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Small Molecule Near-Infrared BODIPY Donors for Organic Tandem Solar Cells

Tian-yi Li[†], Toni Meyer[†], Zaifei Ma^{*}, Johannes Benduhn, Christian Körner, Olaf Zeika, Koen Vandewal, Karl Leo^{*}

Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Technische Universität Dresden, Nöthnitzer Street 61, 01187 Dresden, Germany.

Supporting Information Placeholder

ABSTRACT: Three furan fused BODIPYs with a CF₃ group on the *meso*-carbon are synthesized as near infrared (NIR) absorbing materials for vacuum processable organic solar cells (OSCs). The best single junction device reaches a short-circuit current (j_{sc}) of 13.3 mA cm⁻² and a power conversion efficiency (PCE) of 6.1%. These values are highly promising for an electron donor material with an absorption onset beyond 900 nm. In a tandem solar cell (TSC) comprising a NIR BODIPY sub-cell and a matching “green” absorber sub-cell, complementary absorption is achieved, resulting in PCE of ~10%.

Significant research effort has been put into the development of strongly absorbing donor materials, aiming to enhance the PCE of OSCs based on bulk-heterojunction (BHJ).¹ However, organic small molecules often suffer from narrow absorption bands, resulting in the absorption of only a small fraction of solar radiation. TSCs comprising a stack of two or more complementary absorbing sub-cells are thus advantageous for higher photovoltaic (PV) efficiency. Additionally, the donors in the sub-cells have different optical gaps, which reduces charge carrier thermalization losses.²

When it comes to the realization of highly efficient and long-term stable TSCs, vacuum-deposition technology has been proven to be superior as compared to the solution processing method. The risk of damaging the underlying layers by solvent is avoided and the layer thickness can be easily and precisely monitored with an accuracy of a few nanometers. The latter is particularly important for TSCs, where the optical field within the stack needs to be accurately controlled to ensure matching photo-currents.³

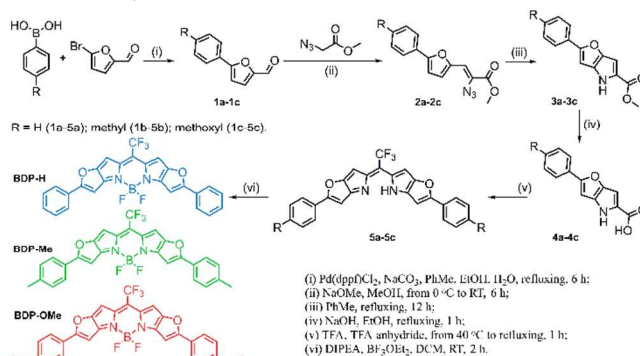
To achieve high-efficiency TSCs using vacuum-deposition, the photo-active small molecules need to have a good sublimation behavior. In addition, their absorption should extend into the NIR (wavelength > 780 nm) region, since there is still abundant solar power in this region. Even though NIR absorbers are extremely important for TSCs, only few organic small molecules exhibit absorption maxima close or beyond 800 nm.⁴ Most efficient vacuum processable small molecule donors, up to now, are visible light (400–700 nm) absorbers.⁵

In addition to bathochromically shifted absorption, a promising NIR small molecular donor should fulfill the following requirements: high thermal stability, high extinction coefficient (> 100,000 L mol⁻¹ cm⁻¹), appropriate highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) energy levels, and a favorable BHJ active layer morphology when combined with electron accepting molecules. In this respect, boron dipyrromethene

(BODIPY) represents a class of promising chromophores due to their large variety of chemical modifications with relatively clear structure-property relationships.⁶ BODIPYs have been applied in OSCs during past years, benefiting from the tunable absorption bands towards the NIR region and their high absorption coefficients. However, PCEs of these OSCs are far from satisfying, which hinders their application in TSCs.⁷

A BODIPY with intense and long wavelength absorption can be achieved by an extension of the π -system and an electron withdrawing group on the *meso*-C.⁸ In this work, three furan fused BODIPYs with CF₃ on the *meso*-C (short for **BDP-H**, **BDP-Me**, **BDP-OMe**) are synthesized. We achieve a PCE over 6% in a single junction OSC, using **BDP-OMe** as donor, with the external quantum efficiency (EQE) spanning the spectral region of 600–900 nm (peaking at 795 nm). By combining this molecule with the “green” absorbing donor **DCV5T-Me**^{5b}, a PCE approaching 10%, and an open-circuit voltage (V_{oc}) as high as 1.70 V are obtained.

