A Supramolecular Artificial Light-Harvesting System with an Ultrahigh Antenna Effect

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An efficient artificial light-harvesting system is fabricated from a cyclic polysaccharide, sulfato-β-cyclodextrin (SCD); an aggregation-induced emission molecule, an oligo(phenylenevinylene) derivative (OPV-I); and a fluorescent dye, nile red (NiR), via noncovalent interactions in an aqueous solution. In this system, the OPV-I/SCD supramolecular assembly acts as a donor, and NiR that is loaded into the OPV-I/SCD assembly acts as an acceptor. Significantly, an efficient energy-transfer process occurs between the OPV-I/SCD assembly and the loaded NiR, leading to an extremely high antenna effect.

In natural photosynthesis, green plants and some photosynthetic bacteria capture, transfer, and store solar energy effectively to achieve photosynthesis.[1] Within these light-harvesting organisms, light is absorbed by a pigment–protein complex consisting of a dense array of chlorophyll molecules. Then, a photoinduced energy migration occurs among the chlorophyll molecules and, subsequently, the excitation energy is transferred to the reaction center, where light energy turns into chemical energy.[2] One of the most remarkable features of natural light-harvesting systems is their densely packed antenna chromophores. Generally, over 200 antenna chromophores (donor) absorb light energy and transfer it to an acceptor at the reaction center.[3] Recently, considerable efforts have been devoted to mimic natural light-harvesting processes by realizing efficient and rapid energy transfer from a donor to an acceptor through a light-induced Förster resonance energy-transfer (FRET) process.[4] For this purpose, two necessary factors should be taken into consideration: 1) the donor should be densely packed without a significant self-quenching effect, and 2) the donor/acceptor ratio should be relatively high. These factors can minimize energy loss and transfer excitation energy with a high efficiency.[3–6] Actually, green plants usually form chlorophyll–protein complexes via noncovalent interactions to perform photosynthesis. Therefore, noncovalent assemblies with high photoinduced energy-transfer efficiencies have

attracted increasing interest, and a variety of supramolecular artificial light-harvesting systems, including dendrimers,[7] organogels,[8] multiporphyrin arrays,[9] biomaterials,[10] and organic–inorganic hybrid materials,[11] have been constructed via noncovalent assembly. However, most of these artificial light-harvesting systems have performed in organic solvents due to the intrinsic hydrophobic effect and the undesired aggregation-caused quenching (ACQ) effect of organic chromophores in water. As a result, the fabrication of a highly efficient light-harvesting system in an aqueous solution is still a challenge.

In this work, we report a novel and highly efficient aqueous light-harvesting system constructed from the noncovalent supramolecular assembly of an oligo(phenylenevinylene) derivative (OPV-I), sulfato-β-cyclodextrin (SCD), and nile red (NiR) (**Scheme 1**). There are several advantages of this system: 1) at a high concentration, OPV-I possesses good aggregation-induced emission (AIE) properties, but does not display the ACQ effect, which enables OPV-I to act as a good donor; 2) SCD greatly lowers the critical aggregation concentration (CAC) of OPV-I, improving the AIE properties of OPV-I and enabling good water solubility of the resultant light-harvesting system; and 3) the hydrophobic dye NiR is loaded in the hydrophobic layer of the OPV-I/SCD nanoparticles and acts as a good acceptor. As a result, the obtained OPV-I/SCD/NiR system shows a high antenna effect, energy-transfer efficiency, and donor/acceptor ratio, and the antenna effect occurs with a trace amount of acceptor (donor/acceptor ratio = 1500:1).

