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Highly Efficient Artificial Light-Harvesting Systems Constructed in Aqueous Solution Based on Supramolecular Self-Assembly

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Abstract: Highly efficient light-harvesting systems are successfully fabricated in aqueous solution based on the supramolecular self-assembly of a water-soluble pillar[6]arene (WP6), a salicylaldehyde azine derivative (G), and two different fluorescence dyes, nile red (NiR) or eosin Y (ESY). The WP6-G supramolecular assembly exhibits remarkably improved aggregation-induced emission enhancement and acts as a donor for the artificial light-harvesting system, and NiR (or ESY) which is loaded within the WP6-G assembly acts as different acceptors. Notably, efficient energy-transfer process takes place from the WP6-G assembly not only to NiR but also to ESY for these two different systems. Furthermore, both of the WP6-G-NiR and WP6-G-ESY systems show ultrahigh antenna effect at a high donor/acceptor ratio.

Photosynthesis is the survival foundation for living creatures, during its primary process, sunlight is captured, transferred, and stored as chemical energy.^[1] This process takes place in chloroplast pigments with highly efficient photon-harvesting owing to the large number of closely packed chlorophylls within the pigment-protein complexes. Subsequently, excitation energy migrates among chlorophyll molecules, which is finally transferred to the reaction center, where the excitation energy is converted into chemical energy.^[2] The large number of closely packed antenna pigments (ca.200) around the reaction center is one of the most remarkable features for natural harvesting systems, which helps organisms thrive even under the extremely low-light conditions.^[3] Inspired by nature, up to now, great progress has been made in mimicking natural light-harvesting process by achieving efficient energy transfer from donors to acceptors through a Förster resonance energy transfer (FRET) process.^[4] In order to fabricate an artificial light-harvesting system with high energy collection efficiency, there are two key factors that should be taken into account: (1) the system should contain multiple donors per acceptor; (2) the donor should be closely packed but without intramolecular fluorescence selfquenching. In nature, green plants rely on non-covalent selfassembly between chlorophyll and protein to form the efficient light-harvesting antenna. So far, the reported artificial light-

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harvesting systems constructed based on covalent bonds (such as porphyrin arrays and dendrimers) always faced multistep synthesis difficulties,^[5] which hampered their scale up and widespread application. Whereas, supramolecular self-assembly paves a promising and facile way for constructing artificial lightharvesting systems. In fact, a variety of artificial light-harvesting systems have been successfully constructed via non-covalent assembly, including supramolecular polymers,^[6] organogels,^[7] biomaterials,^[8] and organic-inorganic hybrid materials.^[9] However, most of these reported artificial light-harvesting systems were fabricated in organic solvents instead of the aqueous environment like in nature. Since the donor chromophores are generally hydrophobic and exhibit undesired aggregation-caused quenching (ACQ) effect, they always show very poor energy transfer efficiency in water.^[10] Up to now, only a few examples of efficient aqueous light-harvesting systems have been delicately fabricated to address this problem. For examples, Zhou and coworkers designed pomegranate-like unimolecular micelle aggregates with porphyrin core structure to effectively inhibit the self-quenching between porphyrin chromophores.^[3c] Liu and coworkers exploited an oligo(phenylenevinylene) derivative to serve as an idea donor, [3b] which exhibited the aggregation-induced emission but without the undesired ACQ effect. Therefore, it is still a very challenging task to design and fabricate highly efficient light-harvesting systems in aqueous environment.

Herein, we report two novel aqueous light-harvesting systems which are fabricated based on the supramolecular self-assembly



Scheme 1. Schematic illustration of the self-assembly of pillar[6]arene-based aqueous light-harvesting systems.

