



Synthesis of multi-armed small molecules with planar terminals and their application in organic solar cells



Dongfeng Dang ^{a, b, *}, Pei Zhou ^a, Manjun Xiao ^{a, c}, Renqiang Yang ^{c, **}, Weiguo Zhu ^{a, ***}

^a Department of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in the Ministry of Education, Xiangtan University, Xiangtan 411105, PR China

^b School of Science, Xi'an Jiao Tong University, Xi'an 710049, PR China

^c Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China

ARTICLE INFO

Article history:

Received 31 March 2016
Received in revised form
17 May 2016
Accepted 20 May 2016
Available online 21 May 2016

Keywords:

Organic solar cells
D-A type small molecules
Planar terminals
Multi-armed small molecules
3D molecules

ABSTRACT

Bi-armed Cz(BT-T-3Cz)₂, tri-armed TPA(BT-T-3Cz)₃ and tetra-armed SF(BT-T-3Cz)₄ with planar terminals were designed, in which carbazole, triphenylamine and spiro-fluorene units were employed as the electron-rich core, respectively, and benzothiadiazole units were introduced as the electron-deficient arms. As displayed, when the electron-deficient arms in molecules increase, improved thermal properties and increased extinction coefficient were obtained. Also as anticipated, the spatial configurations of SMs could affect their photovoltaic performance significantly. The linear Cz(BT-T-3Cz)₂-based solar cells exhibited a PCE value of 3.0%, however, tri-armed TPA(BT-T-3Cz)₃ and tetra-armed SF(BT-T-3Cz)₄ displayed better photovoltaic properties with the PCE values up to 5.25% and 4.37% in their corresponding devices, respectively, indicating that altering the spatial configurations in molecules is an efficient method to enhance their photovoltaic performance in OSCs.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past few years, small molecules (SMs) for bulk hetero-junction organic solar cells (BHJ-OSCs) have attracted much attention for their merits of well-defined molecular structures, ease of purification, no end group contaminants, and good batch to batch reproducibility [1–3]. Recently, great progress with the achievement of encouraging power conversion efficiency (PCE) value up to 10% has been achieved by optimizing the molecular structures and device architectures [4]. However, the overall performances of small molecules-based organic solar cells (SM-OSCs) are still inferior to their polymer counterparts (PSCs) currently. Therefore, to enrich the tool-box of high-performance small-molecules and reduce the performance gap between SM-OSCs and

PSCs, developing novel SMs with broad and strong absorption to sunlight, matched energy levels and high carrier mobility is still urgent needed. As known, using an appropriate electron-rich moiety (D) and an appropriate electron-deficient moiety (A) to construct the D-A type molecules is one of the most straightforward approaches to afford the above mentioned “ideal” molecules [5,6]. For instance, Chen et al. reported series of high performance SMs by utilizing the oligothiophene as D and rhodanine based building block as A, in which DRCN7T displayed an impressive PCE value up to 9.3% in solution-processed SM-OSCs [7]. On the other hand, developing the star-shaped molecules has also been demonstrated as one efficient method to obtain the high performance materials and solar cells. For example, employing the triphenylamine units (TPA) as core, star-shape molecules with broad absorption spectra, fine-tuned energy levels and high charge carrier mobility are designed and synthesized by Roncali [8,9] and Li [10,11] et al., which also display good photovoltaic properties in the SM-OSCs. In addition, incorporating the planar building blocks of anthracene, pyrene or fused-thiophene rings in polymer backbone or SMs is another promising approach to enhance their photovoltaic performance [12–16]. Recently, our group employed the fused-dibenzosexithiophene building block in polymer backbone to produce a highly planar polymer PBTF and it is found that good

* Corresponding author. School of Science, Xi'an Jiao Tong University, Xi'an 710049, PR China.

** Corresponding author. Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China.

*** Corresponding author. Department of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in the Ministry of Education, Xiangtan University, Xiangtan 411105, PR China.

