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Highly Efficient Energy Transfer in Subphthalocyanine−BODIPY Conjugates

Jian-Yong Liu,[†] Hoi-Sze Yeung,[†] Wei Xu,[‡] Xiyou Li,[‡] and Dennis K. P. Ng*[,†]

Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China, and Department of Chemistry, Shandong University, Jinan 250100, China

dkpn@cuhk.edu.hk

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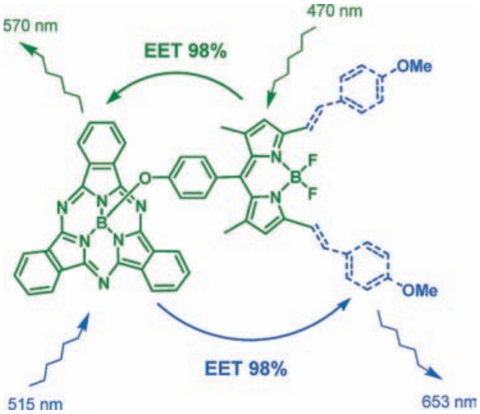
ABSTRACT



Two novel subphthalocyanines substituted axially with a BODIPY or distyryl BODIPY moiety have been synthesized. Both systems exhibit a highly efficient photoinduced energy transfer process, either from the excited BODIPY to the subphthalocyanine core (for the former) or from the excited subphthalocyanine to the distyryl BODIPY unit (for the latter).

Excitation energy transfer (EET) is a vital process in nature. Photosynthetic organisms, for example, make use of chromophore-rich antenna proteins to funnel the captured light energy to the reaction center where it initiates a multistep electron-transfer reaction, leading eventually to the oxidation of water to oxygen and the fixation of carbon dioxide.[1] Energy transfer also plays an important role in many artificial processes such as photochemical conversion of solar energy by artificial photosynthetic systems,[1,2] information processing with a variety of molecular devices and machines,[3] and detection of analytes with molecular-based sensors.[4] Numerous artificial antenna systems with different combinations of chromophores have been studied with a view to enhancing the energy transfer efficiency and facilitating their use in different forms.[1,2a,5] Among the different chromophores, boron dipyrromethene (BODIPY) dyes are of particular interest because of their large extinction coefficients, high fluorescence quantum yields, reasonably long excited singlet-state lifetimes, and good solubility and stability in many solvent systems.[6] More importantly, the BODIPY core can

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[†] The Chinese University of Hong Kong.
[‡] Shandong University.

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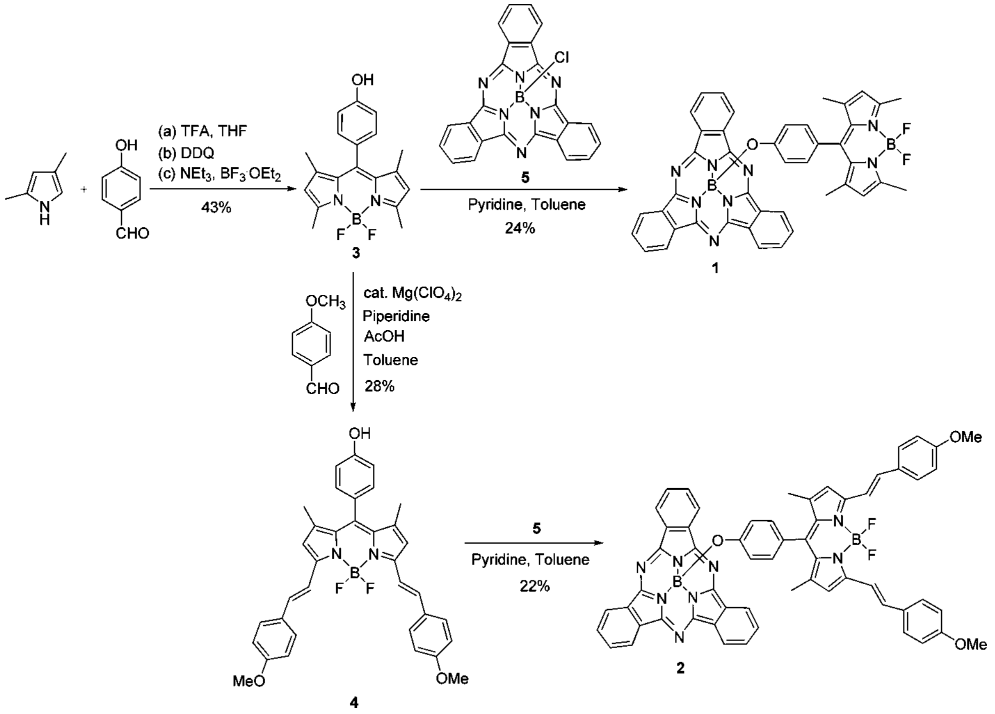
Scheme 1



