Benzothiadiazole-triphenylamine as efficient exciton blocking layer in small molecule based organic solar cells

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We have designed a small molecule based on benzothiadiazole-triphenylamine (BTD-TPA₂), encompasses of an electron-poor benzothiadiazole core with two electron-rich triphenylamine arms. BTD-TPA₂ was synthesized in a facile manner using Suzuki cross-coupling reaction. The molecule was rationally designed to take advantage from the synergistic effect of BTD, which allows the formation of a favorable band gap material, while triphenylamine (TPA) moieties will favour efficient hole extraction and transport properties. A thin layer of BTD-TPA₂ was placed between the photo-active DBP/C₇₀ layer stack and the MoO_x electrical contact. With an optimized interlayer thickness of 35 nm, the attained photovoltaic properties were substantially higher than those of the reference devices. This has its origin in BTD-TPA₂'s dual functionality i.e. efficient exciton blocking and improved hole extraction at the anode contact. The obtained results led to an improved power conversion efficiency of 5.66% for a vacuum deposited bilayer DBP/C₇₀ solar cell, which will be new state-of-the-art for bilayer DBP based solar cells.

Introduction

Organic solar cells (OSCs) have been intensively investigated over the last decades with the aim to further optimize its photovoltaic (PV) performance, currently measuring the power conversion efficiency (PCE) value of up to 15%¹. OSCs represent a competitive edge due to their intriguing features such as low material and fabrication costs^{2,3}, opportunities to use roll-to-roll (R2R) processing techniques^{4,5}, along with the possibility to develop thin, aesthetic, flexible, transparent and portable solar modules^{6–9} as compared to other thin film PV technology. Diverse device architectures have been investigated so far, such as donor and acceptor (D-A) bilayer (planar heterojunction, PHJ) and bulk heterojunction (BHJ) structures, in conjunction with innovative materials, such as polymeric semiconductors and small organic molecules as donor and acceptor materials. Small organic molecules possess numerous benefits, such as high purity, easy processability and low batch-to-batch variation in performance, this allows to explore a range of novel materials to be employed as donor

and acceptor molecules in OSCs^{10,11}. Tetraphenylidibenzoperiflanthene (DBP) as the donor and C₇₀ as the acceptor material, have been well investigated and employed in both efficient bulk¹² and bilayer^{13,14} heterojunction OSCs configurations. DBP is a well-known small organic conjugated material, and was extensively used in opto-electrical devices, and OSCs in particularly^{15–17}. The main advantages of using DBP as donor material in OSCs is it's high optical absorption and relatively deep lying highest occupied molecular orbital (HOMO) level (-5.5 eV¹⁸), which was found to be ideal for efficient exciton splitting at the DBP/fullerene interface, while maintaining relatively high open circuit voltages (V_{oc})^{13,19}. DBP has a strong absorption in the visible region from 300 - 700 nm, with a peak absorption coefficient of $4.2 \times 10^5 \text{ cm}^{-1}$ at $\lambda = 610 \text{ nm}$, a relatively high hole mobility of $\sim 10^{-4} \text{ cm}^2/(\text{V}\cdot\text{s})$ ¹⁹, and an exciton diffusion length of up to $16 \pm 1 \text{ nm}$, as reported by Bergemann et al.²⁰. DBP based devices employing MoO_x as hole extraction layers were found to yield decent performance, though excitons were not blocked at the DBP/MoO_x interface, but were quenched.²¹ A possible strategy for overcoming exciton quenching effects is to introduce an exciton blocking layer (EBL), which can prevent excitons to leave the active layer, and increases the possibility for dissociation at the D-A interface¹⁹. Zhang et al. have reported the use of three well-known small organic hole transporting materials (HTMs), such as 5,10,15-tribenzyl-5H-diindolo[3,2-a:3',2'-c]-carbazole (TBDI), *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) and 1,1'-bis(di-4-tolylaminophenyl)cyclohexane (TAPC), to serve as EBL in DBP based planar hetero-junction cells²². It was reported that the HTM successfully blocked excitons at the donor/hole extraction interface, yielding a PCE of 1.70%, 1.33%, and 1.33%, respectively, whereas the control device without any EBL gave a modest PCE of 1.25%. Patil et al.¹⁴ have recently reported an analogous study in which a ultra-thin layer of *N,N'*-di-1-naphthalenyl-*N,N'*-diphenyl [1,1':4,1'':4'',1''']-

