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Synthesis, Spectral, Electrochemical Properties and Photovoltaic Performance of structurally constrained BODIPY dyes with 4,4-dimethyltriphenylamine at the 2,6-positions

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ABSTRACT

Novel symmetrical D-A-D type of BODIPY derivatives (DTPA-BDP) were synthesized successfully. The introduction of chromophoric units make the molecules absorption wavelengths spanning the ranges of 300-800 nm and shift the emission to 793 nm in red and near-infrared region. Bulk heterojunction solar cells with DTPA-BDPs as electron donor and $PC_{61}BM$ as electron acceptor exhibited photovoltaic properties with a power conversion efficiency of 0.77 %, an open-circuit voltage of 0.70 V.

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Recently, the 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPYs) have received increasing attention due to their outstanding optical properties such as high absorption coefficients, relatively sharp emission bands, high fluorescence quantum yields, excellent chemical and photochemical stability, high solubility, [1] which make BODIPY-based systems as the most promising candidate for light-harvesting applications in solar cells,[**2**] biological labeling[3] and cell imaging.[4] Recently, they have been introduced to render the dye sensitive to the environment.[5] Additionally, straightforward chemical synthesis and structural robustness have enabled finetuning of optical properties of BODIPY dyes *via* systematic structural variations. There have been a lot of researches focusing on the development of new fluorophores with two photon absorption cross sections as well as high fluorescence quantum yields.[6] In order to modulate the optical properties of BODIPY dyes, the following strategies are usually elaborated: (1) extension of π-conjugation of the structure;[7] (2) rigidifying the molecular structure to suppress the free rotation of extended substituents and enhance the coplanarity;[8] (3) introducing electron-donating groups.[9] Recently, there were some reports on BODIPY derivatives be used in dye-sensitizd solar cells (DSCs). [2,10] However, to the best of our knowledge, up to date, the reports on using BODIPY derivatives in such molecular system for construction bulk heterojunction (BHJ) are still rare. [11]

In this paper, in order to extend the conjugation of the BODIPY dyes, triphenylamine groups were introduced to BODIPY by attaching to the pyrrole rings on the 2,6-axis to form the novel symmetrical D-A-D type of DTPA-BDP. The absorption spectral range of these novel DTPA-BDP were shifted to infrared region. And BHJ solar cells were fabricated with DTPA-BDP as donor materials and $PC_{61}BM$ as acceptor materials. It should be noted that adequate solubilizing side chains ensure DTPA-BDP good film ability when blended with $PC_{61}BM$.

DTPA-BDPs were synthesized according to the route illustrated in Scheme 1. Firstly, Dipyrromethanes **1** were prepared in a mild way which was reported by our group in

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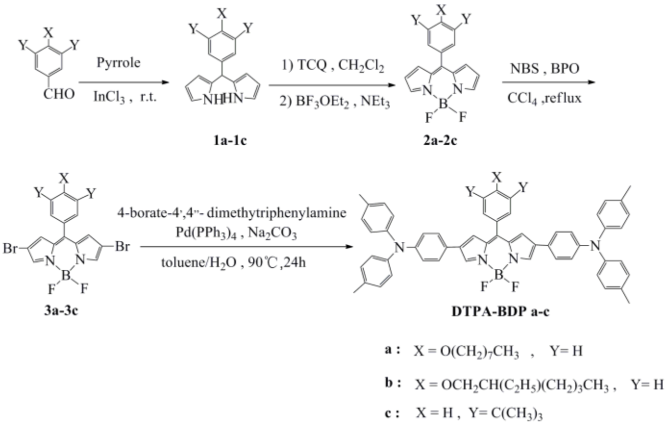
2010.[12] Subsequently, the dipyrromethanes were oxidated by 2,3,5,6-tetrachloro-1,4-benzoquinone (TCQ) and then treated with BF_3OEt_2 to form the important intermediates BODIPY **2**. Bromination of BODIPY **2** at 2,6-positions of pyrrole rings affording the corresponding bromides **3**. Finally, the desired DTPA-BDPs were obtained by Suzuki coupling reactions between bromides **3** and triphenylamine boronic acid. Compared with the traditional synthetic method,[13] this strategy restrain the generation of accessory substances effectively and promote the yields of target products. Using this synthetic strategy, we successfully prepared three DTPA-BDPs: DTPA-BDP **a**, DTPA-BDP **b** and DTPA-BDP **c**.