E-mail addresses: dongfengdang@mail.xjtu.edu.cn (D. Dang), yangrq@qibebt.ac.cn (R. Yang), zhuwg18@126.com (W. Zhu).

photovoltaic performance with a high charge carrier mobility of $0.028 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved owing to its much effective π -electron delocalization [17]. Therefore, considering the merit of these common methods, star-shaped SMs with a D-A architecture by utilizing the planar carbazole units as terminal groups was developed recently by Zhu et al. [18,19] Encouragingly, a high PCE value up to 5.07% with a short-circuit current density (J_{sc}) of 10.08 mA/cm^2 and an impressive open circuit voltage (V_{oc}) up to 0.90 V was achieved in the solution-processed SM-OSCs, indicating that developing the D-A type small molecules with planar terminals is very attractive for SM-OSCs.

However, although good photovoltaic performance has been achieved for SM-OSCs, the relationship between molecular structures and their photovoltaic performance is still not well understood, including the influence of molecular spatial configurations on their photovoltaic properties of SMs. Meanwhile, the tetra-armed SMs as donor materials in solar cells are also seldom investigated. Therefore, to fully investigate the effect of molecular spatial configurations on the properties of SMs and photovoltaic performance of solar cells, 3-carbazolyl terminated bi-armed SMs of $\text{Cz}(\text{BT-T-3Cz})_2$, tri-armed SMs of $\text{TPA}(\text{BT-T-3Cz})_3$ and tetra-armed SMs of $\text{SF}(\text{BT-T-3Cz})_4$ were designed and synthesized in this work with the carbazole (Cz) [20], TPA [21] and spiro-fluorene (SF) [22] units as the core for their high hole mobility, respectively, in which the benzothiadiazole (BT) building block was introduced as the electron-deficient arms for its good electron-withdrawing properties [23,24]. All these molecules displayed a broad absorption spectra covering from 300 to 610 nm with the suitable HOMO and LUMO energy levels due to their efficient intra-molecular D-A charge transfer. Meanwhile, it's observed that when the electron-deficient arms increase in SMs, significantly improved thermal properties and increased extinction coefficient was obtained. It's also worth noting that when the three dimensional (3D) structures was constructed in tri-armed SMs of $\text{TPA}(\text{BT-T-3Cz})_3$ and tetra-armed SMs of $\text{SF}(\text{BT-T-3Cz})_4$, enhanced holes mobility up to 3.9×10^{-4} and $1.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by space charge limited current (SCLC) method was achieved, respectively, in contrast to that of linear typed $\text{Cz}(\text{BT-T-3Cz})_2$. Additionally, the photovoltaic properties of $\text{Cz}(\text{BT-T-3Cz})_2$, $\text{TPA}(\text{BT-T-3Cz})_3$, $\text{SF}(\text{BT-T-3Cz})_4$ were also fully studied by fabricating the solution-processing solar cells with a device structure of ITO/PEDOT: PSS/SMs: $\text{PC}_{71}\text{BM}/\text{Ca}/\text{Al}$. In contrast to the bi-armed $\text{Cz}(\text{BT-T-3Cz})_2$, tri-armed $\text{TPA}(\text{BT-T-3Cz})_3$ and tetra-armed $\text{SF}(\text{BT-T-3Cz})_4$ displayed better photovoltaic performance with a PCE value up to 5.25% and 4.37% in their corresponding OSCs, respectively, implying that the spatial configurations of SMs could affect their photovoltaic performance significantly. Our results here also indicate that altering the spatial configurations of molecules is an efficient and facile method to enhance their photovoltaic performance in OSCs.

2. Experimental section

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros and TCI) and used without further purification unless stated otherwise. Compound 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1) was purchased from Solarmer Materials Inc. Compound 3-(5-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-9-octyl-9H-carbazole (1) [19], compound tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (3) [19] and compound tetra(2,2',7,7'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)spiro-bifluorene (4) [22] were synthesized according to the literature.

