Aqueous Platinum(II)-Cage-Based Light-Harvesting System for Photocatalytic Cross-Coupling Hydrogen Evolution Reaction

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Abstract

Photosynthesis is a process wherein the chromophores in plants and bacteria absorb light and convert it into chemical energy. To mimic this process, an emissive poly(ethylene glycol)-decorated tetragonal prismatic platinum(II) cage was prepared and used as the donor molecule to construct a light-harvesting system in water. Eosin Y was chosen as the acceptor because of its good spectral overlap with that of the metallacage, which is essential for the preparation of light-harvesting systems. Such a combination showed enhanced catalytic activity in catalyzing the cross-coupling hydrogen evolution reaction, as compared with eosin Yalone. This study offers a pathway for using the output energy from the light-harvesting system to mimic the whole photosynthetic process.

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Conflict of interest

The authors declare no conflict of interest.

Keywords

cage compounds; cross-coupling; hydrogen evolution reaction; light harvesting; photocatalysis

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*P*hotosynthesis,[1] as the primary source for the fuel on earth, is a process by which living plants and bacteria absorb, capture, transfer, and store energy from the sun. In this process, the energy from sunlight is captured and funneled by a dense array of chlorophyll molecules to the reaction center, and then converted into chemical energy.[2] So far, many artificial light-harvesting systems mimicking this process have been developed by using a Föster resonance energy-transfer (FRET) process, with the aim of developing clean and sustainable energy.[3-5] Among them, supramolecular systems[5] have received considerable attention not only because of their tunable and functionable molecular structures but also because the energy transfer between chlorophyll and protein in natural systems also relies on supramolecular self-assembly. For example, Yang et al. developed a highly efficient light-harvesting system based on the self-assembly of organic nanocrystals.[5b] Wang, Hu, and co-workers reported light-harvesting systems formed by water-soluble pillar[6]arene-based host-guest interactions.[5g] However, most of these systems just mimicked the FRET process of natural systems. The use of the output energy for photo-catalytic reactions has been rarely addressed. As natural photosynthetic systems also use the transferred energy for chemical reactions, artificial light-harvesting systems with the ability to catalyze chemical reactions for storing and releasing chemical energy are urgently needed.

Metal-organic cages and metallacages[6] represent three-dimensional cagelike structures formed by metal-coordination-driven self-assembly. With precisely controlled inner cavities, such fascinating structures have been widely studied in the past three decades for guest encapsulation, catalysis, and stabilizing reactive intermediates, etc.[7] Recently, Stang et al. developed a series of emissive metallacages[8] through the incorporation of tetraphenylethylene (TPE) derivatives as the building blocks. These metallacages exhibited aggregation-induced emission (AIE) properties[9] because of the restriction of molecular motions that decrease the nonradiative decay. In artificial light-harvesting systems, thousands of donor molecules are generally used for a single acceptor, and may cause fluorescence quenching by dye aggregation. Therefore, the use of AIE-active fluorophores as the donor molecules offers an alternative strategy to avoid the fluorescence quenching upon aggregation and increase the efficiency of light-harvesting systems.

Based on the above discussions, it is inferred that the TPE-based metallacages may behave as good donor molecules for light-harvesting systems because of their highly emissive and AIE-active nature. Through the self-assembly of TPE-based sodium benzoate ligands (**1**), the dipyridyl ligand **2a** or **2b**, and *cis*-Pt(PEt$_3$)$_2$(OTf)$_2$ (**3**), the metallacages **4a** and **4b**, respectively, were prepared in good yields (Scheme 1). Although the inner framework of the metallacages is hydrophobic, the introduction of eight poly(ethylene glycol) (PEG) chains affords **4b** with good solubility in water (> 15.0 mM). This feature allows us to use it as the donor molecule for the FRET process in aqueous light-harvesting systems. By the further self-assembly of **4b** with eosin Y, which serves as the acceptor molecule, through hydrophobic interactions, an efficient light-harvesting system was successfully constructed

in water. Because of the intense absorption of **4b** in the ultraviolet (UV) region, the light-harvesting system can not only use visible light but also exploit UV light through FRET to activate eosin Y, making it exhibit enhanced photocatalytic activity relative to eosin Y alone. For example, the conversions and yields increased twofold in the cross-coupling hydrogen evolution reaction[10] between benzothiazole and diphenylphosphine oxide (Scheme 2) upon irradiation by a Xe lamp. This study offers an example where the output energy of a supramolecular light-harvesting system can be used for chemical synthesis, which is another step towards artificial photosynthesis.

