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Intramolecular Excitation Energy Transfer from Visible-light Absorbing Chlorophyll Derivatives to a Near-infrared-light Emitting Boron Dipyrromethene Moiety

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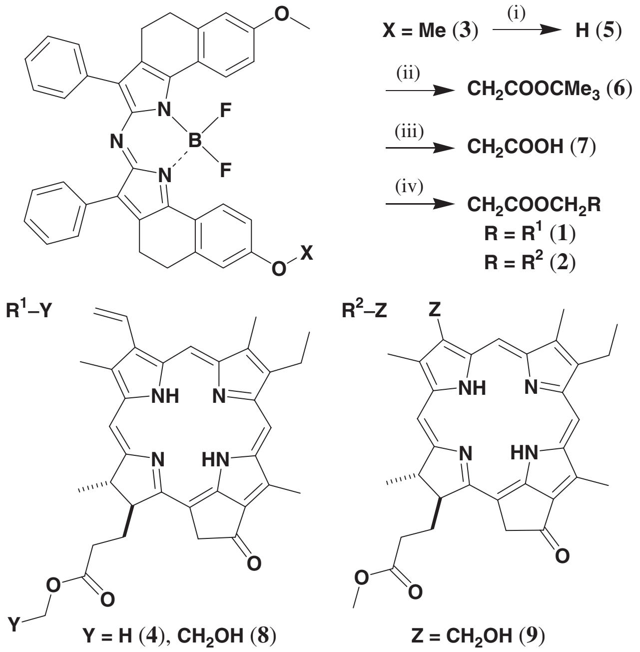
Chlorophyll-*a* derivatives were covalently linked with a π-extended boron aza-dipyrromethene moiety. In the synthetic dyads, photoinduced energy transfer from the former visible-light absorbing chlorin chromophore to the latter highly fluorescent unit in the near-infrared region was observed in a solution. The singlet-excited states of both the units were partially quenched by the charge-separated state, which was pronounced in polar organic solvents.



Scheme 1. Synthesis of chlorin–BODIPY dyads **1**/**2**: (i) BBr_3, CH_2Cl_2; (ii) $BrCH_2COOCMe_3$, K_2CO_3, Me_2CO; (iii) CF_3-COOH, CH_2Cl_2; (iv) RCH_2OH **8**/**9**, EDC–DMAP, CH_2Cl_2.

Understanding of excitation energy transfer in a (supra)-molecule is important for construction of artificial photoactive devices as well as elucidation of natural photosynthetic events. Photoinduced intramolecular energy transfer from a visible-light absorbing porphyrin π-system to near-infrared-light absorbing species including fullerenes and carbon nanotubes has been investigated.[1] Moreover, irradiation of chlorophyllous pigments with visible light induced the migration of the excitation energy to nearby chromophores such as bacteriochlorophyll derivatives, cyanine dyes, and lanthanoid complexes, which emitted light in the near-infrared region.[2]

Boron dipyrromethene (BODIPY) dyes are highly fluorescent and have been used as an efficient excitation energy donor after absorbing visible light. Various reports are available on intramolecular energy transfer from photoexcited BODIPY to porphyrinoid moieties.[3,4] Here we report synthesis of visible-light absorbing chlorophyll-*a* derivatives covalently linked with a near-infrared-light emitting aza-BODIPY moiety and singlet energy transfer from photoexcited chlorin (Chl*) to BODIPY units in synthetic dyads, where such a BODIPY derivative functioned as an energy acceptor from porphyrinoids.