be modified readily to tailor their absorption and emission properties. Light-harvesting BODIPY derivatives conjugated with energy donors such as pyrenes and anthracenes[7] and energy acceptors such as porphyrins,[3a,8] perylenediimides,[9] and extended BODIPYs[10] have been reported. We report herein the preparation and energy-transfer properties of the first BODIPY derivatives linked to a subphthalocyanine unit. Subphthalocyanines are lower homologues of phthalocyanines, and they are also versatile functional dyes with remarkable photophysical and photochemical properties.[11] Several subphthalocyanine$-C_{60}$[12] and subphthalocyanine$-$phthalocyanine[13] dyads have been reported which exhibit an efficient singlet$-$singlet energy-transfer process. The major absorption and fluorescence emission positions of subphthalocyanines (ca. 560$-$570 nm) are complementary with those of BODIPY (ca. 500$-$520 nm) and distyryl BODIPY (ca. 630$-$680 nm). Therefore, the resulting conjugates should absorb over a broad range in the visible region and have a good spectral overlap between the donor emission and the acceptor absorption. Both of these features are desirable for efficient light-harvesting systems.

Two subphthalocyanine-BODIPY derivatives **1** and **2** were prepared according to Scheme 1. The phenol-containing BODIPY **3** was first prepared by treating 2,4-dimethylpyrrole with 4-hydroxybenzaldehyde via sequential condensation, oxidation, and complexation reactions. The preparation of this compound had been reported previously,[14] but by following this procedure, only a tiny amount of product could be obtained in our hands. After several attempts, we found that by changing the solvent from CH_2Cl_2 to THF (which can better solublize the reagents) and using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) instead of tetrachlorobenzoquinone as the oxidizing agent, compound **3** could be obtained in 43% yield. This compound then underwent condensation reaction with 4-methoxybenzaldehyde in the presence of piperidine to give the distyryl BODIPY **4** in 28% yield. Both **3** and **4** were then treated with the commercially available boron(III) subphthalocyanine chloride (**5**) in the presence of pyridine in toluene to afford the substituted products **1** and **2**, respectively. The yields of these products are relatively low probably due to the low reactivity of the BODIPY-appended phenols **3** and **4**. Both conjugates possess good solubility in common organic solvents and could be purified readily by column chromatography followed by size exclusion chromatography and recrystallization (see the Supporting Information for the experimental details and characterization data).

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All of the new BODIPY derivatives **1**, **2**, and **4** were characterized with various spectroscopic methods and X-ray diffraction analyses. The ^{1}H signals for the meso-*p*-phenylene protons of **1** and **2** are significantly upfield-shifted compared with those of their respective precursors **3** and **4** (both by 0.5 and 1.4 ppm for the two doublets), as a result of the shielding effect by the subphthalocyanine ring current. Single crystals of all these compounds were grown by layering hexane onto their CH_2Cl_2 solutions. The distyryl BODIPY **4** crystallizes in the monoclinic system with a *Cc* space group. Its molecular structure (Figure S1 in the Supporting Information) shows typical structural features of BODIPYs[15] with two extended styryl groups. The subphthalocyanine-BODIPY dyad **1** crystallizes with a water molecule in the monoclinic system with a $P2_1/c$ space group, while the dyad **2** crystallizes in the triclinic system with a $P\bar{1}$ space group containing a CH_2Cl_2 solvent molecule. Their molecular structures are shown in Figure 1 and clearly show that the cone-shaped subphthalocyanine unit is axially bound to BODIPY **3** or **4** via the phenoxy group. The B−O bond distances [1.435(5) and 1.440(8) Å for **1** and **2**, respectively] and the average B−N bond distances of the subphthalocyanine core are very similar with those in the subphthalocyanine analogue having an axial 4-(3,6-dioxaheptoxy)phenoxy group [1.440(4) and 1.496(5) Å, respectively].[16] The structural parameters of **4** are not significantly changed upon conjugation to the subphthalocyanine unit.

