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

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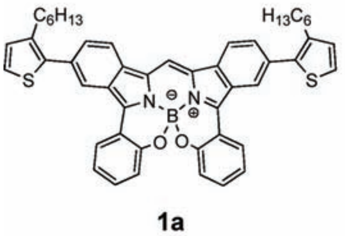
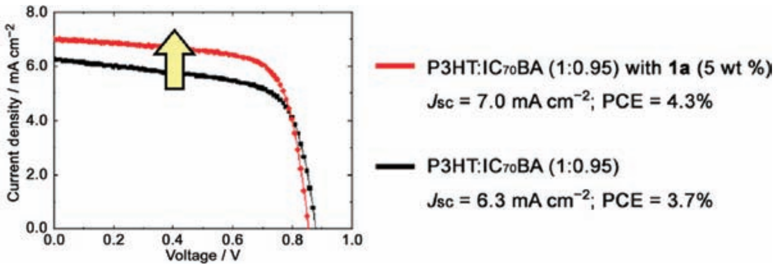
ABSTRACT



1a



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 ($IC_{70}BA$) 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 TiO_2-based solar cells[2] and bulk heterojunction (BHJ) devices.[3] BODIPY dyes have been

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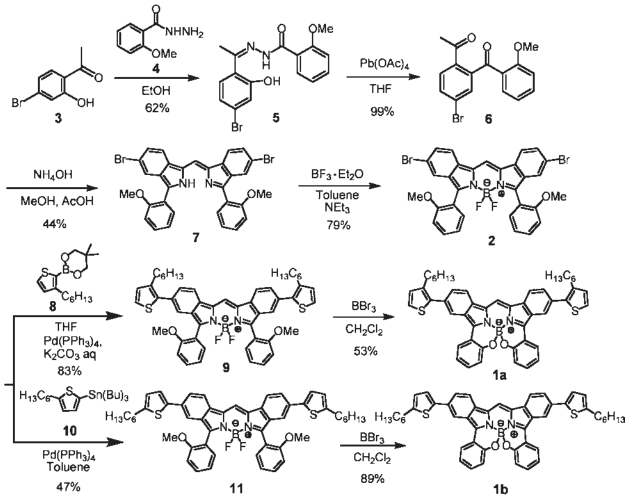
investigated as p-type or donor materials in conjugation with electron-accepting fullerene derivatives to realize solution-processed BHJ solar cells.

Scheme 1. Synthesis of Thiophene-conjugatedboron-dibenzopyrromethenes **1**



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 boron-dibenzopyrromethene dyes[5] in which the formation of a benzo[1,3,2]oxazaborinine based on intramolecular B,O-chelation caused a remarkable bathochromic shift in the absorption band,[6] resulting in the production of near-infrared 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 hexylthiophene-conjugated 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 ($> 10^{-2}$ cm^2 V^{-1} s^{-1}),[8] the film can only absorb short wavelengths under 650 nm. Thus, there is a 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 diketopyrrolopyrrole[9] and phthalocyanines.[10]

Here, we show that the incorporation of **1** at a blend ratio of 5 wt % into a P3HT/IC$_{70}$BA BHJ solar cell (IC$_{70}$BA; indene-C$_{70}$ bis-adduct[11]) 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, BF$_2$-chelation with **7** using BF$_3\cdot$Et$_2$O 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 **8**,[12] followed by demethylation with BBr$_3$ 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 cross-coupling of **2** with the stannic derivative **10**[13] followed by treatment with BBr$_3$. The assignments of these new dyes 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

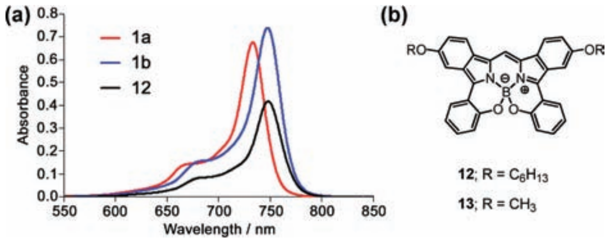


Figure 1. (a) Absorption spectra of **1a**, **1b**, and **12** (5 μM) in THF at 25 °C. (b) Chemical structures of **12** and **13**.