As a chlorophyll derivative that absorbs visible light, methyl pyropheophorbide-*a* (**4**, Scheme 1) was used because of its easy availability, and was prepared by modification of natural occurring chlorophyll-*a*.[5] The synthetic chlorophyllous moiety gave a redmost (Qy) absorption maximum at 667 nm in dichloromethane. For a singlet-excitation energy acceptor from the chlorin chromophore, a π-extended aza-BODIPY derivative **3** possessing $\lambda_{max} = 739$ nm[6] was selected from various reported BODIPYs.[3,7] The dimethoxy compound **3** was treated with boron tribromide and the reaction mixture containing dimethoxy-, monomethoxy–monohydroxy-, and dihydroxy compounds was purified by silica gel flash column chromatography to give the desired mono-ol **5** (55% yield, see experimental details in Supporting Information).[8] The phenol **5** was etherified (54%) and the resulting *tert*-butyl ester **6** was quantitatively cleaved by the action of trifluoroacetic acid. The reactive carboxylic acid **7** was esterified with 2-hydroxyethylpyropheophorbide-*a* (**8**)[9] to afford the desired chlorin–BODIPY dyad **1** (71%). As another hydroxylated chlorin, methyl 3-devinyl-3-hydroxymethylpyropheophorbide-*a* (**9**) was used[10] and the other dyad **2** possessing a shorter covalent linkage was similarly prepared (66%). Full characterization of the present synthetic compounds is described in Supporting Information.[8]

In a diluted dichloromethane solution (1.8 μM), dyad **1** gave the electronic absorption spectrum which was reproduced by the sum of those of chlorin **4** and BODIPY **3** (Figure 1). The superposition indicated no intramolecular interaction between the chlorin and BODIPY units in the ground state as well as no intermolecular interaction among the chromophores due to the low concentration. The observed proton and carbon-13 signals of **1**, **3**, and **4** in their NMR spectra (see the data in Supporting Information[8]) also showed the limited intra- and intermolecular interaction in the composite units of **1** in chloroform-*d* (ca. 1 mM). No interaction in **2** could be detected, although the spacer was shorter than that of **1**.[11]

Photoexcitation of **1** in dichloromethane (1.8 μM) at 410 nm gave a weak emission band at 678 nm from the chlorin chromophore and a prominent band at 752 nm from the

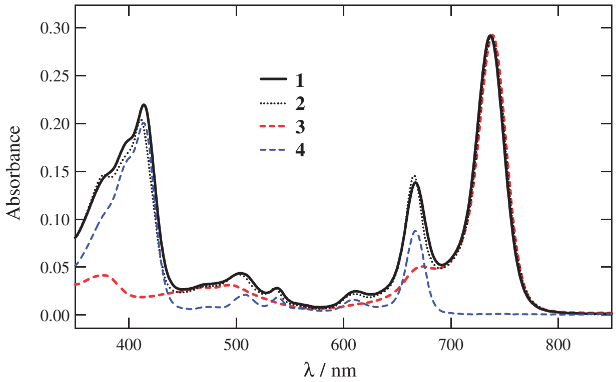


Figure 1. Electronic absorption spectra of Chl–BODIPY **1** with a long spacer (black solid), Chl–BODIPY **2** with a short spacer (black dotted), BODIPY **3** (red broken), and Chl **4** (blue broken) in CH_2Cl_2 (1.8 µM).

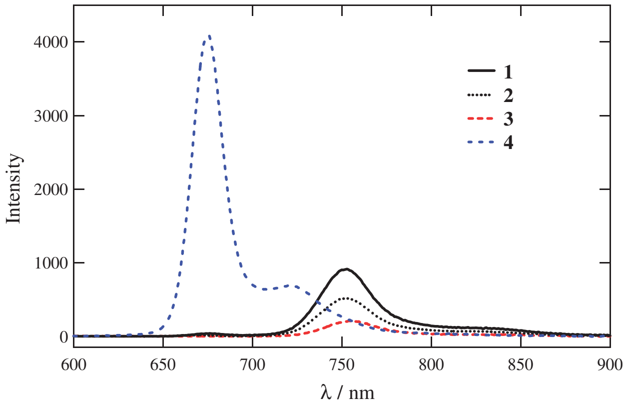


Figure 2. Fluorescence emission spectra of Chl–BODIPY **1** with a long spacer (black solid), Chl–BODIPY **2** with a short spacer (black dotted), BODIPY **3** (red broken), and Chl **4** (blue broken) in CH_2Cl_2 (1.8 µM) with excitation at 410 nm.