Scheme 1. Syntheses of the BODIPYs



The synthetic route of the BODIPYs is presented in Scheme 1. The Suzuki cross-coupling is used to connect the substituted phenyl ring and 5-bromo-2-furaldehyde, providing **1a–c**. The Hemetsberger-Knittel indolization is followed to form the indole ring in **3a–c** via the intermediates **2a–c**. After the hydrolysis of the ester moiety, the acid **4a–c** are dimerized in trifluoromethyl acetic acid with the presence of trifluoroacetic anhydride to synthesize the BODIPY precursors **5a–c**. The BODIPYs are obtained by chelating with the BF₂ moiety using boron trifluoride etherate.

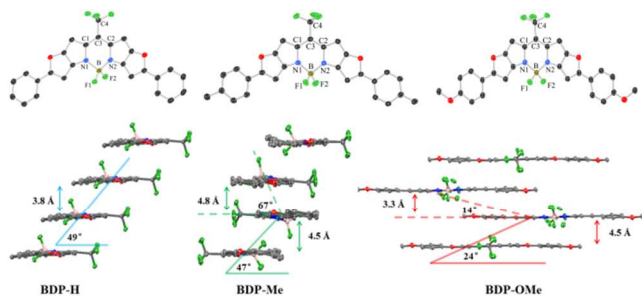


Figure 1. The ORTEP plots (top) and packing configurations (bottom) of the BODIPYs. Hydrogen atoms are omitted.

The molecular geometries of the BODIPYs are depicted in Figure 1. They adopt a planar structure with torsion angles less than 8° between the dipyrromethene and peripheral phenyl rings. The boron atoms are coordinated in a disordered tetrahedron geometry with B-N bonds (1.53–1.55 Å) longer than B-F bonds (1.38–1.40 Å). The packing behavior is obviously influenced by the methyl or methoxyl substituents. The **BDP-H** molecules exhibit a staircase-type stacking arrangement. However, in **BDP-Me**, two parallel molecules form a repeating unit in a sloping ladder-type arrangement. For **BDP-OMe**, a brickwork-type arrangement is observed, comprising an alternating arrangement of a unit consisting of two antiparallel molecules. Consequently, **BDP-H** and **BDP-OMe** have more J-aggregation character. While, **BDP-Me** has more H-type character.⁹ It is known that aggregation in thin films broadens the absorption spectra and a J-/H-aggregation can result in bathochromic/hypsochromic shifts.¹⁰ Moreover, charge transport in OSCs benefits from aggregation, leading to higher overall PCE through improved j_{sc} and FF , even though V_{oc} may decrease slightly.¹¹

For efficient and stable vacuum-deposited OSCs, a high material purity and thermal stability are required. We thus characterized the thermal properties of the BODIPYs by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) (Figure S1). From **BDP-H** to **BDP-Me** and **BDP-OMe**, the decomposition temperature increases from 294°C to 331°C and then decreases to 312°C , as deduced from the TG plots. In the DSC plots, the melting point increases from 290°C for **BDP-H** to 336°C for **BDP-Me**, then decreases to 238°C for **BDP-OMe**. The results indicate that intermolecular interactions increase with the introduction of the methyl group, but decrease upon adding the methoxyl group.

The absorption spectra of the BODIPYs in both solution and solid state (50 nm film) are shown in Figure 2. The optical gaps, molar absorption coefficients and absorption peak wavelengths are listed in Table S3. In solution, the spectra of the dyes exhibit the typical BODIPY narrow absorption profile with a main peak followed by higher-energy and weaker-absorbing phonon replicas. The main peak covers a range from 600 to 750 nm. The bathochromically shifted absorption maxima of **BDP-Me** and **BDP-OMe** (705 nm and 723 nm) reveal the electron donating nature of methyl and methoxyl groups with respect to **BDP-H** (692 nm). As small molecule dyes with restricted conjugated structures, all these compounds have high molar extinction coefficients over $32000\text{ L mol}^{-1}\text{ cm}^{-1}$. This indicates an efficient delocalization of the π electrons. In solid state, the absorption spectra broaden significantly, due to thin film aggregation effects that are promoted by the planarity of the molecules. The absorption coefficients of the materials range between 94000 and 127000 cm^{-1} . Additionally, the optical gaps determined by the absorption onset in films range from

1.32 to 1.37 eV, which is around 0.32 to 0.36 eV lower than in solution.

