Dyes and Pigments 132 (2016) 41–47

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Edge-to-face stacking non-fullerene small molecule acceptor for bulk heterojunction solar cells

Qichao Wu [a], Ling Li [a], Jiefeng Hai [a], Xin Zhang [b], Zhenhuan Lu [a, *], Jianwen Yang [a], Yongping Liu [a, **], Lingzhi Zhang [a], Chuanlang Zhan [b, ***]

[a] Guangxi Key Laboratory of Electrochemical and Magneto-chemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China
[b] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

*Article history:*
Received 21 February 2016
Received in revised form
23 April 2016
Accepted 25 April 2016
Available online 26 April 2016

*Keywords:*
Non-fullerene
Perylene
Small molecule acceptor
Organic solar cells
Edge-to-face interaction

ABSTRACT

Synthesis of a novel small molecule accepter with perylenediimide linked through thiophene ring with triphenylamine is described. Introducing thiophene unit leads to extending the molecular absorption spectrum to the range of 330 nm–700 nm. The molecule showed the lowest unoccupied molecular orbital level (LUMO) of −3.80 eV and the highest occupied molecular orbital level (HOMO) of −5.60 eV. The X-ray Diffraction (XRD) spectra confirmed that the molecule self-assemble in the solid phase by edge-to-face aromatic interaction, and the addition of 1, 8-diiodooctane in the solvent can adjust its stacking, and thus improve the crystallinity and electron mobility. Solution-processed bulk-heterojunction organic solar cells constructed using the small molecule as acceptor and the polymer of PBDTTT-C-T as donor showed the best efficiency of 1.92%.



## 1. Introduction

Solution-processed bulk heterojunction (BHJ) organic solar cells (OSCs) have become a research hotspot in recent two decades, because they have the advantages of low-cost, light-weight, and flexibility. In recent years, many encouraging results have been reported in the literature [1]. For example, the best power conversion efficiencies (PCEs) of the polymer electron donor and fullerene electron acceptor system have achieved 10–11% [2–4], the efficiency of organic small molecule donor and fullerene acceptor system has now reached about 10% [5–7]. These high efficient results are obtained on the basis of the donor materials. In fact, the acceptor material is equally important to the high performance OSCs. However, the development of acceptor materials is relatively slow. At present, fullenrence derivatives are widely used as electron acceptors in OSCs due to their excellent electric properties [8]. However, there are some insufficiencies that limit its further development, such as weak absorption in the visible region, difficult purification procedures and limited energy level variation. On the other hand, organic small molecules have structure and chemical multiplicity, increase probability to broaden solar spectral coverage, purifying and adjusting energy level. Therefore, many researchers are now working on the non-fullerene acceptor materials researches [9–14]. The efficiency of non-fullerene acceptor materials began to develop rapidly since the year 2010. The PCE value first broke through 2% at the end of 2010 [15] and further break through 4% in 2013 [16]. Recently, the PCE of solar cells based on the non-fullerene acceptor has been boosted to 7–8% [17–19]. Compared with fullerene acceptors, however, non-fullerene acceptors are still at the infant stage, and more novel non-fullerene acceptors should be explored.

Perylene diimides (PDIs) is a kind of widely used acceptor unit with excellent photoelectric properties, electron affinity, high electron mobility, light stability, thermal stability, and chemical stability [20]. However, PDI molecules have a strong aggregation ability which is easy to form large size crystal phase [21]. Thus, it is

* Corresponding author. Guilin University of Technology, No. 12 Jiangan Road, Guilin 541004, China.
** Corresponding author. Guilin University of Technology, No. 12 Jiangan Road, Guilin 541004, China.
*** Corresponding author. Institute of Chemistry, Chinese Academy of Sciences, North First Street No. 2, Zhongguancun, Beijing 100190, China.
*E-mail addresses:* zhenhuanlu@glut.edu.cn (Z. Lu), liuyp624@163.com (Y. Liu), clzhan@iccas.ac.cn (C. Zhan).

http://dx.doi.org/10.1016/j.dyepig.2016.04.040
0143-7208/

difficult to blend with the donor materials to form interpenetrating network structure as bulk heterojunction requirement. Therefore, it often links alkyl, attracting/donating electron group or aromatic system to the amide N or the bay region of PDI molecule, with the aim of adjusting the properties of the molecules [22–27]. For example, using the donor units such as thiophene [28], TPA [29] couples to the waist of PDI molecules. Conjugating these aromatic with the aromatic ring of PDI leads to extending the conjugation length and expanding the molecular absorption range. At the same time, the introduction of these donor units can adjust the HOMO/LUMO energy levels of the molecule, and achieve fine tuning donor/acceptor (D/A) pairs with matched energy. Moreover, it can weaken the aggregation ability of PDI derivatives, adjust crystallinity, offer the acceptor not only a good film forming property, and maintain sufficient electron mobility in the blend film as well. In the end, researchers employed a solvent additive, such as 1, 8-diiodooctane (DIO), to control the morphology of the active layer, so finally optimizing the performance of a BHJ device [30–32]. In recent years, many high efficient PDI acceptor materials have been developed following the above-mentioned principle [16,19,33].

In this paper, we reported the synthesis of a novel star-shaped perylenebisimide small molecule, namely **TPA(T-PDI-EG)$_3$**, which was based on perylenediimide, triphenylamine (TPA) and thiophene. This molecule showed excellent absorption on broad solar spectral coverage, and matched the energy level of polymer donor **PBDTTT-C-T**. Above all, we found the small molecules assembling in the solid phase with edge-to-face aromatic interaction, and then studied the aromatic interaction's adjust mechanism of 1, 8-diiodooctane (DIO) additive. Moreover, we used **TPA(T-PDI-EG)$_3$** as acceptor and **PBDTTT-C-T** as donor to fabricate non-fullerene OSCs, and carried out an investigation of the blend film morphology, mobility and photoelectric properties.

