DCN as end group and acceptor unit, and thiophene as the π -bridge. The molecules showed promising photovoltaic performance with a PCE of 1.17% for the bilayer OSC based on the molecules as donor and C₆₀ as acceptor.² Wong et al.¹⁸ reported the linear conjugated D $-\pi$ -A organic molecules with TPAfluorene as donor unit, DCN as acceptor unit and oligothiophene as π -bridge. The molecule films demonstrate broad and strong absorption in the visible region from 360 to 700 nm. The bilayer OSC with the molecules as donor and C₆₀ as acceptor displayed a PCE as high as 2.67%.¹⁸ The results indicate that the D $-\pi$ -A organic molecules with TPA as donor unit and DCN as acceptor unit are promising photovoltaic materials. However, poor solubility of the molecules containing DCN hampers the fabrication of bulk heterojunction OSCs, and the bilayer OSCs mentioned above were fabricated by vacuumevaporation.^{1,18} Obviously, it should be interesting if we can obtain the solution-processable $D-\pi-A$ organic molecules containing TPA and DCN units for the application as donor materials in bulk heterojunction OSCs.

In this work, we designed and synthesized two new starshaped D- π -A molecules with TPA as core and donor unit, DCN as end group and acceptor unit, and 4,4'-Dihexyl-2, 2'-bithiophene or 4,4'-Dihexyl-2,2'-bithiophene vinylene as Scheme 1. Structures of S(TPA-bT-DCN) and S(TPA-bTV-DCN)



 π -bridge, S(TPA-bT-DCN) and S(TPA-bTV-DCN), as shown in Scheme 1. The two hexyl side chains on the π -bridge of bithiophene in the molecules are used to improve solubility and film forming properties of the molecules. The two compounds do show good solubility in common organic solvents as expected, and possess broad visible absorption band. Bulk heterojunction OSCs were fabricated by spincoating the blend solution of the compounds (as donor) and $PC_{70}BM$ (as acceptor). The photovoltaic performance of the OSC device based on a blend of S(TPA-bTV-DCN) and $PC_{70}BM$ (1:2, w/w) exhibited a PCE of 3.0% with a short circuit current density (J_{sc}) of 7.76 mA/cm², a V_{oc} of 0.88 V, and a fill factor (FF) of 43.9%, under the illumination of AM.1.5, 100 mW/cm^2 . The PCE of 3.0% is the highest value for the OSCs based on the solution-processable TPA-containing organic molecules, and it is among the top values in the bulk heterojunction molecule-based OSCs reported so far.

2. Experimental Section

2.1. Materials. All reagents were obtained from Aldrich, Acros, or TCI Chemical Co, and used as received. PC₇₀BM was bought from ADS (American Dye Source Inc.) Tetrahydrofuran (THF) was dried over Na/benzophenoneketyl and freshly distilled prior to use. CHCl3 and triethylamine were dried over a molecular sieve.

2.2. Synthesis. The synthetic routes of the compounds are shown in Scheme 2. The detailed synthesis processes are as follows.

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^{*a*}(I) AgNO₃, KF, DMSO, dark, 60 °C for 24 h; (II) n-BuLi, DMF, THF, -78 °C; (III) Pd(dac)₂, K₃PO₄ (2 mol/L), toluene, 120 °C reflux for 24 h; (IV) Pd(OAc)₂, NaOAc, n-Bu₄NBr, DMF, under N₂, 100 °C for 24 h; (V, VI) malononitrile, CHCl₃, triethylamine, under N₂, 75 °C reflux for 24 h.

