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Design and characterization of Bodipy derivatives for bulk heterojunction solar cells

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ABSTRACT

Two electron rich Bodipy dyes with strong absorptivities in the visible region were designed and synthesized as potential electron donors in bulk heterojunction photovoltaic constructs. Overall efficiency is above 1%, with impressive responsiveness at both UV and near-IR ends of the visible spectrum. Computational studies reveal an unexpected effect of *meso*-substituents on the electron transfer efficiency.

1. Introduction

Bulk heterojunction (BHJ) organic photovoltaic (OPV) technologies are recognized as a promising alternative to traditional liquid electrolyte based dye-sensitized solar cells (DSSCs) following the improved conversion efficiencies during the last decade.[1] In these all-organic cells, electron donor/acceptor moieties are blended together in the photoactive layer and conductive polymers (PEDOT:PSS/polyethylenedioxythiophene:polystyrene sulfonate) are incorporated as replacement to inorganic semi-conductors.[2] BHJ-OPV offers a promising modality towards solvent free, large area, reduced weight, and environmentally friendly OPV constructs.

Common strategy for the fabrication of BHJ-OPV is to combine fullerene derivatives as an electron acceptor (in most cases phenyl-C60/61/70-butryic acid methyl ester; PCBM) with conjugated polymers as electron donors.[1c,2] Conjugated polymers, with their high film forming qualities, resulted in moderate to high efficiencies.[3] However, challenging synthetic problems, structural concerns and purification problems generate a clear impetus to find substitutes for the polymeric component of the photovoltaic cell. Another important issue with the polymers is their large optical band gaps. This causes polymer to mostly absorb at high-energy part of the electromagnetic spectrum within a very narrow wavelength range. Thus, significant effort has been placed to find longer wavelength absorbing polymers.[4] On the other hand, as a reasonable alternative, more suitable smaller molecules were also employed as donors.[5] Among the possible donor molecules, Boradiazaindacene (also known as Bodipy)[6] dyes appear to be promising candidates due to their tunable absorption spectra with high extinction coefficients, multiple modification sites amenable for derivatization, photostability, ease of synthesis and relatively long excited state lifetimes.[7] Bodipy dyes have been widely used in biological labeling and molecular sensors,[8] as sensitizers for photodynamic therapy,[9] energy transfer cassettes and light harvesting,[10] and in logic gates studies.[11] Besides these applications, as a result of their suitable characteristics, Bodipy dyes were also employed in liquid electrolyte,[12] solid state[13] and BHJ-OPV[14] solar cells.

In this work, we revisited the rich Bodipy chemistry and designed two near-IR absorbing donor molecules (**BHJ 1** & **BHJ 2**) to investigate their photovoltaic performance in BHJ-OPV (Fig. 1). The main goal was to obtain panchromatic sensitization by including near-IR absorption.

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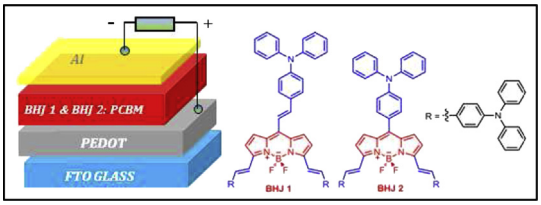

Fig. 1. Structures of sensitizers **BHJ 1** & **BHJ 2** and schematic representation of the BHJ-OPV cell.

2. Results and discussion

Our previous Bodipy sensitizers[12d] clearly showed that the absence of methyl groups on positions 1 and 7 has a positive effect on extended conjugation and favors the electron transfer processes. This is the result of smaller dihedral angle between *meso*-phenyl moieties and the Bodipy core.

In the design of **BHJ 1**, we are not just removing those methyl groups, but also linking the electron donor diphenylamino phenyl moiety at *meso* position with a styryl unit in order to further improve the conjugation and flexibility within the sensitizer. *meso*-Phenyl substituted analogue of **BHJ 2** was also studied to observe the effect of structural modifications on efficiency of the donor. As a final design requirement, additional diphenylamino phenyl groups were incorporated at the 3 and 5 positions of the Bodipy in both **BHJ 1** & **2** to obtain near-IR absorbing dyes and stronger electron donating sensitizers.

BHJ 1 and **BHJ 2** were synthesized according to established protocols. In the case of **BHJ 1** standard Bodipy synthesis procedure with acetyl chloride and 2-methyl pyrrole was applied. In the synthesis of **BHJ 2**, another approach was taken, making use of the reaction of diphenylaminobenzaldehyde and 2-methyl pyrrole. Once the desired Bodipy cores were constructed, targeted compounds were obtained by Knoevenagel condensation reactions in the presence of piperidine and acetic acid.