For **BDP-H** and **BDP-OMe**, the main absorption peaks in thin film are found at 750 nm and 800 nm with shoulders at 671 nm and 712 nm respectively, which can be attributed to the J-aggregation-induced broadening and bathochromic shifts. However, the absorption peaks of **BDP-Me**, at 758 nm and 668 nm, have similar but lower intensities. This can be explained by the combined J-/H-aggregation character of **BDP-Me** as observed in the single crystal packing behavior.

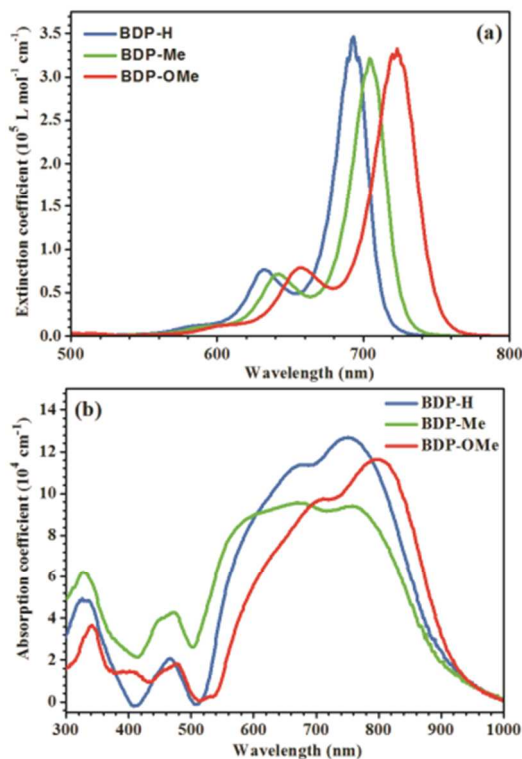


Figure 2. The absorption spectra of the BODIPYs in (a) DCM and (b) neat films.

The electrochemical properties of the BODIPYs are investigated in dichloromethane (DCM) solution using cyclic voltammetry (CV) measurements (Figure S6, Table S3). HOMO/LUMO are calculated using a ferrocene/ferrocenium couple as reference. All the dyes show reversible oxidation peaks and partially reversible reduction peaks. From **BDP-H** to **BDP-Me** and **BDP-OMe**, both oxidation and reduction peaks present negative shifts, demonstrating destabilized HOMO and LUMO energy levels with the introduction of methyl and methoxyl groups. The HOMO energy increases from -5.45 eV to -5.23 eV upon the introduction of methyl and methoxyl group. Meanwhile, their LUMOs range from -3.78 to -3.87 eV allowing charge transfer to the C_{60} acceptor whose LUMO is around -4.0 eV . Still, the driving force is heavily affected by this shift in the LUMO energies, and will affect OSC performance, as will be shown below.

Single BHJ OSCs comprising the new BODIPY derivatives as electron donors and C_{60} as the electron acceptor in a n-i-p device architecture³ are fabricated by vacuum-deposition. We use the device architecture ITO/MH250:W₂(hpp)₄ 7 wt.% (5 nm)/C₇₀ (15 nm)/**BDP-OMe**:C₆₀ (40 nm)/BPAPF (5 nm)/BPAPF:NDP9 10 wt.% (40 nm)/NDP9 (1 nm)/Al (100 nm), where W₂(hpp)₄ and NDP9 are n- and p-dopants and MH250/BPAPF is an electron/hole transporting material. The neat layer of C₇₀ does not only act as hole blocking layer (HBL) but also contributes to photocurrent

generation. We find an optimum BHJ active layer thickness for a donor/acceptor ratio of 1:2 (v/v) and substrate heating to 100 °C is needed to achieve the optimized performance.

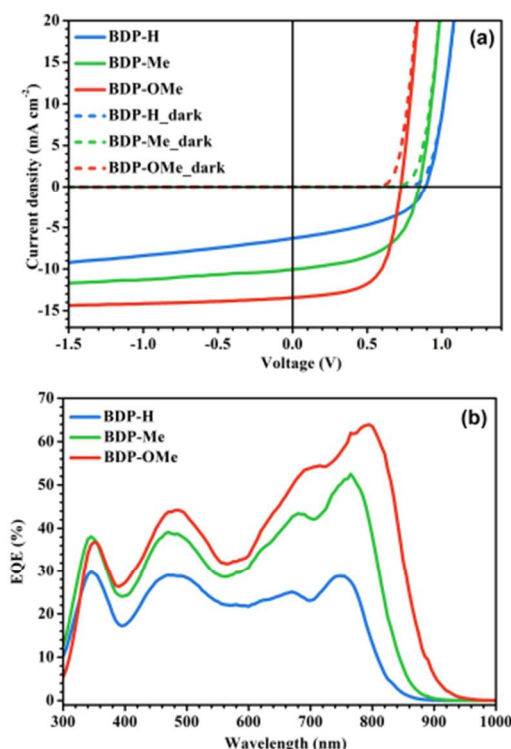


Figure 3. (a) The j - V curves in dark and under AM1.5G illumination and (b) the EQE spectra of the single junction OSCs

