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Facile Synthesis of Biphenyl-Fused BODIPY and Its Property

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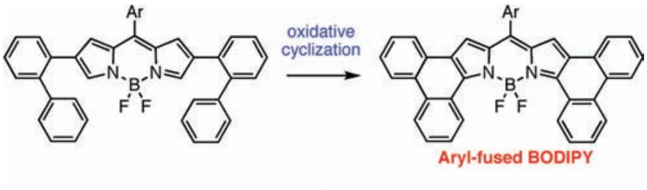
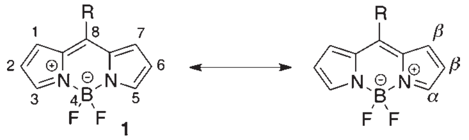
ABSTRACT



A biphenyl-fused BODIPY was synthesized through a facile oxidative cyclization of peripheral aryl-substituents at the β-position of the BODIPY unit. The extended π-system of the fused BODIPY induces near-infrared (NIR) absorption and strong $\pi-\pi$ interactions in the solid state. These features are beneficial for the application of the dye as a functional material. The biphenyl-fused BODIPY dye was demonstrated to exhibit photocurrent conversion ability on the basis of its *n*-type semiconducting property.

Boron dipyrrins (BODIPYs) are currently attracting much interest in a wide variety of research areas such as labeling reagents, fluorescent switches, chemosensors, nonlinear optical materials, and photovoltaics owing to their advantageous photophysical properties such as photostability, large extinction coefficients, and high luminescence efficiency.[1] The parent BODIPY dye (Scheme 1) shows absorption and emission around 500 nm. The addition of near-infrared (NIR) absorbing/emitting property to the BODIPY dye makes BODIPYs more useful materials in applications to solar cells as well as biolabeling.

Scheme 1. General Structure and Numbering of *meso*-Substituted BODIPYs



Hence, various methods to access NIR BODIPY dyes have been developed, including extension of π-conjugation, introduction of intramolecular charge transfer (ICT) character,[2,3] and incorporation of a nitrogen atom in the skeleton.[4] To extend π-conjugation, introduction of π-conjugated fragments such as ethynyl and vinyl groups or fusion of BODIPYs with aryl groups are often employed.

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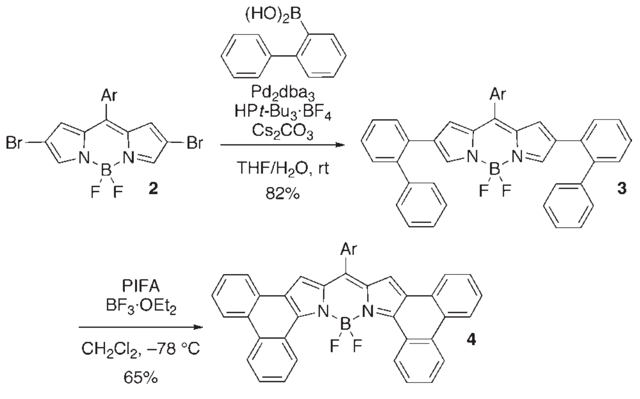
In particular, aryl-fused BODIPY dyes possess high rigidity in their structures. High rigidity of π-systems leads to a high fluorescence quantum yield in solution as well as strong intermolecular $\pi-\pi$ interactions in the solid state, which are beneficial for applications as π-functional materials. The conventional method for synthesis of aryl-fused BODIPY dyes is a condensation−oxidation sequence starting with π-extended fused pyrroles such as furopyrrole.[3a−c] In contrast, the oxidative fusion strategy of BODIPYs with peripheral aryl moieties is considered to be a straightforward alternative route. However, such examples are limited to the recent work by Wu et al., who reported synthesis of perylene- and porphyrin-fused BODIPYs through an oxidative fusion reaction with *meso*-substituents.[3d,e] Along this line, we decided to develop a novel strategy for synthesis of aryl-fused BODIPYs through an oxidative cyclization of β-aryl groups. Here, we report the synthetic procedure as well as application of a biphenyl-fused BODIPY dye as an *n*-type semiconducting material.