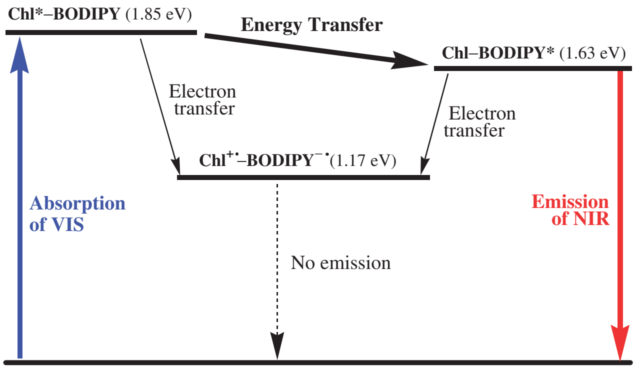
BODIPY unit (Figure 2). Considering that the light at 410 nm was predominantly absorbed by the chlorin moiety, the energy transfer from the photoexcited chlorin to BODIPY units was observed in the dyad **1**. Compared with the fluorescence emission spectrum of an equimolar mixture of **3** and **4**, fluorescence from the chlorin chromophore ($\lambda_{abs} = 667$ and $\lambda_{em} = 678$ nm) was largely (>99%) quenched by the BODIPY unit ($\lambda_{abs} = 737$ and $\lambda_{em} = 752$ nm) in a molecule. Based on the analysis of fluorescence excitation spectrum at 810-nm emission and visible absorption spectrum of dyad **1** (Figure S1).[8] the efficiency of intramolecular energy transfer was estimated to be about 80%. The inconsistency of the quenching value with energy-transfer efficiency indicated the presence (ca. 20%) of other quenching processes in **1**.

In a benzene solution of **1**, the intramolecular fluorescence quenching value of photoexcited chlorin chromophore and singlet-excitation energy-transfer efficiency were determined to be >99 and >95%, respectively. The nearly consistent percentage data indicated that the other quenching pathway was inhibited in a less polar solvent, suggesting that the other fluorescence quenching was ascribable to intramolecular electron transfer. Calculated free energy of photoinduced electron transfer (ΔG_{eT}) from the Rehm–Weller equation[12] showed that the electron transfer from photoexcited chlorin to BODIPY units was preferable: ΔG_{eT} (in CH_2Cl_2) $= -0.68$ (for Chl*–BODIPY → $Chl^{+\bullet}$–$BODIPY^{-\bullet}$) < -0.18 eV (for Chl*–BODIPY → $Chl^{-\bullet}$–$BODIPY^{+\bullet}$).[11]

Table 1. Fluorescence lifetimes (τ_{flu}/ns) of **1**–**3** monitored at 760 nm with excitation at 410 nm

Compound	τ_{flu} (τ_{flu}^{rel})^a [$k_{eT}/10^8\,s^{-1}$]^b		
	Benzene	Dichloromethane	Acetonitrile
1	1.96 (0.55) [2.3]	1.42 (0.43) [4.0]	0.88 (0.27) [8.3]
2	1.68 (0.47) [3.2]	1.03 (0.31) [6.7]	0.59 (0.18) [13.9]
3	3.59 (1.00)	3.31 (1.00)	3.27 (1.00)

$^a\tau_{flu}^{rel} = \tau_{flu}/\tau_{flu}(\mathbf{3})$. $^b k_{eT} = 1/\tau_{flu} - 1/\tau_{flu}(\mathbf{3})$.



Scheme 2. Energy diagram of photoexcited Chl–BODIPY dyad: the values in parenthesis indicate estimated energy levels for dyad **1** in CH_2Cl_2.

