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Protein-Framed Multi-Porphyrin Micelles for a Hybrid Natural–Artificial Light-Harvesting Nanosystem

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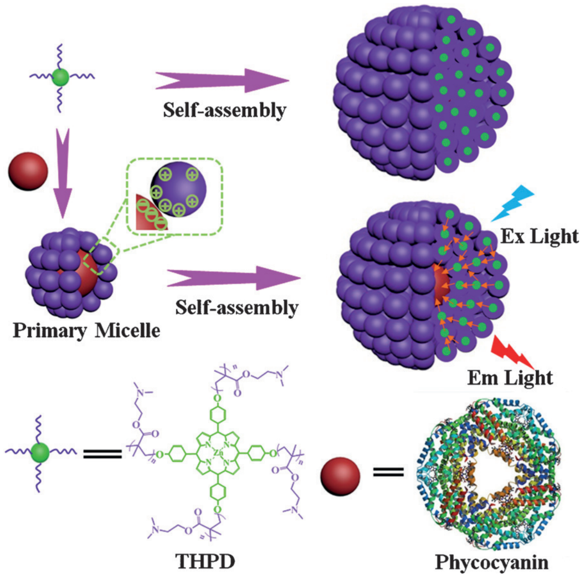
Dedicated to Professor Deyue Yan on the occasion of his 80th birthday

Abstract: *A micelle-like hybrid natural–artificial light-harvesting nanosystem was prepared through protein-framed electrostatic self-assembly of phycocyanin and a four-armed porphyrin star polymer. The nanosystem has a special structure of pomegranate-like unimolecular micelle aggregate with one phycocyanin acceptor in the center and multiple porphyrin donors in the shell. It can inhibit donor self-quenching effectively and display efficient transfer of excitation energy (about 80.1 %) in water. Furthermore, the number of donors contributing to a single acceptor could reach as high as about 179 in this nanosystem.*

Natural photosynthesis is the survival foundation of the living beings. Light-harvesting antenna (LHA), as the initiation of the photosynthesis, can capture light energy and then funnel excitation energy to the reaction center where light energy turns into chemical energy.[1] One of the most remarkable feature of the natural LHA is that weak light can be used by the reaction center because of their specific structure where every acceptor molecule is surrounded by a large number of donors (often ca. 200). Inspired by nature, up to now, great progress has been made in artificial light-harvesting systems.[1,2] The majority of them are worked in organic solutions and are generally based on scaffolds like dendrimers,[3] coordination polymers,[4] and cyclic arrays.[5] In recent years, some aqueous artificial LHA scaffolds, such as DNA,[6] MOFs,[7] gels,[8] virus,[9] proteins,[10] micelles[11] and clay,[12] have also been developed. These LHA systems are like nature ones working in aqueous environment, however, it is difficult for them to obtain clear multi-donors to only one acceptor structure, especially with a ratio more than 100 as the nature does. In addition, it is still very challenging for these aqueous LHAs to inhibit the self-quenching of donors in water due to their great hydrophobicity.

Herein, we report a novel aqueous LH system to address these challenges. Previously, our group disclosed a special multimolecular micelle structure, named as unimolecular micelle aggregate (UMA), through the direct aggregation of unimolecular micelles into a pomegranate-like micellar structure.[13] In the present work, a four-arm star polymer (THPD) with a porphyrin core and four poly(2-(Dimethylamino)ethylmethacrylate) (PDMAEMA) arms was synthesized, which also self-assembled into the pomegranate-like UMAs in water (Scheme 1). Since the obtained THPD micelles have multi-porphyrin donors, a biomimetic LHA system with multiple donors and one acceptor could be constructed if an acceptor was able to be introduced into the core of the THPD micelle. Herein, a natural LHA protein of phycocyanin (PC) was selected as the acceptor. PC, a water-soluble light-absorption protein in cyanobacteria, is composed of two subunits of the α-chain and β-chain. The two subunits form monomers, which aggregate into $\alpha_3\beta_3$ trimers and further into $\alpha_6\beta_6$ hexamers (Scheme 1).[14] The PC was put into the core of the pomegranate-like THPD UMA micelle through a delicate protein-framed electrostatic assembly process (Scheme 1).[15] In this as-prepared hybrid natural–artificial LH system, the porphyrin donors are effectively separated from each other by PDMAEMA arms, which



Scheme 1. Self-assembly of the pomegranate-like porphyrin-phycocyanin light-harvesting nanosystem (Ex Light = exciting light; Em Light = emitted light).

