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A Supramolecular Artificial Light-harvesting System with Twostep Sequential Energy Transfer for Photochemical Catalysis

Min Hao,[#] Guangping Sun,[#] Minzan Zuo,[#] Zuqiang Xu, Yuan Chen, Xiao-Yu Hu,* and Leyong Wang*

Abstract: An artificial light-harvesting system with sequential energy-transfer process is successfully fabricated in aqueous environment based on the supramolecular strategy. Self-assembled from the host-guest complex formed by water-soluble pillar[5]arene (WP5) and a bola-type tetraphenylethylene-functionalized dialkyl ammonium derivative (TPEDA), as well as two fluorescent dyes, Eosin Y (ESY) and Nile Red (NiR), the obtained supramolecular vesicles can achieve efficient energy transfer from the AIE guest TPEDA to ESY at a high energy-transfer efficiency and donor/acceptor ratio. Moreover, ESY can function as a relay to further transfer the energy to the second acceptor NiR and realize the two-step sequential energy-transfer process with good efficiency. By properly tuning the ratio between the donor and acceptors, bright white light emission can be successfully achieved with a CIE coordinate of (0.33, 0.33). More importantly, to better mimic the natural photosynthesis and make full use of the harvested energy, the WP5 TPEDA-ESY-NiR system can be utilized as a nanoreactor, where photocatalysed dehalogenation of α -bromoacetophenone can be realized with 96% yield in aqueous medium.

Introduction

Light-harvesting systems play an important role in natural photosynthesis for converting light energy into chemical energy,^[1] which paves a prospective way for the exploitation of renewable energy resources. In recent years, more and more attention has been paid to mimic natural light-harvesting systems because of their considerable potential applications in the field of biological imaging and optoelectronic devices.^[2] Inspired by nature, there are two crucial prerequisites to realize efficacious energy transfer from a donor to an acceptor through the Förster resonance energy transfer (FRET) process.^[3] Firstly, the donor should be not only densely packed but also needs to, in the meantime, avoid intramolecular self-quenching of fluorescence caused by the aggregation-caused quenching (ACQ) effect. Secondly, the ratio of the donor and acceptor should be relatively high to make sure that multiple donors correspond to one acceptor. It is noteworthy that efficient natural

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light-harvesting systems are constructed by non-covalent interactions between chlorophyll and protein. Therefore, compared with traditional artificial light-harvesting systems via covalent bonds, supramolecular light-harvesting systems constructed by noncovalent interaction are usually easy to be fabricated without multiple synthesis.^[4]

So far, most research has focused on the construction of lightharvesting systems in organic solvents^[5] rather than in the aqueous environment as the natural photosynthesis system. Since the energy donors are usually hydrophobic, the organic system can avoid the ACQ effect induced by water, and thus high energy transfer efficiency can be achieved compared with that in aqueous solution. Therefore, fabricating efficient lightharvesting systems in water to mimic the natural processes remains a challenging task, which has aroused great interest among researchers.^[6] For instance, Liu et al. demonstrated that an oligo(phenylenevinylene) derivative could effectively inhibit the ACQ effect and exhibited outstanding energy transfer efficiency in water.^[7] Our group has previously reported an artificial light-harvesting system based on a salicylaldehyde azine derivative which showed aggregation-induced emission (AIE) effect instead of the ACQ phenomenon.^[8] However, most of these systems contain only one-step direct FRET process from donors to acceptors, while the natural light-harvesting system with excellent efficiency is characterized by multichannel information communication.^[9] Besides, the use of harvested solar energy for further photochemical catalysis has been rarely addressed. Thus, to better understand and mimic the natural light-harvesting antenna systems, establishing the multi-step sequential FRET systems with the capability to convert solar energy into chemical energy in aqueous environment is of great significance.^[10]