Fluorescence lifetimes (τ_{flu}) of the BODIPY unit in dyad **1** were dependent upon the solvents (Table 1). The values of τ_{flu} in **1** ($\tau_{flu}(\mathbf{1})$) decreased with an increase of solvent polarity; the decrease would also be due to the electron-transfer quenching. Estimated ΔG_{eT} supported the preferable intramolecular electron transfer from photoexcited BODIPY to chlorin units: ΔG_{eT} (in CH_2Cl_2) $= -0.46$ (for Chl–BODIPY* → $Chl^{+\bullet}$–$BODIPY^{-\bullet}$) $<$ $+0.05$ eV (for Chl–BODIPY* → $Chl^{-\bullet}$–$BODIPY^{+\bullet}$).[13] From the electron transfer rate (k_{eT}) $= 1/\tau_{flu}(\mathbf{1}) - 1/\tau_{flu}(\mathbf{3})$, the k_{eT} values were calculated to be 2.3, 4.0, and 8.3 × $10^8\,s^{-1}$ for benzene, dichloromethane, and acetonitrile, respectively. An energy diagram for photoexcited chlorin–BODIPY dyads is drawn in Scheme 2. Unfortunately, the analysis of fluorescence profiles at 760 nm gave no clear rise constant in the present measurements (ps time scale), so the rate of excitation energy transfer from Chl* to BODIPY in dyad **1** was not determined.

Quantum yields (Φ_{flu}) of fluorescence emission from BODIPY* by photoexcitation of Chl in dyad **1** were dependent on the solvents and decreased with an increase of their polarities as expected (Table 2). This decrease is explained by 1) less formation of BODIPY* through intramolecular energy transfer from primarily produced and partially electron-transfer quenched Chl* and/or 2) more quenching of BODIPY* through intramolecular electron transfer in a polar solvent.

In dyad **2** which possessed a shorter spacer between Chl and BODIPY units, similar behavior in fluorescence data was

Table 2. Fluorescence quantum yields (Φ_{flu}) of **1**–**3** monitored at an emission band of the BODIPY moiety (720–850 nm) with excitation at 410 nm

Compound	Φ_{flu} ($\Phi_{flu}{}^{rel}$)[a]		
	Benzene	Dichloromethane	Acetonitrile
1	0.10 (0.53)	0.08 (0.38)	0.02 (0.11)
2	0.09 (0.47)	0.05 (0.24)	0.01 (0.06)
3	0.19 (1.00)	0.21 (1.00)	0.18 (1.00)

[a] $\Phi_{flu}{}^{rel} = \Phi_{flu} / \Phi_{flu}(\mathbf{3})$.

observed. Estimated k_{eT} values for Chl–BODIPY* → Chl$^{+\bullet}$–BODIPY$^{-\bullet}$ in **2** were larger than those in **1** (Table 1), because the average distance between the two units in **2** was shorter than that of **1** in a solution. Smaller Φ_{flu}s of **2** are also interpreted by more efficient intramolecular electron transfer in **2**.

In conclusion, intramolecular singlet energy transfer from photoexcited chlorin (porphyrinoid) chromophore to BODIPY unit was first shown in synthetic dyads. In the photoexcited molecule, electron-transfer quenching processes were also observed, which were regulated by the solvent polarity as well as the length of the covalently linked spacer between Chl and BODIPY moieties.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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11 Similarly, the electronic absorption spectrum of **1** in a diluted acetonitrile solution was consistent with the sum of those of **4** and **3**.

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13 Based on the following data: E^{ox} (**3**) = 0.34, E^{red} (**3**) = −1.07, E^{ox} (**4**) = 0.37, and E^{ox} (**4**) = −1.60 V (vs. $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$, in 0.1 M $(C_4H_9)_4NClO_4/CH_2Cl_2$); $E^{0,0}$ (**3**) = 1.63 and $E^{0,0}$ (**4**) = 1.85 eV; factors for Coulombic stabilization and ion-pair solvation = −0.27 eV reported in ref. 4b.