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inhibits self-quenching of donors and keep them stable in water. In addition, like the natural system, a regular structure with about 179 effective donors but one acceptor was constructed in this synthetic LH system, which showed excellent energy-funneling properties in water. Porphyrins are stable and have broad absorption and large extinction coefficient in the visible light region. Thus, they are not only widely existed in chlorophyll a and chlorophyll b of the natural LHAs, but also have been widely used as artificial LHA chromophores.[16] Herein, a porphyrin-based four-arm star polymer of THPD was constructed as donors through an oxyanionic polymerization of PDMAEMA arms from the core of 5,10,15,20-tetrakis(4-hydroxyphenyl) zinc porphyrin (ZnTHPP).[17] The detailed syntheses and characterizations of the synthetic intermediates as well as THPDs were shown in the supporting information (see Figures S1–S5 in the Supporting Information). As we know, short PDMAEMA arms cannot support the total segregation of porphyrin chromophores between THPDs, while too longer arms will prevent THPDs from self-assembly. Therefore, the THPDs with a moderate degree of polymerization of 21 for PDMAEMA arms, a total molecular weight around 14 kD, and a polydispersity of 1.19 were synthesized.

THPDs can undergo self-assembly in aqueous solution at a pH of 6.2 since each of them has a hydrophobic ZnTHPP core and four hydrophilic PDMAEMA arms in this condition. The critical micellar concentration (CMC) of THPDs was determined to be 0.05 mg mL^{-1} (Figure S6). When the concentration was below CMC, for example 0.04 mg mL^{-1}, the typical transmission electron microscope (TEM) image in Figure 1 a showed that spherical particles with an average diameter of about 3.8 nm existed in solution, which was also supported by dynamic light scattering (DLS) analysis showing an average hydrodynamic diameter (D_h) of 5.3 nm (inset of Figure 1 a). These results indicate THPDs form unimolecular micelles below the CMC. In contrast, when the THPD concentration was above the CMC, spherical micelles with an average diameter of 76 nm, as counted from 200 particles in the TEM images, were observed (Figures 1 b and S7a), which agreed well with the scanning electron microscope (SEM) result (Figure S7b). However, the micelle size measured by TEM was smaller than that from DLS measurement (D_h = 112 nm, Figure S7c) since the micelles were in a dried state during the TEM measurement.

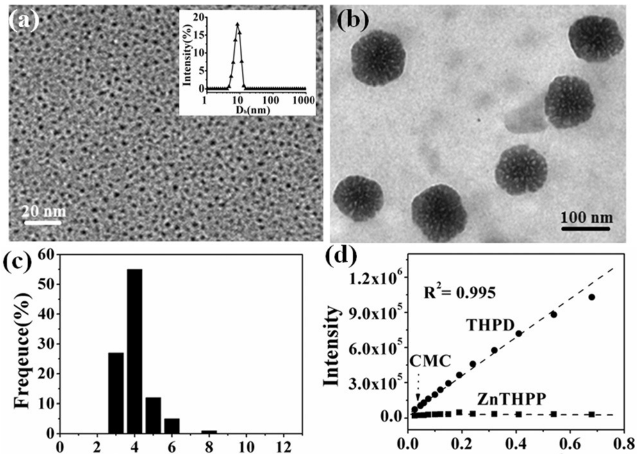

Figure 1. Characterizations of THPD micelles. a) Representative TEM images as well as the DLS curve (inset) of THPD unimolecular micelles. b) A typical TEM image of THPD multimolecular micelles at a concentration of 0.50 mg mL^{-1}. c) The size distribution of small spherical particles inside the THPD multimolecular micelles from image (b). d) The fluorescence emission intensity (exited at λ = 426 nm) as a function of the concentration of ZnTHPP and THPD aqueous solutions.