Herein, we report the fabrication of a novel artificial lightharvesting system based on the noncovalent supramolecular assembly between a water-soluble pillar[5]arene (WP5) and a bola-type tetraphenylethylene-functionalized dialkyl ammonium derivative (TPEDA),^[11] which could realize two-step sequential energy-transfer process in aqueous environment (Scheme 1). Due to the unique property of AIE effect, TPE analogues in the aggregated form can exhibit high emission,^[12] which makes TPEDA a remarkable donor in water. Meanwhile, WP5 could function as an ideal host towards TPEDA to lower its critical aggregation concentration as well as strengthen the AIE effect. When WP5 was added into the aqueous solution of TPEDA, stable host-guest inclusion complex could be formed and further self-assembled into supramolecular nanoparticles. Driven by the noncovalent interaction, an energy acceptor, the hydrophobic fluorescent dye Eosin Y (ESY), could be successfully entrapped into the hydrophobic core of the formed WP5 TPEDA $\ensuremath{\text{vesicles.}}^{[13]}$ Because of the well overlap between the emission band of the WP5 TPEDA complex and the absorption band of ESY, efficient one-step energy-transfer process could take place from WP5 DTPEDA vesicles to ESY. Furthermore, a two-step sequential energy-transfer process could also be realized by the simultaneous encapsulation of another carefully selected

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hydrophobic dye Nile Red (NiR) as the second energy acceptor. Thus, this two-step energy-transfer process could initially take place from WP5¬TPEDA vesicles to ESY and then to NiR at a high energy-transfer efficiency and donor/acceptor ratio ([TPEDA]/[ESY]/[NiR] = 200:1:1). In addition, strong white light emitting^[13–15] can also be achieved with the fabricated WP5¬TPEDA-ESY-NiR supramolecular system. Significantly, due to the AIE enhanced FRET process, undesired fluorescence quenching could be avoided and the harvested solar energy could be utilized to promote the photocatalysed dehalogenation of α -bromoacetophenone with 96% yield in aqueous medium.



Scheme 1. Schematic illustration of the self-assembly of pillar[5]arene-based aqueous light-harvesting system with two-step sequential energy transfer.

Results and Discussion

The synthesis of **WP5**^[16] and pentyltrimethylammonium bromide $(G_M)^{[17]}$ were according to the reported methods, and guest TPEDA molecule was prepared by taking 4hydroxybenzophenone as the starting material (Scheme S1 and Figure S1-S8, Supporting Information). Initially, ¹H NMR spectroscopic studies was conducted to investigate the hostguest binding ability between WP5 and TPEDA (Figure S9, Supporting Information). Considering the complicated structure of TPEDA may hamper the investigation of host-guest association, G_M with the same binding site as TPEDA was utilized as the model compound. Figure S9 revealed that the protons of the alkyl chain moiety (H₂, H₃, H₄, H₅, and H₆) of G_M underwent manifest upfield shift due to the shielding effect of the WP5 hydrophobic cavity, while the signals of the phenyl protons (H_a) and methylene protons (H_b) of WP5 shifted downfield slightly. These results convincingly demonstrated that G_M threaded into the electron-rich cavity of WP5. Moreover, the association constant (K_a) between WP5 and TPEDA was determined to be $(1.69 \pm 0.27) \times 10^5$ M⁻¹ by Isothermal Titration Calorimetry (ITC) (Figure S10, Supporting Information). Such high binding affinity may attribute to the cooperative C-H··· π , electrostatic as well as hydrophobic interactions, leading to the formation of stable amphiphilic host-guest complex.

Before exploring the energy-transfer process, we first studied the self-assembly behavior of the WP5_TPEDA complex. Neither Tyndall effect nor strong fluorescence could be observed from the freshly prepared TPEDA solution (Figure S11, Supporting Information). However, in the presence of WP5, notable opalescence with obvious Tyndall effect could be observed, suggesting the formation of large amounts of WP5 TPEDA supramolecular nanoparticles. Moreover, the free TPEDA solution exhibited very dim fluorescence. On the contrary, the WP5 TPEDA solution showed significantly enhanced fluorescence (Figure S11 and Figure S16, Supporting Information), indicating that WP5 could induce the self-assembly behavior of TPEDA, and the close-packed structure could restrict the intramolecular rotation of TPEDA, which in return resulted in the obvious AIE effect. Then the best molar ratio of TPEDA and WP5 for aggregation was tested to be 5:1 ([TPEDA]/[WP5]) by UV-visible spectroscopy (Figure S13, Supporting Information). What's more, the critical aggregation concentration (CAC) of WP5 TPEDA assembly was confirmed to be 0.014 mM at the best molar ratio (Figure S14, Supporting Information). The size and morphology of assemblies were investigated by dynamic light scattering (DLS) and transmission electron microscope (TEM) measurements, respectively. WP5 TPEDA nano-aggregates showed a narrow size distribution with an average diameter of 180 nm (Figure 1a). TEM images revealed a dark spherical structure (Figure 1b) with a similar diameter as the DLS results, suggesting the formation of multilayer vesicular structure. Zeta potential measurements gave a relatively high positive ζ -potential (19.84)



