DOI: 10.1002/ange.201107723

Energy Transfer

Artificial Light-Harvesting System Based on Multifunctional Surface-Cross-Linked Micelles**

Hui-Qing Peng, Yu-Zhe Chen, Yan Zhao, Qing-Zheng Yang, Li-Zhu Wu, Chen-Ho Tung, Li-Ping Zhang, and Qing-Xiao Tong**

In the natural photosynthetic centers of bacteria and plants, antenna chromophores absorb solar light and transfer the excitation energy to the reaction center by highly efficient singlet–singlet energy transfer.[1–6] Spatial organization of individual chromophores is key to such efficiency: chromophores need to be separated enough to minimize self-quenching without sacrificing the dipole–dipole coupling-mediated energy transfer.[1,2] In addition to its important role in photosynthesis, efficient transfer of energy from multiple chromophores to a single acceptor is of potential significance to solar cells, photocatalysts, optical sensors and light-emitting devices.[7–10] For these reasons, there has been a great deal of interest in mimicking the natural light-harvesting process.[11–37] A variety of scaffolds have been used including dendrimers,[11–17] organogels,[18,19] porphyrin arrays/assemblies,[20–23,34] biopolymer assemblies,[24–28] and organic–inorganic hybrid materials.[29–32]

Although impressive results have been obtained with the above scaffolds, the multistep synthesis of the complex architectures hampers their scale up and widespread application. Nature relies on a combination of covalent and noncovalent interactions to create the photosynthetic centers. Covalent structures possess excellent stability and noncovalent self-assembled constructs provide order and synthetic efficiency. Herein, we report a biomimetic approach to construct artificial light-harvesting systems. We combined two self-assembling strategies and covalent fixation to prepare a highly efficient antenna system from readily available building blocks. The entire synthesis was achieved by a one-pot reaction, and the product precipitated spontaneously out of the reaction mixture at the end of the reaction.

The synthesis of the light-harvesting system is shown in Scheme 1, and is based on the recently reported method to cross-link surfactant micelles.[38,39] Our model antenna chromophore is 9,10-bis(4-methylphenyl)anthracene (DPA), a compound with high fluorescence quantum yield (90 %).[40] Eosin Y disodium salt (EY) is the energy acceptor. Cationic surfactant, 4-(dodecyloxy)benzyltripropargylammonium bromide (**1**),[38] forms micelles at concentrations of above 0.14 mM in water. Because the surface of the micelle is covered with a dense layer of alkynyl groups, 1,4-diazidobutane-2,3-diol (**2**)[38] could easily capture the micelle by 1,3-dipolar cycloaddition with a Cu^I catalyst.[41] When **1** and **2** were used in a 1:1 ratio, the resulting surface-cross-linked micelles (SCMs) are water-soluble nanoparticles with numerous alkynes on the surface. Surface functionalization occurred readily upon addition of a THF solution of DPA–N$_3$ (obtained from commercially available DPA by partial bromination and azidation, see the Supporting Information). After 18 hours at room temperature, the DPA-functionalized SCMs (DPA–SCMs) precipitated spontaneously from the 2:1 THF/water mixture, apparently as a result of the increased hydrophobicity of the product. The IR spectrum of the DPA–SCMs showed nearly complete disappearance of the alkyne peaks in the starting SCMs (Figure S1, in the Supporting Information). DLS (dynamic light scattering) indicated an increase in size for the SCMs upon DPA-functionalization (Figure S2, in the Supporting Information).

The absorption band of the DPA–SCMs is at 330–420 nm in THF and the emission band at 390–520 nm. These spectra match almost exactly with those of the free, monomeric DPA in solution (Figure S3, in the Supporting Information). Therefore, the DPA concentration ([DPA]$_{\text{SCMs}}$) in this system can be determined from the absorption spectrum and the molar coefficient extinction of DPA.

