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Comparative study on triphenylamine-based bi-armed and four-armed small molecule donors for solution processed organic solar cells

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ABSTRACT

A novel four-armed triphenylamine (TPA)-based molecule named $(TPATh)_4TPA_2B$ with 4,7-bis(4-diphenylaminophenyl)-2,1,3-benzothiadiazole unit as the central building block and triphenylamine-3-dodecylthiophene unit as the arms and a bi-armed TPA-based molecule named $(TPATh)_2(MTPA)_2B$ with the same central building block and arms as those of $(TPATh)_4TPA_2B$ were designed and synthesized by Pd-catalyzed Stille reaction. The thermal stability, photophysical and electrochemical properties of these small molecules are studied. Moreover, they are evaluated in solution processed bulk-heterojunction organic solar cells (OSCs). The device performances of the OSCs based on these small molecule donors and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) were studied. With the same core, the four-armed molecule has the higher absorption and better miscibility with $PC_{71}BM$ than that of bi-armed molecule, while the bi-armed molecule $(TPATh)_2(MTPA)_2B$ has the higher hole mobility. The power conversion efficiency of the OSCs based on $(TPATh)_4TPA_2B$ as donor and $PC_{71}BM$ as acceptor is 1.3% with open-circuit voltage 0.71 V.

1. Introduction

In recent years bulk heterojunction (BHJ) organic solar cells (OSCs) based on small molecules or polymers as donors and fullerene derivatives as acceptor have attracted widespread attention due to their low cost, light weight and easy fabrication to flexible devices [1–9]. Compared with polydisperse conjugated polymers, the solution processed small molecules have the advantages in well-defined molecular structure, definite molecular weight, high purity and monodispersity without batch to batch variations [4–8]. The power conversion efficiency (PCE) more than 8% has been achieved from the OSCs based on a solution-processed linear small molecule and $PC_{71}BM$ [10]. However, few soluble small molecules used as electron donors in OSCs demonstrated decent PCEs compared with their polymer counterparts and therefore more molecules need to be synthesized and evaluated in OSCs.

Due to its good electron donating and high hole-transporting abilities, triphenylamine (TPA) is regarded as a promising unit for hole-transporting, light-emitting and photovoltaic materials [11–14]. Owing to the noncoplanarity of the three phenyl substituents, TPA is widely used as a core for tri-armed molecules. Combining TPA with linear conjugated systems, amorphous materials with isotropic optical and charge-transport properties could be obtained [15]. At present, various TPA-based star-shaped molecules were used as donor in solution-processed OSCs and the PCE more than 4% was reported [16–18]. When a linear conjugated molecule containing two TPAs was used as a core instead of TPA, four-armed molecules could be attained with longer conjugated length [19–21]. Besides, with four arms holding the fullerene balls, better miscibility with PCBM in BHJ OSCs can be expected.

In our previous work, we reported the synthesis of a four-armed TPA-based molecule [Th_4(DTPAB)] with a linear conjugated molecule (TPA-benzothiadiazole-TPA) containing two TPAs units as the core and 4-hexylthiophene as arms and its application in BHJ OSCs [22]. Th_4(DTPAB) has longer conjugated length compared with that of star-shaped TPA molecule containing similar arm structure, so that Th_4(DTPAB) has good miscibility with commercial PCBM to

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achieve optimum morphology in the active layer for BHJ OSCs. To further study the relationship between structure and properties of four-armed TPA molecules, here we design and synthesize another four-armed TPA-based small molecule $(TPATh)_4TPA_2B$ with 4,7-bis(4-diphenylaminophenyl)-2,1,3-benzothiadiazole unit as core and TPA-3-dodecylthiophene unit as arms. Moreover, a linear bi-armed TPA-based small molecule $(TPATh)_2(MTPA)_2B$ with the same core and arms as those of $(TPATh)_4TPA_2B$ was synthesized to study the effect of arms number on absorption, energy level, hole mobility, morphology and photovoltaic properties of the molecules. The OSCs based on blends of $(TPATh)_4TPA_2B$: $PC_{71}BM$ show better device performances than that of $(TPATh)_2(MTPA)_2B$: $PC_{71}BM$ under the same preparation condition.

2. Experimental

2.1. Materials and measurement

Measurement of molecular weight was carried out on an autoflex III smart bean matrix-assisted laser desorption/ionization time of flight mass spectrometry. Elemental analysis was performed on a FlashEA1112 elemental analysis instrument. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 in deuterated chloroform (CF) solution at 298 K. The thermogravimetry (TG) curves were recorded on a Netzschsta409P with a heating rate of 10 °C min^{-1} in a N_2 atmosphere. UV–visible absorption spectra were recorded on a UV-2550 spectrophotometer. Electrochemical measurements of the small molecule films were performed in a 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP)–acetonitrile (CH_3CN) solution using a glass–carbon electrode at a scan rate of 50 mV s^{-1} against a calomel reference electrode with a CHI610A electrochemical workstation. Topographic images of the films were characterized by atomic force microscopy (AFM, XE-100 Park System).

4,7-Bis(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole [23], 4-(3-dodecyl-2-thienyl)-N,N-diphenyl benzenamine, 4,7-bis(4-(di(4-bromophenyl)amino)phenyl)-2,1,3-benzothiadiazole and tributyl(4-(diphenylamino)phenyl)stanne [24] were prepared following published procedures.