SCD was commercially available, and OPV-I was obtained in 82% yield (Figures S1–S6, Supporting Information). The solvent-dependent aggregation behavior of OPV-I was investigated by fluorescence spectroscopy. As shown in **Figure 1**a, when the water content was less than 80%, the solution of OPV-I barely fluoresced, and its fluorescence spectra were nearly unchanged, indicating that no self-aggregation of OPV-I occurred. However, with an increasing volume fraction of water from 80 to 100 vol% (Figure 1b), the fluorescence intensity of OPV-I greatly enhanced, accompanied by an obvious bathochromic shift of the emission maximum, from 450 to 540 nm. In an aqueous solution, OPV-I emitted strong yellow fluorescence when excited at 365 nm, owing to the AIE of OPV-I.[12]

With the addition of SCD, the fluorescence intensity of OPV-I increased 3.7 times (Figure S9, Supporting Information), and the fluorescence enhancement was clearly observed by the naked eye (**Figure 2**). In control experiments, the fluorescence of OPV-I was moderately enhanced (1.6 times) with

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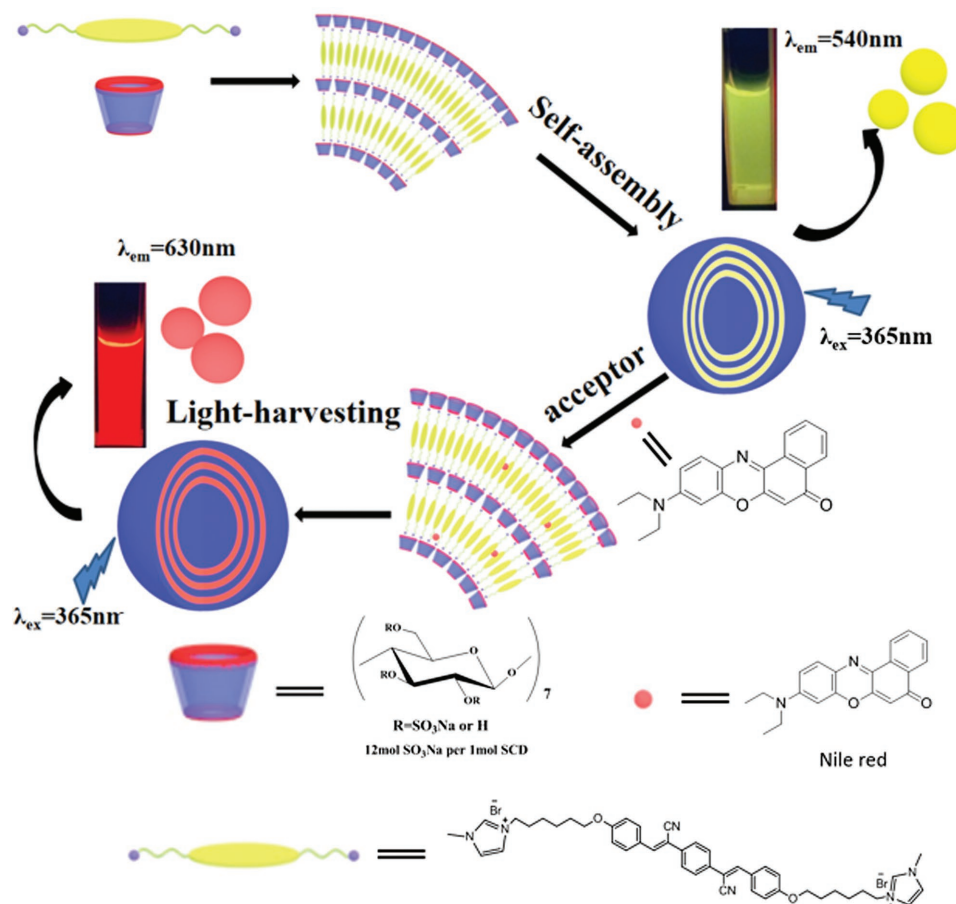
Scheme 1. Construction of the light-harvesting system.

the addition of another anionic macrocyclic molecule, *p*-sulfonatocalix[4]arene (SC4A), but was nearly unchanged or slightly quenched with the addition of a neutral macrocyclic molecule, such as native *β*-CD or cucurbit[7]uril (CB[7]). It is well documented that sulfonatocalixarenes can promote the self-aggregation of aromatic or amphiphilic molecules by lowering the CAC, enhancing the aggregate stability and compactness,