Scheme 2 shows the synthetic route and condition for a biphenyl-fused BODIPY. Suzuki−Miyaura coupling of 2,6-dibromo BODIPY **2**[5] with 2-biphenylboronic acid afforded biphenyl BODIPY **3** in 82% yield. Oxidative cyclization of biphenyl BODIPY **3** by PIFA−$BF_3 \cdot OEt_2$[6] at −78 °C proceeded smoothly to furnish biphenyl-fused BODIPY **4** as a sole product in 65% yield.

Figure 1a,b shows the absorption and emission spectra of fused BODIPY **4** in CH_2Cl_2, which exhibit substantial red-shifts in comparison to biphenyl BODIPY **3** due to a decrease in the HOMO−LUMO gap (vide infra). BODIPY **4** showed an intense absorption band at 673 nm with rather high absorption coefficients ($\varepsilon(\lambda_{max}) = 1.4 \times 10^5\ M^{-1}\ cm^{-1}$) (Table 1). The fluorescence quantum yield of **4** is high enough, despite the rather small HOMO−LUMO gap ($\Phi = 0.51$). The lower fluorescence quantum yield of **3** could be due to partial charge transfer character of **3** (Supporting Information).

Scheme 2. Synthesis of a Biphenyl-Fused BODIPY[a]



[a] Ar = 2,4,6-trimethylphenyl, PIFA = [Bis(trifluoroacetoxy)iodo]benzene.

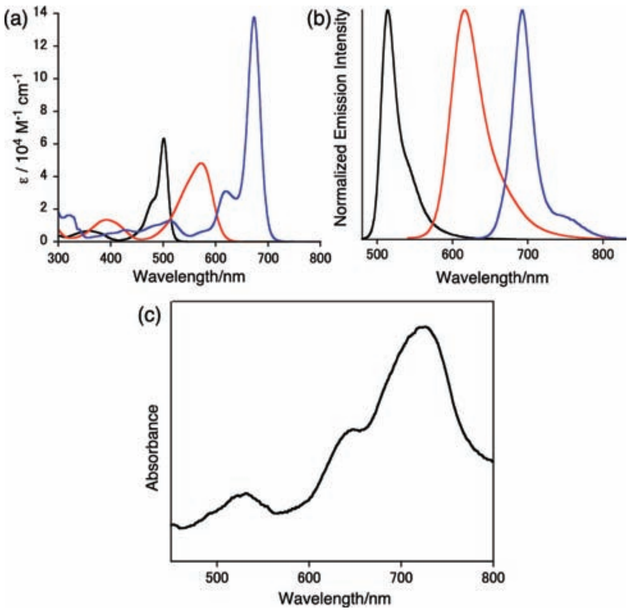


Figure 1. (a) UV−vis absorption spectra of **1** (R = 2,4,6-trimethylphenyl; black), **3** (red), and **4** (blue). (b) Fluorescence spectra of **1** (black), **3** (red), and **4** (blue) measured in CH_2Cl_2. (c) UV−vis absorption spectrum of thin film state of **4**.

Single crystal X-ray diffraction analysis revealed the molecular structure of **4** (Figure 2). BODIPY **4** exhibited π-interactions through peripheral fused-biphenyl moieties, in which the interplanar distance is 3.48 Å. Interestingly, the BODIPY units adopt a 1-D infinite stack (Figure 2c), which is known to be favorable for organic semiconductors.[7] The intermolecular $\pi-\pi$ interactions in the solid state were further confirmed by the UV−vis absorption spectrum in

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the solid state. As shown in Figure 1c, the UV–vis absorption spectrum of compound **3** in thin film exhibited a substantial red shift in comparison to that in solution ($\Delta\lambda$ = 34 nm). No emission was observed in the solid state.

Table 1. Summary of Optical Properties of BODIPYs in Solution

compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_f
1	501	6.3×10^4	514	0.92^a
2	538	5.8×10^4	577	0.14^a
3	573	4.8×10^4	616	0.58
4	673	1.4×10^5	692	0.51

[a] Values taken from ref 5.