The formation of **4a** and **4b** was confirmed by multi-nuclear NMR spectroscopy (^{31}P{^{1}H} NMR and ^{1}H NMR) and electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS). As depicted in Figures 1a-c, the ^{31}P{^{1}H} NMR spectra displayed two doublets of equal intensity with concomitant ^{195}Pt satellites at δ = 5.54 and 0.32 ppm for **4a**, δ = 5.45 and 0.31 ppm for **4b**, revealing the formation of charge-separated metallacages.[8] In the ^{1}H NMR spectra, significant downfield shifts were observed for α-pyridyl protons H^1 (from δ = 8.61 to 8.92 ppm) and β-pyridyl protons H^2 (from δ = 7.72 to 8.06 ppm; Figures 1e,f), as compared with the free dipyridyl ligand **2a**, because of the coordination of the pyridyl moieties to the Pt^{II} ions. Analogous downfield shifts were also observed for **4b**, as α-pyridyl protons H^7 shifted from δ = 8.65 to 8.95 ppm and β-pyridyl protons H^8 shifted from δ = 7.75 to 8.09 ppm (Figures 1 g,h). Ethoxy protons H^4 and H^5 of **4a** and H^{10} and H^{11} of **4b** shifted upfield, and is probably due to the shielding effect of the cage. ESI-TOF-MS affirmed the presumptive stoichiometry of **4a** by showing isotopically well-resolved peaks at *m/z* = 2407.7954, 1768.7821, 1385.1743, 1129.1058 and 809.5500 (Figure 1d; see Figure S9 in the Supporting Information), corresponding to [M–3 OTf]$^{3+}$, [M–4OTf]$^{4+}$, [M–5OTf]$^{5+}$, [M–6OTf]$^{6+}$ and [M–8OTf]$^{8+}$, respectively. Although all the attempts to get the ESI-TOF-MS of **4b** failed, probably because of the polydispersity of PEG chains along with multiple charge states, we can compare the ^{31}P{^{1}H} NMR and ^{1}H NMR spectra of **4a** and **4b** to conclude that both the metallacages were successfully prepared.

The photophysical properties of **4a** and **4b** in different solvents were collected (see Figure S12). Both cages show an intense absorption peak centered at about 292 nm with a shoulder at 356 nm in almost all the tested solvents, indicating that the solvents have little influence on the absorption. The metallacages **4a** and **4b** are emissive even in dilute solutions because the metal-coordination bonds restrict the rotation of the phenyl groups on the TPE units,[8] thus decreasing the nonradiative decay to give bright emission. It is worth noting that **4b** shows a strong emission peak centered at 511 nm with quantum yield ($Φ_f$) of 23.8% in water. Moreover, similar to previously reported TPE-based metallacages,[8] it is also AIE-active (see Figure S12). These characteristics make it a good energy donor for aqueous light-harvesting systems.

The self-assemblies formed by **4b** in water were studied by transmission electron microscopy (TEM), confocal laser scanning microscopy (CLSM), and dynamic light scattering (DLS) measurements. It can be seen clearly that **4b** forms spherical micelles with an average diameter of 140 nm at 10.0 μM (Figure 2a). Moreover, because **4b** is emissive in water, nanoparticles with bright emission and diameter of 190 nm were visualized by CLSM (Figure 2b). The critical aggregation concentration (CAC) of **4b** was measured to be 8.83 ×

10^{-6} M by plotting the optical transmittance versus the concentration of **4b** at 400 nm (Figures 3c; see Figure S13). DLS measurements showed that **4b** formed large-sized aggregates with averaged hydrodynamic diameters (D_h) of 185 nm (Figure 2d), consistent with the TEM and CLSM results. In the micelles, the hydrophobic inner framework of **4b** forms the core and the PEG chains form the corona, and they further assembled into spherical nanoparticles through hydrophobic interactions (Scheme 2).

Eosin Y was used as the acceptor for **4b** to construct an aqueous light-harvesting system because the absorption of eosin Y overlaps well with the emission of **4b** in water (Figure 3a). With the gradual addition of eosin Y to the aqueous solution of **4b**, the emission intensity at 511 nm, derived from **4b**, decreased, while a new emission band at 550 nm, ascribed to eosin Y, appeared and increased when excited at 365 nm (Figure 3b). These phenomena suggested that efficient energy transfer took place from **4b** to eosin Y. This process was also evidenced by the images taken by CLSM. When the light-harvesting system was irradiated at 405 nm, a FRET process took place from **4b** to eosin Y, therefore some red nanoparticles derived from eosin Y were observed even though eosin Y itself cannot be excited at 405 nm (Figure 3c; see Figure S14). The fluorescence decay measurements were also carried out to study the light-harvesting process. The fluorescence lifetime (τ) of the assembly formed by **4b** and eosin Y ($\tau_1 = 2.45$ ns, $\tau_2 = 5.69$ ns) was shorter than that of **4b** ($\tau_1 = 2.76$ ns, $\tau_2 = 6.30$ ns), giving more evidence for the efficient energy transfer from **4b** to eosin Y.[5] When the molar ratio of **4b**/eosin Y is 20, the energy-transfer efficiency reached 45%, which is comparable to previously reported supramolecular light-harvesting systems in aqueous solution.[5g]