Scheme 1. Synthesis of DTPA-BDP a-c.

The color conversions from BODIPY **2** to DTPA-BDP dyes under ambient light in the process of synthesizing DTPA-BDPs were shown in Figure 1. It indicated that the absorption wavelengths changed by introducing functional groups to BODIPY. And we believe that such straightforward functionalization and derivatization methodologies are likely to enhance their impressive versatility.[14]

Figure 1. The color conversions of the DTPA-BDP dyes under ambient light

With these novel DTPA-BDPs in hand, we subsequently studied the optical properties of all three DTPA-BDPs and found that these covalently assembled light harvesters showed two major absorption bands which were derived from two different chromophores.

In the D-π-D type (Donor-π bridge-Donor) dyes DTPA-BDPs, a central BODIPY core with a considerable electron-accepting nature was connected with two triphenylamino groups. We expected that a strong red emission by direct two photon excitation would be achieved by using the strong fluorescent BODIPY dyes and high electron-donating groups. An efficient π conjugated spacer is one of the most important reasons for contributing to facilitate the electronic flow. With this in mind, we tested their absorption spectra using a ultraviolet-visible spectrometer. In CH_2Cl_2 solution, DTPA-BDP **a-c** showed two obvious absorption peaks. The first one at ~310 nm corresponds to the $\pi\rightarrow\pi^*$ transition in short wavelength regions. The second band of long wavelength regions at 648nm, 653nm, 559nm, respectively, is attributed to the intramolecular charge transfer (ICT) interaction between the donor units and the acceptor units in the main chain. Compared with the absorption spectrum in CH_2Cl_2 solution, the dyes in solid film displayed a red-shift absorption peak at 313 nm and 666nm, 676nm, 573nm, respectively (Figure 2, Table 1). We could see that DTPA-BDP **a**, DTPA-BDP **b** and DTPA-BDP **c** display similar absorption features.

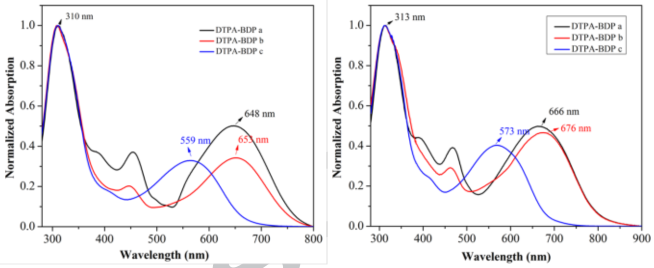


Figure 2. Normalized absorption spectra of DTPA-BDP **a-c** in CH_2Cl_2 solution (left) and thin films on quartz surface (right).

Table1. Photophysical Properties of DTPA-BDP a-c in CH_2Cl_2 at Room Temperature.

Entry	solution[a]			film[b]	
	λ_{max} (nm)	lg ε	λ_{em} (nm)	λ_{max} (nm)	λ_{onset} (nm)
a	310,648	5.2 , 4.9	793	313,666	824
b	310,653	5.1, 4.7	743	313,676	820
c	310,559	5.1, 4.6	681	313,573	696

a. In CH_2Cl_2, *b*. Deposited onto quartz substrate by spin-coating technique from CH_2Cl_2 solution

The fluorescence properties of all BODIPY dyes were studied in CH_2Cl_2 solution at room temperature. A comparison of the emission spectra of these dyes was shown in Supporting Information and the normalized fluorescence spectra of DTPA-BDP **a-c** were shown in Figure 3. BODIPY dyes with 4,4-dimethyltriphenyl amine at the 2,6-positions resulted in near-infrared and deep-red emissive BODIPY copolymeric dyes with emission maxima of 793nm, 743nm and 681nm, respectively. It can be explained as the basis of photoinduced energy transfer from the BODIPY $\pi\rightarrow\pi^*$ excited state to the lower lying singlet excited state of the triphenylamine and/or to the existence of new nonradiative pathways form the BODIPY $\pi\rightarrow\pi^*$ state to the ground state. On the other hand , DTPA-BDP **a-c** gave low fluorescent quantum yields. These could be attributed to the increased internal conversion according to the energy gap law that states the non-radiative deactivation probability of S_0-S_1 increases as the energy gap of $S_0\rightarrow S_1$ decreases in a highly extended conjugating system.