5-Bromo-5'-formyl-4,4'-dihexyl-2,2'-bithiophene (4). 5,5'-Dibromo-4,4'-dihexyl- 2,2'-bithiophene (3) (13 g, 26.42 mmol) was dissolved in 200 mL THF in a well-dried flask under the protection of N₂ flow. N-Butyl lithium (9.2 mL, 26.96 mmol, 2.93 M in hexane) was added dropwise by syringe at -78 °C. After the addition, the reaction mixture was stirred at -78 °C for 2 h and DMF (2 mL, 26.42 mmol) was added dropwise, then the mixture was warmed to room temperature. After stirring for 12 h, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried over Na₂SO₄. After solvent removal, the residue was purified by column chromatography on silica gel (petroleum/CH₂Cl₂, 15:1) to give 6.2 g of compound 4 with a yield of 53.1%. GC/MS: 441 (M^+) . ¹H NMR (400 MHz, CDCl₃): δ ppm 9.98 (s, 1H), 7.03 (s, 1H), 7.02 (s, 1H), 2.07 (t, 2H), 2.26 (t, 2H), 1.64-1.70 (m, 2H), 1.55-1.60 (m, 2H), 1.32-1.37 (m, 12H), 0.89 (t, 6H).

Tris{4-[5-(5-formyl-4-hexyl-2-thienyl)-3-hexyl-2-thienyl]phenyl}amine (5). A mixture of 5-bromo-5'-formyl-2,2'-bithiophene (4) (2.68 g, 6.06 mmol), K_3PO_4 (24 mL, 2 M in aqueous solution), degassed toluene (40 mL), Pd(dac)_3 (21 mg), [(CH_3)_3C]PHBF_4 (27 mg, and Monomer 1 (1.18 g, 1.89 mmol) were stirred under the protection of N_2 flow. The solution was kept at 120 °C for 24 h. The mixture was poured into water, extracted with dichloromethane, and washed by water, dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum/CH₂Cl₂, 1:1) to produce 1.09 g of compound **5** with a yield of 43.5%. MALDI-TOF MS: 1325.7, calcd for $C_{81}H_{99}NO_3S_6$ 1325.6. ¹H NMR (400 MHz, CDCl₃): δ ppm 10.02 (s, 3H), 7.42 (d, 3H), 7.41 (d, 3H), 7.29 (d, 3H), 7.20 (d, 3H), 7.08 (s, 3H), 7.253 (s, 3H), 2.95 (t, 6H), 2.70 (t, 6H), 1.71 (m, 12H), 1.31 (m, 36H), 0.9 (t, 18H).

Tris{4-[2-(5-(5-formyl-4,4'-dihexyl-2-thienyl)-3-hexyl-2-thienyl)vinyl]phenyl}amine (6). A mixture of Monomer **2** (730.5 mg, 2.26 mmol), Pd(OAc)₂ (31 mg), NaOAc (5.56 g, 67.84 mmol), 5-bromo-5'-formyl-2,2'-bithiophene (**4**) (3 g, 6.79 mmol), and *n*-Bu₄NBr (1.05 g, 3.26 mmol) was dissolved in degassed DMF (75 mL). The solution was kept under a nitrogen atmosphere at 100 °C for 24 h. The mixture was poured into water. The precipitate was filtered, washed with water and dissolved in dichloromethane, and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum/CH₂Cl₂, 1:1) to produce 2.10 g of Compound **6** with a yield of 66.2%. MALDI-TOF MS: 1403.6, calcd for C₉₇H₁₀₅NO₃S₆ 1404.6. ¹H NMR (400 MHz, CDCl₃): δ ppm 9.98 (s, 3H), 7.38–7.40 (d, 6H), 7.01–7.12 (m, 12H), 6.90 (d, 6H), 2.92 (t, 6H), 2.66 (t, 6H), 1.62–1.70 (m, 12H), 1.26–1.32 (m, 36H), 0.89 (t, 18H). *Tris*{4-[5-(5-*dicyanomethylidenemethyl-4-hexyl-2-thienyl*]*phenyl*}*amine* (*S*(*TPA-bT-DCN*)). To a solution of Tris{4-[5-(5-formyl-4-hexyl-2-thienyl]*-3-hexyl-2-thienyl*]*phenyl*}*amine* (**5**) (1 g, 0.75 mmol) in 50 mL of chloroform were added malonodinitrile (149 mg, 2.26 mmol) and 0.5 mL triethylamine, and the mixture was refluxed at 75 °C for 24 h under nitrogen. After the solution was cooled to room temperature, dichloromethane was added, the solution was washed with water and dried over MgSO₄. After solvent removal, the residue was purified by column chromatography on silica gel (dichloromethane) to give 0.80 g S(TPA-bT-DCN) (yield: 72%) of black red solid. MALDI-TOF MS: 1470.60, calcd for C₉₁H₁₀₃N₇S₆ 1469.63. ¹H NMR (400 MHz, CDCl₃): *δ* ppm 7.83 (s, 3H), 7.38–7.40 (d, 6H), 7.33 (s, 3H), 7.22–7.25 (d, 6H), 7.10 (s, 3H), 2.74 (t, 6H), 2.68 (t, 6H), 1.64 (m, 12H), 1.31 (m, 36H), 0.90 (t, 18H).