2.1.1. 4,7-Bis(4-(N-(4-bromophenyl)-N-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole (*1*)

Under a N_2 atmosphere, 4,7-bis(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole (0.3 g, 0.48 m mol) and CF (15 ml) were added into the 50 ml flask successively, then N-bromosuccinimide (0.21 g, 1.2 mmol) was added into the flask in the dark, and the reaction mixture was stirred overnight in the dark. The reaction mixture was poured into water, extracted with dichloromethane. The organic layer was washed with saturated sodium chloride solution and dried with anhydrous Na_2SO_4. Then the solvent was removed, the residual solid was purified by column chromatography (silica gel, petroleum ether/CF (1:1)) to give a red solid (0.264 g, 67%). ESI-MS: 808. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85–7.87 (d, 2H), 7.70–7.79 (d, 4H), 7.46–7.50 (m, 4H), 7.31–7.33 (d, 4H), 7.16–7.17 (d, 4H), 7.06–7.08 (d, 4H), 6.94–6.96 (d, 4H), 2.31–2.36 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.53, 142.03, 138.18, 132.70, 130.79, 128.58, 125.03, 123.27, 117.11, 24.30. Elem. Anal. for $C_{62}H_{58}N_4S_3$ Calc.: C, 77.95; H, 6.12; N, 5.86; S, 10.07. Found: C, 78.03; H, 6.26; N, 5.78; S, 9.93.

2.1.2. 4-[3-Dodecyl-5-(tributylstannyl)-2-thienyl]-N,N-diphenyl benzenamine (*2*)

To a solution of 4-(3-dodecyl-2-thienyl)-N,N-diphenyl benzenamine in anhydrous THF at −78 °C, n-BuLi was added drop wise and the mixture was stirred at this temperature for 2 h under N_2. Then tributyltin chloride was added, and the mixture was stirred at −78 °C for 1 h. Then the mixture was warmed to room temperature and stirred overnight. The resulting mixture was poured into saturated aqueous sodium hydrogen carbonate, and the organic phase was separated and washed with saturated aqueous brine and then dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure to give the product as pale-yellow oil, the product was used directly in the next step without further purification (yield: 90%).

2.1.3. Linear bi-armed TPA-based small molecule $(TPATh)_2(MTPA)_2B$

4,7-Bis(4-(N-(4-bromophenyl)-N-(4-methylphenyl)amino)phenyl)-2,1,3-benzothiadiazole (0.26 g, 0.32 mmol), 4-[3-dodecyl-5-(tributylstannyl)-2-thienyl]-N,N-diphenyl benzenamine (2 g, 2.6 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg) and tetrahydrofuran (20 ml) were added successively into a 100 ml three-necked flask under an N_2 atmosphere, then the reaction mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic layer was washed with saturated sodium chloride solution and dried over anhydrous Na_2SO_4. Then the solvent was removed, the crude product was purified by column chromatography (silica gel, petroleum ether/CF (2:1)) to give a red solid (0.51 g, 26%). MALDI-TOF MS: *m/z* 1638.181 (100%) M^+ (calcd. 1638.32). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 2H), 7.83–7.89 (m, 4H), 7.63–7.69 (m, 2H), 7.37–7.41 (m, 4H), 7.28–7.35 (m, 12H), 7.13–7.19 (m, 20H), 7.03–7.09 (m, 8H), 6.94–6.97 (d, 4H), 2.78 (s, 4H), 2.35–2.43 (m, 6H), 1.64–1.73 (m, 4H), 1.27–1.33 (m, 36H), 0.88–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.32, 142.52, 139.94, 130.75, 129.36, 124.52, 123.48, 31.82, 31.14, 29.76, 29.65, 29.60, 29.56, 29.49, 29.38, 29.00, 24.35, 22.70, 14.14. Elem. Anal. for $C_{112}H_{114}N_4S_7$ Calc.: C, 75.60; H, 7.09; N, 3.46; S, 13.85. Found: C, 75.82; H, 7.26; N, 3.37; S, 13.55.

2.1.4. Four-armed small molecule $(TPATh)_4TPA_2B$

Synthesis of the small molecule $(TPATh)_4TPA_2B$ was carried out using palladium-catalyzed Stille couplings. Carefully purified 4,7-bis(4-(di(4-bromophenyl)amino)phenyl)-2,1,3-benzothiadiazole (0.235 g, 0.25 mmol), 4-[3-dodecyl-5-(tributylstannyl)-2-thienyl]-N,N-diphenyl benzenamine (1.178 g, 1.5 mmol) (3) and $Pd(PPh_3)_2Cl_2$ (10 mg) were dissolved in a mixture of toluene under an argon atmosphere. The mixture was refluxed with vigorous stirring for 48 h. Then the reaction solution was cooled to room temperature and poured into water, extracted with dichloromethane, the organic layer was washed with brine, dried over anhydrous sodium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, petroleum ether/CF (1:1)) to produce the title product as an orange solid (0.322 g, 50%). MALDI-TOF MS: *m/z* 2597.161 (100%) M^+ (calcd. 2597.76). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92–7.95 (d, 4H), 7.78 (s, 2H), 7.53–7.55 (d, 8H), 7.26–7.34 (m, 36H), 7.19–7.21 (d, 4H), 7.14–7.16 (d, 16H), 7.03–7.11 (m, 16H), 2.66–2.69 (t, 8H), 1.63–1.70 (m, 8H), 1.25 (s, 72H), 0.86–0.89 (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.52, 146.94, 129.75, 129.29, 124.62, 123.08, 31.92, 31.04, 29.70, 29.65, 29.62, 29.56, 29.50, 29.36, 29.00, 22.70, 14.14. Elem. Anal. for $C_{178}H_{186}N_8S_5$ Calc.: C, 82.31; H, 7.17; N, 4.32; S, 6.20. Found: C, 82.23; H, 7.56; N, 4.09; S, 6.12.

2.2. Device fabrication and characterization

Hole mobility of the small molecule films was measured using space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS)/small molecules/MoO_3 (10 nm)/Al (100 nm). Hole mobility was