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quaterphenyl]-4,4'-diamine (4P-NPD) was effectively used as EBL in DBP/C₇₀ inverted planar heterojunction solar cells, reaching a PCE of 3.69% for the optimized EBL thickness versus a PCE of 2.97% for the EBL-free reference cell. In this work, we have introduced 4,4'-(2,1,3-Benzothiadiazole-4,7-diyl) bis(*N,N*-diphenylaniline) (BTD-TPA₂) as an EBL, sandwiched between the electron donor (DBP) and hole transporting layer (MoO₃) in a classical planar hetero-junction solar cells. The use of BTD-TPA₂ demonstrate its dual functionality i.e. efficient exciton blocking and improved hole extraction at the anode and electron co-donor effect. The obtained results led to an improvement in the device performance in terms of PCE, and an enhanced PCE of 5.66% for bilayer DBP/C₇₀ solar cells was obtained with an optimized EBL thickness of 35 nm (15mM BTD-TPA₂), which is among the highest reported PCEs to date for bilayer DBP based solar cells.

Figure 1. a) Band alignment and b) molecular structure of the materials used in this study.

Results and discussion

Figure 1, represents the architecture of the devices studied in this work along with the molecular structure of the materials used. MoO₃ was employed as hole transporting layer in the OSCs, due to its efficient and stable hole extraction capabilities^{23,24}. A thin layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) was used as electron transporting material and hole blocking layer at the interface between the acceptor C₇₀ and Ag cathode. BCP is a wide band gap electron transporting material, which also acts as a physical barrier in order to prevent damage to the active organic layer by the metal deposition. In a report, the Ag metal:BCP hybrid complex formed upon Ag evaporation, possess favorable states (LUMO level of the complex) inside the bandgap of BCP, leading to an efficient electron extraction in such OSCs²⁵. In the past, benzothiadiazole

(BTD) based polymers and small molecules have been widely employed in opto-electrical devices, such as organic light emitting diodes (OLEDs) due to its fluorescent properties^{26,27}, while the development of D-A structures in combination with triphenylamine (TPA) moieties have been extensively employed as dye/active materials in dye sensitized solar cells (DSSC)^{28,29}/OSCs^{30,31}. BTD-TPA₂ is a small organic molecule, having an electron-poor benzothiadiazole core with two electron-rich triphenylamine arms, and has been explored as red light-emitting material in OLED application^{32,33}.

Scheme 1. Synthetic route adopted for the synthesis of BTD-TPA₂.

BTD-TPA₂ was synthesized in a facile manner using a Suzuki cross-coupling reaction (scheme 1). ¹H-NMR spectrum of synthesized BTD-TPA₂ was recorded in CD₂Cl₂ and is shown in Fig. S1 (Supporting Information). The presence of triphenylamine (TPA) moieties provides an amorphous thin film with efficient hole transport properties, while the presence of the BTD core lead to the suitable frontier orbital energy matching with the donor of HOMO³⁴. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) curves and cyclic voltammetry (CV) measurements are reported in Fig. S2 (Supporting Information), showing a HOMO level of -5.54 eV and a LUMO level of -3.24 eV is higher than the LUMO level of DBP, allowing the use of BTD-TPA₂ as exciton blocking material and potential donor in such devices. (chemical structure and band alignment are shown in Figure 1).

To optimize the thickness of the films, varying concentrations (eight different samples) of BTD-TPA₂ were prepared in chlorobenzene, and were spin-coated (under similar conditions) to form an interfacial layer between the thermally evaporated layers of MoO₃ and DBP (structure depicted in Figure 1). The concentrations of BTD-TPA₂ were chosen in such a way to allow for the formation of thin layer and was in the range of 1.25 mM – 40 mM (corresponding thickness was between 15– 65 nm). To elucidate the effect of BTD-TPA₂, reference devices (without EBL, labelled as 0 mM) were also fabricated. The fabricated devices has following structure: ITO/BTD-TPA₂ (0–40 mM)/DBP (20 nm)/C₇₀ (30 nm)/BCP (10 nm)/Ag (100 nm). The employment of BTD-TPA₂ as EBL gave notable enhancements in the PV performance of the devices, as shown in Table 1, while statistical values are reported in Table S1 (Supporting Information).

Table 1. PV parameters for the OSCs employing EBL layer (using different concentrations of BTDT-TPA₂ in chlorobenzene). Devices structure: ITO/BTD-TPA₂ (0-65 nm)/DBP (20 nm)/C₇₀ (30 nm)/BCP (10 nm)/Ag (100 nm).