Tris{4-[2-(5-(5-dicvanomethylidenemethyl-4-hexyl-2-thienyl)-3-hexyl-2-thienyl)-vinyl]phenyl]amine (S(TPA-bTV-DCN)). The synthesis procedure for S(TPA-bTV-DCN) is similar to that of S(TPA-bT-DCN) but using precursor 6 instead of 5. To a solution of 6 (1.4 g, 1 mmol) in 50 mL of chloroform, malonodinitrile (0.2 g, 3.03 mmol), and 0.5 mL of triethylamine were added, and the mixture was refluxed at 75 °C for 24 h under nitrogen. After the solution was cooled to room temperature, dichloromethane was added, and the solution was washed with water and dried over MgSO₄. After solvent removal, the residue was purified by column chromatography on silica gel (dichloromethane) to give 1.09 g S(TPA-bTV-DCN) (yield: 70%) of a black purple solid. MALDI-TOF MS: 1548.70, calcd for C₉₇H₁₀₉N₇S₆ 1547.68. ¹H NMR (400 MHz, CDCl₃): δ ppm 7.80 (s, 3H), 7.41 (d, 6H), 7.23 (s, 3H), 7.08 (m, 12H), 6.91 (d, 6H), 2.73 (t, 6H), 2.67 (t, 6H), 1.64 (m, 12H), 1.30 (m, 36H), 0.91 (t, 18H).

2.3. Measurements. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEXIII. Absorption spectra were taken on a Hitachi U-3010 UV–vis spectrophotometer. The film on quartz used for UV measurements was prepared by spin-coating a 1% chloroform solution of the samples. The thermogravimetric analysis (TGA) measurement was performed on a Perkin-Elmer TGA-7 apparatus. The electrochemical cyclic voltammetry was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L 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.

2.4. Fabrication and Characterization of Organic Solar Cells. The organic solar cells were fabricated in a sandwich geometry consisting of a bottom indium tin oxide (ITO) glass positive electrode, a photosensitive layer composed of a blend of the organic molecule as donor and PC70BM as acceptor, and a top Ca/Al negative electrode. Patterned ITO glass with a sheet resistance of ca. 10 Ω sq⁻¹ was purchased from CSG HOLD-ING Co., LTD (China). The ITO glass was cleaned in an ultrasonic bath of acetone and isopropanol, and then treated in an ultraviolet-ozone chamber for 30 min (Ultraviolet Ozone Cleaner, Jelight Company, USA). Then a thin layer (30 nm) of PEDOT: PSS (poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)) (Baytron PVP A1 4083, Germany) was spin-coated at 4000 rpm on the ITO glass and baked at 150 °C for 30 min in the air. Subsequently, the photosensitive active layer was prepared in a drybox by spin-coating the blend chlorobenzene solution of S(TPA-bT-DCN) or S(TPA-bTV-DCN) and $PC_{70}BM$ (1:2 w/w, 18 mg/mL) on the top of the PEDOT: PSS layer with a spin speed of 2000 rpm. The thickness of the



Figure 1. TGA plots of S(TPA-bT-DCN) and S(TPA-bTV-DCN).



Figure 2. UV-vis absorption spectra of S(TPA-bT-DCN) and S(TPA-bTV-DCN) in chloroform solution and in film state.

photosensitive layer was ca. 80 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisted of Ca (~10 nm) capped with Al (~100 nm) was thermal-evaporated under a shadow mask in a base pressure of ca. 1×10^{-4} Pa. The device active area of the PSCs is 4 mm². The current–voltage (*I–V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in glovebox under simulated AM1.5G irradiation (100 mW cm⁻²) using a Xenon-lamp-based solar simulator (from Newport Co., Ltd.).