Most interestingly, the obtained micelles seemed to be formed by the aggregation of small particles (Figure 1 b), and the size of these small particles inside the micelles were ranging from 3 to 6 nm in diameter based on the statistical analyses of 200 particles (Figure 1 c), which matched well with that of the THPD unimolecular micelles. Thus, the THPD micelles should have a so-called UMA structure as shown in Scheme 1.[13] In other words, the THPD micelles were formed through the direct aggregation of THPD unimolecular micelles.

Such a UMA structure can effectively inhibit the self-quenching between porphyrin chromophores. ZnTHPPs are not water-soluble and will undergo serious aggregation-caused quenching (ACQ) with the increase of concentration. The SEM measurement also showed the formation of large aggregates from ZnTHPPs in water (Figure S8). As expected, ZnTHPPs almost had no fluorescence emission in water because of the strong ACQ effect (Figure 1 d).[18] In contrast, the fluorescent intensity of THPD aqueous solution increased linearly with the concentration (Figures 1 d and S9) up to 0.51 mg mL^{-1} (ten times higher than CMC). Besides, the UV absorbance peaks of THPDs in water were almost kept at the same positions in spite that they were in the unimolecular micelle state below the CMC or in the UMA state above the CMC (Figure S10). The time-resolved fluorescence analyses showed no apparent change between the decay lifetime of THPD unimolecular micelles (τ = 1.35 ns) and UMA micelles (τ = 1.32 ns; Figure S11). All these data support the self-quenching of porphyrins in THPD micelles is inhibited, which should be attributed to the UMA structure in the micelles. In such UMA micelles, each porphyrin chromophore was spatially separated from one another by the PDMAEMA shells, which greatly decreased the π–π stacking of chromophores. However, when the concentration of THPD was higher than 0.51 mg mL^{-1}, the fluorescent intensity was deviated from linear relationship with concentration probably due to the common inner-filter effect of the fluorescence between chromophores.[19]

As shown above, THPDs formed multi-porphyrin micelles with a UMA structure and a good fluorescence property in water. In addition, the energy migration ability between porphyrins in the THPD micelles was also proved by a small additional rise-time component in time-resolved profile of THPD micelles (Figure S11).[20] Then, we wanted to introduce PCs as the acceptors into THPD micelles to construct hybrid LH systems. PCs formed spherical nanoparticles with a diameter of about 13 nm according to typical TEM (Figures S12) and atomic force microscope (AFM) images (Figure S13). The Zeta potential value of PCs at the pH of 6.2 is −31.1 mV (Figure S14), which means PC is negatively charged. These results are consistent with literatures.[14] In addition, the fluorescence emission spectrum of THPDs and the UV absorption spectrum of PCs were well overlapped (Figure S15). Thus, THPD and PC are complementary donor and acceptor candidates and might be combined into a LH system through an electrostatic self-assembly process since THPD micelles are positively charged (the zeta potential value is 35.3 mV at pH 6.2, Figure S16).

We wanted to set up a LH system with only one PC acceptor but multiple THPD donors. In order to ensure this, a classical electrostatic self-assembly method as developed by Grzybowski was adopted here.[21] A small amount of aqueous solution of negatively charged PCs was added into the aqueous solution of massive positively charged THPDs with vigorous stirring (the concentration of THPDs is 0.04 mg mL^{-1}). In this way, PCs were separated from each other by many surrounding THPD molecules. We expected that at the beginning THPD unimers in solution would be immediately adsorbed onto the surface of every PC particle though electrostatic interaction to form primary micelles, and then every primary micelle would act as a nucleating agent to take more and more THPD molecules to form a THPD-PC complex micelle.