It is known that eosin Y can be used as a photosensitizer to catalyze C–H arylation of heteroarenes and cross-coupling hydrogen evolution reactions.[10] To use the output energy to mimic the whole photosynthetic process, we employed the above light-harvesting system as a photocatalyst for the cross-coupling reaction between benzothiazole (**5**) and diphenylphosphine oxide (**6**) in water. For eosin-Y-based photocatalytic reactions, green light or visible light is generally used as the light source[10b] because eosin Y shows little absorption in the UV region. However, in our system, because **4b** exhibits strong absorption in the UV region, it can serve as an antenna to transfer the energy from the UV light to eosin Y, indicating that we can directly use solar light (here we used Xe lamp as the solar light simulator) to trigger the photocatalytic reaction. As shown in Figures 4 a and b, both the conversion of **5** and the yield of **7** increased dramatically by using the light-harvesting system compared with those of eosin Y alone. After a 12 hour reaction, the conversion of **5** reached 88% and the yield of **7** reached 65% when using the light-harvesting system as the photocatalyst. In comparison only 40% conversion and 33% yield were obtained by using eosin Y alone. Nearly no catalytic activity was observed for **4b**. The FRET process increases the number of excited photocatalysts (eosin Y*) which undergo the catalytic cycle (Figure 4c) to increase the catalytic activity. Meanwhile, hydrogen was produced by the combination of dissociated hydrogen radicals, offering a pathway to store the energy from the light. Moreover, the photobleaching effect of eosin Y upon long-time irradiation was also decreased because of the formation of supramolecular micelles, which trap eosin Y and protect it from the damage of trace singlet oxygen.[11] All these results suggest that a light-

harvesting system with good ability to catalyze organic reactions in water was successfully constructed. We believe that this strategy can also be applied in other light-harvesting systems to increase the photocatalytic activities of dye photosensitizers.

In summary, two TPE-based tetragonal prismatic platinum(II) cages were prepared and characterized by ^{31}P NMR and ^{1}H NMR spectroscopy, ESI-TOF-MS, UV absorption, and fluorescence spectroscopy. By the incorporation of PEG chains on the pillars of the metallacage, it exhibits good water-solubility and is highly emissive in water. The metallacage was further used as an energy donor for eosin Y to prepare an efficient light-harvesting system in water through a FRET process. More importantly, the light-harvesting system shows good photocatalytic activity for cross-coupling hydrogen evolution reaction, offering the products in yields almost twofold that of using eosin Y alone. This study not only gives a type of metallacage-based structure as an energy donor for the construction of efficient light-harvesting systems, but also utilizes the output energy for photocatalytic reactions to prepare useful hydrocarbons and release gas, and will pave the way for the fabrication of artificial photosynthetic systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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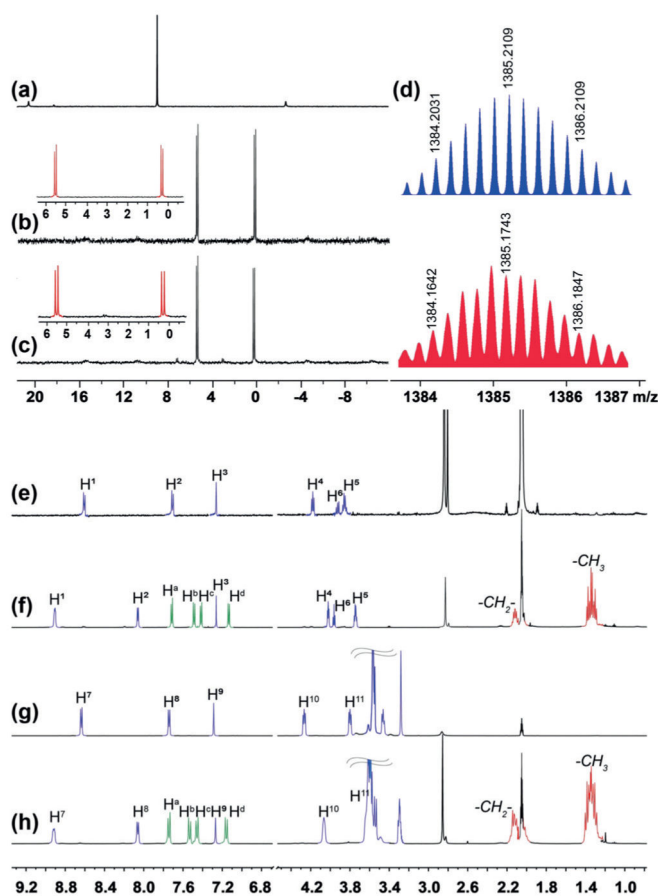[11]. DeRosa MC, Crutchley RJ, Coord. Chem. Rev 2002, 233–234, 351–371.