3. Results and Discussion

3.1. Synthesis and Thermal Stability. S(TPA-bT-DCN) and S(TPA-bTV-DCN) were synthesized by the synthetic routes shown in Scheme 2. Monomers 1, 2 and 3 were synthesized according to literatures.^{14,19} Compound 5 was prepared from Monomers 1 and 4 through Suzuki reaction with a yield of 39.8%. Compound 6 was synthesized from Monomer 2 and 4 by Heck reaction with a yield of 62.9%. Finally, S(TPA-bT-DCN) and S(TPA-bTV-DCN) were obtained by Knoevenagel condensation of malononitrile with the appropriate aldehyde. Both S(TPA-bT-DCN) and S(TPA-bTV-DCN) are soluble in common organic solvents, such as CHCl₃, THF, chlorobenzene, and toluene.

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Table 1. Optical Absorption and Electrochemical Properties and Electronic Energy Levels of S(TPA-bT-DCN) and S(TPA-bTV-DCN)

compds	$\lambda_{solution} (nm)$	$\lambda_{\rm film} ({\rm nm})$	$(E_g^{opt})_{film} (eV)$	$E^{\text{red}}_{\text{onset}}$ (V ^a) /LUMO(eV)	$E^{\text{ox}}_{\text{onset}}(V^a)$ /HOMO(eV)	$E_{\rm g}^{\rm cv}\left({\rm eV}\right)$
S(TPA-bT-DCN)	296, 342, 504	312, 402, 563	1.83	-1.37/-3.34	0.51/-5.22	1.88
S(TPA-bTV-DCN)	298, 357, 518	320, 421, 585	1.65	-1.29/-3.42	0.32/-5.03	1.61

^a The reference electrode is Ag/Ag⁺

The thermal stability of S(TPA-bT-DCN) and S(TPAbTV-DCN) was investigated by TGA analysis. The temperatures with 5% weight loss are 358 °C for S(TPA-bT-DCN) and 347 °C for S(TPA-bTV-DCN), as shown in Figure 1. The stability of S(TPA-bT-DCN) and S(TPAbTV-DCN)) is good enough for the applications in optoelectronic devices.

3.2. Optical Properties. Figure 2 shows the UV-vis absorption spectra of S(TPA-bT-DCN) and S(TPAbTV-DCN) in solutions and solid films. The absorption peak wavelengths (λ) of the two compounds were summarized in Table 1. The absorption spectrum of S(TPAbT-DCN) solution shows three absorption peaks at 296, 342, and 504 nm, respectively, covering a broad wavelength range from 260 to 600 nm, which is benefited from its D- π -A molecular structure. The two UV absorption peaks at 296 and 342 nm correspond to the $\pi - \pi^*$ absorption of S(TPA-bT-DCN), and the strong visible absorption peak at ca. 504 nm is attributed to the intramolecular charge transfer (ICT) transition between the TPA-bithiophene donor unit and DCN acceptor unit. The spectrum of S(TPA-bT-DCN) with two UV peaks and a visible peak agrees with that of a similar molecule (molecule 5) in ref 2. The absorption spectrum of the S(TPA-bT-DCN) film red-shifted in comparison with its solution, which results from the aggregation of the molecules in the solid film state. The three absorption peaks of the S(TPA-bT-DCN) film red-shifted to 312, 402, and 563 nm, respectively. The relatively lower intensity of the $\pi - \pi^*$ transition and the higher intensity of the ICT band in the absorption spectra agree with that reported by Roncali et al.² S(TPA-bTV-DCN) shows similar and redshifted absorption spectra to that of S(TPA-bT-DCN). The three absorption peaks of S(TPA-bTV-DCN) film red-shifted to 320, 421, and 585 nm, respectively. The absorption spectrum of the S(TPA-bTV-DCN) film covers a broad wavelength range in the visible region from 380 to 750 nm, which is beneficial to the application as photovoltaic materials. In comparison with S(TPA-bT-DCN), the red-shift of the absorption spectra of S(TPAbTV-DCN) should result from the vinylene linkage between TPA and bithiophene in it. Probably, the vinylene linkage in S(TPA-bTV-DCN) could eliminate torsional interactions between TPA and bithiophene, and extend the conjugation length of each branch in the molecule. leading to the red-shifted and broader absorption spectrum.²⁰ The absorption edges of S(TPA-bT-DCN) and S(TPA-bTV-DCN) films are at ca. 674 nm and ca. 752 nm, corresponding to the band gaps of 1.83 and