of a water-soluble pillar[6]arene (WP6), a salicylaldehyde azine derivatives (G), and two different fluorescence dyes, nile red (NiR) or eosin Y (ESY). Since the salicylaldehyde azine derivatives are highly emissive in aggregates through the combined mechanism of aggregation induced emission (AIE) and excited-state intramolecular proton transfer (ESIPT), which can avoid ACQ effect and make the designed compound G an excellent donor. Upon addition of WP6 to the aqueous solution of G, it was found that the trimethylammonium terminals of G could form stable inclusion complex with WP6 and further selfassembled into spherical nanoparticles, which can not only significantly lower the critical aggregation concentration of G but also can remarkably improve the AIE effect of G. Hydrophobic fluorescent dye NiR or ESY, which acts as an idea acceptor, was successfully loaded within the hydrophobic interior of the obtained nanoparticles. To our delight, efficient energy-transfer process took place from the WP6-G assembly not only to NiR but also to **ESY** for these two different systems. Furthermore, both of the WP6-G-NiR and WP6-G-ESY systems show ultrahigh antenna effect at a high donor/acceptor ratio.

WP6 was synthesized according to reported method.^[11] and G was obtained by using 2,4-dihydroxybenzaldehyde as starting Since shows water material. G poor solubility. butyltrimethylaminium bromide (G_M) was used as a model compound to study the host-guest complexation between WP6 and G. As shown in Figure S7, upon adding equal equivalent of **WP6** to the solution of G_{M_1} the signals of phenyl protons (H₁) and methylene protons (H₂ and H₃) from WP6 shifted downfield slightly. Whereas, the signals derived from N-methyl protons (Ha) and butyl protons (Hb, Hc, Hd, and He) of $\textbf{G}_{\textbf{M}}$ shifted upfield remarkably and showed obvious broadening effect due to the shielding effect of the electron-rich cavities of pillar[6]arene. The above observations demonstrated that the alkyl chain of G_M was encapsulated into the hydrophobic cavity of WP6. Moreover, a 1:1 binding stoichiometry between WP6 and G_M for the WP6⊃G_M inclusion complex was measured by Job's plot method (Figure S8, Supporting Information), and the association constant (K_a) between WP6 and G_M was determined to be 2.31. \times 10² M⁻¹ by ¹H NMR titration experiments (Figure S9, Supporting Information).



Figure 1. (a) Fluorescence spectra of **G** (1×10^{-4} M) in a DMSO/H₂O mixed solution with different vol% ($\lambda_{ex} = 365$ nm); (b) Fluorescence intensity of **G** at 510 nm in the presence of different faction of water from 10 to 100%. Inset: photographs of **G** (1×10^{-4} M) in DMSO/H₂O = 9:1 (left) and in water (right) under UV lamp irradiation.

The fluorescence of ${\bf G}$ was first studied in a DMSO/water mixed solution with different water fractions to investigate its

solvent-dependent aggregation behavior. The emission of **G** (1 × 10^{-4} M) was very weak in DMSO, and it increased slowly when the water content was less than 80 vol%. However, when the water content increased from 80 to 100 vol%, the fluorescence intensity of **G** enhanced significantly caused by the intriguing AIE effect due to the formation of aggregates at this concentration.^[12] And the aqueous solution of **G** (1 × 10^{-4} M) showed strong yellow fluorescence under 365 nm excitation.

Based on the above-mentioned result, we wonder whether WP6 could induce G to assemble into higher-order aggregates and lead to remarkable emission enhancement of G in aqueous solution. Interestingly, upon addition of WP6 to the aqueous G solution, obvious Tyndall effect could be observed, indicating the existence of plentiful nanoparticles (Figure S10b, Supporting Information). Moreover, the fluorescence intensity of G increased significantly, and the fluorescence enhancement could be clearly perceived by the naked eye (Figure S10d, Supporting Information), which suggests that WP6 could induce G to assemble into tightly stacked aggregates and resulted in the AIE effect via restriction of intramolecular rotation of G around the N-N bond.^[12] In the control experiment, neither Tvndall effect nor fluorescence enhancement could be observed, when the building subunit of WP6 was added to the G solution (Figure S11, Supporting Information), indicating that the macrocyclebased host-guest recognition is crucial for inducing G to assemble. Then, the critical aggregation concentration (CAC) of G with WP6 for the formation of supramolecular aggregates was measured by monitoring optical transmittance. The CAC of free **G** was determined to be 1.4×10^{-4} M, and the transmittance of **G** at 500 nm showed no discernible change when the concentration of G is below its CAC (Figure S12, Supporting Information). However, upon gradual addition of WP6 to the G solution (2 \times 10⁻⁵ M, below its CAC), the solution transmittance at 500 nm underwent first decrease and then an inverse increase, and an inflection point with the molar ratio 4:1 ([G]/[WP6]) was observed when plotting the optical transmittance at 500 nm versus WP6 concentration (Figure S13, Supporting Information), which indicates that the best mixing ratio of G and WP6 for the assembly was 4:1. Moreover, keeping the mixing ratio of G and WP6 at their best molar ratio, the CAC for WP6-G assembly was determined to be 5×10^{-6} M (Figure S14, Supporting Information), which means that the CAC value of G decreased at least 28-fold in the presence of WP6.