Photophysical and electrochemical characterization data of the sensitizers in solution are listed in Tables 1 and 2. Electronic absorption spectra (Fig. 2 top) of both dyes show strong and broad ($S_0 \rightarrow S_1$) absorption bands in the red and near-IR region of the spectrum with high extinction coefficients. As expected, extended conjugation in **BHJ 1** result in red-shifted peak centered around 748 nm. Very low fluorescence intensity ($\phi_f \approx 1\%$) of **BHJ 1** can be attributed to the rotation of the double bond around the dihedral axis in the excited state. More rigid **BHJ 2** on the other hand, shows

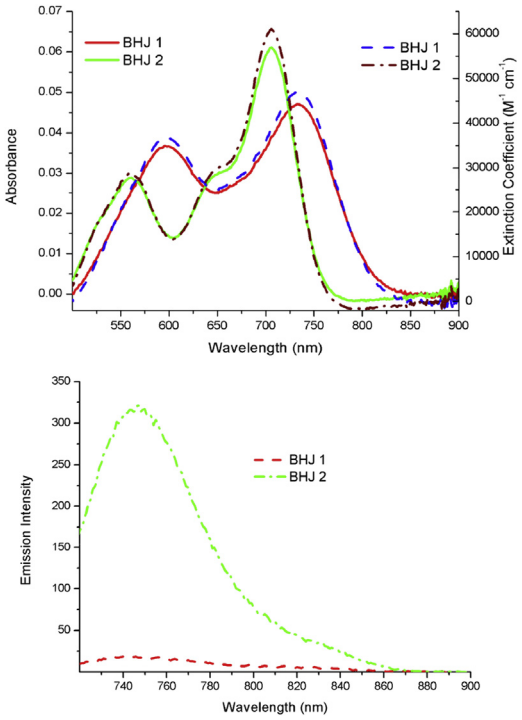

Fig. 2. (top) Electronic absorption and (bottom) emission spectra of **BHJ 1** (red & blue) and **BHJ 2** (green & dark red) in $CHCl_3$.

clear emission peak around 750 nm (Fig. 2 bottom) with moderate fluorescence quantum yield ($\phi_f \approx 24\%$).

Cyclic voltammetry data (CV) were acquired in chloroform (10^{-3} M). A three-electrode cell was used consisting of glassy carbon supporting electrode, platinum wire counter electrode, and Ag/AgCl reference electrode. Data were taken with ferrocene as the internal reference electrode. CV spectra (Fig. 3) of sensitizers show both reversible oxidation and reduction peaks (Table 2). The lowest unoccupied molecular (LUMO) energy of **BHJ 1** and **BHJ 2** are −3.59 and −3.42 eV, respectively. LUMO energies of dyes are clearly higher than the LUMO energy of PCBM (≈−3.90 eV), which suggests an efficient electron transfer from excited donor to acceptor PCBM. Another remarkable result of the CV study is that the highest occupied molecular orbital (HOMO) energy levels of the sensitizers are deeper than the commonly used P3HT (poly(3-hexylthiophene-2,5-diyl)) conjugated polymer[16] suggesting an improved oxidative stability for **BHJ 1** and **2**.

Table 1
Photophysical characterization of **BHJ 1** and **2**

Dye	λ_{abs}/(nm)[a]	ε_{max}/(M^{-1} cm^{-1})[a]	λ_{ems}/(nm)[a]	ϕ_f/(%)[b]
BHJ 1	748	37,000	755	1
BHJ 2	710	46,000	750	24

[a] Data were acquired in $CHCl_3$.
[b] Reference compound: tetrastyryl dye 2 in Ref. 15 (ϕ_f=42%) in $CHCl_3$.

Table 2
Photophysical and electrochemical characterization of **BHJ 1** and **2**

Dye	E_{ox}/(V)[a]	E_{red}/(V)[a]	E_{HOMO}/(eV)[a]	E_{LUMO}/(eV)[a]	$E_{band\ gap}$/(eV)[a]
BHJ 1	0.60	−0.82	−5.00	−3.59	1.41
BHJ 2	0.58	−0.97	−4.96	−3.42	1.54

[a] Solutions were prepared in $CHCl_3$ (10^{-3} M).

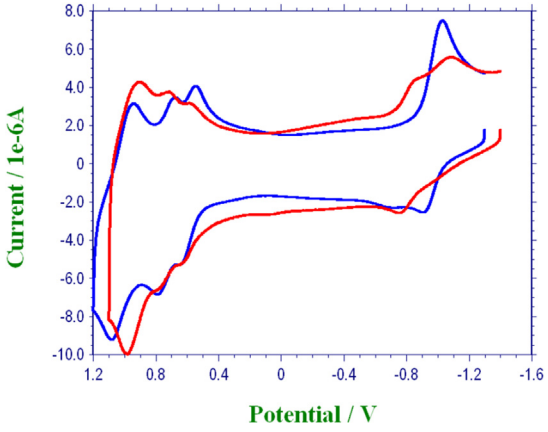

Fig. 3. Cyclic voltammograms of **BHJ 1** (red) and **BHJ 2** (blue).