Figure 3. Cyclic voltammograms of S(TPA-bT-DCN) and S(TPA-bTV-DCN) film on Pt electrode in an acetonitrile solution of 0.1 mol/L Bu_4NPF_6 (Bu = butyl) with a scan rate of 100 mV/s.

1.65 eV, respectively. The detailed optical data of S(TPAbT-DCN) and S(TPA-bTV-DCN) are listed in Table 1.

3.3. Electronic Energy Levels. The electronic energy levels of the organic semiconductors are crucial for their photovoltaic performance,²¹ and the electrochemical onset oxidation potentials and onset reduction potentials are corresponding to the ionization potential (IP) and electron affinity (EA) of the organic semiconductors respectively.²² In the simple HOMO-LUMO energy diagram of the organic photovoltaic donor and acceptor materials, the HOMO energy level can be estimated from IP with HOMO = -IP and the LUMO energy level can be estimated form EA with LUMO = -EA. To measure the electronic energy levels of the compounds, we carried out electrochemical cyclic voltammetry for the two compounds. Figure 3 shows the cyclic voltammograms of S(TPA-bT-DCN) and S(TPA-bTV-DCN) films on a Pt electrode. The onset reduction potential (E^{red}_{onset}) , the onset oxidation potential (E^{ox}_{onset}) and the electrochemical bandgap (E_g^{cv}) of the compounds are also listed in Table 1. The HOMO, LUMO energy levels and the electrochemical band gap of S(TPA-bT-DCN) were estimated to be -5.22, -3.34, and 1.88 eV, respectively, from the onset oxidation and reduction potentials according to the following equations:²³ $E_{\text{HOMO}} = -\text{IP} = -e (E^{\text{ox}}_{\text{onset}} + 4.71) (eV), E_{\text{LUMO}} = -\text{EA} = -e (E^{\text{red}}_{\text{onset}} + 4.71)$ (eV), and $E_g = IP - EA$. For S(TPA-bTV-DCN), The HOMO and LUMO energy levels and the electrochemical band gap were estimated to be -5.03, -3.42, and 1.61 eV, respectively. The electrochemical band gaps of

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Figure 4. Current density-voltage characteristics of the OSCs based on the blend of S(TPA-bT-DCN) or S(TPA-bTV-DCN)/PC70BM (1:2, w/w) with Ca/Al as the negative electrode at dark and under the illumination of AM 1.5, 100 mW/cm².

S(TPA-bT-DCN) and S(TPA-bTV-DCN) are in agreement with the optical measurements. Compared with the HOMO (-5.87 eV) and LUMO (-3.91 eV) energy levels for $PC_{70}BM$,²⁴ the two compounds are suitable for the application as donor materials with PC70BM as acceptor in OSCs. In addition, the deeper HOMO level of the two compounds is beneficial to higher open circuit voltage (V_{oc}) of the OSCs with them as donor materials, because the $V_{\rm oc}$ is usually proportional to the difference between the LUMO level of the acceptor and the HOMO level of the donor.25,26