To prove the assumption, TEM measurements were performed to track the intermediates during this electrostatic self-assembly process. In the TEM image, PC particles look much paler than THPDs since there is one Zn atom with a high electron density in each THPD molecule. The TEM image in Figure S17 displayed some particle intermediates at the beginning of self-assembly process of THPDs and PCs with a molar ratio of 200:1, and each of them has a light core partly or completely covered with a dark thin layer. The light cores have a diameter in the range from 10 nm to 15 nm, which agrees well with the size of PCs, while the dark thin layer should come from the adsorbed THPD molecules. In other words, the PC-cored primary micelles did form at the initial step of the co-assembly process. Finally, numerous core–shell micelles (Figure 2a) with a D_h of 93 nm (Figure 2b) were obtained. The light core was assigned to the PC, while the dark shell was formed by the aggregation of small nanoparticles according to the magnified view (Figure 2c). The diameter of these small particles in the micelle shell is ranging from 3 nm to 6 nm when counted from 100 particles (Figure 2d), which agrees well with the size of THPD unimers. So, the final THPD-PC complex micelle should be composed of a PC core and a shell of THPD molecules with a UMA structure (Scheme 1).

The core–shell structure of the THPD-PC complex micelles was much clearer (Figure 2e) under high-resolution TEM (HRTEM) in spite that the details in the shell as shown in the biological TEM (Figure 2a and c) were lost. Fortunately, the line scanning element analyses of one selected THPD-PC micelle show the micelle shell has more zinc and carbon contents derived from ZnTHPP moieties, while the micelle core has more nitrogen content derived from the peptide bonds of PC (Figure 2f) under HRTEM. Thus, as a support of the biological TEM, the HRTEM results also prove the THPD-PC micelle has a structure of one-PC core and a multi-THPD shell.

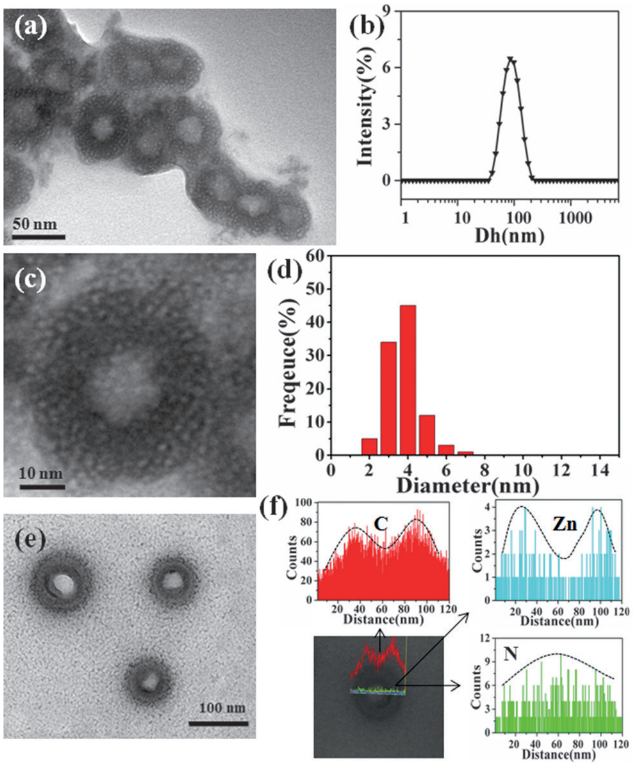

Figure 2. Structural characterizations of THPD-PC complex micelles. a) A typical biological TEM image of THPD-PC micelles. b) The DLS curve of THPD-PC micelles. c) The magnified view of a typical THPD-PC micelle. d) A statistical size distribution of small particles inside the shell of THPD-PC micelles. e) The HRTEM image of THPD-PC micelles, f) Line scanning element analyses of one THPD-PC micelle (bottom left), including carbon element (top left), zinc element (top right) and nitrogen element (bottom right).

