



Improvement of intramolecular charge transfer within a donor–acceptor blend by doping novel synthesized benzothiadiazole small molecules in solid state



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ABSTRACT

Three electron-deficient small molecules based on 2,1,3-benzothiadiazole (BTD) units namely, 4,7-bis(3-methoxyphenyl)-2,1,3-benzothiadiazole (**BT1**), (3-{7-[3-(dimethylamino)phenyl]-2,1,3-benzothiadiazole-4-yl}phenyl)dimethylamine (**BT2**) and 3,3'-(2,1,3-benzothiadiazole-4,7-dyl)dianiline (**BT3**) were synthesized and their photophysical properties were investigated systematically to understand their potential usage in ternary organic solar cells (OSCs) as additive material to enhance the cell efficiency. All these molecules show broad absorption bands in 350–750 nm on glass substrate and their optical band gaps were calculated to be around 2.50–2.80 eV. BTD fluorescence dynamics were measured in polymer:BT1:fullerene blends with varying emission wavelengths of active layer. Fluorescence emission and time resolved measurements indicated photoinduced energy shift from **BT1** dye to fullerene and also from polymer to **BT1** dye upon excitation of the active layer.

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1. Introduction

New family of organic semiconductors is in progress for the development of cheap and high performance photovoltaic materials. Polymers containing 2,1,3-benzothiadiazole (BTD) units have been successfully used in organic solar cells (OSCs). One of these, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] [PCPDTBT], in blends with [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM), has been reported as giving satisfyingly a high power conversion efficiency (PCE) of 3.2% and external quantum efficiency of 38% [1]. Cell efficiency of bulk-heterojunction solar cells (BHJCs) based on poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) blends has been enhanced by the addition of small fractions of PCPDTBT polymer and efficiency has been reached to a value of 2.8% [2]. Efficient BHJCs have been fabricated using a benzothiadiazole-thiophene co-polymer, PCDTPT, in blends with PCBM giving impressive performances with PCE values around 6.0–6.5% [3,4].

BTDs are one of the most used groups in conjugated systems because of their high fluorescence activity, efficient electron-withdrawing capacity, well-ordered crystal structures and high

reduction potentials [5]. Many groups have preferred the BTD containing polymers or co-polymers blending with different mass ratios of PCBM acceptor to fabricate efficient OSC devices [6–13]. BTD units in these polymers contribute the cell performance by lowering the band gap and improving the absorption covering the entire solar spectra [14,15]. Also, small molecule BTD derivatives play an important role in OSC technologies. As compared to the polymeric counterparts, many of small molecules have well-defined molecular structures and are easy to re-synthesize, functionalize and purify [16]. There are several families of solution processable BTD small molecules that have been used as donor materials in BHJ solar cells in literature [17–28]. Among these studies, Wang and co-workers have reported a promising result with an impressive V_{oc} of 1.04 V and a PCE of 3.85% by fabricating a device with blended PC₆₁BM and BTD-triphenylamine type small molecule [29]. Horie and co-workers have used a BTD/cyclopentadithiophene small molecule as a sensitizer in a ternary blend with classical P3HT:PC₆₁BM type OSCs and obtained a high cell efficiency value of 4.1% [30].

Detailed analysis of photophysical process within donor and acceptor sites in blend is necessary to clarify the charge transfer contribution of BTD small molecule to overall performance for these OSC devices described above. P3HT:PC₆₁BM blends have granted a convenient model to understand the photophysics and charge generation dynamics in many donor–acceptor groups in

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OSC devices [31–35]. In these systems, it is known that excitons are conveyed to the interface, where they separated into charge carriers, by charge transfer from donor P3HT to acceptor PCBM. In a ternary system, where one component (BTD small molecule) acts as sensitizer and the others as charge transporting system components (P3HT/PC₆₁BM). BTD contribution to overall charge shift has not been discussed yet. Samuel and co-workers have investigated the singlet exciton diffusion and decay dynamics in conjugated PCDTPT polymers blended with fullerene acceptor. They have reported that exciton diffusion occurs into the polymer inside at very low concentrations of fullerene, whereas Förster-type energy transfer to the fullerene is the main process at higher fullerene concentrations [36].

In this report, we have managed to synthesize three kinds of new BTD derivatives with different donor substituents, as shown in Fig. 1. Also, we have focused on photoinduced energy or electron transfer process between donor and acceptor components in P3HT:BTD:PC₆₁BM ternary structure using fluorescence emission and time resolved measurements. We have compared the photo-physical properties of BTD dyes on thin films with in solutions of different polarities.

