LETTERS 2011 Vol. 13, No. 17 4574–4577

ORGANIC

Near-Infrared Absorbing Boron-dibenzopyrromethenes that Serve As Light-Harvesting Sensitizers for Polymeric Solar Cells

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Received July 1, 2011



Hexylthiophene-conjugated boron-dibenzopyrromethenes with benzo[1,3,2]oxazaborinine rings, 1, that absorb near-infrared light with relatively high molecular extinction coefficients have been synthesized. The incorporation of 3-hexylthiophene-conjugated dye 1a at a blend ratio of 5 wt % into a polymeric solar cell based on a P3HT/indene $-C_{70}$ bisadduct (IC₇₀BA) bulk heterojunction structure improved power conversion efficiency from 3.7 to 4.3%. The present work suggests that well-defined near-infrared absorbing BODIPY analogues can potentially be used as photosensitizers in polymeric solar cells.

Much attention has been devoted to the chemistry of BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene).¹ BODIPY, which can be easily modified by a synthetic process, is considered greatly promising for a variety of applications such as fluorescence probes, emitting materials, chemosensors, and light-harvesting materials because of its high molecular extinction coefficients of absorption, high fluorescence quantum yield, and high photostability. Its structure can be controlled during synthesis, enabling the fine-tuning of its optical properties. In this context, increased efforts to apply BODIPY to organic photovoltaic cells have led to the synthesis of BODIPY derivatives

for applications to TiO₂-based solar cells² and bulk heterojunction (BHJ) devices.³ BODIPY dyes have been

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investigated as p-type or donor materials in conjugation with electron-accepting fullerene derivatives to realize solution-processed BHJ solar cells.

 $\begin{array}{l} \textbf{Scheme 1. Synthesis of Thiophene-conjugated boron-dibenzo-pyrromethenes 1} \end{array} \\ \end{array}$



From the viewpoint of achieving high power conversion efficiency (PCE), near-infrared absorbing dyes are one of the most important research candidates because approximately 50% of the radiation intensity of sunlight is in the near-infrared region from 700 to 2000 nm.⁴ However, to the best of our knowledge, few studies have focused on solar cells containing near-infrared absorbing BODIPY dyes.^{2e}

We have currently synthesized new types of borondibenzopyrromethene dyes⁵ in which the formation of a benzo[1,3,2]oxazaborinine based on intramolecular B.Ochelation caused a remarkable bathochromic shift in the absorption band,⁶ resulting in the production of nearinfrared absorbing dyes. The synthetic path that we employed enabled us to introduce several functional groups at the 5-position of the isoindole moiety. Our continuous efforts to determine the applicability of the dye to photovoltaic devices led to our discovery that hexylthiopheneconjugated dye 1 could serve as a sensitizer in a BHJ solar cell. The prototype BHJ system is based on a blend of regioregular poly(3-hexylthiophene) (P3HT) as a donor and a fullerene derivative as an acceptor, with reported PCEs of up to 4-5%.⁷ Although P3HT has a high field effect hole mobility ($> 10^{-2}$ cm² V⁻¹ s⁻¹),⁸ the film can only absorb short wavelengths under 650 nm. Thus, there is a

(5) Kubo, Y.; Minowa, Y.; Shoda, T.; Takeshita, K. Tetrahedron Lett. 2010, 51, 1600–1602. high demand for near-infrared absorbing dyes capable of acting as a photosensitizer in BHJ solar cells to enhance the light-harvesting capability. Despite this necessity, so far, only a few near-infrared dyes have been reported, such as diketopyrrolopyrrole⁹ and phthalocyanines.¹⁰

Here, we show that the incorporation of 1 at a blend ratio of 5 wt % into a P3HT/IC₇₀BA BHJ solar cell (IC₇₀BA; indene-C₇₀ bis-adduct¹¹) leads to increased carrier generation in the near-infrared region, resulting in the enhancement of the short circuit current and thus the PCE of the device. These are the first examples of BODIPY analogues that improve the photovoltaic performance of polymeric solar cells.