Furthermore, the fluorescence changes of G with different amounts of WP6 were monitored. As shown in Figure 2b, the fluorescence of G (2 \times 10⁻⁵ M) first increased upon addition of WP6, reaching a maximum at a WP6 concentration of 5×10^{-6} M, which is coincidental with the best molar ratio of G and WP6, and then the fluorescence decreased upon further addition of WP6. The increase in fluorescence indicated the formation of aggregates by mixing G and WP6. Compared with free G, the fluorescence intensity of G with the presence of WP6 increased 30 times at the maximum point, indicating that the AIE effect of G was significantly improved by WP6 at the best mixing ratio. Such a WP6-improved AIE effect of G was also in accoredance with the sharp increase of fluorescence quatum yield of the obtained WP6-G assembly (5.32%, Table S3, Supporting Information).¹² Whereas, further addition of excessive amount of WP6 led to the formation of a simple 2:1 WP6⊃G inclusion

intensity.

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complex and accompanied by the disassembly of the aggregates, resulting in an obvious decrease in the fluorescence



Figure 2. (a) Fluoresence spectra of **G** $(2 \times 10^{-5} \text{ M})$ upon increasing the concentration of **WP6** $(0 - 2 \times 10^{-5} \text{ M})$. (b) Dependence of fluorescence intensity at 514 nm on the **WP6** concentration $(0 - 2 \times 10^{-5} \text{ M})$ with a fixed concentration of **G** $(2 \times 10^{-5} \text{ M})$. Inset: photographs of **G** $(2 \times 10^{-5} \text{ M})$ (left) and the mixture of **G** $(2 \times 10^{-5} \text{ M})$ and **WP6** $(5 \times 10^{-6} \text{ M})$ (right) under UV lamp irradiation.

Subsequently, the morphology and size of the formed aggregates were investigated by dynamic light scattering (DLS), transmission electron microscopy (TEM), and scanning electronic microscopy (SEM) measurements. DLS results showed that the WP6-G complex (at the best mixing ratio) formed well-defined aggregates with a narrow size distribution, giving an average diameter of 109 nm (Figure 3a). The TEM and SEM images showed spherical morphology with a dark core and the diameters around 100 nm (Figure 3c), indicating that they formed spherical nanoparticles. Confocal fluorescence images further showed that these nano-aggregates exhibited strong fluorescence (Figure 3b). The formation of **WP6-G** nanoparticles proceed as follows: Upon addition of WP6, miaht supramolecular inclusion complex was formed by WP6 and G based on electrostatic and hydrophobic interactions. Since the



Figure 3. (a) DLS data of WP6-G assembly at 25 °C. (b) Fluorescence microscopic image of the WP6-G aggregates. (c) TEM image of WP6-G assembly. (d) SEM image of WP6-G assembly. ([WP6] = 5×10^{-6} M, [G] = 2×10^{-5} M).

salicylaldehyde azine groups tend to form π - π stacked structure^[13] and the complexation with **WP6** could counterbalance the original charge repulsion of **G**, then free **G** and complexed **G** integrate together to form curved aggregate, which further self-assemble to form a multilayer sphere with alternating shell structure as illustrated in Scheme 1.^[14] Moreover, the ζ -potential experiment suggested that these nanoparticles have a relatively high negative ζ -potential (–29.6 mV, Figure S16, Supporting Information), indicating the existence of repulsive forces among these nanoparticles which can enhance their stability.