Consistent with the literature,[15] the installation of new substituents on the BODIPY core greatly affects the spectroscopic charateristics of the chromophore. In comparison to the starting BODIPY **2**, the installation of bromo-substituents onto the BODIPY core lead to an up to 41 nm red-shift of the absorption maximum and an up to 48 nm red-shift of the emission maximun as shown in Supporting Information. These may be due to the heavy atom effect, which facilitates the $S_1\rightarrow T_1$ intersystem crossing. Similar to it, the installation of triphenylamino groups at 2,6 positions also show large red-shift of the absorption and emission spectra. Thus, the different arylated moieties at the meso position of BODIPY **2** and BODIPY **3** do not significantly affect the absorption and emission spectral maxima, only for DTPA-BDPs, the electron-donating oxoalkyl groups make DTPA-BDP a and b have longer maximum absorption and emission wavelength. This difference may arise from the fact that the arylated moiety is not coplanar with the BODIPY core due to steric hindrance with the substitution position is structurally unique.

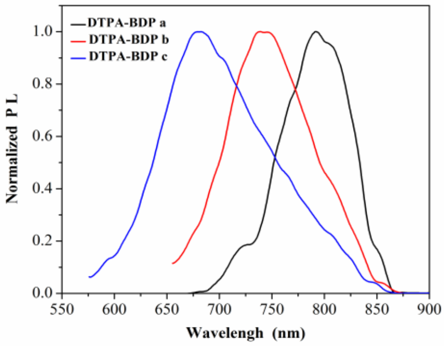


Figure 3. Normalized fluorescence spectra of DTPA-BDP **a** (black, λ_{exc} = 648 nm), DTPA-BDP **b** (red, λ_{exc} = 653 nm), DTPA-BDP **c** (blue, λ_{exc} = 559 nm) recorded in CH_2Cl_2.

Furthermore, In order to investigate the electrochemical behaviors of DTPA-BDP **a-c**, the electronic states of compounds DTPA-BDP **a-c** were studied through cyclic voltammetry in CH_2Cl_2 (Figure 4) and the results were summarized in Table 2. The potentials were reported versus ferrocene as internal standard and potentials were calibrated by addition of 0.63 V to the potential (vs. SCE) vs. Fc/Fc^+.[16] It can be seen that the E^{ox}_{onset} and E^{ox}_p of the three dyes were all measured as around 0.95 V and 1.1 V (Table 2), indicating that the different branched chains of electron donating groups had no effect on the E^{ox}. The corresponding HOMO (highest occupied molecular orbital) energy level of DTPA-BDPs were calculated (-5.36eV, -5.34 eV and -5.35eV, respectively) from the equation $E_{HUMO} = E^{ox}_{onset} + 4.4$ eV. Three dyes were actually located at very low energy.The important factor for this was that stronger electron donating group would result in more intensive ICT process.

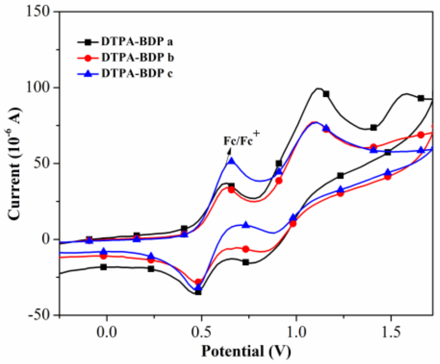


Figure 4. Cyclic voltammograms of DTPA-BDP **a-c** in CH_2Cl_2, containing 0.1M nBu_4NPF_6 as the supporting electrolyte recorded at scan speed of 50 mV/s, Fc^+/Fc refers to the ferricinium/ferrocene couple used as internal reference

By neglecting any entropy change during light absorption, the reduction potential vs. NHE (E_{red}), which corresponds to the lowest unoccupied molecular orbital (LUMO vs. NHE), can be obtained from E^{ox}_{onset} and E_g .

Table 2. Solution Electrochemical Properties of DTPA-BDP **a-c**.