Electrochemical properties of BODIPY **3** and **4** were examined by cyclic voltammometry (Table 2). In the case of **3**, a quasi-reversible oxidation wave and reversible reduction wave were observed at 0.89 and −1.34 V, respectively. In the case of **4**, reversible oxidation and reduction waves were observed at 0.80 and −1.05 V, respectively (vs Fc/Fc$^+$). Remarkably, reduction of **4** occurred at rather positive potential. Consequently, expansion of π-conjugation and the electron-withdrawing boron atom significantly lowered the LUMO level (−3.75 eV) of **4**,[8] which is almost equal to representative *n*-type semiconducting materials such as perylene bisimides and fullerenes.

Table 2. Summary of Electrochemical Properties of BODIPYs[a]

compound	$E_{1/2}^{red1}$/V	$E_{1/2}^{ox1}$/V	LUMO level/eV[b]
3	−1.34	0.89	−3.46
4	−1.05	0.80	−3.75

[a] Measurements were performed in CH_2Cl_2 solution containing $TBAPF_6$ (0.1 M) as a supporting electrolyte with a scan rate of 100 mV/s. Platinum, platinum wire, and Ag/AgClO$_4$ electrodes were used as working, counter, and reference electrodes, respectively. [b] Values from the vacuum level were estimated by the following equation: LUMO level = $-(4.8 + E_{1/2}^{red})$ eV

Because an application of a BODIPY skeleton as *n*-type semiconducting materials has not been reported so far, except for BODIPY-polymers,[9,10]the *n*-type semiconducting property was examined. To evaluate the intrinsic charge-carrier mobility, we measured the flash-photolysis time-resolved microwave conductivity (FP-TRMC) of the polycrystalline film of **4**.[11] The TRMC measurement of transient photoconductivity confirms that **4** has actually good carrier mobility (a minimum mobility; μ_{min} = 9×10^{-3} cm^{-1} V^{-1} s^{-1}) determined by the maximum yield of photogenerated charge carriers upon excitation at 355 nm derived from transient photocurrent traces.

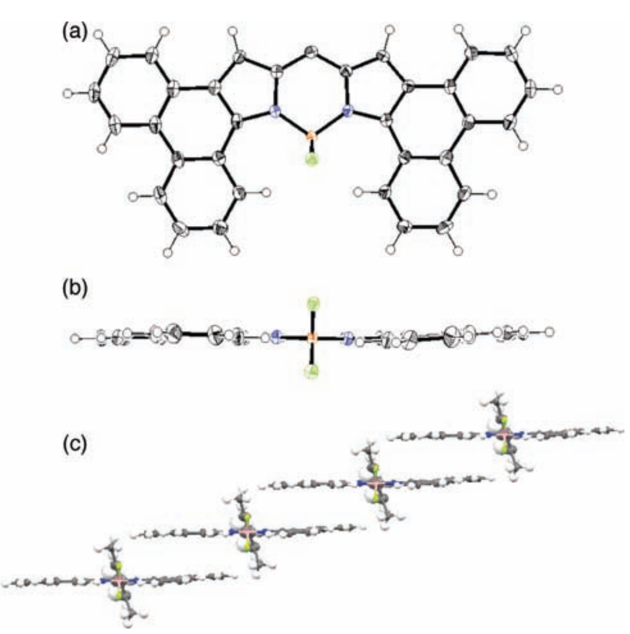

Figure 2. X-ray crystal structure of **4**. (a) Top view of **4**, (b) side view of **4**, and (c) packing structure of **4**. The thermal ellipsoids were scaled to the 50% probability level. *meso*-Aryl substituents were omitted for clarity except (c).