The current density-voltage (j - V) characteristics and EQE spectra of the optimized OSCs are plotted in Figure 3(a) and 3(b). The corresponding PV parameters are listed in Table 1. The lowest V_{oc} (0.73 V) is obtained from the solar cell based on **BDP-OMe**, and the highest V_{oc} is obtained from the device based on **BDP-H** (0.89 V), agreeing well with the destabilization of the HOMO energy levels of these BDP materials.

The highest PCE of 6.1% is obtained from the **BDP-OMe** device with a j_{sc} as high as 13.3 mA cm^{-2} , and a FF of 63%. However, the PCE of the **BDP-H** based solar cell is low, only 2.5%, due to a low j_{sc} of 6.1 mA cm^{-2} and a low FF of 45%. The poorer performance of the solar cell based on **BDP-H** could be due to low exciton separation efficiency at the D/A interface, since the LUMO of **BDP-H** is very similar to that of the C_{60} , providing insufficient driving force for charge generation. In addition, we also notice a stronger trap assisted recombination loss in the device based on **BDP-H**, compared to that in the **BDP-OMe** device, see Figure S8 and S9, for more detailed discussions.

The maximum EQE of **BDP-Me** (765 nm, 53%) is almost double than that of the **BDP-H** device (750 nm, 29%). The EQE peak value for the **BDP-OMe** device is 64% at 795 nm. This value is remarkable considering that the volume content of BODIPY molecules in the blend layer is only 30%, which is equivalent to roughly a 13 nm thick pure film. Furthermore, the high EQE and j_{sc} of the device indicate that the photogenerated excitons are efficiently separated into free charge carriers. AFM images (Figure S10) confirm that **BDP-OMe** and C_{60} are well intermixed, providing enough D/A interfaces for exciton dissociation. It is also worth to note that interpenetrating pathways in the active layer seem to be resolved in the AFM image. Therefore, a decent FF is achieved, leading to a high PCE of 6.1%.

Table 1. PV parameters of single junction OSCs

Donor	V_{oc} (V)	j_{sc} (mA cm^{-2})	FF (%)	PCE (%)	EQE_{max} (%) ^[a]
BDP-H	0.89	6.1	45	2.5	29
BDP-Me	0.85	9.9	54	4.6	53
BDP-OMe	0.73	13.3	63	6.1	64

^[a] The peak values in the main absorption region of BODIPY donors

Inspired by the promising PV performance of the NIR absorbing **BDP-OMe**, vacuum-deposited TSCs are fabricated with **BDP-OMe** as donor for the rear sub-cell and **DCV5T-Me** as donor for the front sub-cell. The absorption spectra of thin films blended with C_{60} are shown in Figure 4(a). **DCV5T-Me** covers the spectral range from 400 nm to 700 nm, which complements that of **BDP-OMe**. Together these materials cover the complete visible region and part of NIR until 900 nm. Additionally, the optimized **DCV5T-Me** single junction device has a j_{sc} around 13.2 mA cm^{-2} which is close to that of **BDP-OMe** cell.³ Such matching currents are essential when fabricating a TSC with serial connected sub-cells.

In both sub-cells, C_{60} is employed as acceptor. In the rear subcell, C_{70} is used as HBL and additional absorber, similarly as in the single junction device. On the p-side, the hole transporting material BPAPF is chosen as exciton reflecting and electron blocking layer. The n-type electron transporting layer is MH250 doped with 7 wt.% $W_2(hpp)_4$ and p-type HTL was BPAPF doped with 10 wt.% NDP9. An additional 1 nm of NDP9 was used to enhance hole extraction. The mixed layer of Bphen and Cs forms another p-n recombination contact with the underlying p-doped layer. It is also used to prevent diffusion of metal atoms from the electrode into the organic layer upon deposition. Ag is chosen as electrode material instead of the commonly used Al due to its higher reflectance.