Figure 1.
Partial ^{31}P {^1H} NMR spectra (121.4 MHz, CD$_3$COCD$_3$, 295 K) of **3** (a), **4a** (b), and **4b** (c).
d) Experimental (red) and calculated (blue) ESI-TOF-MS spectra of **4a**: [M-5OTf]$^{5+}$. Partial
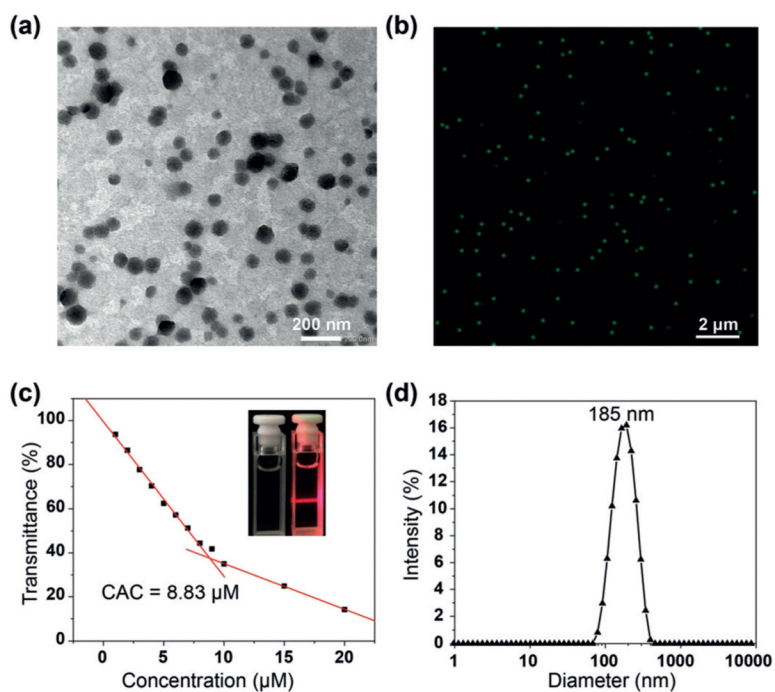^1H NMR spectra (400 MHz, CD$_3$COCD$_3$, 295 K) of **2a** (e), **4a** (f), **2b** (g), and **4b** (h).