and regulating the degree of order in the aggregates. This unique self-assembly strategy is called calixarene-induced aggregation.[13] Therefore, we deduced that the enhanced fluorescence of the OPV-I/SCD system is mainly attributed to the SCD-induced aggregation of OPV-I, which consequently led to the aggregation-induced emission enhancement (AIEE) of OPV-I, but without the inclusion of OPV-I into the SCD cavity.
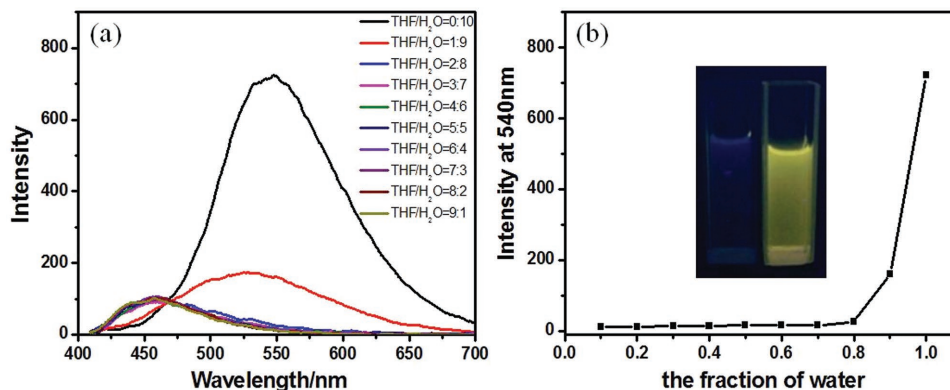

Figure 1. a) Fluorescence emission spectra of OPV-I (0.03×10^{-3} M) in Tetrahydrofuran(THF)/H_2O (λ_{ex} = 365 nm). b) Fluorescence intensity of OPV-I at 540 nm with various fractions of water from 10 to 100 vol%. Inset: photographs of OPV-I (0.03×10^{-3} M) in THF:H_2O = 9:1 (left) and in water (right) under UV light (365 nm).

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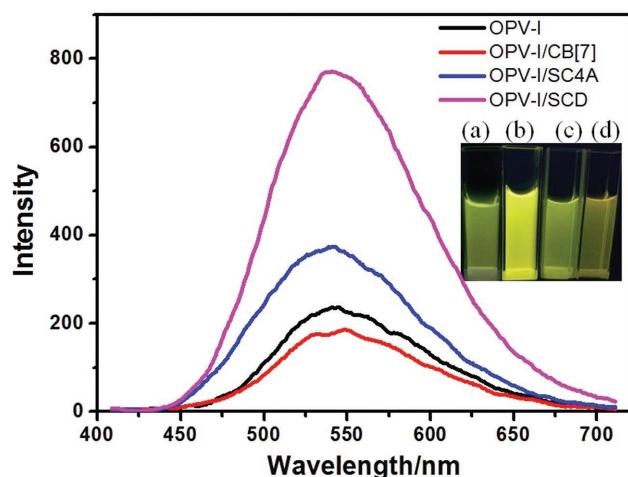**Figure 2.** Fluorescence spectra of OPV-I with the addition of SCD, SC4A, and CB[7] in an aqueous solution (λ_{ex} = 365 nm). Inset: photographs of a) OPV-I, b) OPV-I/SCD, c) OPV-I/SC4A, and d) OPV-I/CB[7] under UV light (365 nm) ([OPV-I] = 0.03 × 10^{-3} M, [SCD] = [SC4A] = [CB[7]] = 0.015 × 10^{-3} M).

Additionally, electrostatic interactions between the host and guest may play an important role. Because the negative charge density of SCD was higher than that of SC4A, the OPV-I/SCD system displayed a higher induced aggregation ability and larger fluorescence enhancement.