Besides the morphology observation, the self-assembly process between PCs and THPDs was further tracked by time-dependent DLS and fluorescence emission measurements (Figure S18), and all results support an electrostatic self-assembly process as summarized in Scheme 1. At the beginning, each PC was worked as a core to frame the coating of a thin layer of THPD molecules driven by the electrostatic interactions, and thus a primary micelle was obtained. Since the positive charge of the THPD layer in the primary micelle was partly neutralized by the PC core, the hydrophobicity of these coated THPD molecules increased. As a result, the primary micelles further attracted the aggregation of more THPD molecules onto the surface driven by the hydrophobic interactions to form a core–shell complex micelle. This process was similar to the self-assembly process of THPDs except that a primary micelle pre-existed in here, and thus a UMA structure was also formed in the shell of the complex micelle. Since the final obtained core–shell micelle was framed by the PC protein, we called it as a protein-framed multi-porphyrin micelle.

There are also some factors that play important roles in the self-assembly of PC-THPD micelles. First, the concentration of THPD is very important. If the concentration was too low (much lower than 0.04 mg mL^{-1}), only small core–shell micelles with thin THPD shells were obtained. While, if the concentration of THPDs was higher than the CMC, THPDs themselves formed the micelles with a UMA structure, and the PC-THPD core–shell micelles were difficult to form. Second, the feed ratios of THPD:PC is also important. A series of PC-THPD core–shell complex micelles were also obtained by changing the ratios from 500:1 to 2000:1 through the same PC-framed electrostatic self-assembly process, and the micelle size increased with the increase of the ratios (Figures S19 and S20). However, there is a size self-limiting mechanism in the self-assembly of THPD-PC micelles,[22] and they will stop growing when the feed ratio is above 1000:1, which is probably attributed to the equilibrium of the hydration repulsion and hydrophobic attraction interactions between the free THPD molecules and the already existing micelles at the critical condition.

The light-harvesting property of the as-prepared THPD-PC complex micelles was also carefully investigated. Compared with the fluorescent emission of THPDs and PCs (Figure 3 a), the fluorescence emission spectra of THPD-PC complex micelles excited at 456 nm showed a typical Förster resonance energy transfer (FRET) phenomenon with one isoemissive point: the fluorescence emission peak of THPD donors at 620 nm decreased, while that of PC acceptors at 660 nm increased with the increase of the PC concentrations (Figure 3 b and the corresponding peak-differentiation-imitating analyses in Figure S21). The excitation wavelength was set at 456 nm for the FRET measurements, which is not the maximum absorption wavelength of THPDs ($\lambda_{max} = 426$ nm). However, PCs have the weakest absorption at this excitation wavelength (Figure S22), which can better avoid the emission interference for the energy-transfer process. The FRET efficiency of these LH systems was calculated and listed in Table S1, which reached the maximum of 80.1 % in the complex micelle system with a THPD:PC molar ratio of 200:1 (see the Supporting Information).