Concentration/ thickness BTD-TPA ₂	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
40 mM/65 nm	870	6.81	39.00	2.32
30 mM/45 nm	940	7.86	46.71	3.14
20 mM/40 nm	940	8.84	54.56	4.56
15 mM/35 nm	950	9.53	62.73	5.66
10 mM/30 nm	940	9.66	56.38	5.13
5 mM/25 nm	950	7.69	63.42	4.62
2.5 mM/20 nm	950	7.34	61.88	4.31
1.25 mM/15 nm	860	6.56	68.92	3.88
0 mM/ 0 nm	900	6.69	64.86	3.91

Figure 2. Summary of the photovoltaic parameters obtained as a function of BTD-TPA₂ concentration.

Figure 3. a) J-V characteristics and b) EQE measurements of OSCs fabricated with BTD-TPA₂ exciton blocking layer deposited from solution at different concentrations.

Enhancement in the short-circuit current density (J_{sc}) were obtained for all the devices fabricated by using BTD-TPA₂ as EBL. For the optimal thickness of BTD-TPA₂, (15 mM with a corresponding thickness of 35 nm) the current density value obtained was nearly 42% higher than the J_{sc} of the reference devices, i.e. an increment was observed from 6.7 mA/cm² for the EBL-free reference devices to 9.5 mA/cm² for the best device containing BTD-TPA₂. Thus, the enhancement in the photocurrent indicates the efficacy of the exciton-blocking properties of the BTD-TPA₂. The trend for the different BTD-TPA₂ concentrations are distinct, (Figure 2 and Figure 3a). The PV behaviour obtained from the thinnest EBL (1.25 mM solution, corresponds to a 15 nm thick layer) shows no significant improvement, yielding an V_{oc} of 860 mV, J_{sc} of 6.56 mA/cm², Fill Factor (FF) of 68.92% with an overall PCE of 3.88%, which are on par with the reference devices (PCE = 3.91%). By increasing the concentration and thus thickness, i.e. to 2.5 mM and 5 mM (20 and 25 nm thick layers, respectively), a modest increase of the current density was registered due to the exciton blocking behavior of BTD-TPA₂, with a J_{sc} of 6.69

mA/cm² for the reference device to 7.34 mA/cm² and 7.69 mA/cm² of the devices prepared with BTD-TPA₂ at 2.5 mM and 5 mM, respectively. The significant improvements were recorded with the devices containing the EBL deposited from the solution at 15 mM concentrations, gave an impressive overall PCE of 5.66%, which corresponds to an enhancement of over 42% with respect to the reference device. Notably, by further increasing the concentrations to 20, 30 and 40 mM (i.e. to 40, 45 and 65 nm), a reverse trend was obtained, and lower device performance was recorded, i.e. PCE of 4.56%, 3.14% and 2.32%, respectively. V_{oc} remains largely constant, though an increase of 40-50 mV for devices including the BTD-TPA₂ layers (between 2.5 mM to 30 mM) was recorded. A drop in FF was obtained, in case of thicker layers, deposited from 30 and 40 mM concentration. This we assigned to enhancement in series resistance caused by hampering of hole transport through the thicker EBL layer. These trends are also in accordance with the EQE measurements (Figure 3b). The maximum light harvesting abilities was attributed to the defined optimal concentration of BTD-TPA₂, i.e. 15 mM, showing a maximum conversion of over

60% in the 550-650 nm range, which corresponds to the peak of DBP absorption, whereas an almost constant increment in the EQE spectrum was observed over the range of 300-650 nm. We expect that a co-donor effect may take place, allowing excitons generated in the BTDP-TPA₂ layer (absorbing at shorter wavelengths as compared to DBP in the range 400-550 nm) to be dissociated into free carriers. From the measured EQE curves, the integrated value of J_{SC} was extracted for each configuration (Figure S3) and values are listed in Table S1. The integrated current density was consistent with the average values of current density registered by the J - V measurements (Table S1).

To further confirm, whether codonor effect takes place, we have calculated the change in EQE as a function of wavelength and its corresponding integrated photocurrent contributed by the BTDP-TPA₂ as co-donor (Figure S4 and S5). It can be deduced from the figure, that in case of a thin layer (1.25 mM corresponds to 15 nm thin film) and for thicker layer (40 mM corresponds to 65 nm thick), we observe a decreases in Δ EQE, thus we don't expect any contribution from photon. However, increase in Δ EQE can be observed from 2.5 mM to 15 mM (corresponds to 20 nm – 35 nm thin layer), which we assign due to the co-donor effect of BTDP-TPA₂. Beyond this concentration, for 20, 30 mM concentration, (corresponds to 40, 45 nm thick layer), no enhancement in Δ EQE was observed and the contribution decreases. It can be concluded that co-donor effect occurs when thin EBL layer (20-35 nm) was employed, and this effect is inefficient in case of thick layers (40-65 nm). We

expect that for thin layers, the exciton generated in the blocking layer are capable to reach and dissociate at DBP interface and this dissociation efficiency could be expected to drop for thicker layers (40-65 nm very thick layer), where instead the blocking improves further (as seen from PL).

