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Donor–acceptor–π–acceptor based charge transfer chromophore as electron donors for solution processed small molecule organic bulk heterojunction solar cells

P. Gautam [a], R. Misra [a,*], S.A. Siddiqui [b], G.D. Sharma [c,*]

[a] Department of Chemistry, Indian Institute of Technology Indore, MP 452017, India
[b] Department of Electrical Engineering, Vivekanand Institute of Technology (VIT), NRI Road, Jagatpura, Jaipur, Rajasthan 303012, India
[c] R & D Center for Engineering and Science, JEC Group of Colleges, Jaipur Engineering College, Kukas, Jaipur, Rajasthan 302028, India

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ABSTRACT

Two benzothiazole (BT) based donor–acceptor–π–acceptor (D–A–π–A) molecular system denoted as BT3 and BT4 have been designed, synthesized and their optical and electrochemical properties were investigated. The **BT4** show wider absorption profile and lower bandgap as compared to **BT3** due to the strong electron withdrawing ability of dicyanoquinodimethane (DCNQ) as compared to tetracyanobutadiene (TCBD). The solution processed bulk heterojunction solar cells were fabricated using **BT3** and **BT4** as electron donor and $PC_{71}BM$ as electron acceptor. The organic solar cells optimized dichloromethane (DCM) processed **BT3**:$PC_{71}BM$ (1:1) and **BT4**:$PC_{71}BM$ (1:1) showed PCE of 2.56% and 3.68%, respectively. The higher PCE of **BT4**:$PC_{71}BM$ is related to the wider absorption of the blend and better ordered domain sizes in the blend as compared to **BT3**:$PC_{71}BM$. The devices processed with 1,8-diiodoctane (DIO) additives showed PCE of 3.77% and 5.27%, for **BT3**:$PC_{71}BM$ and **BT4**:$PC_{71}BM$ blends, respectively.

1. Introduction

Bulk heterojunction, comprised of a blend of electron donor (polymers or small molecules) and electron acceptor (fullerene derivatives) have attracted considerable attention due to their potential for fabrication of low cost devices with high power conversion efficiency (PCE) [1]. The power conversion efficiencies (PCE) of polymer/fullerene BHJ solar cells have increased over the past two decades and approached 9.2% in single junction cells [2], and more than 10% for tandem solar cells [3]. In spite of the high PCE of these organic solar cells, polymer donor materials always suffer from batch to batch variations, difficulty of purification, and polydispersity [4]. Compared to polymers, the small molecules have advantages including a well defined molecular structure, definite molecular weight and high purity without batch to batch variations [5], and have garnered lots of attention for solution processed organic BHJ solar cells [6]. Solution processed BHJ organic solar cells based on small donor molecules have shown outstanding PCE of over 8% in the recent years [7]. These results indicate that small molecule based BHJ organic solar cells have a great potential. At present, an impressive PCE of 12% has been achieved for a vacuum processed triple junction tandem small molecule organic solar cell (SMOSC) [8].

In order to obtain high PCE in organic solar cells based on small molecules, the synthesis of low bandgap small molecules containing electron donating (D) and electron accepting (A) groups have become a widely used strategy

* Corresponding authors.
E-mail addresses: rajneeshmisra@iiti.ac.in (R. Misra), sharmagd_in@yahoo.com, gdsharma273@gmail.com (G.D. Sharma).

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over the past few years [9]. In the case of D–A based organic material, the intramolecular charge transfer (ICT) between the D and A unit in the material effectively extends the light absorption to the near infrared (NIR) region of the solar spectrum. However, it decreases the absorption of the material in the visible region resulting in the reduction in short circuit current density (J_{sc}) [10]. This issue can be overcome by incorporating an additional electron rich (1A/2D system) or electron deficient unit (2A/D system) as a third unit in the material, which can extend the range of light absorption through the appearance of new $\pi \rightarrow \pi^*$ or lCT peak, respectively. Moreover, the Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels can be controlled by tuning the strength of the three different units because the degree of electron donating and accepting ability affects the HOMO and LUMO energy levels, respectively, of the materials.

Two small molecules **BT3** and **BT4** having A1–π–A2–D molecular structure with the same A1 (benzothiazole), π-linker (phenyl) and D triphenylamine (TPA) but different A2, i.e. tetracyanobutadiene (TCBD) and dicyanoquinodimethane (DCNQ) for **BT3** and **BT4** were synthesized, and their optical, electrochemical and theoretical properties were investigated. These small molecules were applied as donor along with $PC_{71}BM$ as acceptor for the fabrication of solution processed bulk heterojunction organic solar cells and showed PCE of 2.56% and 3.68% for **BT3**:$PC_{71}BM$ and **BT4**:$PC_{71}BM$ blends cast from DCM solvent. Through the incorporation of 1,8-diiodoctane (DIO) additive during the spin coating of active layer the PCE of organic solar cells has been enhanced up to 3.77% and 5.27%, for **BT3**:$PC_{71}BM$ and **BT4**:$PC_{71}BM$ blends, respectively.