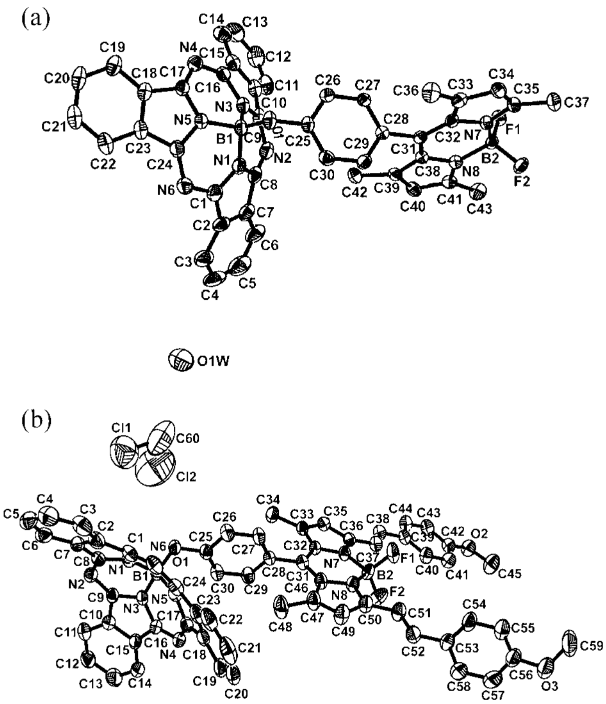

Figure 1. Molecular structures of (a) **1** and (b) **2** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Figure 2 shows the normalized absorption spectra of the dyad **1**, BODIPY **3**, and the subphthalocyanine with an axial 4-methanoylphenoxy group **6**, which was prepared by the substitution reaction of **5** with 4-hydroxybenzaldehyde (Scheme S1 in the Supporting Information). The latter two compounds were used as the references. The dyad **1** shows two major absorption bands at 502 and 563 nm, which are virtually unshifted compared with those of **3** and **6**. Similarly, the electronic absorption spectrum of the dyad **2** is essentially the same as the sum of the spectra of the two reference compounds **4** and **6** (Figure S2 in the Supporting Information). These observations indicate that the two chromophores in **1** and **2** do not have significant ground-state interactions.

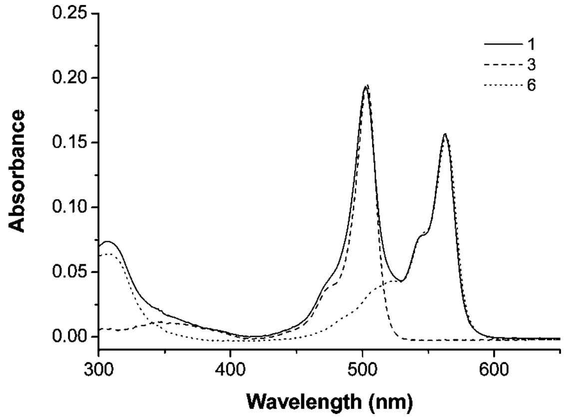

Figure 2. Normalized absorption spectra of compounds **1**, **3**, and **6** in toluene. The spectra of **1** and **3** were normalized at 502 nm, while those of **1** and **6** were normalized at 563 nm.

Efficient energy transfer via a Förster mechanism requires a good spectral overlap between the energy donor (D) emission and the energy acceptor (A) absorption.[17] BODIPY−subphthalocyanine and subphthalocyanine−distyryl BODIPY are excellent donor−acceptor pairs which fulfill this requirement (see Figure S3 showing the overlap between the fluorescence spectrum of BODIPY **3** and the absorption spectrum of subphthalocyanine **6** and Figure S4 showing the fluorescence spectrum of subphthalocyanine **6** and the absorption spectrum of distyryl BODIPY **4** in the Supporting Information). As a result, it is expected that both the dyads **1** and **2** should exhibit an efficient through-space energy transfer.

The energy transfer process of **1** and **2** in toluene was studied by steady-state and time-resolved fluorescence spectroscopy. Table 1 compiles the fluorescence as well as the electronic absorption data of these dyads and the reference compounds in toluene. As shown in Figure 3, excitation of BODIPY **3** at 470 nm gives a strong fluorescence emission at 514 nm. However, this signal virtually

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Table 1. Absorption and Fluorescence Data for the Dyads **1** and **2** and the Reference Compounds **3**, **4**, and **6** in Toluene

compd	λ_{max}/nm (log ε)	λ_{em}/nm	Φ_F[a]	τ_F/ns
1	502 (5.06), 563 (4.96)	570[b]	0.015[c]	2.4[d,e]
2	562 (5.02), 645 (5.10)	653[f]	0.013[c]	0.1[c], 4.0[d]
3	503 (4.99)	514[b]	0.94	4.3
4	647 (5.11)	653[f]	0.73	3.9
6	564 (4.99)	571[f]	0.75	2.3