The thickness of the EBLs at different concentrations was measured with the help of atomic force microscopy (AFM) as shown in Figure S7. The average values from the measurement of each film deposited atop of 10 nm of thermally evaporated MoO_x are listed in Table S2. The measured thickness was in the range of 15 nm (1.25 mM) – 65 nm (40 mM). The best PV behavior was obtained from the deposition of 30-35 nm BTDP-TPA₂ as EBL, corresponding to a concentration of 10-15 mM.

Figure 4a shows the UV-vis absorption spectra for BTDP-TPA₂ layers deposited from the different concentrated solutions sandwiched between the thermally evaporated MoO_x and DBP layers. As expected, with the increase of concentration (and so the thickness of BTDP-TPA₂ layers), the absorption in the range of 400-500 nm and 300-350 nm sequentially increases, which corresponds to the absorption of the synthesized molecules, as shown in Figure 4a (black dotted line). Additionally, with the increase in the thickness of the EBL, a small reduction in the absorption of the peak at 610 nm was observed. As BTDP-TPA₂ lacks absorbance in this range, we expect that this relatively small absorption change could occur due to changes in the orientation of the DBP molecules when deposited on top of BTDP-TPA₂, as compared to on top of the MoO_x layer.

Figure 4. a) UV-Vis absorption spectra of the BTDP-TPA₂ layers sandwiched between MoO_x and DBP layers (solid lines) and BTDP-TPA₂ alone (dashed line) and b) sensitive-EQE measurements of the DBP/C₇₀-based reference device (black line) and two devices with BTDP-TPA₂ using the best concentration (15 mM, red and blue lines) are shown.

Due to the relatively strong absorption of BTDP-TPA₂ in the 400-550 nm range, which is complementary to the DBP main absorption at 550-650 nm, its usage as single donor and as co-donor with DBP was evaluated. For this purpose, two different thicknesses were selected to be evaluated as donor layer, 40 nm and 35 nm, which corresponds to 20 mM and 15 mM solutions respectively, and were deposited by spin-coating in a similar condition. Similarly, in order to evaluate its

behavior as DBP co-donor, the concentrations of BTDP-TPA₂ (15 and 20 mM) were kept alike and were probed together with an ultra-thin layer of DBP (5 nm). On one hand, it can be deduced from data (Fig. S7 and Table S3 in Supporting Information) that the donor properties of the BTDP-TPA₂ are less appealing compared to the reference donor DBP, resulting in devices with a PCE of maximum 2.44% for BTDP-TPA₂ with 40 nm thickness, while a PCE of 3.91% was obtained for the

reference DBP device. On the other hand, the use of BTDA-TPA₂ as co-donor with an ultrathin layer of DBP showed a slight improvement in device PCE, especially for the devices with higher concentration of BTDA-TPA₂, i.e. 20 mM, resulting in a J_{SC} of up to 8.01 mA/cm² and a PCE of up to 4.19%. No significant change in terms of V_{OC} was observed. These results suggest that the use of BTDA-TPA₂ as donor with DBP is a less useful strategy as compared to its exciton blocking properties. However, when used as exciton blocking layer, the co-donor effect will also be present, depending on the thickness of the EBL layer (Figure S7). As slight variations in the DBP absorption and open-circuit voltage was detected, which points towards a possible structural modified donor layer. Thus, sensitive external quantum efficiency measurements (sEQE) were conducted to elucidate if the integrated BTDA-TPA₂ layer affects the interface energetics and the properties of the charge-transfer (CT) states at the donor/acceptor interface in the solar cells. In Figure 4b, sEQE measurements of the DBP/C₇₀-based reference device (black line) and for the configuration containing BTDA-TPA₂ in the best concentration (15 mM, red and blue lines) are shown. The two devices with the same concentration of BTDA-TPA₂ show an identical behavior. The signal at low photon energies around 1.5 eV originates from the weak absorption related to CT state between the C₇₀ and DBP layers. From the sEQE measurements, the energy (E_{CT}) and the reorganization energy (λ) of the CT state were determined by fitting low energy part of the spectrum as described by Vandewal et al.³⁵. These parameters mainly

determine the V_{OC} ^{36,37}. Since no difference for both E_{CT} and λ in the reference DBP/C₇₀ device and the BTDA-TPA₂/DBP/C₇₀-based devices was found, we conclude that the interface energetics of DBP/C₇₀ remains unchanged with the use of BTDA-TPA₂, suggesting that the main function of the layer is to provide efficient hole extraction and exciton blocking at anode, in addition to the small co-donor effect. Additionally, it suggests that non-radiative voltage losses are reduced due to reduced non-radiative recombination at the hole contact and resulted in an increase V_{OC} .