To clarify whether BODIPY **4** can be used as an *n*-type semiconducting material for a device application, a *p*–*n* heterojunction solar cell was fabricated.[12,13] Tetrabenzoporphyrin (BP) was employed as an electron donor.[14] The current density–voltage (*J*–*V*) characteristics under AM 1.5G simulated solar illumination at an intensity of 100 mW/cm^2 and corresponding external quantum efficiency (EQE) spectrum are shown in Figure 3. The device actually showed a performance with an open-circuit voltage (V_{oc}) of 0.51 V, a shot-circuit current density (J_{sc}) of

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(8) The LUMO level was estimated by using the following equation: LUMO level = $-(4.8 + E_{1/2}^{red})$ eV. Wong, W.-Y.; Wang, X.-Z.; He, Z.; Djurii, A. B.; Yip, C.-T.; Cheung, K.-Y.; Wang, H.; Mak, C. S. K.; Chan, W.-K. *Nat. Mater.* **2007**, *6*, 521.

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2.9 mA/cm^2, and a fill factor (FF) of 0.35. The power conversion efficiency (PCE) of 0.52% was obtained. This means that biphenyl-fused BODIPY **4** can act as an *n*-type semiconducting material as expected from the packing structure as well as low LUMO level.

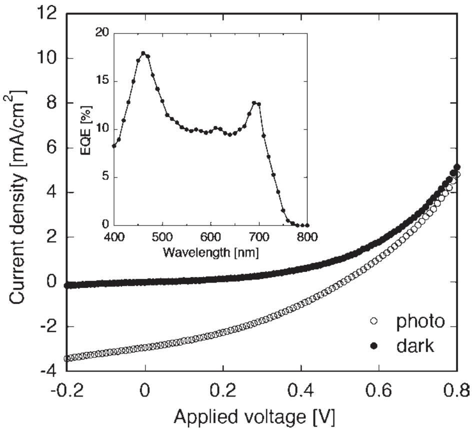

Figure 3. *J*–*V* curves for the device; glass/ITO/PEDOT:PSS/BP/BODIPY **4**/NBphen/Al. Photocurrent is measured under AM1.5G illumination (100 mW/cm^2, 1 sun). Inset: External quantum efficiency (EQE) as function of wavelength of the OPV device.

To understand the carrier mobility, frontier orbitals of **4** were calculated at the B3LYP/6-31G(d) level by the DFT method (Figure 4). Both HOMO and LUMO of **4** are well delocalized on the fused biphenyl moiety, offering effective orbital interactions between the stacked π-systems. We also evaluated transfer integrals of HOMO and LUMO (tHOMO and tLUMO) on the basis of the crystal structure of **4** by is the Amsterdam Density Functional (ADF) program package (PW91/DZP level of theory).[15,16]

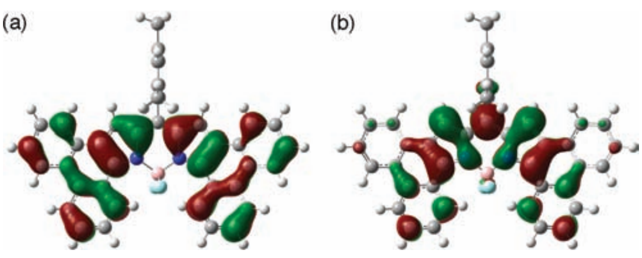

Figure 4. (a) HOMO and (b) LUMO of **4** calculated at the B3LYP/6-31G(d) level.

The calculated tHOMO (54.7 meV) and tLUMO (68.8 meV) are substantially large in the 1-D infinite stack to support high carrier mobility of BODIPY **4**. On the basis of these analyses, fused BODIPY **4** would also act as a hole-transporting material.

In summary, we have developed a novel synthetic procedure for a biphenyl-fused BODIPY through Suzuki–Miyaura coupling–oxidative cyclization sequence. The biphenyl-fused BODIPY has a low LUMO level and exhibits strong π–π interactions in the solid state. These features allow the use of the biphenyl-fused BODIPY as an *n*-type organic photovoltaic (OPV) material. Synthesis of aryl-fused BODIPYs toward further applications in materials science is currently underway.

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Supporting Information Available. General procedures, spectral data for compounds, and CIF file for the X-ray analysis of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.