As the WP6-G assembly showed remarkably enhanced fluorescence in aqueous solution, it will be an idea candidate to fabricate aqueous artificial light-harvesting systems, which could avoid fluorescence self-quenching of the aggregated donor chromophores in aqueous solution. Hydrophobic fluorescence dye nile red (NiR) was first selected as a fluorescent acceptor, since the absorption band of NiR is largely overlapped with the fluorescence band of the WP6-G assembly (Figure S17, Supporting Information). As show in Figure 4a, with the gradual addition of NiR to the WP6-G assembly, the fluorescence intensity of the WP6-G assembly decreased, while the fluorescence emission of NiR (acceptor) increased when excited at 365 nm. In contrast, the emission of free NiR was negligible upon direct excitation at 365 nm or even at 580 nm (Figure S18, Supporting Information). The quatum yield of WP6-G-NiR assembly also showed a sharp increase (10.69%, Figure S20, S21 and Table S3, S4, Supporting Information), probably becacuse NiR accepts and emits the maximum possible amount of excitation energy.^{6d} Therefore, the above phenomenon indicates that energy transfer takes place from the WP6-G assembly to the encapsulated NiR. Moreover, fluorescence decay experiments were performed to support the occurrence of light-harvesting process. The decay curve of G (Figure 4b, blue line) was fitted as a double exponential decay with fluorescence lifetimes of $\tau_1 = 0.32$ ns and $\tau_2 = 1.62$ ns, both of which were related to the tightly stacked G (Table S1 and S2, Supporting Information). For the WP6-G assembly (Figure 4b, green line), the fluorescence lifetimes increased to $\tau_1 = 0.70$ ns and $\tau_2 = 1.95$ ns due to WP6-induced aggregation of G. With respect to the WP6-G-NiR assembly (Figure 4b, red line), the fluorescence lifetimes decreased to τ_1 = 0.61 ns and τ_2 = 1.69 ns, which further validates that energy transfer takes place from the WP6-G donor to NiR acceptor (Table S1, Supporting Information).^[3b] These results also jointly suggested that NiR was encapsulated within the WP6-G nanoparticles. Moreover, the morphology and size distribution of NiR-loaded WP6-G assembly were similar to that of WP6-G nanoparticles based on the DLS and TEM results (Figure S15c and 15d, Supporting Information).

Furthermore, the energy transfer efficiency and antenna effect which are widely used empirical parameters to evaluate the efficiency of a light-harvesting system, were investigated for the **WP6-G-NiR** assembly.^[3c] The energy transfer efficiency, which was estimated from the fluorescence quenching rate of **G** in the aggregated structure, reached 55% when the mixing molar ratio of donor/acceptor was at 150:1 (Figure S22, Supporting Information). Notably, the antenna effect at this mixing ratio was calculated to be 25.4 (Figure S23 Supporting Information), which

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indicates that the **WP6-G** nanoparticles function as an excellent light harvesting antenna in aqueous environment.



Figure 4. (a) Fluorescence spectra of WP6-G ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M) in water with different concentrations of NiR. Inset: photographs of WP6-G and WP6-G-NiR ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [NiR] = 1.3×10^{7} M). (b) Fluorescence decay profiles of G (blue line), WP6-G (green line), and WP6-G-NiR (red line). ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [NiR] = 1.3×10^{7} M). (c) Fluorescence spectra of WP6-G ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [NiR] = 1.3×10^{7} M). (c) Fluorescence spectra of WP6-G ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [NiR] = 1.3×10^{7} M) in water with different concentrations of ESY. Inset: photographs of WP6-G and WP6-G-ESY ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [ESY] = 1×10^{7} M). (d) Fluorescence decay profiles of G (blue line), WP6-G (green line), and WP6-G-ESY (yellow line). ([WP6] = 5×10^{6} M, [G] = 2×10^{5} M, [ESY] = 1.0×10^{7} M).