A frequent issue in light-harvesting systems with multiple donors is the self-quenching and/or excimer formation caused by the proximity of the chromophores. These pathways interfere with the energy transfer and lower the overall efficiency, and often require elaborate strategies to overcome.[15,42] Excitingly, the fluorescence quantum yield was 0.80 and 0.90 for the micelle-bound DPA and the free chromophore, respectively (see the Supporting Information). Clearly, neither self-quenching nor excimer formation was significant in the highly crowded system. We suspect there are

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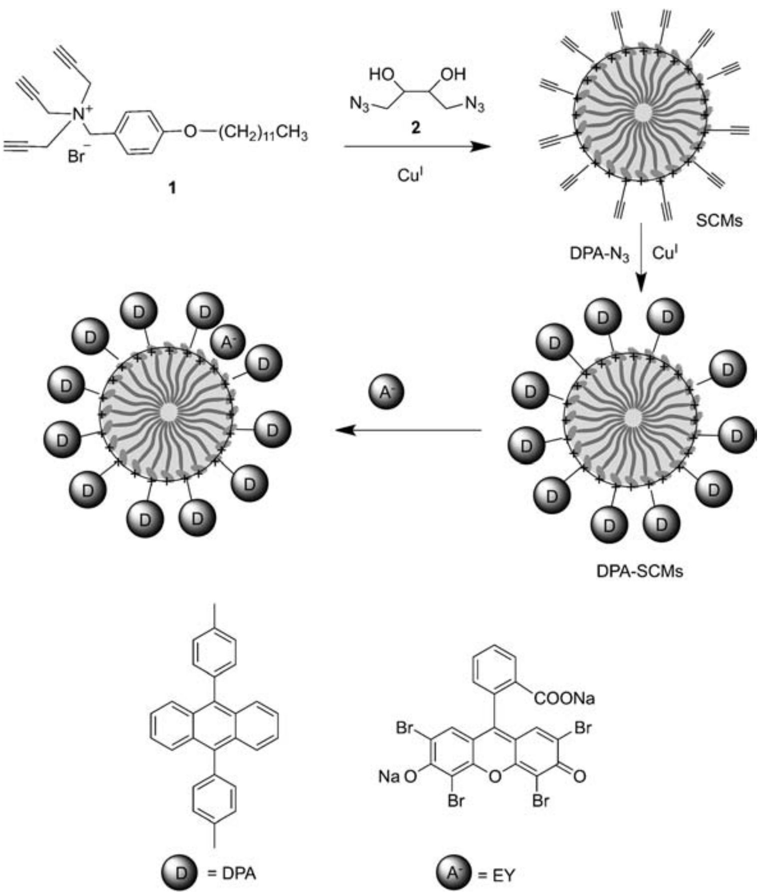
[*] H.-Q. Peng,[+] Dr. Y.-Z. Chen,[+] Prof. Q.-Z. Yang, Prof. L.-Z. Wu, Prof. C.-H. Tung, Prof. L.-P. Zhang
Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry
Chinese Academy of Sciences
29 Zhongguancun East Road, Beijing 100190 (China)
E-mail: qzyang@mail.ipc.ac.cn
H.-Q. Peng,[+] Prof. Q.-X. Tong
Department of Chemistry, Shantou University
Shantou, Guangdong 515063 (China)
E-mail: qxtong@stu.edu.cn
Prof. Y. Zhao
Department of Chemistry, Iowa State University
Ames, IA 50011-3111 (USA)

[+] These authors contributed equally to this work.

[**] We thank Prof. Roman Boulatov (UIUC) for his useful discussion. We are grateful for financial support from the National Natural Science Foundation of China (91027041, 21102155, 21072202, 20973189), the Chinese Academy of Sciences, and the Bureau of Basic Sciences of CAS (KJCX2-EW-W09). Y.Z. thanks the U.S. Department of Energy-Office of Basic Energy Sciences (grant DE-SC0002142) for partial support of the research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107723.



Scheme 1. Preparation of DPA-functionalized SCMs and the construction of a light-harvesting system by introducing EY through electrostatic interactions.

three reasons for the observed results. First, the two phenyl groups at the 9 and 10 positions of DPA are forced out of the anthracene plane by steric interactions, and the nonplanarity of the chromophore may make it difficult to form stacked structures. Second, as only short and aromatic (i.e., triazole) linkages are used to connect DPA to the SCMs, the DPA on the SCM surface had limited freedom. Therefore, it is possible that the preferred orientation/distance of the self-quenching or excimer formation for the surface-bound DPA simply could not be achieved in our structure. Third, the positively charged SCMs by electrostatic repulsion would reduce the chance of intermicellar interactions of the DPA.

