ORGANIC LETTERS

2008
Vol. 10, No. 1
29−32

Highly Efficient Energy Transfer in the Light Harvesting System Composed of Three Kinds of Boron–Dipyrromethene Derivatives

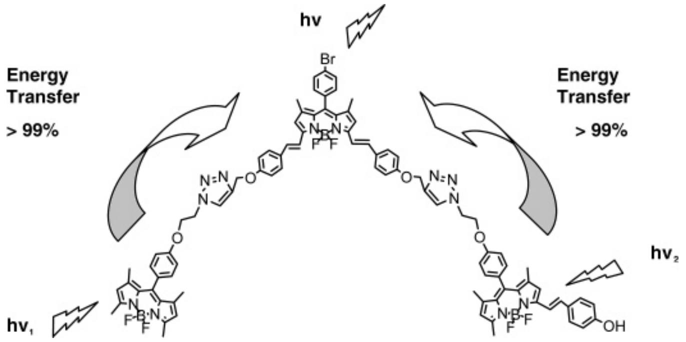
Xiaolin Zhang,[†] Yi Xiao,*,[†] and Xuhong Qian[‡]

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China, and State Key Laboratory of Bioreactor Engineering and Shanghai Key Laboratory of Chemical Biology, East China University of Science and Technology, Shanghai 200237, China

xiaoyi@chem.dlut.edu.cn

Received October 17, 2007

ABSTRACT



A light-harvesting system containing three kinds of BODIPY fluorophores was synthesized. It exhibited very strong absorption in the region from 300 to 700 nm, and the energy transfer within it was highly efficient.

The light harvesting system, which absorbs light and funnels energy to the reaction center, plays a very important role in natural photosynthesis.[1] Many artificial light-harvesting molecules are synthesized in succession.[2] An ideal light-harvesting system absorbs light efficiently in a relatively broad region covering most of the sunlight spectrum. In order to achieve this, the integration of multiple excellent chromophores is necessary, and the energy transfer within the system should be efficient. The development of highly efficient light-harvesting systems remains a challenging task as many aspects need improvment like the choice of the chromophores with proper spectra overlaps and suited energy levels, linker types, connection sites, and synthesis strategy, etc.

Boron−dipyrromethene (BODIPY) dyes,[3] which are widely applied as fluorescent sensors[4b] and labeling reagents,[3] have remarkable properties such as high absorption coefficient, high fluorescence yield, and excellent photostability, etc.[4] The long wavelength BODIPYs, in particular, have advan-

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[†] Dalian University of Technology.

[‡] East China University of Science and Technology.