2.2. Synthesis

2.2.1. Synthesis of compound $\text{Cz}(\text{BT-T-3Cz})_2$

Under nitrogen atmosphere, palladium(0)tetrakis(triphenylphosphine) [$\text{Pd}(\text{PPh}_3)_4$] (10.0 mg) was added to a solution of 3-(5-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-9-octyl-9H-carbazole (compound 1, 0.11 g, 0.19 mmol) and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (compound 2, 50 mg, 0.076 mmol) in ethanol (5 mL), toluene (40 mL) and potassium carbonate (K_2CO_3) aqueous solution (2 M, 1.5 mL). Then the mixture was heated and stirred for 20 h at 80°C . After that the reaction was quenched with water and extracted with dichloromethane (DCM) at room temperatures (RT). The combined organic layer was dried over anhydrous magnesium sulfate (MgSO_4) and then distilled to remove off the solvent. Then the residue was purified by column chromatography on silica gel using PE (petroleum ether)-DCM ($V/V = 1:1$) as eluent to give a dark red solid (62.9 mg, 60.3%). $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 8.50 (s, 2H), 8.43 (s, 2H), 8.33 (d, $J = 7.0$ Hz, 2H), 8.23 (d, $J = 7.0$ Hz, 4H), 8.09 (d, $J = 7.0$ Hz, 2H), 7.95 (d, $J = 7.3$ Hz, 2H), 7.89 (t, $J = 7.4$ Hz, 4H), 7.59–7.44 (m, 6H), 7.36–7.27 (m, 4H), 4.82 (s, 1H), 4.37 (t, $J = 6.4$ Hz, 4H), 2.61–2.45 (m, 2H), 2.15–2.01 (br, 2H), 1.98–1.84 (m, 4H), 1.51–1.15 (m, 44H), 0.99–0.67 (m, 12H). MALDI-MS (m/z): 1391.76 for $[\text{M}]^+$.

2.2.2. Synthesis of $\text{TPA}(\text{BT-T-3Cz})_3$

Compound $\text{TPA}(\text{BT-T-3Cz})_3$ was synthesized according to the synthetic procedure of $\text{Cz}(\text{BT-T-3Cz})_2$ as a purple solid with a yield of 50.6%. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 8.44 (s, 3H), 8.18 (m, 6H), 8.01 (d, $J = 8.0$ Hz, 9H), 7.85 (d, $J = 8.4$ Hz, 3H), 7.79 (d, $J = 7.3$ Hz, 3H), 7.53–7.39 (m, 18H), 7.29 (br, 3H), 4.32 (t, $J = 6.8$ Hz, 6H), 2.00–1.81 (m, 6H), 1.47–1.04 (br, 30H), 0.96–0.78 (br, 9H). MALDI-MS (m/z): 1725.15 for $[\text{M}]^+$.

2.2.3. Synthesis of compound $\text{SF}(\text{BT-T-3Cz})_4$

Compound of $\text{SF}(\text{BT-T-3Cz})_4$ was synthesized according to the synthetic procedure of $\text{Cz}(\text{BT-T-3Cz})_2$ as a dark red solid with a yield of 57.8%. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 8.36 (s, 4H), 8.16 (m, 8H), 7.99 (s, 4H), 7.75 (d, $J = 6.6$ Hz, 4H), 7.60 (s, 4H), 7.54–7.2 (m, 32H), 4.36–4.16 (br, 8H), 1.95–1.75 (br, 8H), 1.45–1.12 (br, 40H), 0.95–0.76 (br, 12H). MALDI-MS (m/z): 2291.12 for $[\text{M}]^+$.

2.3. Characterization and measurement

Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 analyzer and differential scanning calorimeter (DSC) was measured on a TA Q200 instrument under nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$. The theoretical study was performed on the 6–31G** basis set in Gaussian09 using the density functional theory (DFT), as approximated by the B3LYP. UV-Vis spectra were measured on a Perkin-Elmer Lambda 25 spectrometer. Cyclic voltammograms (CV) were performed with a three electrode electrochemical cell in a 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (TBAPF_6) solution with a scan 100 mV s^{-1} at room temperature under argon atmosphere. A platinum wire and Ag/AgCl (0.1 M) as were used as counter electrode and reference electrode. The thin films on the Pt disk, formed by drop-casting the molecule solution in chloroform (analytical reagent, 10 mg/mL), were used as the working electrode. Surface morphologies were recorded by atomic force microscopy (AFM) on a Veeco-DI Multi-mode NS-3D apparatus in a trapping mode under normal air condition at room temperature.

Download English Version:

<https://daneshyari.com/en/article/175361>

Download Persian Version:

<https://daneshyari.com/article/175361>

[Daneshyari.com](https://daneshyari.com)