The Förster radius (R_0), defined as the theoretical donor–acceptor distance at the 50 % energy-transfer efficiency, was estimated to be 3.6 nm for DPA–EY and 2.5 nm for DPA–DPA (see the Supporting Information).[24,43] Our previous estimates[38,39] suggest that the average distance between the residual alkynyl groups in SCMs is less than 2 nm. The high density of DPA on the SCM surface thus makes it extremely easy to shuttle energy from DPA to DPA and ultimately to the EY acceptor. To test the hypothesis, we titrated a THF solution of DPA–SCM with EY. The expectation was that the negatively charged EY would assemble spontaneously on the surface of the positively charged DPA–SCM by electrostatic interactions. No matter which DPA chromophore absorbs light, energy migration should occur readily from donor to donor and finally to the acceptor.

As EY was added to the DPA–SCMs, the DPA absorption, at 330–420 nm, stayed nearly constant while that of EY, at 450–570 nm, increased gradually (Figure 1 a). Importantly, the titration lowered the donor emission at 430 nm while enhancing that of the acceptor at 550 nm when the donor was selectively excited at 375 nm. In the absence of DPA–SCM, irradiation of EY at 375 nm yielded negligible emission since EY has negligible absorption at this wavelength (Figure 2 a, dotted trace). The results indicated Förster energy transfer from DPA to EY despite the low concentrations of the two—$[\mathrm{DPA}]_{\mathrm{SCMs}} = 23\ \mu\mathrm{M}$ and $[\mathrm{EY}]_{\max} = 1.34\ \mu\mathrm{M}$. Additional evidence for the energy transfer was obtained in a reverse titration of EY by DPA–SCMs (Figure S4, in the Supporting Information) and from the excitation spectrum of the EY in the presence of DPA–SCMs (Figure 2 b). The excitation spectrum of the acceptor was nearly identical to the absorption spectrum of DPA–SCM, thus demonstrating that the donor contributed directly to the acceptor emission.

The electrostatic assembly of the EY on the DPA–SCM surface was confirmed by control experiments. Energy transfer was absent under similar conditions when free DPA was titrated by EY (Figure 2 a, and Figure S5 in the Supporting

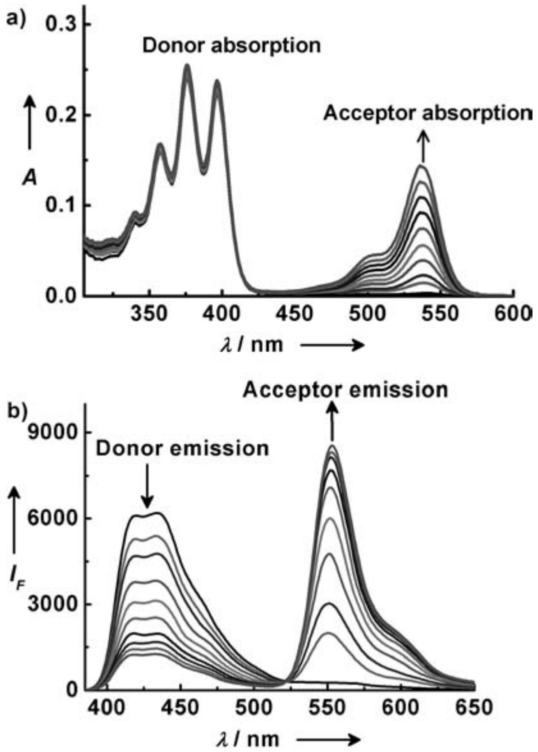


Figure 1. Absorption (a) and fluorescence (b) spectra of DPA–SCM in THF with different concentrations of EY. $[\mathrm{DPA}]_{\mathrm{SCMs}} = 23.0\ \mu\mathrm{M}$. [EY] was 0.00, 0.08, 0.17, 0.33, 0.50, 0.67, 0.84, 1.00, 1.17, and 1.34 μM from bottom to top. $\lambda_{\mathrm{ex}} = 375$ nm.