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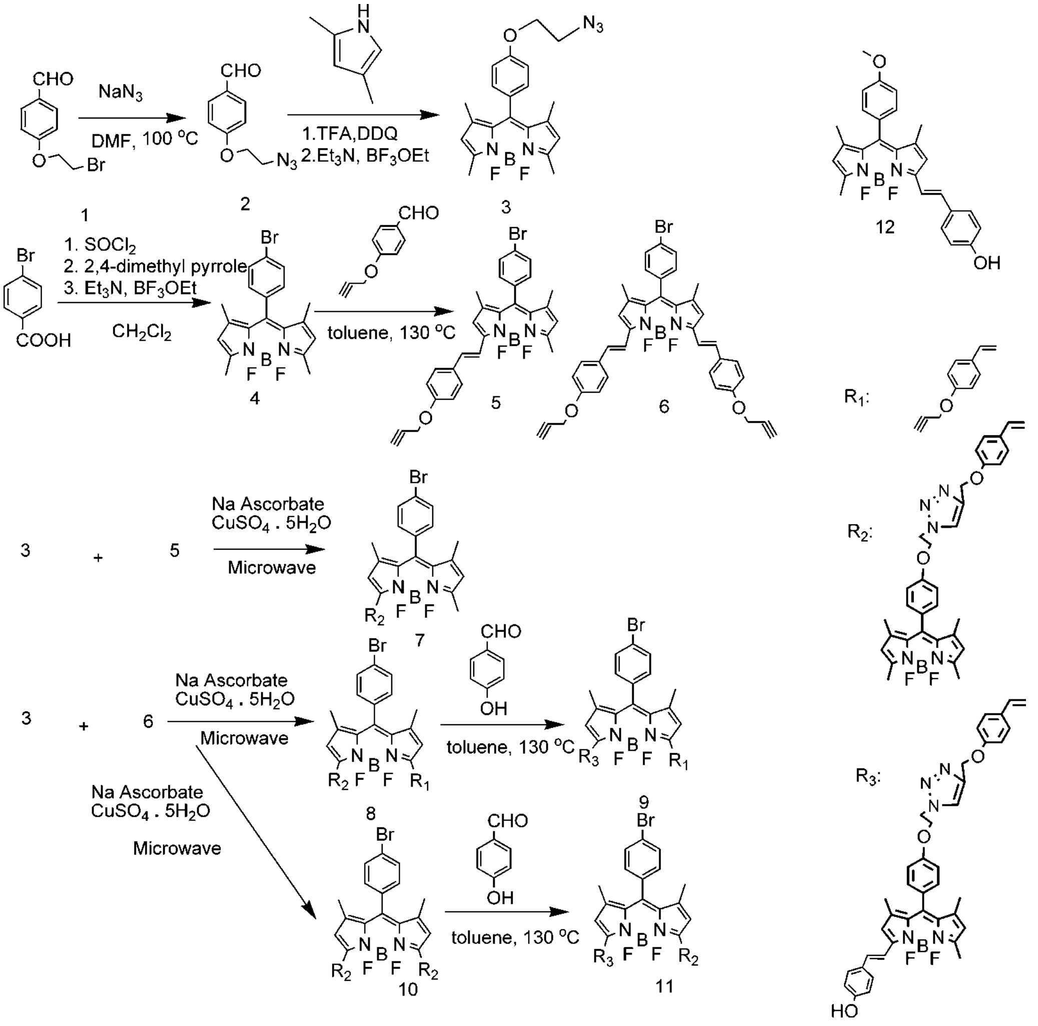
10.1021/ol702381j CCC: $40.75

Scheme 1. Synthetic Routes and Chemical Structures of the Compounds



tages over many other popular long wavelength dyes in these aspects. For example, in the long wavelength region, BODIPYs have a higher molar absorption coefficient than porphyrins and better photostability than cyanine dyes, etc. Thus, we believe that BODIPYs should be very competitive candidates in the design of light-harvesting systems.[5] However, there have been few reports on light-harvesting systems using a long wavelength BODIPY as the energy acceptor.[6] In the past, the synthetic difficulty might be the main hindrance. But, recently, considerable progress has been made in the efficient syntheses of BODIPYs especially for methyl-substituted long wavelength BODIPYs,[7] which endows BODIPYs with a better prospect in the design of light-harvesting systems.

Here, we designed and synthesized the first boron−dipyrromethene-based light-harvesting system (compound **11**, shown in Scheme 1) containing three kinds of BODIPY dyes (yellow-green BODIPY, pink BODIPY, and purple BODIPY with the absorption maximum at 501, 568, and 647 nm, respectively) to absorb the light energy in corresponding regions. Its intense absorption from the visible to near-infrared region covers the strong radiation scope of sunlight. Furthermore, its good photostability, solubility, and efficient energy transfer (99%) within it make compound **11** promising as a light-harvesting system.

Click chemistry, 1,3-dipolar cycloaddition of azides and alkynes using catalyst copper(I), was chosen as the strategy to connect the three BODIPYs.[8] There were two considerations: one was the high yield of the click reactions; the

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other was the mild conditions which could be tolerable for the boron complex.

The syntheses of the target compound **11** and reference compounds **5**−**10** and **12** are depicted in Scheme 1. Compound **1** reacted with NaN_3 in DMF to produce compound **2**, which further reacted with 2,4-dimethylpyrrole in the presence of TFA and DDQ, followed by the addition of $BF_3{\cdot}Et_2O$, to produce compound **3**. Compound **5** and **6**, synthesized through two steps according to the previous procedure,[7] reacted with compound **3** to produce the corresponding compounds in the presence of sodium ascorbate and $CuSO_4{\cdot}5H_2O$ in a 1:1 mixture of ethanol and water in the microwave reactor.