The induced aggregation behavior of SCD toward OPV-I was qualitatively and quantitatively investigated by optical transmittance, Tyndall effect, zeta potential, dynamic light scattering (DLS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) measurements. Without SCD, the CAC of OPV-I was 0.12 × 10^{-3} M (Figure S12, Supporting Information). In the presence of SCD, the optical transmittance (at 500 nm) of OPV-I decreased owing to the formation of a large supramolecular assembly (Figure S13, Supporting Information), and an inflection point at 0.025 × 10^{-3} M was observed on the plot of optical transmittance at 500 nm versus the concentration of OPV-I, corresponding to a CAC value for OPV-I of 0.025 × 10^{-3} M in the presence of SCD. This means that the CAC value of OPV-I decreased 4.8 times with the addition of SCD. Moreover, the preferable mixing ratio between SCD and OPV-I was also determined. By gradually adding SCD to an OPV-I solution at a fixed concentration of 0.042 × 10^{-3} M, the optical transmittance of the OPV-I/SCD solution at 500 nm decreased rapidly and then gradually increased thereafter to a quasiplateau, and the minimum was reached at a SCD concentration of 0.007 × 10^{-3} M (Figure S14, Supporting Information). The rapid decrease of the optical transmittance indicated that a large aggregate formed between OPV-I and SCD. Then, the addition of an excess amount of SCD led to the formation of a simple inclusion complex accompanied by the disassembly of the aggregate, resulting in an increase in the optical transmittance.[14] As a result, the preferable molar ratio for the supramolecular assembly was SCD:OPV-I = 1:6. Moreover, a similar phenomenon was also observed in the SC4A/OPV-I system, and the CAC value of OPV-I was 0.03 × 10^{-3} M in the presence of SC4A (Figure S15, Supporting Information), accompanied

by a preferable molar ratio of SC4A/OPV-I of 1:2 (Figure S16, Supporting Information). However, the optical transmittance of CB[7]/OPV-I at 500 nm showed no appreciable changes (Figure S17, Supporting Information). These results further confirmed that SCD displayed the highest induced aggregation ability toward OPV-I among the examined macrocyclic molecules.

In addition, a simple mixture of SCD with OPV-I (molar ratio = 1:6) in an aqueous solution exhibited an obvious Tyndall effect (Figure S19, Supporting Information), indicating the formation of large aggregates. In control experiments, neither SCD nor OPV-I exhibited a Tyndall effect, revealing that both SCD and OPV-I did not form large self-aggregates under the same conditions. The DLS results illustrated the existence of large aggregates of OPV-I/SCD with an average diameter of ≈147 nm, accompanied by a narrow size distribution (**Figure 3**b). The TEM and SEM images showed several spherical nanoparticles with diameters ranging from 50 to 150 nm (Figure 3c,d). There was no critical evidence to prove that the inside of these spheres was hollow or solid; thus, we classified them as a type of nanoparticle. A possible rationale for the multilayer structure may be as follows: free OPV-I molecules cannot form a large self-aggregate. Upon the addition of SCD, one SCD and several OPV-I form a complex. Subsequently, various complexes integrate together to form a large multilayer aggregate that curves to generate a multilayer sphere with alternating shell structure. The resulting aggregates were simultaneously stabilized by several noncovalent interactions, including host–guest, electrostatic, and π–π interactions, and the synergetic contribution of these noncovalent interactions endowed the OPV-I molecules with good aggregation stability, short aggregation distance, and a high-order degree of aggregation. It is noteworthy that, since SCD existed as a mixture of CDs randomly substituted by sulfonate groups with an average degree of substitution of 12, the resultant OPV-I/SCD nanoparticles were inhomogeneous to some extent. Zeta potential measurements gave an average zeta potential of the OPV-I/SCD assembly of −18.65 mV (Figure 3a), indicating that the surfaces of the nanoparticles were negatively charged.