Entry	E_g [a] (eV)	E^{ox}_{onset} [b] (eV)	E^{ox}_p [c] (v)	E_{red} [d] (v) vs.	HOMO/LUMO[e] (eV)
a	1.92	0.96	1.12	-0.96	-5.36/-3.44
b	1.90	0.94	1.08	-0.96	-5.34/-3.44
c	2.19	0.95	1.09	-1.24	-5.35/-3.16

a. Energy band gap, determined from UV-vis absorption spectra. At absorption maxima ($E_g = 1240/\lambda max$)

b. E^{ox}_{onset}, onset oxidation potential

c. E^{ox}_p , oxidation peak potential

d. E_{red} the reduction potential ,was calculated from $E^{ox}_{onset} - E_g$.

e. HOMO = $-(E^{ox}_{onset} + 4.4$ eV); LUMO = HOMO + E_g eV.

The above-discussed results indicated that the photophysical and electrochemical properties of these dyes were excellent and their performance as electron donor in BHJ solar cells would be feasible. We expect that these dyes would become valuable candidates to the applications of BHJ solar cells as a series of new metal-free organic dyes.

BODIPY derivatives BHJ solar cells were fabricated using DTPA-BDP **a-c** as the electron donor materials and fullerene derivatives as the electron acceptor materials through the conventional spin-coating process. The cell structure was ITO/ PEDOT:PSS (30 nm)/donor:acceptor (80 nm)/LiF (0.7 nm)/Al(100 nm). The effective device area was 7×10^{-2} cm^2, as defined by a shadow mask. Figure 5 shows typical current density-voltage (*J-V*) characteristics of two optimized devices at a ratio of 1:3 between DTPA-BDPs and $PC_{61}BM$ under 1,000 W m^{-2} air mass 1.5 global (AM 1.5 G) illumination. Device parameters such as short-circuit photocurrent densities (J_{SC}), open-circuit voltage (V_{OC}), fill factor (*FF*) and solar energy-to-electricity conversion yields (PCE) were deduced from the *J–V* characteristics and summarized in Table 3. A maximal PCE of 0.77 % with an V_{OC} of 0.70 V, a J_{SC} of 3.46 mA cm^{-2} and a *FF* of 0.32% was achieved in the DTPA-BDP **a**:$PC_{61}BM$-based device. All the PCE of BHJ solar cells were obtained without the thermal annealing. The FF values of this series of solar cells, from 0.32 to 0.23, which are relatively lower than the devices employing the state-of-the-art dye N719 (FF = 0.61),[17] suggesting the charge transfer within the cells was hindered once the charges in the active layer are formed.[18] Device performance was also very sensitive to atmosphere (oxygen and moisture) exposure, which likeky resulted in the presence of traps and worsening of fill factor.

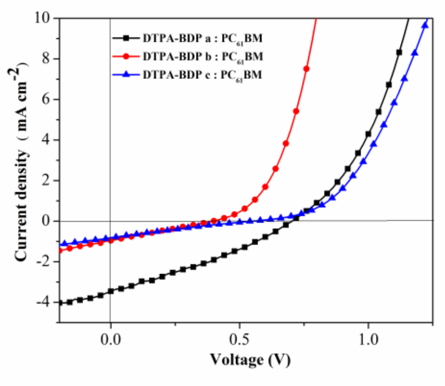


Figure 5. Current density-voltage (*J-V*) characteristics of the devices at a 1:3 weight ratio between BODIPYs and $PC_{61}BM$ under simulated AM 1.5G illumination (1000 W m^{-2})

Table 3. Photovoltaic Performances of the Devices Fabricated with Donor (DTPA- BDP **a**, DTPA- BDP **b**, DTPA- BDP **c**,)/C_{61}–PCBM BHJ Film.

Donor	Acceptor	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF %	PCE %
a	$PC_{61}BM$	3.46	0.70	0.32	0.77
b	$PC_{61}BM$	0.96	0.40	0.24	0.09
c	$PC_{61}BM$	0.81	0.54	0.23	0.10

In Conclusion, three novel BODIPY dyes (DTPA-BDP **a-c**) with 4,4-dimethyltriphenylamine at the 2,6-positions were successfully synthesized, which displayed PCEs 0.77% with a maximum Voc of 0.70V. Moreover, the interesting optical and electrochemical properties of these BODIPY dyes were also investigated. All dyes are emissive in near-infrared region. We believed that BODIPY dyes with 4,4-dimethyltriphenylamine at the 2,6-positions would improve light-harvesting assemblies. The further molecular design of molecular disks can enhance the PCE values of BHJ solar cells by optimizing the organized structures of donors for efficient charge mobility in the active layers.

Acknowledgments

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Supplementary Material

Experimental procedures, structural proofs, and spectral data for all new compounds are provided.

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