Figure 1. DLS data of (a) **WP5 TPEDA** assembly, (c) **WP5 TPEDA-ESY** assembly, and (e) **WP5 TPEDA-ESY-NiR** assembly in water at 25 °C. TEM images of (b) **WP5 TPEDA** assembly, (d) **WP5 TPEDA-ESY** assembly, and (f) **WP5 TPEDA-ESY-NiR** assembly. [**WP5**] = 1.0×10^{-5} M, [**TPEDA**] = 5.0×10^{-5} M, [**ESY**] = 2.5×10^{-7} M and [**NiR**] = 2.5×10^{-7} M. Scale bar: 200 nm.

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mV, Figure S15, Supporting Information), suggesting that the electrostatic repulsive force around the surfaces of the nanoparticles can prevent their agglomeration and further improve the stability of the nanoparticles in aqueous solution.

Since WP5 could obviously induce the AIE effect of TPEDA, the fluorescence intensity of the system was significantly enhanced with a fluorescence quantum yield of 15.63% (Figure S18a and Table S2. Supporting Information), indicating that WP5 TPEDA assembly can be served as an ideal donor for the construction of an artificial light-harvesting system in aqueous solution. ESY, a hydrophobic fluorescent dye, was expected to be a promising acceptor due to the following benefits: on one hand, the absorption band of ESY overlaps very well with the fluorescence emission of the WP5 DTPEDA assembly (Figure S19a, Supporting Information). On the other hand, since the WP5 TPEDA inclusion complex tends to form tightly stacked π - π stacking assembly, **ESY** can be easily entrapped into the hydrophobic layer of the obtained WP5 - TPEDA vesicles via noncovalent interaction, thus the distance between the donor and acceptor will be significantly shortened, which ensures the efficient FRET effect. Accordingly, the obtained ESY-loaded WP5 TPEDA assembly had an obviously increased average diameter (Figure 1c and 1d) compared with the blank nanoparticles. Subsequently, the fluorescent behavior of the ESY-loaded vesicles was investigated. As shown in Figure 2a, with the increasing concentration of ESY, the fluorescence intensity of TPEDA (donor) at 480 nm decreased gradually, while the fluorescence emission of ESY (acceptor) at 550 nm increased when excited at 365 nm. In addition, the fluorescent color changed from light blue of WP5 TPEDA vesicles to bright yellow-green of WP5 TPEDA-ESY system (Figure 2a and Figure S12c, Supporting Information). These phenomena are consistent with the efficient energy transfer from the donor to the acceptor. To further confirm the light-harvesting properties, fluorescence decay experiments were conducted. The decay curve of WP5 TPEDA assembly was fitted as a double exponential decay (Figure 2b), which showed the fluorescence lifetimes of $\tau_1 = 1.79$ ns and $\tau_2 = 5.40$ ns (Figure S17a and Table S1, Supporting Information). In addition, the fluorescence lifetimes of WP5 \supset TPEDA-ESY system decreased to $\tau_1 = 1.15$ ns and τ_2 = 3.64 ns (Figure S17b and Table S1, Supporting Information), indicating that the WP5 TPEDA-ESY system functions as an artificial light-harvesting system in which the energy can be transferred from WP5_TPEDA assembly to the acceptor ESY. To quantitatively evaluate the efficiency of a lightharvesting system, it is very necessary and important to know its energy transfer efficiency and antenna effect. According to the fluorescence quenching rate of WP5 TPEDA assembly, energy



Figure 2. (a) Fluorescence spectra of **WP5 TPEDA** assembly in water with different concentrations of **ESY**. Inset: photographs of **WP5 TPEDA** assembly and **WP5 TPEDA-ESY** assembly. (b) Fluorescence decay profiles of **WP5 TPEDA** assembly (black line), and **WP5 TPEDA-ESY** assembly (red line). [**WP5**] = 2×10^{-5} M, [**TPEDA**] = 1×10^{-4} M, [**ESY**] = 5×10^{-7} M.