To assess the efficiency of energy transfer, the compounds were studied by UV/vis absorption and time-resolved fluorescence spectroscopy in CH_2Cl_2. The photophysical data are summarized in Table 1. The absorption spectra of compounds **11** and reference compounds **3**, **6**, and **12** at equal absorbance values are shown in Figure 1. The spectrum of compound **11**, as expected, was essentially equal to the sum of the other three spectra, which showed the absorption characteristic maxima of all three BODIPY chromophores. The spectrum was composed of absorption bands of yellow-green BODIPY, pink BODIPY, and purple BODIPY. Thus, the absorption properties of compound **11** were determined by the individual patterns of the parent chromophoric units, and there was no interaction between the chromophores in the ground state.[2d] Compared with the most widely used light-harvesting systems based on porphyrins, the absorption peaks that composed compound **11** had higher molar extinction coefficient and broader absorption band. The absorption spectrum of compound **11** spanned a very broad region from 300 to 700 nm which overlapped the strong radiation scope of sunlight. (The absorption spectra of other compounds are described in the Supporting Information.)

Table 1. Photophysical Properties of Compounds in CH_2Cl_2

compd	ϵ (λ_{max})/(M^{-1} cm^{-1}) (nm)	λ_{em}/nm	Φ_f	τ/ns
3	56600 (501)	511	0.65	3.97
5	89882 (572)	583	0.54	4.42
6	82989 (644)	656	0.20	4.67
7	62010 (501), 80596 (572)	586	0.56^a	4.34
8	69883 (501), 92355 (644)	659	0.24^a	4.73
9	82176 (568), 73340 (644)	658	0.18^b	3.74
10	126706 (501), 87456 (646)	660	0.22^a	4.67
11	60436 (502), 80542 (568), 67724 (647)	662	0.22^a	3.50
12	90100 (567)	581	0.58	4.51

[a] λ_{ex} = 490 nm. [b] λ_{ex} = 560 nm.

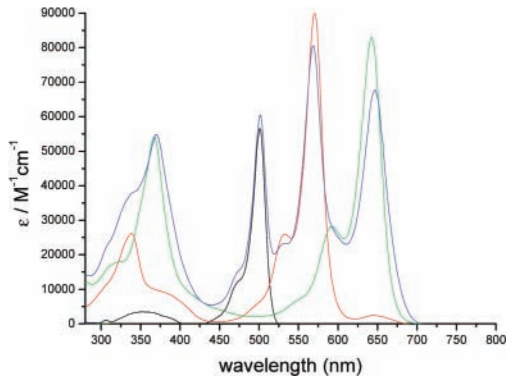

Figure 1. Absorbance spectra of compounds **3** (black, solid), **6** (green, solid), **11** (blue, solid), and **12** (red, solid) in CH_2Cl_2.

Upon photoexcitation of compound **11** at λ_{ex} = 490 nm (exclusive absorption of the yellow-green BODIPY unit) or λ_{ex} = 560 nm (exclusive absorption of the pink BODIPY unit), fluorescence emission of the central purple BODIPY dye at 660 nm was observed (Figure 2). The emission peaks were very weak from the yellow-green BODIPY at 520 nm and pink BODIPY at 586 nm, respectively. The quantum yields of compound **11** were measured to be 0.22, 0.21, and 0.20 for three different excitation wavelengths (490 nm, 560 nm, 635 nm), which were also close to that of the compound **6**. Obviously, the fluorescence quantum yields did not vary significantly whether the compounds were excited at the donor's or acceptor's absorbance. The absence of the quantum yield dependence suggested almost complete energy transfer from the donor to the acceptor.[9]