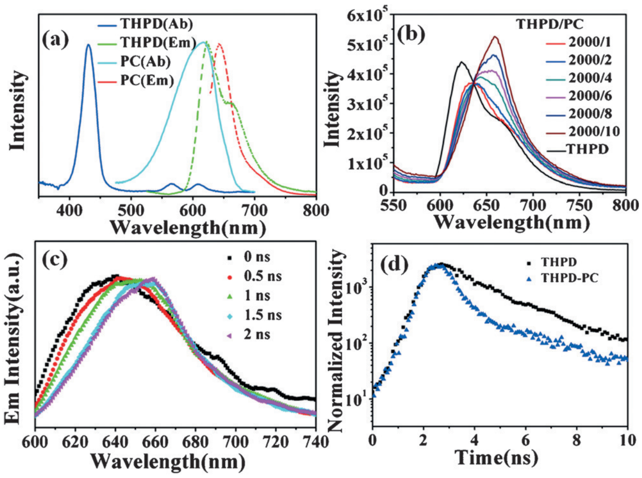

Figure 3. Optical property characterizations of THPD-PC complex micelles. a) Normalized absorption (solid lines) and fluorescence emission (dashed lines) spectra of PC and THPD. b) The fluorescence spectra of PC-THPD complex micelles excited at 456 nm in aqueous solution at the different donor-to-acceptor ratios. c) The time-resolved fluorescence spectra of PC-THPD complex micelles at 0 ns, 0.5 ns, 1 ns, 1.5 ns and 2 ns after excitation. d) The fluorescence decay profiles of pure THPD (black) and PC-THPD complex micelles (blue). The excitation wavelength was 456 nm in images (b)–(d), and the monitored wavelength in image (d) is 620 nm (the donor emission maxima). The ratio between THPD and PC is 200:1 for the complex micelles in images (c) and (d).

The time-resolved fluorescence spectra for THPD-PC LH system at a feed ratio of 200:1 and excited at 456 nm were examined to further reveal the energy-transfer process (Figure 3 c). The obtained emission spectrum was similar to that of THPDs at the beginning (set as 0 ns), and then with the continuous excitation, the spectrum transferred to that of PCs after 2 ns, which directly supported the energy was transferred from the excited THPD donors to PC acceptors effectively. Furthermore, the fluorescence lifetime decay curves of THPD donors and PC acceptors at 620 nm were fitted as a single exponential decay with a lifetime of $\tau_D = 1.32$ ns (Figure 3 d) and $\tau_A = 1.43$ ns (Figure S23), respectively. However, the lifetime of THPD-PC micelles exhibited a typically biexponential decay with $\tau_1 = 0.51$ ns and $\tau_2 = 1.46$ ns, respectively (Figure 3 d). The long lifetime τ_2 is close to that of acceptors, and thus we believe the short lifetime τ_1 is from the donors. Such a prominent shortening of the donor lifetime suggests that nonradiative energy transfer takes the dominant place in the energy-transfer mechanism from the donors to the acceptors in the THPD-PC complex micelles. The time-resolved fluorescence curves of the THPD-PC micelles and PC acceptors monitored at 680 nm support the same results (Figure S24).

In addition, in the THPD-PC micellar LH system with a THPD/PC ratio of 200:1, the energy-transfer rate constant k_{ET} between THPD donor and PC acceptor was calculated to be 3.03×10^9 s^{-1} (see the Supporting Information). The overlap integral J was calculated to be 1.40×10^{13} M^{-1} cm^{-1} nm^4 for energy transfer between THPD and PC ($J_{D\text{-}A}$), and 1.16×10^{12} M^{-1} cm^{-1} nm^4 for energy transfer between THPDs ($J_{D\text{-}D}$; see the Supporting Information). Herein, both the k_{ET} and J are large enough to keep the effective energy migration among donors and energy transfer from the donor to the acceptor.[2,12] The Förster radius between donor and acceptor ($R_{0(D\text{-}A)}$) was estimated to be 2.90 nm (see the Supporting Information), which indicates that PC acceptors are very closely surrounded by THPD donors in PC-THPD hybrid LH nanosystem. The average number of THPD molecules that quenched by each PC was calculated to be 179 (see the Supporting Information), which is comparable to that in natural LHA systems.

In summary, the work reports a novel core–shell micellar light-harvesting nanosystem consisting of one phycocyanin acceptor in the center and many porphyrin donors packed in a pomegranate-like model in the shell through the protein-framed aqueous electrostatic self-assembly. It can avoid self-quenching among the porphyrin donors and afford efficient energy transfer from up to 179 porphyrin donors to one phycocyanin acceptor in water. Such a regular multi-donor and one-acceptor structure is similar to that of natural light-harvesting antenna. Thus, we believe this work might throw new light onto the construction of biomimetic highly efficient aqueous light-harvesting nanosystem with a high donor and acceptor ratio. In addition, it is well anticipated that the energy-transfer efficiency of the present light-harvesting nanosystem in water can be further improved by delicately matching the donor with acceptor, and the related work as well as the potential applications of the nanosystem in photocatalytic water splitting are still ongoing.

Acknowledgements

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