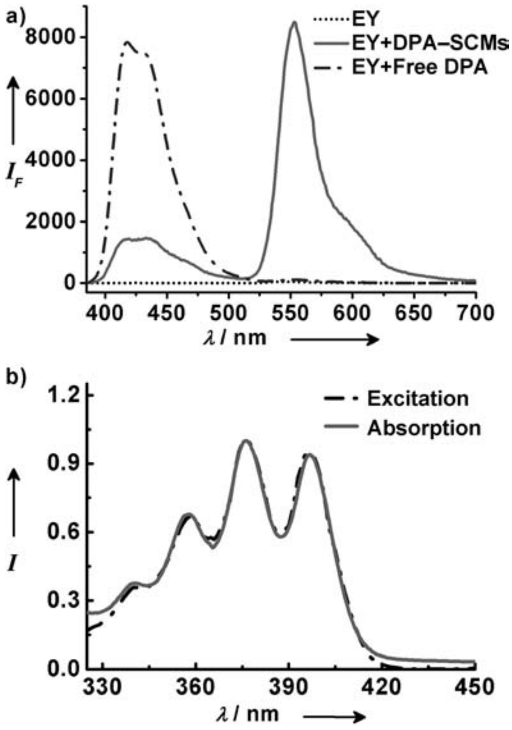


Figure 2. a) Fluorescence spectra ($\lambda_{ex} = 375$ nm) of EY/DPA–SCM (1.4 μM/23 μM, solid trace) and EY/free DPA (9.9 μM/98 μM, dash-dot trace). The fluorescence spectrum (dotted trace) of EY is shown for comparison. b) Normalized excitation spectrum of EY/DPA–SCM ($\lambda_{em} = 550$ nm, dash-dot trace) and absorption spectrum of DPA–SCM (solid trace). [EY] = 1.4 μM. [DPA] = 23.0 μM. THF was used in all spectroscopic measurements.

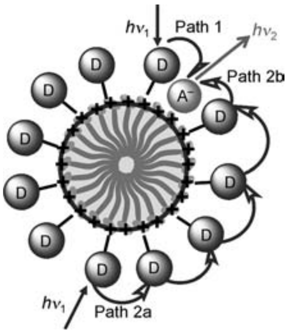


Figure 3. The two main pathways involved in the light-harvesting system: 1) Direct energy transfer from donor to acceptor (path 1); 2) Energy migration from donor to donor (path 2a), then energy transfer to acceptor (path 2b). D and A represent donor and acceptor, respectively.

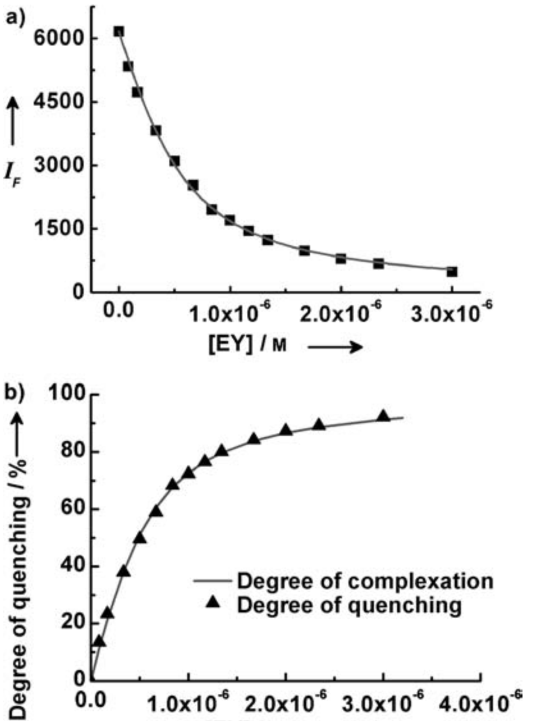


Figure 4. a) The nonlinear least-squares analysis of I_F versus the concentration of EY according to equation: $I_F = I_0 + ((I_{lim} - I_0)/(2c_0))\,(c_0 + c_{EY} + (1/K_a) \cdot ((c_0 + c_{EY} + (1/K_a))\,2 - 4\,c_{EY}c_0)\,(1/2))$, in which I_F is the observed emission intensity of DPA–SCM, I_0 the emission intensity of DPA–SCM in the absence of EY, I_{lim} the emission intensity of the fully complexed DPA–SCM (assumed to be zero in the curve fitting), c_0 the concentration of $(DPA)_n$, and c_{EY} the concentration of EY.[45] b) Comparison of the degree of complexation and the degree of quenching. The degree of complexation was calculated from K_a and c_0 obtained from the curve fitting and the degree of quenching ($=1-I_F/I_0$) calculated from the observed emission intensity.