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transfer efficiency was calculated to be 74.39% at the molar ratio of donor/acceptor = 200:1 (Figure S19b, Supporting Information). Moreover, the antenna effect was calculated to be 11.5 at such a high donor/acceptor ratio (Figure S21, Supporting Information) and the fluorescence quantum yield was tested to be 7.27% (Figure S18b and Table S2, Supporting Information). The above results indicated that the **WP5TPEDA** assembly could function as a promising light harvesting antenna in aqueous environment.

Considering that the photosynthetic light-harvesting system in nature consists of multichromophoric assemblies for multi-step sequential energy transfer rather than the simple one-step energy transfer,^[18] we further investigated the possibility of sequential energy transfer process of the fabricated supramolecular system. After systematic screening, NiR was selected as a suitable acceptor for WP5_TPEDA-ESY system (Figure 1e and 1f), because the absorption band of ESY overlaps well with the fluorescent emission of the WP5 - TPEDA-ESY assembly. When the second acceptor NiR was added to the WP5 TPEDA-ESY system, the emission intensity at 550 nm ascribed to ESY decreased and a new emission band of NiR at 610 nm appeared at the same time (Figure 3a, for full spectra, see Figure S26 in Supporting Information). Moreover, the fluorescent color changed from bright yellow-green of WP5 TPEDA-ESY assembly to off-white of WP5 TPEDA-ESY-NIR assembly (Figure 3a and Figure S12d, Supporting Information). These observations indicated that a sequential energy transfer process took place from WP5 TPEDA-ESY system to NiR, and ESY may function as a crucial bridge to realize this sequential energy transfer in a relay mode. The fluorescence quantum yield of WP5 TPEDA-ESY-NiR system was tested to be 5.01% (Figure S18c and Table S2, Supporting Information), and the energy-transfer efficiency was calculated to be 56.28% with the molar ratio of donor/acceptor I/acceptor II = 200:1:1 (Figure S20b, Supporting Information). The antenna effect was then calculated to be 3.5 at such a high donor/acceptor ratio (Figure S22, Supporting Information). To further confirm the crucial role of ESY as a bridge for sequential energy transfer, WP5 - TPEDA-NiR assembly was used as a control treatment, as seen in Figure S24, the emission band of the NiR could hardly be observed, indicating the very low harvesting antenna effect between WP5 DTPEDA and NiR. The above results also confirmed that the WP5 DTPEDA-ESY-NiR assembly could function as sequential harvesting antenna in aqueous environment.

Furthermore, fluorescence lifetime decay tests were also performed to investigate the energy transfer process for the



Figure 3. (a) Fluorescence spectra of **WP5DTPEDA-ESY** assembly in water with different concentrations of **NiR**. Inset: photographs of **WP5DTPEDA-ESY** assembly and **WP5DTPEDA-ESY-NiR** assembly. (b) Fluorescence decay profiles of **WP5DTPEDA-ESY** assembly (red line), and **WP5DTPEDA-ESY-NiR** assembly (blue line). **[WP5]** = 2×10^{-5} M, **[TPEDA]** = 1×10^{-4} M, **[ESY]** = 5×10^{-7} M.

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WP5⊃**TPEDA-ESY-NiR** systems. The decay curve of the **WP5**⊃**TPEDA-ESY-NiR** assembly showed the lifetimes of τ_1 = 1.05 ns and τ_2 = 2.68 ns (**Figure 3b**). Therefore, the fluorescence lifetime showed an initial decline from **WP5**⊃**TPEDA** assembly to **WP5**⊃**TPEDA-ESY** assembly and a further decrease from **WP5**⊃**TPEDA-ESY** assembly to **WP5**⊃**TPEDA-ESY-NiR** assembly. These results can also jointly validate the encapsulation of fluorescent dyes **ESY** and **NiR** into the **WP5**⊃**TPEDA** vesicles as well as the sequential energy transfer in the relay mode.