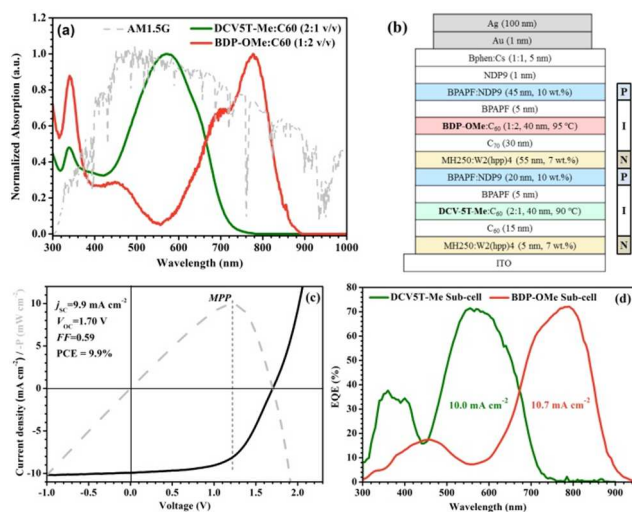


Figure 4. (a) The absorption spectra of **BDP-OMe** and **DCV5T-Me** mixed with C_{60} . The AM1.5G solar spectrum is shown for comparison. (b) the optimal TSC geometry and (c) j - V characteristics; (d) EQE spectra of the two sub-cells.

The optimized TSC device architecture is shown in Figure 4(b) and the j - V curve obtained from the optimized TSC is plotted in Figure 4(c). A high PCE of 9.9% is obtained from the TSC with a FF of 59%, a j_{sc} of 9.9 mA cm^{-2} . The V_{oc} of the TSC equals the sum of the V_{oc} values of the sub-cells (0.96 V and 0.73 V)³ and is as high as 1.70 V. Despite the high PCE, a slight S-kink in the j - V curve is observed, which limits the FF of the TSC. The S-kink is

related to a charge injection barrier at the active layer/contact interface, see Figure S12 for details.

In order to reveal the contribution of each sub-cell to the photo-current, EQE measurements are conducted using 518 nm and 689 nm light bias as illustrated in Figure 4(d). The photo-currents derived from the EQE spectra for the **DCV5T-Me** sub-cell (10.0 mA cm⁻²), and **BDP-OMe** sub-cell (10.7 mA cm⁻²) are found to match, which results in a high j_{sc} of 9.9 mA cm⁻² for the TSC. This demonstrates that the j_{sc} of a serial TSC is indeed controlled by the sub-cell with lower j_{sc} value.¹² It is also observed that a wide spectral region from 500 to 900 nm is covered by the EQE spectra with the maxima over 70%. This demonstrates an excellent complementary of the two absorbers.

To conclude, we synthesized and studied three furan fused BODIPYs with a CF₃ group on the *meso*-C for application in OSCs. The methyl or methoxyl group on the peripheral phenyl rings influences the packing behavior of these three donors significantly, which results in different optical properties. Their absorption bands cover a wide range from 500 to 950 nm in thin films. These BODIPYs are examined in vacuum-processed single junction BHJ OSCs, presenting PCEs from 2.5% to 6.1%. It is found that their PV performance increases along with the destabilization of the BODIPY's LUMO energy level and the steric volume of the substituents on phenyl rings. The optimized **BDP-OMe** device yields a high j_{sc} of 13.3 mA cm⁻² and a V_{oc} of 0.73 V. We further use **BDP-OMe** as the long wavelength absorber in vacuum-processed TSC combined with **DCV5T-Me** as complementary absorber from the visible to the NIR region. The TSC shows a j_{sc} of 9.9 mA cm⁻² and a V_{oc} of 1.70 V. With a reasonable *FF* of 59%, a high PCE of 9.9% is achieved. This work demonstrates that **BDP-OMe** is an outstanding NIR absorber for vacuum-deposited organic PV applications and further modifications may lead to more promising BODIPY molecules for OSCs.

ASSOCIATED CONTENT

Supporting Information

Synthesis details, experimental procedures, device fabrication and characterizations (PDF)

CIF file for **BDP-H/Me/OMe** (cif)

AUTHOR INFORMATION

Corresponding Author

*zaifei.ma@iapp.de

*karl.leo@iapp.de

ORCID

Tian-yi Li: 0000-0003-4247-5840

Zaifei Ma: 0000-0002-3100-1570

AUTHOR CONTRIBUTION

[†]T. Li and T. Meyer contributed equally to this work

Notes

The authors declare no competing financial interests.

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TOC Graphic