Information). Moreover, when DPA–SCM was added to a neutral Bodipy[44] acceptor, no energy transfer was observed, even though the DPA–Bodipy Förster radius was similar to that for DPA–EY (Figure S6 in the Supporting Information).

The majority of the DPA fluorescence was quenched by a few percent of EY (Figure 1b). One acceptor, therefore, must have quenched multiple donors in our system. If we assume *n* DPA fluorophores could be quenched by one EY, we could treat $(DPA)_n$ as one unit and model the quenching by a 1:1 binding isotherm. This model combines the direct quenching (Figure 3, path 1) and the energy-migration-assisted energy-transfer pathway corresponding to the antenna effect (Figure 3, path 2) and may be expressed as Equation (1).

$$(\mathrm{DPA})_n + \mathrm{EY} = (\mathrm{DPA})_n\,\mathrm{EY} \qquad (1)$$

The quenching data indeed fit well to the 1:1 binding isotherm (Figure 4a). Nonlinear least-squares curve fitting afforded an association constant $K_a = (4.1 \pm 0.2) \times 10^6\,\mathrm{M}^{-1}$ and the $(DPA)_n$ concentration $c_0 = (4.8 \pm 0.4) \times 10^{-7}\,\mathrm{M}$. Since the concentration of DPA in the solution was $2.3 \times 10^{-5}\,\mathrm{M}$ based on optical density, the number of DPA chromophores in the light-harvesting unit was calculated to be $n = 48 \pm 4$.

The number of the DPA chromophores per light-harvesting unit was in excellent agreement with the aggregation number of surfactant in the SCM. According to the previous DLS study, an SCM on average contained 40–50 cross-linked surfactants.[38] Since a 1:1 stoichiometry was employed in the preparation of the SCMs for **1** and **2**, the SCM on average contained one residual alkyne group per surfactant. Assuming complete functionalization of these alkyne groups by DPA–N_3, a value of $n = 48 \pm 4$ for the light-harvesting unit strongly suggests that the light-harvesting unit was indeed the DPA–SCM nanoparticle, on which highly efficient energy migration took place.

Figure 4b compares the degree of complexation (i.e., percentage of DPA–SCMs with a bound EY) and the degree of quenching. The degree of complexation was calculated from K_a and c_0 obtained by the nonlinear least-squares curve fitting. The degree of quenching was obtained from the observed emission intensity. As shown by Figure 4b, the two sets of data overlap perfectly, thus indicating that every bound EY completely quenched the excited DPA, regardless of its location on the DPA–SCM.

Because the diameter of the DPA–SCM is about 20 nm according to DLS (Figure S2), the energy transfer to EY could not all take place through the Förster mechanism but, instead, happens through both direct quenching (Figure 3, Path 1) and energy-migration (Path 2) pathways.[24,37] The majority of DPA chromophores on the surface of the DPA–SCMs were not in the immediate vicinity of a bound EY. Path 2 thus must be the dominant process responsible for the quenching.

In summary, we have prepared a highly efficient light-harvesting system by combining two self-assembling strategies (micellization and electrostatic attraction) and covalent capture. Inexpensive starting materials and simple chemistry were employed. The synthesis was achieved by a one-pot reaction at RT. The modularity of the preparation makes it straightforward to vary the donor, the acceptor, and the ratio between the two. A high density of the antenna chromophore was achieved without self-quenching and excimer formation, affording extremely efficient energy transfer. The construction of our light-harvesting system is considerably simpler compared to most of those reported in the literature, making it a potentially useful platform for optical, photovoltaic, or photocatalytic devices.

Received: November 2, 2011

Keywords: click chemistry · cross-linked micelles · energy transfer · light-harvesting system · self-assembly

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