



Synthesis of star-shaped non-fullerene acceptors and their applications in organic solar cells



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ARTICLE INFO

Keywords:

Star-shaped molecule
Non-fullerene acceptor
Organic solar cells
Narrow bandgap
Triphenylamine

ABSTRACT

Star-shaped planar acceptors have many advantages than linear planar ones such as stronger absorption, higher solubility and better film-forming properties, which are expected to have better solar cell performance. So far, most of star-shaped small molecule acceptors have a bandgap larger than 1.8 eV which cannot make use of near-infrared sunlight. In this work, three star-shaped small-molecular acceptors (TPA-ID, TPA-IC and TPA-ICF) with triphenylamine as core, 1,1-dicyanomethylene-3-indanone derivative as terminal group and 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']-dithiophene as bridge group were synthesized. These materials exhibit excellent solubility, high thermal stability and high extinction coefficient. TPA-IC and TPA-ICF have narrow bandgap (1.48 and 1.52 eV) and high HOMO energy levels (-5.31 eV and -5.36 eV) that matches well with that of typical donor PBDB-T. A PCE of 4.61% was achieved from photovoltaic device with a structure of ITO/ZnO/PBDB-T:TPA-IC(1:1.5)/MoO₃/Ag with a high V_{oc} of 0.90 V. The V_{oc} loss of this device is only 0.64 eV. The current device performance is limited by the low electron mobility of the acceptor which restricts absorber layer thickness.

1. Introduction

Over the past two decades, fullerene-based acceptors have been dominant in organic solar cells (OSCs) research field and devices with power conversion efficiencies (PCEs) over 11% have been achieved [1,2]. However, fullerene acceptors have low LUMO (lowest unoccupied molecular orbital) energy level and weak absorption, which limits device open circuit voltage (V_{oc}) and short-circuit current density (J_{sc}). In order to overcome these obstacles, non-fullerene n-type organic semiconducting materials have been developed [3–10]. Based on molecular structure, non-fullerene acceptors can be divided into polymer and small molecule. The efficiency of solar cells based on polymer acceptors has reached 10.1% [11], whereas small molecule ones have achieved efficiency higher than 14% [12–16], demonstrating the superior of small molecules over polymers acceptors. The breakthrough of non-fullerene small-molecular solar cells is mainly attributed to acceptor's better absorption and matched energy level with that of donors, bringing higher short-circuit current density and open circuit voltage. In addition, small-molecular non-fullerene acceptors have definite molecular structure, simple preparation/purification processes, and good phase-separation with donors, motivating researchers to

explore new type of small-molecular acceptors for higher efficiency OSCs.

The state-of-the-art small molecular acceptors are mostly based on linear planar structure. Star-shaped small-molecular acceptors have many advantages than linear planar ones such as stronger absorption, higher solubility and better film-forming properties [17–20], which are expected to have better solar cell performance. In 2012, using triphenylamine (TPA) as core and diketopyrrolopyrrole (DPP) as terminal group, Zhan [21] group designed and synthesized star-shaped small-molecular acceptors; solar cell using one of star-shaped small-molecular acceptors (S(TPA-DPP)) as acceptor and poly(3-hexylthiophene) (P3HT) as donor achieved a PCE of 0.81%. Due to the strong electron donating ability of triphenylamine, the triphenylamine-based compounds usually have high HOMO and LUMO energy levels. The high LUMO (-3.3 eV for S(TPA-DPP)) mismatches with that of state-of-the-art donors, such as PTB7-Th (-3.68 eV) and PBDB-T (-3.39 eV), and limits device performance [3]. Yang [22] and Zhan [23] groups replaced DPP with a stronger electron withdrawing group perylene diimide (PDI) to reduce the LUMO energy level and solar cell with a PCE of 6.10% was achieved using TPA-PDI-Se as acceptor and PDBT-T1 as donor. Due to the wide bandgap of TPA-PDI-Se (1.94 eV) which

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<https://doi.org/10.1016/j.synthmet.2018.08.017>

Received 17 July 2018; Received in revised form 23 August 2018; Accepted 27 August 2018