## 2. Experimental section

### 2.1. Measurements and characterization

$^1$H NMR and $^{13}$C NMR spectrums were recorded by a Bruker DMX-400 spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by a Bruker BIFLEX III. Elemental analysis was performed on a flash EA1112 analyzer. The electrochemical cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) dichloromethane (DCM) solution with a scan speed at 50 mV/s. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The reference value (Ag/AgCl), which is used for the estimation of HOMO-LUMO energy values, is −4.4 eV *vs.* vacuum. Atom force microscopy (AFM) was investigated by Brucker Multimode 8 using tapping-mode with a scan speed of 1 Hz. Transmission electron microscopy (TEM) tests were performed on a JEM-2011F operated at 200 kV. The TEM specimens were prepared by transferring the spin-coated films to the 200 mesh copper grids. The X-ray Diffraction (XRD) spectrum was recorded by a Rigaku D/max-2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Kα radiation. The absorption spectrum was measured on Shimadzu, Lambda750 UV–vis spectrophotometer. The solution spectrum was obtained using a 1 cm optical length quartz cell and the film spectrum was obtained via the transmission mode. The thickness of the solid films was measured by atom force microscopy. Thermally evaporated deposition was performed on a high vacuum evaporation coating machine (ZHD-300M2, Beijing Technol Science Co., Ltd.). Density functional theory (DFT) calculations were performed with the Gaussian 09 program, using the B3LYP functional. All-electron double-ξ valence basis sets with polarization functions 6-31G* were used for all atoms. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency.

### 2.2. Fabrication and characterization of the photovoltaic cells

Solar cell devices with a typical configuration of indium tin oxide (ITO)/Poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS)/**PBDTTT-C-T:TPA(T-PDI-EG)$_3$**/Ca/Al was fabricated as follows: The ITO glass was pre-cleaned with deionized water, CMOS grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating with UV-ozone for 1 h. Then the ITO glass was modified by spin-coating PEDOT: PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) layer, 30 nm) on it. After the ITO glasses were dried in oven at 150 °C for 15 min, the active layer was spin-coated on the ITO/PEDOT:PSS using a blend solution of **TPA(T-PDI-EG)$_3$** and **PBDTTT-C-T** (30 mg/mL in o-dichlorobenzene (*o*-DCB), variants with donor/acceptor weight ratio, and different contents of DIO, respectively). Ca (20 nm) and Al (80 nm) electrode was then subsequently thermally evaporated on the active layer under the vacuum of $1 \times 10^{-4}$ Torr. The active area of the device was 0.06 cm$^2$, and the thicknesses of the active films were ~90 nm. The devices were characterized under the illumination of simulated AM 1.5 G, 100 mW/cm$^2$ using a solar simulator (Newport Oriel 91192). The current–voltage (*I*–*V*) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. The EQE measurements were performed in air using solar cell QE/IPCE measurement system (Solar Cell Scan100, Zolix Instruments Co., Ltd.) with a scan increment of 20 nm per point.

### 2.3. Materials

All reagents and chemicals were purchased from commercial sources (TCI, Acros, Sigma, or Alfa) and used without further purification except statements. Solvents (toluene and tetrahydrofuran) were distilled by standard procedures before used for organic synthesis. The polymer of PBDTTT-C-T (Mn = 20,000 g/mol, PDI = ~3) was purchased from Solarmer company.

### 2.4. Synthesis

**1** and **2** were synthesized following our reported procedure [34,35]. A mixture of **1** (268.2 mg, 0.35 mmol) and **2** (98.3 mg, 0.1 mmol) was dissolved in dry toluene (20 mL). Catalytic amounts of $Pd[P(C_6H_5)_3]_4$ was added and the reaction mixture was stirred at 110 °C for 36 h. The mixture was extracted with dichloromethane (DCM), washed with water. Then, DCM layer was dried over $Na_2SO_4$. After removal of DCM, the residue was applied to chromatography with $CH_2Cl_2$/ethanol (50:1) as eluents to afford the desired products **TPA(T-PDI-EG)$_3$** as a black solid (148.0 mg, 0.058 mmol, yield = 58%).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ ppm: 9.59–8.30 (m, 18H), 7.68–7.22 (br, 18H), 4.71–4.60 (m, 6H), 4.22–3.96 (m, 12H), 4.04–3.96 (m, 6H), 3.64 (s, 9H), 2.02–1.93 (m, 6H), 1.46–1.31 (m, 48H), 1.03–0.90 (m, 36H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 164.09, 163.68, 163.50, 157.20, 149.57, 147.41, 147.04, 135.30, 134.19, 133.46, 132.94, 131.68, 131.48, 130.61, 130.24, 129.38, 128.91, 128.68, 127.85, 127.58, 127.46, 127.39, 124.92, 124.33, 123.94, 123.57, 122.51, 121.85, 121.54, 120.58, 117.74, 71.01, 69.51, 59.70, 44.69, 38.29, 38.19, 31.17, 31.01, 29.08, 28.95, 24.44, 24.26, 23.39, 23.34, 14.44, 14.37, 10.96, 10.84; MS (MALDI-TOF): *m/z* = 2552.2 $[M+H]^+$; Elemental analysis: calcd (%) for $C_{159}H_{159}N_7O_{18}S_3$: C 74.83, H 6.28, N 3.84, S 3.77; found C 74.76, H 6.27, N 3.83, S 3.78.