3.4. Photovoltaic Properties. Bulk-heterojunction OSCs were fabricated by using S(TPA-bT-DCN) or S(TPA-bTV-DCN) as electron donor, $PC_{70}BM$ as electron acceptors^{27–29} with a donor/acceptor weight ratio of 1:2. The device structure is ITO/PEDOT: PSS/photoactive layer/Ca/Al. Figure 4 shows the typical current-voltage curves of the OSCs at dark and under the illumination of AM 1.5, 100 mW/cm^2 . The photovoltaic performance data of the OSCs, including V_{oc} , J_{sc} , FF, and PCE values, are summarized in Table 2. The OSC device based on S(TPA-bTV-DCN) demonstrated a $V_{\rm oc}$ of 0.88 V, a $J_{\rm sc}$ of 7.66 mA/cm², a FF of 43.9%, corresponding to a PCE of 3.0%, under the illumination of AM 1.5, 100 mW/cm². In comparison, the photovoltaic performance of the OSC based on S(TPA-bT-DCN) showed a $V_{\rm oc}$ of 0.84 V, a $J_{\rm sc}$ of 5.21 mA/cm², a FF of 30.8%, corresponding to a PCE of 1.4%, under the same experimental conditions. Obviously, the broader absorption of S(TPA-bTV-DCN) with vinylene bridge plays an

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Table 2. Photovoltaic Performance of ITO/PEDOT:PSS/S(TPA-bT-DCN) or S(TPA-bTV-DCN): PC70BM (1:2, w/w)/Ca/Al under the Illumination of AM 1.5, 100 mW/cm²

active layer	$V_{\rm oc}\left({\rm V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE (%)
S(TPA-bT-DCN): PC ₇₀ BM	0.84	5.21	30.8	1.4
S(TPA-bTV-DCN): PC ₇₀ BM	0.88	7.76	43.9	3.0

important role for the better photovoltaic performance. As mentioned above, the absorption edge of the S(TPA-bTV-DCN) film is ca. 78 nm red-shifted than that of S(TPA-bT-DCN) film. The higher J_{sc} value of 7.66 mA/cm² for the OSC based on S(TPA-bTV-DCN) should be benefitted from the broad absorption band. The HOMO energy level (-5.22 eV) of S(TPA-bT-DCM) is 0.19 eV lower than that (-5.03 eV) of S(TPA-bTV-DCM), which should lead to higher Voc of the OSC based on S(TPA-bT-DCM) as donor because the $V_{\rm oc}$ depends on the difference between the LUMO level of the acceptor and the HOMO level of the donor.^{30,31} But the V_{oc} value of the OSC based on the S(TPA-bT-DCM) is similar to that of S(TPA-bTV-DCM). Probably, other factors such as morphology of the photoactive layer, hole mobility of the molecules, etc. influenced the $V_{\rm oc}$.

4. Conclusion

Two star-shaped D $-\pi$ -A molecules containing TPA donor unit and DCN acceptor unit with 4,4'-dihexyl-2, 2'-bithiophene (bT) or 4,4'-dihexyl-2,2'-bithiophene vinylene (bTV) as π bridge, S(TPA-bT-DCN) and S(TPA-bTV-DCN), were synthesized. Solution-processability of the two compounds was realized for the DCN containing molecules by the two hexyl side chains on the bithiophene bridges in the molecules. The absorption spectrum of the S(TPA-bTV-DCN) film covers a broad wavelength range in the visible region from 380 to 750 nm, which is red-shifted by ca. 40 nm than that of the S(TPA-bT-DCN) film, benefitted from the vinylene bridges between TPA and bithiophene units in it. The PCE of the bulk heterojunction OSC based on a blend of S(TPA-bTV-DCN) and PC₇₀BM (1:2, w/w) reached 3.0% with a J_{sc} of 7.76 mA/cm² and a V_{oc} of 0.88 V, under the illumination of AM.1.5, 100 mW/cm². Although the PCE of the OSC based on S(TPA-bT-DCN) as donor is 1.4% under the same experimental conditions. The PCE of 3.0% for S(TPA-bTV-DCN) is the highest value for the OSCs based on the solution-processable TPA-containing organic molecules, and it is among the top values for the solutionprocessed molecule-based OSCs reported so far. The results indicate that the structural modifications with the hexyl side chains and the vinylene bridge in the DCN-containing starshaped molecules improve the solution-processability, absorption and photovoltaic properties of the molecules significantly, and the star-shaped organic molecules with TPA core and DCN end groups are promising donor materials for high-performance bulk heterojunction OSCs.

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