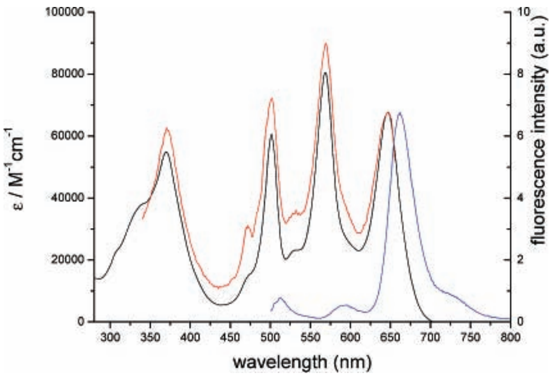

Figure 2. (a) Absorption spectra of compound **11** (black, solid). (b) Corresponding fluorescence emission spectra (blue, solid) and (c) fluorescence excitation spectra (red, solid).

In the fluorescence excitation spectrum of compound **11**, all absorption bands of the parent chromophores were observed. Moreover, the overlay of the excitation spectrum and absorption spectrum for compound **11** showed a close match throughout the spectrum. This indicated a high yield of singlet-state energy transfer in the compound.[10] (The fluorescence spectra of the other compounds are described in the Supporting Information.)

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Table 2. Calculation Data of Energy Transfer for Compounds

	compound (in CH_2Cl_2)		
parameter	**7**	**8**	**9**
J^a/M^{-1} cm^{-1} nm^4	1.57×10^{15}	3.60×10^{14}	3.58×10^{15}
$R_0{}^b$/Å	49.4	38.6	55.6
R^c/Å	17.43	17.43	17.43
E (energy transfer efficiency)/%	99.8	99.2	99.9
k_T (the rate of the energy transfer)/s^{-1}	1.30×10^{11}	2.97×10^{10}	2.33×10^{11}

[a] The overlap integral of the donor emission and the acceptor absorption spectra. $J = \int_0^\infty I_D(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda$. [b] Calculated according to the following equation[6,11] (see the Supporting Information): $k^2 = 2/3$, $n(CH_2Cl_2) = 1.4240$. [c] Distance between the D and A groups (estimated using standard bond lengths).

The rate and efficiency of Förster resonance energy transfer (FRET) depend on many factors: the extent of spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the quantum yield of the donor, orientation factors, and the distance between the donor and the acceptor.[12] In order to access the energy transfer rate and yields in light harvesting system **11**, we calculated those in the reference compounds **7**, **8**, and **9**, respectively (see the calculation details in the Supporting Information). Within compounds **8** and **9**, the yellow-green and pink BODIPY parts acted as donors, respectively, and the purple BODIPY part served as the acceptor, which could simulate the energy transfer from the yellow-green and pink donors to purple BODIPY acceptor in the harvesting system **1**1. Förster radii R_0 of the compounds were found to be significantly greater than the calculated donor−acceptor distance; hence, the calculated energy transfer yields were high. Seen from the Table 2, the energy transfer yields were all over 99%, and the rate constants were all over 10^{10} s^{-1}. The yields of energy transfer within compounds **7** and **9** were slightly higher than that within compound **8**. The rates of energy transfer within compound **7** and **9** were several fold higher than that within compound **8**. These differences were ascribed to the better spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor in compounds **7** and **9** than that in compound **8**. The data of reference compounds indicated that in our trichromophore system **11**, energy transfer from any of the donors (yellow-green BODIPY or pink BODIPY) to the acceptor (purple BODIPY) was highly efficient. The ignorable energy loss can be attributable to the high quantum yields of the donors, the high molar extinction absorption coefficient of the acceptor, and the good spectral overlap.

In conclusion, we synthesized a novel light−harvesting system containing three kinds of BODIPY fluorophores. It exhibited very strong absorption in a broad region from 300 to 700 nm. Within this system, energy transfer from each donor to the acceptor was highly efficient. This study demonstrated the potential of the boron−dipyrromethene derivatives in solar energy collection.

Acknowledgment. We thank the NSF of China for the financial support (Nos. 20406004, 20572012, and 20536010).

Supporting Information Available: Experimental details, spectral data, and energy transfer calculation of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL702381J

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