To elucidate the effects of the implemented layers on the hole extraction properties, J - V measurements of hole only devices with the different thicknesses of the BTDA-TPA₂ layers were conducted. The results from the hole only devices are shown in Figure 5a. In the developed configuration, holes were injected into the device through the Ag electrode and extracted out of the device at the ITO electrode. Devices with the thickest BTDA-TPA₂ layer (40 mM) show the lowest extraction properties, corresponding to a lower current density, and are at par with the EBL-free devices. Devices with BTDA-TPA₂ layers deposited from the 10-15 mM concentrations presented the highest hole extraction efficiencies, demonstrating that the hole contact improves with the introduction of BTDA-TPA₂ layer (up to 15 mM), but it decreases again due to the increased series resistance, arises with the use of thicker layers (obtained using BTDA-TPA₂ above 15 mM).

Figure 5. a) J - V characteristics of the hole only devices (HODs), fabricated with the architecture: ITO/MoO_x(10 nm)/BTDA-TPA₂(different thickness)/DBP (20 nm)/Ag (100 nm); b) Photoluminescence measurements of the layer stack: Quartz/ MoO_x (10 nm)/BTDA-TPA₂/ DBP (15 nm).

To illustrate the exciton blocking properties of BTDA-TPA₂, photoluminescence (PL) measurements were made to compare the PL intensity of DBP using different concentrations of BTDA-TPA₂. The excitation wavelength was centred between 330 nm and 380 nm. Figure 5b depicts the PL measurements of the layer stack: Quartz/ MoO_x (10 nm)/BTDA-TPA₂/ DBP (15 nm). The PL intensity of DBP (600-800 nm) with an emission maximum at 635 nm, increases linearly up to a certain concentration (10mM corresponds to 30 nm thickness), and beyond the 10mM BTDA-TPA₂ concentration, PL signal increases rapidly up to 20 mM (40 nm thick EBL). At higher concentrations 30 mM and 40mM (corresponding thickness 45 & 65 nm respectively), the PL

intensity reaches to the spectrometer detection limit, as shown in figure S8.

With an increase in the thickness of BTDA-TPA₂ layer, exciton quenching at the MoO_x interface will decreased, which leads to an increased PL intensity. This directly demonstrates its effective exciton blocking capabilities by inhibiting charge recombination at the DBP donor and MoO_x interface. We noted that in addition to the DBP signal, a PL signal from the BTDA-TPA₂ layers (centered at 585 nm) arises at a concentration of 5mM (25nm thickness). This PL signal further increases on increasing the BTDA-TPA₂ layer thickness, and surpasses the intensity of the DBP main peak for concentrations above 15 mM. The

enhancement in PL emission at 585 nm also indicates that BTDP-TPA₂ participates simultaneously in the light absorption and exciton generation in the BTDP-TPA₂ layer and suggests its co-donor effect.

Conclusions

We put forward small organic molecules based on BTDP-TPA₂, which was synthesized using simple Suzuki cross-coupling reaction and was employed as an effective exciton blocking material. The incorporation of BTDP-TPA₂ significantly improve the photovoltaic performance of DBP/C₇₀ based solar cells. By tuning the concentration of BTDP-TPA₂, we have found that the optimal BTDP-TPA₂ thickness for device integration was around 30–35 nm. Significant improvements in the short-circuit current density were recorded, with an astonishing increment up to 45%, as compared to the J_{SC} of the reference devices. This allowed to achieve notable increase in PCE from 3.91% to 5.66%, which is one of the highest efficiency obtained to date in DBP based bilayer solar cells. In order to elucidate the involved mechanisms, PL measurements were performed to confirm the exciton blocking properties of BTDP-TPA₂, while hole-only devices revealed improved hole contact at low BTDP-TPA₂ thickness, with an optimal performance at 30–35 nm thick layer. Additionally, sEQE measurements revealed no difference in the interface energetics at the DBP/C₇₀ interface upon EBL integration, suggesting that the integrated EBL only affects the hole extraction and exciton blocking properties at anode. This study put forward the design of BTDP-TPA₂ molecules for its application as efficient exciton blocking materials in organic solar cells, to further push the device performances.

Conflicts of interest

There are no conflicts to declare.

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