The synthetic path of **1** is shown in Scheme 1, the key intermediate being dibromo- and dimethoxy-substituted boron-dibenzopyrromethene difluoride 2. The synthesis of 2 starts with the reaction of commercially available 4-bromo-2-hydroxyacetophenone 3 with hydrazine 4 to yield 5 in 62% yield, followed by the oxidation reaction with lead tetraacetate to give 6, and then condensation with ammonia to afford benzo-fused dipyrrin 7 in a moderate yield of 44%. Subsequently, BF₂-chelation with 7 using $BF_3 \cdot Et_2O$ was carried out to afford 2 in 79% yield. As for the preparation of 3-hexylthiophene-conjugated dye 1a, Suzuki cross-coupling of 2 was employed with borylthiophene derivative $\mathbf{8}^{12}$ followed by demethylation with BBr₃ to realize spontaneous cyclization to afford 1a in 53% yield. On the other hand, 5-hexylthiophene derivative 1b, being a regioisomer of 1a, could be prepared via Stille crosscoupling of **2** with the stannic derivative 10^{13} followed by treatment with BBr₃. The assignments of these new dyes



Figure 1. (a) Absorption spectra of **1a**, **1b**, and **12** $(5 \mu M)$ in THF at 25 °C. (b) Chemical structures of **12** and **13**.

were carried out using spectroscopic data (see Supporting Information); for example, the resonance arising from thiophene protons for **1a** in d_6 -DMSO was exhibited at 7.13 (2H, d, J = 5.16 Hz) and 7.56 (2H, d, J = 5.10 Hz). Figure 1 shows the absorption spectra of **1** in THF, where

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 Table 1. Optical Properties and Theoretical Data of Borondibenzopyrromethenes

dye	$\lambda_{\max} \ (obs)^a / \ nm$	$\lambda_{\rm max}$ (calcd)/nm	HOMO ^b / eV	LUMO ^b / eV	$rac{arepsilon(\mathrm{obs})^a}{\mathrm{M}^{-1}\mathrm{cm}^{-1}}$	f (calcd)
1a	733	622	-4.707	-2.568	135000	0.621
1b	747	635	-4.616	-2.519	148000	0.662
12^{9}	748				83400	
13 ⁹	746	642	-4.445	-2.408	82900	0.468

 $^a\mathrm{Spectra}$ were measured in THF. $^b\mathrm{Values}$ were calculated using DFT.

the effect of the inserted thiophene on the absorption property can be compared with the corresponding hexyloxy derivative **12**.⁵ Dye **1a** absorbed near-infrared light with a λ_{max} value of 733 nm and with the molecular extinction coefficient (ε) being calculated to be 1.35 × $10^5 \text{ M}^{-1}\text{cm}^{-1}$. When compared to **12**, albeit with a hypshochromic shift of 15 nm, the ε value of **1a** was found to be 1.6 times larger, which is favorable for light-harvesting. The absorption properties of **1b** were also elucidated ($\lambda_{\text{max}} =$ 747 nm, $\varepsilon = 1.48 \times 10^5 \text{ M}^{-1}\text{ cm}^{-1}$); the bathochromic shift, with an enhanced molecular extinction coefficient compared to **1a**, can be interpreted to be caused by steric effects between the isoindole segment and thiophene rings in the chromophore (*vide infra*).

For a better understanding of the spectral properties, the transition energies and oscillator strength (f) were calculated using TD-DFT (time-dependent density functional theory). The resulting data is summarized in Table 1 with the data for the methoxy derivative 13^5 for comparison. Geometry optimization was carried out using the B3LYP hybrid function with the 6-31G(d,p) basis set. The trend of the calculated λ_{max} was almost consistent with that of spectra observed in THF. Although the first absorption band was characterized as a mixture of several configurations, it can mainly be ascribed to the HOMO-LUMO transition. Replacement of the methoxy group at the 5-position of isoindole with hexylthiophene led to significant stabilization of both the HOMO and the LUMO energy levels. In addition, the calculations indicated that the π -systems extended by incorporating the thiophene caused the significant increase in the oscillator strength of 1 compared to 13 from 0.468 to 0.621 for 1a and from 0.468 to 0.662 for 1b. The position of the hexyl substituent on the thiophene ring was found to influence the HOMO energy level more effectively than the LUMO energy level; the HOMO energies of 1a and 1b were calculated to be -4.707and -4.616, respectively. This alteration was due to steric effects between thiophene and isoindole rings, as inferred from the geometry optimization in Figure 2, which shows that the HOMO level is more stable. These calculations clarified the effect of thiophene-insertion on the absorption property of the dibenzopyrromethene chromophore.