2. Experimental details

2.1. Device fabrication and characterization

The BHJ organic solar cells were prepared using indium tin oxide (ITO) coated glass substrate as anode, Al as cathode and a blended film of **BT3** or **BT4**:$PC_{71}BM$ between the two electrodes as photoactive layer as follows. Firstly, ITO-coated glass substrates were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried in an oven for 12 h. An aqueous solution of PEDOT:PSS (Heraeus, Clevios P VP,Al 4083) was spin cast on the ITO substrates obtaining a film of about 40 nm thick. The PEDOT:PSS film was then dried for 10 min at a temperature of 120 °C in ambient conditions. Then, 10 mg/mL solutions of **BT3** or **BT4**/$PC_{71}BM$ blends in different solvents were prepared with different weight ratios spun cast on the top of the PEDOT:PSS layer, and dried at 80 °C for 10 min. The solvents include dichloromethane (DCM) and DCM containing 1%, 2%, 3% and 4% (*v*%) DIO. The thickness of the photoactive layer was about 100 ± 10 nm. Finally ~90 nm thick Al electrodes were deposited on the top of BHJ film under reduced pressure (<10^{-6} Torr). All the devices were fabricated and tested in ambient atmosphere without encapsulation. The active area of the devices is about 0.20 cm^2.

The current–voltage characteristics of the devices were measured using a computer controlled Keithley 238 source meter in the dark as well as under an illumination intensity of 100 mW/cm^2. A xenon light source coupled with AM1.5 optical filter was used as light source to illuminate the surface of the devices. The incident photon to current efficiency (IPCE) of the devices were measured illuminating the device through the light source and monochromator and resulting current was measured using Keithley electrometer under short circuit condition.

3. Results and discussions

3.1. Synthesis and characterization of BT3 and BT4

The synthesis of donor–acceptor–π–acceptor (D–A–π–A) benzothiazoles (BTs) BT3 and BT4 are shown in Scheme 1. The condensation of 2-aminothiophenol with 4-bromobenzaldehyde in DMSO at 190 °C for 1 h resulted in bromo BT1 with 52% yield [9e]. The donor triphenylamine unit was incorporated via Pd-catalyzed Sonogashira cross-coupling reaction of BT1 with 4-ethynyl-N-N-diphenyaniline which resulted in compound BT2 with 70% yield. The [2 + 2] cycloaddition–retroelectrocyclization reaction of acetylene linked compound BT2 with TCNE and TCNQ yielded BT3 and BT4, respectively (Scheme 1) [9f]. The details of synthesis and characterization can be found in supporting information.

3.2. Optical and electrochemical properties

The normalized absorption spectra of dilute solutions of **BT3** and **BT4** in dichloromethane (DCM) and of thin films deposited on quartz glass are shown in Fig. 1 and the summary of optical data, i.e. absorption peak wavelengths (λ_{max}) and optical bandgap $\left(E_g^{opt}\right)$ are complied in Table 1. The solution of **BT3** exhibits two absorption bands with absorption peaks at 400 nm and 480 nm having molar extinction coefficients of $3.38 \times 10^4\ M^{-1}\ cm^{-1}$ and $2.82 \times 10^4\ M^{-1}\ cm^{-1}$, respectively, whereas **BT4** exhibits two absorption bands having absorption peaks at 342 nm and 663 nm with molar extinction coefficients of $2.31 \times 10^4\ M^{-1}\ cm^{-1}$ and $2.05 \times 10^4\ M^{-1}\ cm^{-1}$ respectively, and an additional shoulder at 450 nm. Compared to BT3, BT4 exhibits a wider and red-shifted absorption band in the longer wavelength region, attributed to the strong electron withdrawing capability of DCNQ. The absorption spectra of these small molecules in thin films showed broadening and red-shifting of the optical absorption in the low energy band as compared to the absorption spectra in solution. This can be attributed to greater π-electron delocalization and enhanced inter-chromophore interactions in solid state [11]. The optical bandgaps were estimated from the onset of absorption spectra in long wavelength region and are 1.95 eV and 1.45 eV, for **BT3** and **BT4**, respectively. The lower value of optical bandgap may be attributed to the strong electron withdrawing nature of DCNQ unit in **BT4**.

The redox properties of BT3 and BT4 have been investigated in dichloromethane and the results are summarized