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Table 1. Optical Properties and Theoretical Data of Boron-dibenzopyrromethenes

dye	$\lambda_{\max}$ (obs)^a / nm	$\lambda_{\max}$ (calcd)/nm	HOMO^b/ eV	LUMO^b/ eV	ε (obs)^a M^{-1} cm^{-1}	f (calcd)
1a	733	622	−4.707	−2.568	135 000	0.621
1b	747	635	−4.616	−2.519	148 000	0.662
12[9]	748				83 400	
13[9]	746	642	−4.445	−2.408	82 900	0.468

^{a}Spectra were measured in THF. ^{b}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 $\lambda_{\max}$ value of 733 nm and with the molecular extinction coefficient (ε) being calculated to be 1.35 × 10^5 $M^{-1}cm^{-1}$. 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 ($\lambda_{\max}$ = 747 nm, ε = 1.48 × 10^5 $M^{-1}cm^{-1}$); 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 $\lambda_{\max}$ 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 −4.707 and −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.

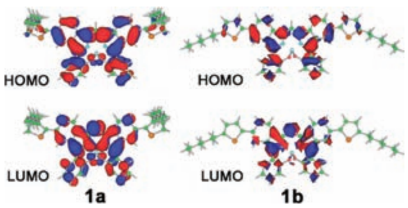

Figure 2. HOMO and LUMO surface plots for **1a** and **1b**.

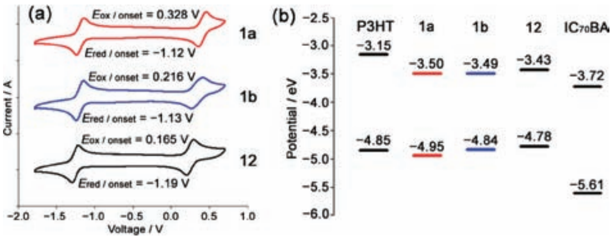

Figure 3. (a) Cyclic voltammograms of **1a**, **1b**, and **12** measured in acetonitrile/*o*-dichlorobenzene (2:3 v/v) containing 0.1 M $TBAPF_6$ at room temperature. Ferrocene (Fc) was used as an internal reference. (b) HOMO and LUMO energies of dyes **1a**, **1b**, **12**, P3HT, and $IC_{70}BA$. The HOMO and LUMO levels of the dyes were calculated from the CV measurements in acetonitrile/*o*-dichlorobenzene (2:3 v/v); HOMO [eV] = $-(E_{ox} - E_{Fc/Fc+} + 4.8)$; LUMO [eV] = $-(E_{red} - E_{Fc/Fc+} + 4.8)$.

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.

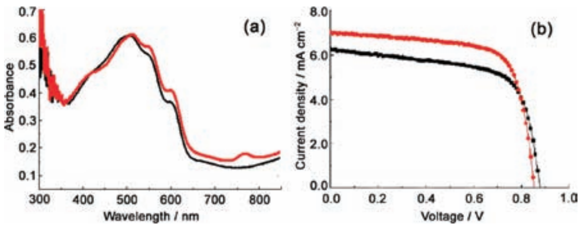

Figure 4. (a) Absorption spectra of BHJ film comprising P3HT:$IC_{70}BA$ (1:0.95) (black curve) and the BHJ film with 5 wt % of **1a** (red curve); (b) $J-V$ curves of devices with the BHJ film (black curve) or the BHJ film with 5 wt % of **1a**.

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 light-harvesting sensitizers in P3HT/$IC_{70}BA$-based BHJ solar cells, wherein $IC_{70}BA$ 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 $IC_{70}BA$ 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 $IC_{70}BA$ 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_w = 38000, PDI = 1.74, 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/$IC_{70}BA$ binary blended cell device was also fabricated. Figure 4a shows the absorption spectra of the activated layer; it was found that P3HT/$IC_{70}BA$ with 5 wt % of **1a** showed a greater optical absorbance in the near-infrared region than did P3HT/$IC_{70}BA$ 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/$IC_{70}BA$/**1a** ternary system exhibited a significant increase in both the short-circuit current (*J*sc) from 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 *J*sc 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/$IC_{70}BA$ 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/$IC_{70}BA$ 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 light-harvesting behavior.

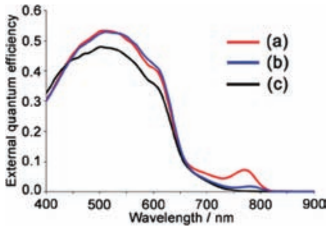

Figure 5. EQE spectra of the devices made using (a) BHJ film comprising P3HT:$IC_{70}BA$ (1:0.95) with 5 wt % of **1a**, (b) BHJ film with 5 wt % of **1b**, and (c) BHJ control film.

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 BODIPY-based 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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