Subsequently, the emission behavior of the WP5-TPEDA-ESY-NIR assembly was investigated. Since the WP5 - TPEDA assembly acts as an AIE fluorophore, it may show concentration-dependent fluorescence in a certain color range. As expected, the color of the WP5_TPEDA-ESY-NIR nanoparticle solution turned from bluish violet to light blue (Figure 4a) as the WP5 TPEDA assembly changed from high concentration $(1 \times 10^{-4} \text{ M})$ to low concentration $(5 \times 10^{-5} \text{ M})$. This is probably because the WP5 TPEDA inclusion complex at high concentration presents a closely compact form to induce the remarkable AIE effect. However, at low concentration, WP5 TPEDA inclusion complex prefer to keep a more loose form and the AIE effect is decreased. Consequently, the fluorescent color changed accordingly. Moreover. the WP5 TPEDA-ESY-NIR assembly also showed ratio-dependent fluorescent changes. As the ratio of ESY increased (from 100:1:1 to 100:10:1), the color of the system changed from light blue to bright yellow, indicating more efficient energy transfer process from WP5 TPEDA assembly to ESY. Thus, the sample could display a strong white-light emission at a concentration of 5×10^{-5} M (TPEDA) with the ratio of [TPEDA]/[ESY]/[NiR] = 100:5:2 (Figure 4b). The color coordinate of the resulting WP5 TPEDA-ESY-NIR system was calculated as (0.33, 0.33) in the CIE (Commission Internationale de l'Eclairage) xy chromaticity diagram, which is exactly the pure white point and could be perceived as white light-emitting materials. Under this condition, the energy-transfer efficiency from WP5 TPEDA assembly to ESY was calculated up to 92.45% (Figure S23a, Supporting Information) and the sequential energy-transfer efficiency from WP5 TPEDA-ESY assembly to NiR was 74.78% (Figure S23b, Supporting Information), indicating the successful construction of a white light-emitting material based on a sequential energy transfer process in supramolecular systems. Moreover, this white-light emission system was very stable after



Figure 4. (a) CIE chromaticity coordinates of equal ratio WP5 \supset TPEDA-ESY-NiR assembly at different concentrations (red arrow, from 5 × 10⁻⁵ M to 1 × 10⁻⁴ M), equal concentration WP5 \supset TPEDA-ESY-NiR assembly at different ratios (blue arrow, from 100:1:1 to 100:10:1), and the white-light-emitting coordinate. (b) Fluorescence spectra of the white-light-emitting coordinate. Inset: corresponding fluorescent image. [WP5] = 1 × 10⁻⁵ M, [TPEDA] = 5 × 10⁻⁵ M, [ESY] = 2.5 × 10⁻⁶ M and [NiR] = 1 × 10⁻⁶ M.

storing for 24 hours, which might be suitable for further application in light-emitting materials (Figure S25, Supporting Information).

To better mimic the natural photosynthesis process and make full use of the harvested energy, the WP5 - TPEDA-ESY-NIR system was utilized as a nanoreactor to catalyze the dehalogenation of a-bromoacetophenone in aqueous medium. It is known that organic dves can be used successfully in the photoredox catalysis with specific light region due to their limited absorption in other regions.^[19] However, in the WP5 TPEDA-ESY-NIR system, the fluorescent chromophores exhibit sequential harvesting antenna effect from the UV region to the visible light region, thus full solar light spectrum can be used to catalyze the chemical reaction. Accordingly, a Xenon lamp was used as a solar light simulator for the photocatalysis reaction.^[20] Upon irradiation, the light energy can be transferred from the donor to NiR through sequential FRET process. Meanwhile, the WP5 TPEDA-ESY-NIR vesicles could function as а nanoreactor to provide favorable space for the photocatalysis reaction and makes it possible to perform organic reactions in aqueous environment (Figure 5). As shown in Table 1, the photocatalytic activities of fluorescent chromophores alone and the light-harvesting system were both investigated. After optimizing the reaction conditions (Table S3 and Figure S31-S33, Supporting Information), for the WP5_TPEDA-ESY-NIR group, the yield of product acetophenone reached 96% after eight-hour irradiation, which was dramatically increased compared with the ESY + NiR group (Table 1 and Figure S27-28, Supporting Information). And very low yield was obtained for the TPEDA group as well as for the blank control without catalyst (Table 1 and Figure S29-S30, Supporting Information). Moreover, nearly



Figure 5. A plausible mechanism for the dehalogenation reaction using WP5_TPEDA-ESY-NIR assembly as a nanoreactor in aqueous medium.

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Entry	Conditions	Light irradiation	Yield [%] ^[b]
1	None ^[a]	Yes	10
2	TPEDA	Yes	13
3	ESY + NIR	Yes	31
4	WP5⊃TPEDA-ESY-NiR	Yes	96
5	WP5⊃TPEDA-ESY-NiR	No	n.d.