Figure 2. HOMO and LUMO surface plots for 1a and 1b.



Figure 3. (a) Cyclic voltammograms of **1a**, **1b**, and **12** measured in acetonitrile/*o*-dichlorobenzene (2:3 v/v) containing 0.1 M TBAPF₆ at room temperature. Ferrocene (Fc) was used as an internal reference. (b) HOMO and LUMO energies of dyes **1a**, **1b**, **12**, P3HT, and IC₇₀BA. The HOMO and LUMO levels of the dyes were calculated from the CV measurements in acetonitrile/*o*-dichlorobenzene (2:3 v/v); HOMO [eV] = $-(E_{\rm ox} - E_{\rm Fc/Fc+} + 4.8)$; LUMO [eV] = $-(E_{\rm red} - E_{\rm Fc/Fc+} + 4.8)$.

The electrochemical properties of 1 were further examined by cyclic voltammetry (CV). Figure 3a shows the reference electrode in acetonitrile/o-dichlorobenzene (2:3 v/v) with 0.1 M tetrabutylammonium hexafluorophosphate $(TBAPF_6)$ as the supporting electrolyte at a scan rate of 50 mV s⁻¹. The measurements were calibrated using a ferrocene value of -4.8 eV as the standard.¹⁴ The formal potential of Fc/Fc^+ was measured as 0.18 V against Ag/Ag⁺. The dyes tested here showed fully reversible oxidation and reduction behaviors. The anodic scan showed that the onset oxidation potential for 1a or 1b occurred at 0.329 or 0.216 eV, respectively, which corresponded to an ionization potential (HOMO level) of -4.95 eV for 1a and -4.84 eV for 1b. Similarly, the onset reduction potential of 1a or 1b allowed us to estimate the electron affinity (LUMO level) to be -3.50 eV for **1a** or -3.49 eV for **1b**. Although both have similar LUMO levels, the HOMO level of 1a was lower than that of 1b, implying that the HOMO level was sensitive to the position of the hexyl substituent on the thiophene ring of the dye, which was consistent with the result of DFT calculations (vide supra). In addition, hexylthiophene-conjugated dyes 1a and 1b showed lower HOMO and LUMO

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⁽¹⁶⁾ Taken into the absorption enhancement at about 600 nm of BHJ film with **1a** account (Figure 4a), the addition of **1a** could also control the nanoscale crystallinity of P3HT in the polymer cells, leading to improvement of carrier mobility arising from P3HT.



Figure 4. (a) Absorption spectra of BHJ film comprising P3HT: IC₇₀BA (1:0.95) (black curve) and the BHJ film with 5 wt % of **1a** (red curve); (b) J-V curves of devices with the BHJ film (black curve) or the BHJ film with 5 wt % of **1a**.

levels than did hexyloxy dyes 12 (HOMO = -4.78 eV; LUMO = -3.43 eV), which supported our calculation results (*vide supra*).

The absorption and electrochemical properties of dyes 1 make them promising for practical applications as lightharvesting sensitizers in P3HT/IC70BA-based BHJ solar cells, wherein IC₇₀BA is employed as an acceptor because of its higher LUMO energy level of -3.72 eV than that of $PC_{60}BM$.¹¹ The energy diagrams of the dyes are shown in Figure 3b along with the values of $P3HT^{15}$ and $IC_{70}BA$. For dye 12, the high-lying HOMO level at -4.78 eV causes a lack of driving force for charge-carrier generation. On the other hand, the HOMO level of 1a(-4.95 eV) is estimated to be lower than that of P3HT by 0.1 eV, enabling it to avoid charge trapping on the dye. Furthermore, the LUMO level of -3.50 eV may be sufficiently high for electron injection into the IC₇₀BA acceptor. This implies that when dye 1a is located at the interface between P3HT and $IC_{70}BA$, the excitons generated in **1a** could donate holes to P3HT and electrons to IC70BA in the device. In addition, the energy diagram suggests that 1b could act as a photosensitizer in the device; however, a negligible difference between the HOMO levels of P3HT and those of 1b may lead to a less effective charge-carrier function.