It is reasonable to expect that the OPV-I/SCD assembly can load a model substrate within the interior of the nanoparticles. NiR, a dye molecule showing strong fluorescence in hydrophobic environments, was selected as a model substrate to construct a supramolecular triad light-harvesting system owing to the following advantages: 1) the absorption band of NiR well overlapped with the fluorescence emission of the OPV-I/SCD assembly (**Figure 4**a), which is favorable for the FRET process (Figure S20, Supporting Information), and 2) because the binding between NiR and the CD cavity was very weak,[15] a small amount of NiR could be loaded into the hydrophobic layer of the OPV-I/SCD assembly rather than encapsulated in the cavity of SCD. As shown in Figure 4b, with the gradual addition of NiR to the OPV-I/SCD assembly, the fluorescence of OPV-I/SCD (donor) decreased, but the fluorescence emission of NiR (acceptor) increased when excited at 365 nm. The bright-red fluorescence assigned to the emission of NiR was readily observed by the naked eye even in the presence of a trace mount of NiR (donor/acceptor ratio up to 1500:1). In control experiments, the free NiR or the NiR/SCD mixture barely fluoresced under the
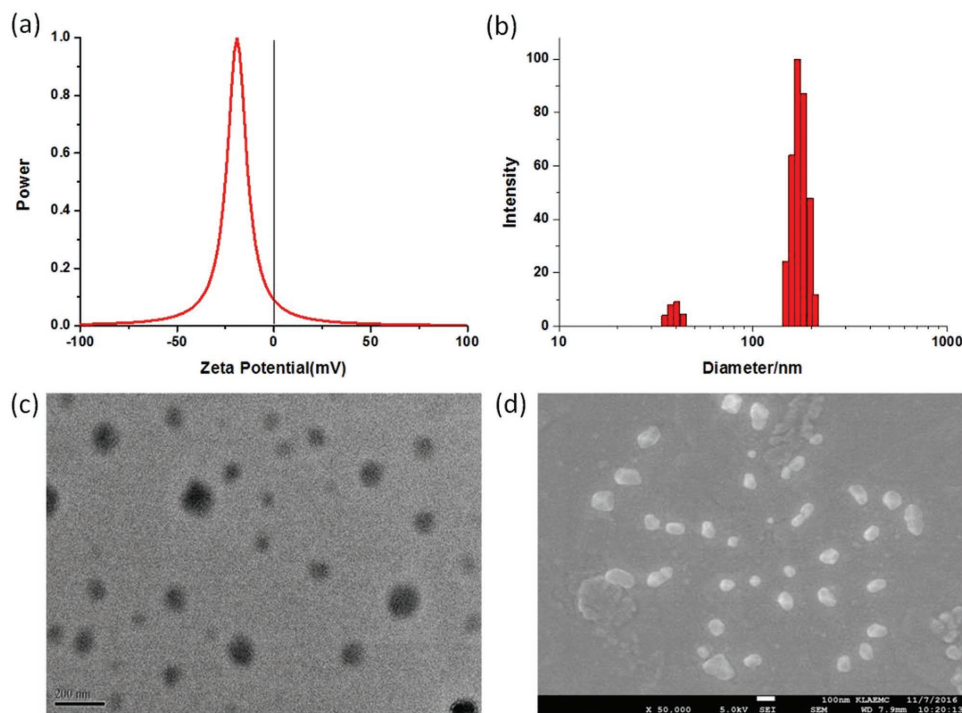
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Figure 3. a) Zeta potential of the OPV-I/SCD assembly in water. b) DLS of the OPV-I/SCD assembly in water. c) TEM and d) SEM images of the OPV-I/SCD assembly.

same conditions (λ_{ex} = 365 nm; Figure S21, Supporting Information), and the fluorescence of free NiR was negligible, even upon excitation at 540 nm, compared with that of the OPV-I/SCD/NiR triad assembly (Figure S24, Supporting Information). In addition, fluorescence lifetime experiments showed that the decay curve of OPV-I followed a double exponential decay with a fluorescence lifetime of τ_1 = 2.00 ns and τ_2 = 12.23 ns. We deduce that the longer fluorescence lifetime is assigned to OPV-I, and the shorter one is assigned to partly deprotonated OPV-I, as this lifetime was nearly unchanged, but its content increased upon increasing the pH. In the OPV-I/SCD system,