[a] Dehalogenation reaction of α -bromoacetophenone without catalyst. [b] Yield determined by GC using appropriate calibrated internal standards.

no catalytic activity was observed in dark for the WP5 - TPEDA-ESY-NIR group. The high catalytic efficiency for the WP5_TPEDA-ESY-NIR system in aqueous medium may be due to the fact that the loading of dyes into the hydrophobic layer of the supramolecular vesicles could minimize the photobleaching effect upon long-time irradiation. What's more, the AIE effect of the donor and the appropriate arrangement of the dyes within restricted space can avoid the undesired fluorescence quenching, which is highly beneficial to improve the light-useefficiency. Moreover, the wide region of the solar light can be used to synergisticly trigger the photocatalysis. These results suggest that the WP5_TPEDA-ESY-NiR nanoreactor with good photocatalytic ability can function as an efficient light-harvesting system to make full use of the harvested solar energy and convert it into chemical energy in aqueous phase. Thus, we believe that such an efficient light-harvesting system with twostep energy transfer process would provide a new insight into the fabrication of artificial photosynthetic systems.

Conclusion

In summary, a sequential light-harvesting system with outstanding efficiency based on facile supramolecular strategy has been designed in aqueous solution. Owing to WP5-induced self-assembly process, the obtained WP5 TPEDA host-guest amphiphile further assembled into supramolecular nanoparticles, which exhibited significant AIE effect with dramatically enhanced fluorescence compared to the free TPEDA solution. After noncovalently encapsulation of the hydrophobic fluorescent dye ESY, an artificial light-harvesting system was successfully fabricated with efficient FRET process that occurred from the donor (WP5 TPEDA assembly) to the acceptor (ESY). What's more, when a second hydrophobic fluorescent dye NiR was further entrapped into the WP5 TPEDA assembly, a lightharvesting system with two-step sequential energy transfer could be achieved from WP5 TPEDA to ESY and then to NiR. More importantly, by tuning the ratio of these two different dyes, the WP5 TPEDA-ESY-NiR system could realize white light emission at a proportion of 100:5:2 (TPEDA/ESY/NiR). Furthermore, the harvested energy of the WP5 - TPEDA-ESY-NIR system with two-step energy transfer process could be further utilized to catalyze the dehalogenation of αbromoacetophenone in water with an excellent yield of 96% compared with the control group using organic dyes alone. Therefore, such an efficient sequential light-harvesting system fabricated in aqueous solution shows great potential applications in mimicking natural photosynthesis featuring facile integration and multi-step energy transfer process.

Experimental Section

Preparation of the Supramolecular Assembly Solutions. The blank WP5 TPEDA assembly solution was prepared as follows: TPEDA (0.38 mg) was dissolved in DMSO (50 µL). Subsequently, the above solution was added to the WP5 aqueous solution (0.02 mM, 5 mL) during ultrasonication within 30 s to generate the assembly solutions in water. The WP5 TPEDA-ESY and WP5 TPEDA-NiR assembly solutions were prepared as follows: TPEDA (0.38 mg) was dissolved in ESY (50 µM)-containing or NiR (50 µM)-containing DMSO solution (50 µL), respectively. The above mixed solutions were added separately to WP5 aqueous solution (0.02 mM, 5 mL) during ultrasonication within 30 s to generate the assembly solutions in water. The WP5_TPEDA-ESY-NIR assembly solution was prepared as follows: TPEDA (0.38 mg) was dissolved in DMSO solution (50 µL) containing ESY (50 µM) and NiR (50 µM). The above mixed solution was added to the WP5 aqueous solution (0.02 mM, 5 mL) during ultrasonication within 30 s to generate the assembly solution in water.

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Keywords: Host-guest interaction • Supramolecular selfassembly • Artificial light-harvesting • Sequential energy transfer • White light emission

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RESEARCH ARTICLE

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An artificial light-harvesting system with two-step sequential energy transfer process in a relay mode is successfully fabricated in aqueous environment based on the supramolecular strategy, which can be used as a nanoreactor for efficient photochemical catalysis. Moreover, bright white light emission can be successfully achieved with a CIE coordinate of (0.33, 0.33).



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