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cannot make use of near-infrared sunlight, the J_{sc} ($10.24 \text{ mA}\cdot\text{cm}^{-2}$) of PBDB-T:TPA-PDI-Se device is limited. In 2018, using 4,8-di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-PTh) as core, Yang [24] group developed a new star-shaped small-molecular acceptors named BPT-S and device based on BPT-S displayed a PCE of 8.28%. Later, Peng group [19,25] used truxene as the core and developed a series of star-shaped wide bandgap small molecular acceptors; a PCE of 10.18% was achieved using para-TrBRCN as acceptor. This is the highest efficiency organic solar cell based on star-shaped small-molecular acceptors. So far, most of star-shaped small-molecular acceptors have a bandgap larger than 1.8 eV [22,24,25], which cannot make use of near-infrared sunlight. In this work, we have used electron-rich triphenylamine as core and strong electron withdrawing groups 1,3-indandione (ID) [26–28], 1,1-dicyanomethylene-3-indanone (IC) [29,30] and 5,6-difluoro-1,1-dicyanomethylene-3-indanone (ICF) [31–33] as terminal group to design star-shaped narrow bandgap small-molecular acceptors. Due to the strong electron donating ability of triphenylamine, these materials were expected to have high HOMO energy levels, which could reduce the energy gap between the HOMO energy levels of acceptor and donor and thus improve V_{oc} . With increase of electron-withdrawing ability of terminal group, the band gap of the compound would become narrower [34–36]. These terminal groups (ID, IC and ICF) have stronger electron-withdrawing property than PDI, so we expected the new star-shaped small-molecular acceptors will have narrower bandgap than TPA-PDI-Se (1.94 eV) [22]. In addition, in order to increase the conjugation degree, we had selected 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b]-dithiophene as a bridge to connect core and terminal group. Three star-shaped small-molecular acceptors (TPA-ID, TPA-IC and TPA-ICF) with bandgaps of 1.83, 1.54 and 1.48 eV were synthesized and a PCE of 4.61% had been obtained from PBDB-T/TPA-IC solar cells.

2. Experimental section

2.1. Materials and methods

All reagents were obtained from commercial sources and used without further purification unless otherwise specified. Tris(4-bromophenyl)amine (98%), bis(pinacolato)diboron (98%), 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b]-dithiophene (98%), 1,3-indandione (98%), 1,1-dicyanomethylene-3-indanone (98%) and 5,6-difluoro-1,1-dicyanomethylene-3-indanone (98%) were purchased from Zhengzhou Alfachem Co., Ltd. [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (99.8%) was obtained from Meryer (Shanghai) Chemical Technology Co., Ltd. N-butyllithium (1.6 M solution in hexane) and tetrakis(triphenylphosphine)palladium were bought from J&K Scientific Ltd. N-bromosuccinimide (98%) was purchased from Alfa Aesar. PBDB-T was purchased from Solarmer Energy, Inc.

^1H and ^{13}C NMR spectra were performed on Bruker Daltonics Avance III NMR instrument with tetramethylsilane (TMS) as internal reference. Relative molecular mass was measured on Bruker Daltonics autoflex speed MALDI-TOF. Thermogravimetric analysis (TGA) was performed on a Netzsch TG209 at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ with a nitrogen flow rate of $20 \text{ mL}\cdot\text{min}^{-1}$. UV-vis spectra were measured on a PerkinElmer Lambda 35 spectrophotometer. The electrochemical properties of the star-shaped small-molecular acceptors were investigated on CHI660E electrochemical workstation with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte and acetonitrile as solvent. Platinum wire, glassy carbon, and Ag/AgCl were used as auxiliary electrode, working electrode and reference electrode, respectively. The small-molecular acceptors were coated on a glassy carbon electrode from CH_2Cl_2 solution. The scan rate was $50 \text{ mV}\cdot\text{s}^{-1}$. Ferrocene (Fc) was used as the internal standard and the onset potential of Fc/Fc^+ was measured to be 0.36 V ($E_{\text{Fc}/\text{Fc}^+} = 0.36 \text{ V}$). The HOMO and LUMO energy levels were calculated from the onset oxidation ($E_{\text{ox}}^{\text{onset}}$) and onset reduction ($E_{\text{red}}^{\text{onset}}$) potentials by equations: $E_{\text{HOMO}}^{\text{HOMO}} =$

$-(E_{\text{ox}}^{\text{onset}} - E_{\text{Fc}/\text{Fc}^+} + 4.8) \text{ eV}$ and $E_{\text{LUMO}}^{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} - E_{\text{Fc}/\text{Fc}^+} + 4.8) \text{ eV}$. X-ray diffraction (XRD) spectra were performed with a Bruker Daltonics D8 Advance A25 X-ray diffractometer. The samples for XRD measurement were prepared by drop-casting solution of star-shaped small-molecular acceptors in CH_2Cl_2 on quartz glass substrates. Lamellar stacking distance of star-shaped small-molecular acceptors were calculated by Bragg's law: $2d\sin\theta = n\lambda$, d is the stacking distances, θ is the degree of diffraction peaks, λ is the wavelength of X-ray and n is the diffraction order number and the value of n usually is 1. The current density-voltage (J - V) curves of the solar cells were measured under AM 1.5 simulated sunlight using a Keithley 2400 source meter. The external quantum efficiency (EQE) of the solar cells were measured on Enlitech QE-R3018 using calibrated Si (Enli technology Co. Ltd.) as reference. Atomic force microscope (AFM) height and phase images were measured on Icon dimension atomic force microscope.