2. Experimental section

2.1. General procedures

¹H NMR and ¹³C NMR were performed using a Bruker 400 MHz spectrometer. FT-IR spectra were carried out using a Perkin Elmer-Spectrum BX spectrophotometer preparing KBr pellets. UV-vis spectra were recorded using a UV-vis-NIR spectrometer (Perkin Elmer Lambda 950) in solutions and on thin films. Fluorescence and life time measurements were obtained using a FLSP 920 Edinburgh fluorescence phosphorescence spectrophotometer. The fluorescence life times were determined by the single photon timing method using a laser which has been used to excite the samples at 472 nm. The Edinburgh Instruments F900 exponential tail fit method [37] was used for calculations. Single photon timing method was used to obtain the fluorescence decay histograms in 10,000 data channels. The fitted decay curve was settled by the fitting parameters such as $\chi^2 < 1.2$ goodness of fit. The instrument response function (IRF) was determined using a Ludox scattering solution.

To investigate the electrochemical characteristics of synthesized **BT1-3** dyes, cyclic voltammetry (CH instruments-Electrochemical

Workstation) measurements were performed with a standard three-electrode electrochemical compartment in 100 mM [TBA][PF₆] solution in Me-CN as the supporting electrolyte. Ag/AgCl, glassy carbon and Pt wire electrodes were used as reference, working and counter electrodes, respectively. The scan rate was at 50 mV/s. Ferrocene-ferrocenium (Fe/Fe⁺) couple which was exhibited at about +0.55 V was used as internal reference for the calculation of the onset values of E_{red} . HOMO and LUMO energy levels of **BT1-3** dyes were calculated by the formulas [38]:

$$E_{\text{LUMO}} = -(4.8 + E_{\text{red}}^{\text{onset}}), \quad E_{\text{red}}^{\text{onset}} = E_{\text{red}}^0 - E_{\text{ox}}^0(\text{ferrocene}), \quad E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$$

PC₆₁BM and other photoactive components were dissolved at concentrations of 1 wt% from *o*-dichlorobenzene (oDCB) solution in different mass ratios. Active layer was coated onto the glass surface by spinning and, then the coated substrate was dried at 75 °C for 30 min under vacuum.

2.2. Materials

Chloroform, silica gel, tetrakis(triphenylphosphine)palladium(0), hydrogen bromide solution (47%) were purchased from Merck Company. Benzene, sodium carbonate, bromine were purchased from Carlo Erba. Ethanol, 2,1,3-benzothiadiazole, magnesium sulfate, 3-(*N,N*-dimethylamino)-phenylboronic acid, 3-aminophenylboronic acid hemisulfate were purchased from Sigma-Aldrich. 3-methoxybenzeneboronic acid (from Alfa Aesar) and NaHSO₃ (Riedel-de-Haën) were used as received. Other organic solvents were analytical grade and used without further purification.

2.3. Synthesis

2.3.1. Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole (**BT**) [39]

To a 250 mL two-necked round bottom flask were added benzothiadiazole (2 g, 14.7 mmol) and 30 mL of HBr (47%). A solution containing Br₂ (10.17 g, 63.6 mmol) in 20 mL of HBr was added dropwise for 1 h. After total addition of the Br₂, the solution was refluxed at 120 °C for 6 h. Precipitation of an orange solid was noted. The mixture was allowed to cool to room temperature and sufficient saturated solution of NaHSO₃ was added to consume completely any excess Br₂. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et₂O and dried under vacuum, affording the desired

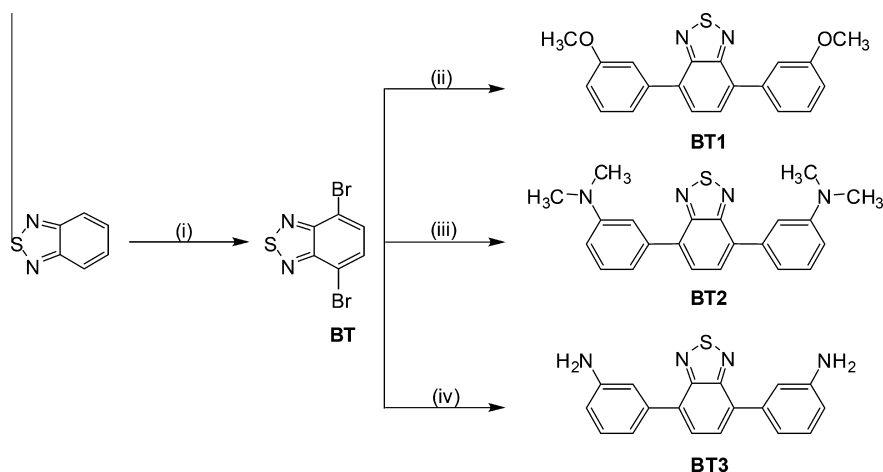


Fig. 1. Synthetic pathways of the studied molecules. (i) Br₂/HBr, 120 °C, 93%; (ii) 3-methoxybenzene boronic acid, Na₂CO₃, ethanol/benzene, Pd(PPh₃)₄, 85 °C, 85%; (iii) 3-(*N,N*-dimethylamino)phenyl boronic acid, Na₂CO₃, ethanol/benzene, Pd(PPh₃)₄, 85 °C, 84%; (iv) 3-aminophenyl boronic acid hemisulfate, Na₂CO₃, ethanol/benzene, Pd(PPh₃)₄, 85 °C, 75%.

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