Moreover, we also used hydrophobic eosin Y (ESY) as a fluorescent acceptor to fabricate another light-harvesting system with WP6-G assembly, since the absorption band of ESY is also largely overlapped with the fluorescence band of the WP6-G assembly (Figure S24, Supporting Information). Upon gradual addition of ESY to the WP6-G assembly, the fluorescence intensity of the WP6-G assembly decreased, whereas the fluorescence emission of ESY increased when excited at 365 nm (Figure 4c). On the contrary, the emission of free ESY was negligible upon direct excitation at 365 nm or even at 510 nm (Figure S25, Supporting Information). The quatum yield of WP6-G-ESY assembly also showed a sharp increase (10.69%, Figure S20, S21 and Table S3, S4, Supporting Information), which is probably also becacuse ESY accepts and emits the maximum possible amount of excitation energy.^{6d} Thus, the above phenomenon clearly indicated the occurrence of energy transfer between the WP6-G assembly and ESY. Subsequently, the fluorescence decay measurements further validate the lightharvesting process. Herein, to make sure that the fluorescence mostly corresponds to the donor, the monitored wavelength was selected at 500 nm, which is little lower than the donor emission maxima (513 nm). Similar to the values of the WP6-G assembly monitored at 513 nm, the assembly monitored at 500 nm (Figure 4d, green line) also showed fluorescence lifetimes of $T_1 = 0.81$ ns and $\tau_2 = 1.99$ ns (Table S5, Supporting Information). However, the fluorescence lifetimes of the WP6-G-ESY assembly (Figure 4d, yellow line) decreased to $\tau_1 = 0.44$ ns and $\tau_2 = 1.43$ ns (Table

S5, Supporting Information), confirming the energy transfer from the WP6-G donor to ESY acceptor. These results also indicated that ESY was loaded within the WP6-G nanoparticles. In addition, the morphology and size distribution of WP6-G-ESY assembly were also similar to that of the WP6-G assembly (Figure S15e and S15f, Supporting Information). The energy transfer efficiency was estimated to be 42% when the mixing molar ratio of donor/acceptor was at 200:1 (Figure S27, Supporting Information). And the antenna effect was calculated to be 28.0 at such high donor/acceptor ratio (Figure S28, Supporting Information), indicating the ESY-loaded nanoparticle could also function as an excellent light harvesting antenna in aqueous environment.

In conclusion, highly efficient artificial light-harvesting systems were fabricated in aqueous environment based on a facile supramolecular self-assembly strategy. The easily obtained **WP6-G** supramolecular assembly showed significantly enhanced fluorescence due to an enhanced AIE effect. After simply mixing WP6-G assembly with hydrophobic fluorescence dve NiR or ESY, two atrtifical light-harvesting systems were successfully constructed based on the highly efficient FRET process that takes place from the donor (WP6-G assembly) to the acceptor (NiR or ESY). More importantly, both of these two artificial light-harvesting systems showed very high antenna effect (25.4 for WP6-G-NiR assembly and 28.0 for WP6-G-ESY assembly) with high donor/acceptor ratio (up to 150:1 for WP6-G-NiR system and 200:1 for WP6-G-ESY system), which are similar to that of natural light-harvesting system. Therefore, these highly efficient aqueous artificial light-harvesting systems are very important and versatile platform for mimicking photosynthesis.

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Highly Efficient Artificial Light-Harvesting Systems Constructed in Aqueous Solution Based on Supramolecular Self-Assembly

Highly efficient light-harvesting systems are successfully fabricated in aqueous solution based on the supramolecular self-assembly of a water-soluble pillar[6]arene (WP6), a salicylaldehyde azine derivative (G), and two different fluorescence dyes, nile red (NiR) or eosin Y (ESY). The WP6-G supramolecular assembly exhibits remarkably improved aggregation-induced emission enhancement and acts as a donor for the artificial light-harvesting system, and NiR (or ESY) which is loaded within the WP6-G assembly acts as different acceptors. Notably, efficient energy-transfer process takes place from the WP6-G assembly not only to NiR but also to ESY for these two different systems. Furthermore, both of the WP6-G-NiR and WP6-G-ESY systems show ultrahigh antenna effect at a high donor/acceptor ratio.