2.2. Synthesis

2.2.1. Compound 3

In a 250 mL two-necked flask, compound 1 (0.75 g, 1.20 mmol) and compound 2 (3.14 g, 7.68 mmol) were dissolved in a mixture of THF (100 mL) and water (25 mL). After NaHCO_3 (0.80 g, 9.60 mmol) and Pd (PPh_3)₄ (83 mg, 0.072 mmol) were added, the solution was heated to 80°C and refluxed for 72 h under argon. After the reaction finished, CH_2Cl_2 (100 mL) was added and the solution was washed with water ($200 \text{ mL} \times 3$). Then the organic phase was dried over anhydrous Na_2SO_4 . After removal of the solvent by rotary evaporation, the crude product was purified by silica gel column chromatography (eluted with petroleum ether: CH_2Cl_2 (v:v 1:3)) to obtain compound 3 as the brown solid (0.57 g, yield 55%). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.82 (s, 3 H), 7.59–7.55 (m, 9 H), 7.19 (s, 3 H), 1.91 (m, 12 H), 1.20–1.18 (m, 12 H), 0.95–0.88 (m, 36 H). 0.68–0.65 (m, 18 H), 0.60–0.55 (m, 18 H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 182.47, 163.12, 157.18, 148.49, 148.16, 146.65, 142.85, 134.76, 129.71, 126.67, 124.59, 117.86, 54.12, 42.42, 34.71, 33.42, 27.74, 26.73, 22.02, 13.15, 9.76. HR-MS (MALDI-TOF) m/z calculated for $\text{C}_{96}\text{H}_{123}\text{NO}_3\text{S}_6$: 1529.723, found: 1530.412.

2.2.2. TPA-ID

In a 50 mL two-necked flask containing compound 3 (0.20 g, 0.13 mmol) and compound a (0.10 g, 0.52 mmol), acetic anhydride (2.5 mL) were added. The solution was heated to 140°C and refluxed for 72 h under argon. After the reaction finished, dichloromethane (100 mL) were added and the solution was washed with water ($200 \text{ mL} \times 3$). Then organic phase was dried over anhydrous Na_2SO_4 . After removal of the solvent by rotary evaporation, the crude product was purified by silica gel column chromatography (eluted with petroleum ether: CH_2Cl_2 (v:v, 1:2)) to obtain TPA-ID as the brown solid (0.15 g, yield 55%). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 7.88–7.79 (m, 12 H), 7.69–7.64 (m, 6 H), 7.55–7.51 (m, 6 H), 7.20 (s, 3 H), 7.14 (d, $J = 12.00 \text{ Hz}$, 6 H), 1.91 (m, 12 H), 1.20–1.18 (m, 12 H), 0.95–0.88 (m, 36 H). 0.68–0.65 (m, 18 H), 0.60–0.55 (m, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 190.42, 164.74, 158.53, 154.06, 150.15, 146.81, 142.03, 140.40, 138.41, 136.53, 135.52, 134.53, 129.76, 126.71, 124.64, 122.32, 121.47, 118.33, 66.75, 42.42, 34.71, 33.40, 27.71, 26.72, 22.07, 13.18, 9.69. HR-MS (MALDI-TOF) m/z calculated for ($\text{C}_{123}\text{H}_{135}\text{NO}_6\text{S}_6$): 1913.861, found: 1913.034.

2.2.3. TPA-IC

In a 50 mL two-necked flask containing compound 3 (0.20 g, 0.13 mol) and compound b (0.14 g, 0.53 mmol), CHCl_3 (25 mL) and pyridine (1 mL) were added. Under the protection of Ar atmosphere, the solution was heated to 80°C and refluxed for 24 h. After removal of the solvent by rotary evaporation, the crude product was purified on silica gel column chromatography (eluted with petroleum ether: CH_2Cl_2 (v:v, 1:2)) to obtain TPA-IC as the black solid (0.16 g, yield 50%). ^1H NMR

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