these fluorescence lifetimes increased to τ_1 = 3.57 ns and τ_2 = 16.43 ns, indicating that both OPV-I and its partly deprotonated derivative participated in the assembly with SCD. However, in the case of the OPV-I/SCD/NiR triad, the fluorescence lifetimes decreased to τ_1 = 2.75 ns and τ_2 = 10.52 ns (Figure S25, Supporting Information). Such an obvious decrease of the fluorescence lifetime suggested an energy transfer from the donor to the acceptor.[5b] Therefore, these results jointly indicated that NiR was loaded into the interior of the OPV-I/SCD assembly, and an energy transfer occurred between the OPV-I/SCD assembly and the loaded NiR. Furthermore, the size
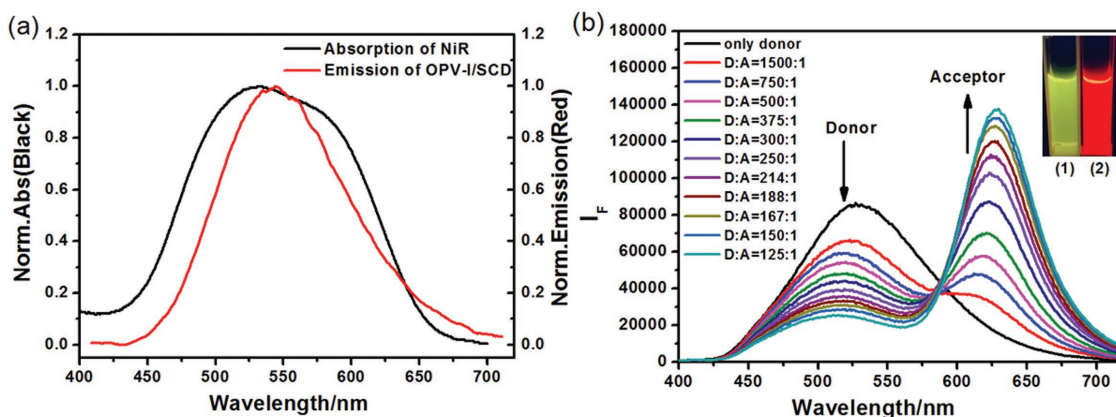

Figure 4. a) Normalized emission spectrum of OPV-I/SCD and absorption spectrum of NiR. b) Fluorescence spectra of OPV-I/SCD ([OPV-I] = 0.03 × 10^{-3} M, [SCD] = 0.005 × 10^{-3} M) in water with different concentrations of NiR. The concentrations of NiR were 0.00, 0.2 × 10^{-7}, 0.40 × 10^{-7}, 0.60 × 10^{-7}, 0.8 × 10^{-7}, 1.0 × 10^{-7}, 1.2 × 10^{-7}, 1.4 × 10^{-7}, 1.6 × 10^{-7}, 1.8 × 10^{-7}, 2.0 × 10^{-7}, and 2.4 × 10^{-7} M. Inset: 1) photographs of OPV-I/SCD, and 2) OPV-I/SCD/NiR under UV light (365 nm) ([OPV-I] = 0.03 × 10^{-3} M, [SCD] = 0.005 × 10^{-3} M, [NiR] = 2.4 × 10^{-7} M).

distribution and morphology of the OPV-I/SCD/NiR triad were similar to that of OPV-I/SCD through the DLS and TEM measurements (Figure S22, Supporting Information).

It is also interesting to investigate the energy-transfer efficiency and antenna effect of the OPV-I/SCD/NiR triad, as these parameters are very important to evaluate the light-harvesting ability of an artificial system.[5a] Through a simple calculation based on Figures S23 and S24 (Supporting Information), the energy-transfer efficiency (ΦET) was calculated as 72%, and the antenna effect was calculated to be 32.5 at a donor/acceptor ratio of 125:1. Significantly, this antenna effect value was much higher than the corresponding values of recently reported artificial light-harvesting systems in aqueous environments.[5]

In conclusion, an artificial light-harvesting system was conveniently constructed based on a supramolecular assembly strategy. The OPV-I/SCD supramolecular assembly was conveniently fabricated, and the fluorescence properties of OPV-I were improved from an enhanced AIE. Interestingly, by simply mixing the acceptor (NiR) with the OPV-I/SCD assembly, a highly efficient FRET process occurred between the OPV-I/SCD assembly and NiR, leading to the in situ formation of an artificial light-harvesting system. Most importantly, this artificial light-harvesting system exhibited a very high antenna effect (up to 32.5) and donor/acceptor ratio (up to 125:1) that are similar to a natural light-harvesting system. This highly effective aqueous light-harvesting system is very significant for mimicking artificial photosynthesis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

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