The dyes presented in our study were characterized in BHJ solar cell devices. The device was fabricated with the configuration ITO/PEDOT:PSS (40 nm)/P3HT $(M_{\rm w} = 38000, \text{PDI} = 1.74, \text{regioregularity} = 91\%):IC_{70}$ BA (1:0.95) with a blend of 5 wt % dye 1a (100 nm)/Ca (10 nm)/Al (80 nm). The active layer was spin-coated and annealed at 150 °C for 20 min. As a control device, a P3HT/IC₇₀BA binary blended cell device was also fabricated. Figure 4a shows the absorption spectra of the activated layer; it was found that P3HT/IC70BA with 5 wt % of **1a** showed a greater optical absorbance in the near-infrared region than did P3HT/IC₇₀BA binary blended BHJ film. In particular, a new absorption band was clearly observed at ca. 760 nm. The photovoltaic devices were characterized under 100 mW cm⁻² AM 1.5G irradiation; the current-density vs voltage (J-V)curves were measured using SourceMeter (Serious 2400 Keithley Instruments Inc.) and are shown in Figure 4b. The P3HT/IC₇₀BA/1a ternary system exhibited a significant increase in both the short-circuit current (Jsc) from



Figure 5. EQE spectra of the devices made using (a) BHJ film comprising P3HT:IC₇₀BA (1:0.95) with 5 wt % of **1a**, (b) BHJ film with 5 wt % of **1b**, and (c) BHJ control film.

6.3 to 7.0 mA cm⁻¹ and the fill factor (FF) from 0.67 to 0.71, as compared to the **1a**-free device. The increase in Jsc with 1a is ascribable to an increase in photogenerated carriers. Indeed, the external quantum efficiency (EQE), as shown in Figure 5, exhibited a peak at ca. 760 nm, indicating that 1a dispersed in the BHJ layer could lead to efficient exciton dissociation and carrier generation. Subsequently, the incorporation of 1a (5 wt %) into a P3HT/ IC₇₀BA bulk heterojunction solar cell improved the PCE from 3.7 to 4.3%.¹⁶ Although the corresponding hexyloxy dye 12 never exhibited light-harvesting capability, as inferred from the energy diagram in Figure 3b, 5-hexylthiophene-conjugated dye 1b exhibited a moderate effect as a sensitizer; the PCE value of the P3HT/IC₇₀BA BHJ device with 5 wt % of **1b** was 4.0%, which was moderately larger than that of the control device (PCE = 3.7%). Note that the EQE spectrum of the 1b-containing device exhibited a diminished peak signal in the near-infrared region. This low efficiency maybe attributable to low carrier generation, possibly due to the higher-lying HOMO level, which is close to that of P3HT. Furthermore, we have to consider the steric bulkiness of the dye system as being a major factor in its performance as a light-harvesting sensitizer in polymeric solar cells.¹⁷ In the case of **1a**, steric hindrance between thiophene and isoindole moieties could prevent dye-aggregation in the film to provide an effective lightharvesting behavior.

In conclusion, we have described the first examples of BODIPY analogues, thiophene-conjugated boron-dibenzopyrromethenes, that can serve as light-harvesting sensitizers in polymeric solar cells. We believe that the synthetic flexibility of BODIPY and its analogues can lead to the development of highly efficient sensitizers for photovoltaic conversion in BHJ solar cell devices. Future work will include not only structural optimization of BODIPYbased sensitizers but also further investigation of the mechanism behind its light-harvesting effect.

Supporting Information Available. Detailed experimental procedures of synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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