[a] Using *N*,*N*′-di-*n*-hexyl-1,7-bis(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic diimide in $CHCl_3$ as the reference ($\Phi_F = 1$). [b] Excited at 470 nm. [c] Due to the donor part. [d] Due to the acceptor part. [e] The lifetime for the donor part is too short to be determined. [f] Excited at 515 nm.

cannot be seen upon excitation of the dyad **1** at the same position. Instead, an emission at 570 nm appears, which is due to the subphthalocyanine unit of **1**. The intensity is stronger than that caused by **6** at a similar concentration (Figure 3). These observations indicate the presence of an efficient singlet−singlet energy transfer process in **1**, from the excited BODIPY part to the subphthalocyanine unit. This was confirmed by the excitation spectrum monitored at 570 nm, which resembles the absorption spectrum of **1** (Figure S5 in the Supporting Information). The fluorescence quantum yield (Φ_F) of **3** in toluene is 0.94, while that of the BODIPY part of **1** is greatly reduced to 0.015 (Table 1). According to the equation $\Phi_{ENT} = 1 - \Phi_{F(dyad)}/\Phi_{F(donor)}$,[18] where Φ_{ENT} is the energy transfer quantum yield, $\Phi_{F(dyad)}$ and $\Phi_{F(donor)}$ are the fluorescence quantum yields of the dyad (the donor part) and the donor without connecting to the acceptor, respectively, the value of Φ_{ENT} was estimated to be 0.98, showing that this is a very efficient process in **1**. In fact, the fluorescence lifetime (τ_F) of the donor part of **1** was too short to be determined (<50 ps) compared with the value of 4.3 ns for **3** (Table 1).

For the dyad **2**, similar results were obtained, but the energy donor is now switched to the subphthalocyanine unit. As shown in Figure S6 in the Supporting Information, excitation of **2** at 515 nm only shows a very weak emission at ca. 570 nm assignable to the subphthalocyanine emission, together with a rather strong emission at 653 nm, which is due to the distyryl BODIPY moiety. The excitation spectrum of **2** monitored at 653 nm also resembles its absorption spectrum (Figure S7 in the Supporting Information). The fluorescence lifetime for the subphthalocyanine part in **2** (0.1 ns) is much shorter than that of **6** (2.3 ns), showing the presence of a very efficient competition pathway. By taking the fluorescence quantum yields of **6** (0.75) and **2** (0.013 for the donor part), the value of Φ_{ENT} was also found to be 0.98. Hence, photoinduced singlet−singlet energy transfer is also a very efficient process for this dyad.

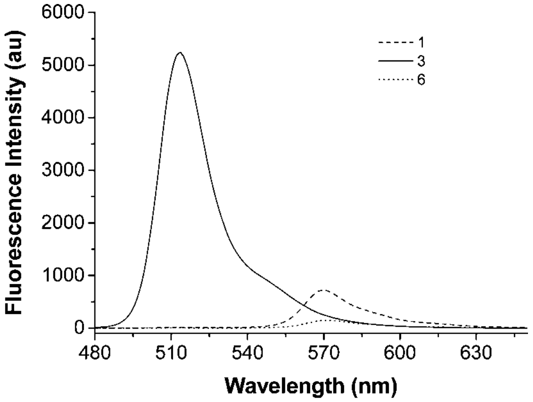

Figure 3. Fluorescence spectra of **1**, **3**, and **6** (in toluene) at equal absorbance at 470 nm for **1** and **3** and at 563 nm for **1** and **6**. All of the compounds were excited at 470 nm.

In conclusion, we have synthesized and characterized two novel conjugates of subphthalocyanines and BODIPY derivatives. Due to the good spectral overlap between the energy donor emission and the energy acceptor absorption, these dyads exhibit a highly efficient photoinduced energy transfer process with an energy transfer quantum yield of 98%.

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Supporting Information Available: Experimental procedure, characterization data, and ^{1}H and ^{13}C{^{1}H} NMR spectra for **1**−**4** and **6**; molecular structure of **4**; normalized absorption and fluorescence spectra of **2**, **4**, and **6**; spectral overlap between the emission of **3** and the absorption of **6** and that between the emission of **6** and the absorption of **4**; normalized absorption and excitation spectra of **1** and **2** (all in toluene). This material is available free of charge via the Internet at http://pubs.acs.org.

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