Figure 2.
a) TEM and b) CLSM images of **4b** in water ($c = 10.0$ μM, $\lambda_{ex} = 405$ nm). c) Concentration-dependent optical transmittance at 400 nm of **4b** in water. Inset: Tyndall effect of **4b** in water ($c = 10.0$ μM). d) DLS data of **4b** in water ($c = 10.0$ μM).
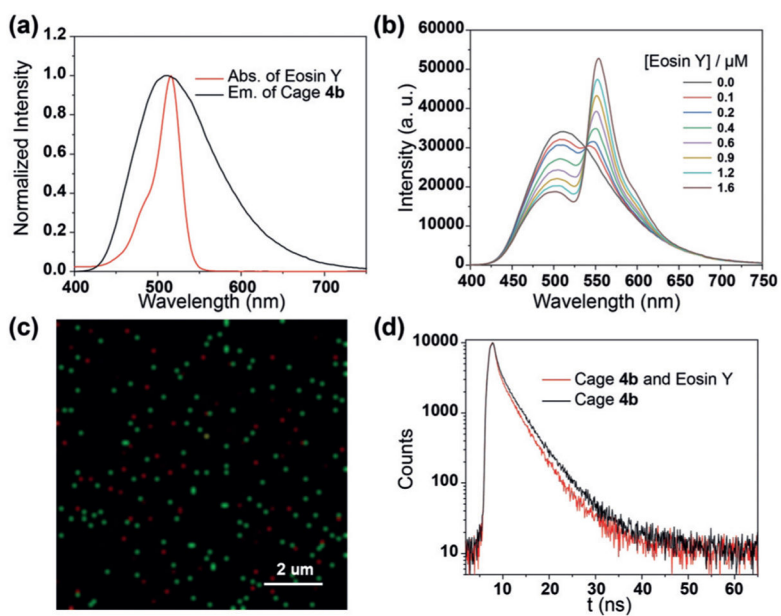
Figure 3.
a) Normalized absorption spectrum of eosin Y and emission spectrum of **4b**. b)
Fluorescence spectra of **4b** ($c = 30.0$ μM) in water with different concentrations of eosin Y
($\lambda_{ex} = 365$ nm). c) CLSM image of **4b** ($c = 10.0$ μM) and eosin Y ($c = 5.0$ μM) in water (λ_{ex}
= 405 nm). d) Fluorescence decay profiles of **4b** (blank line), **4b** and eosin Y (red line).
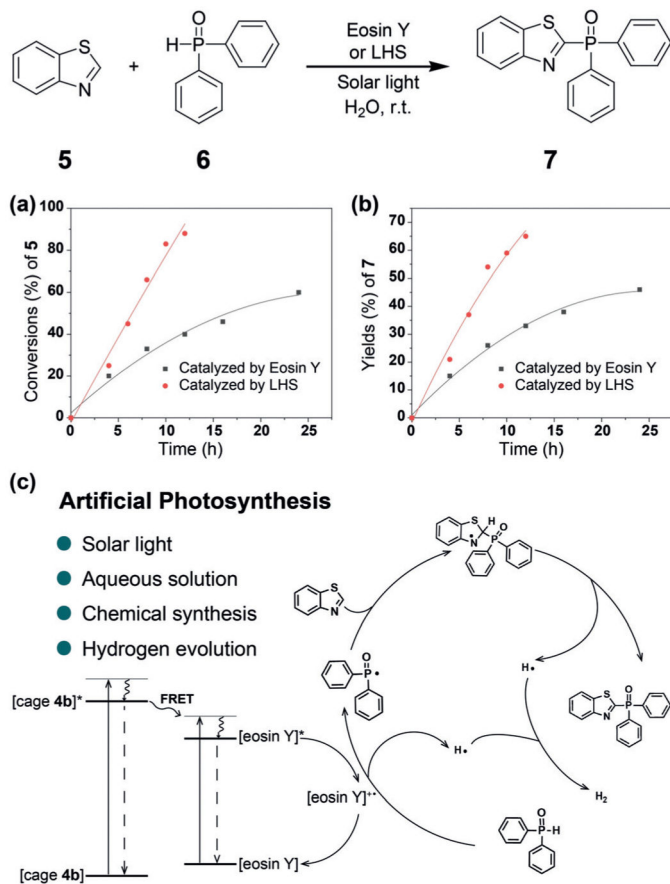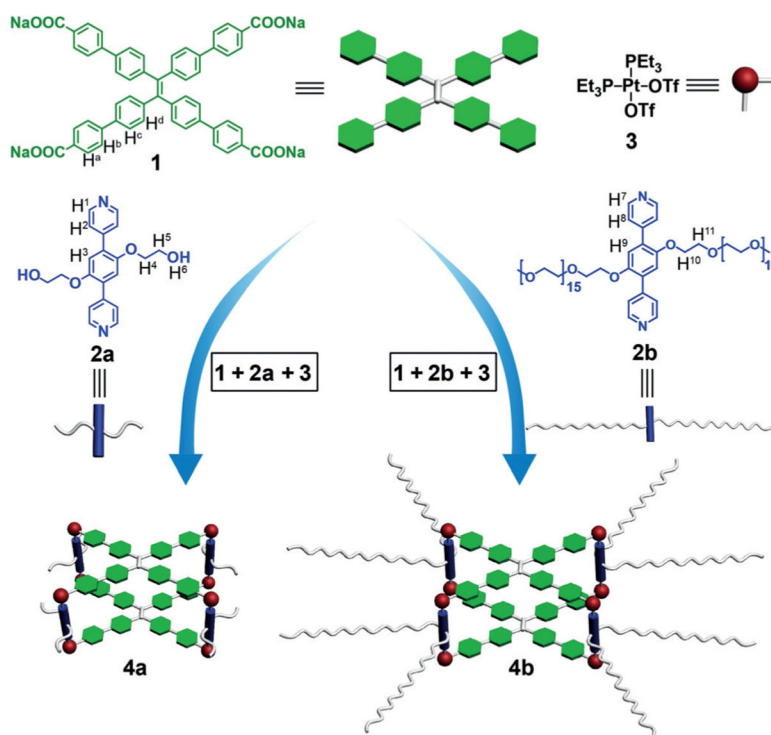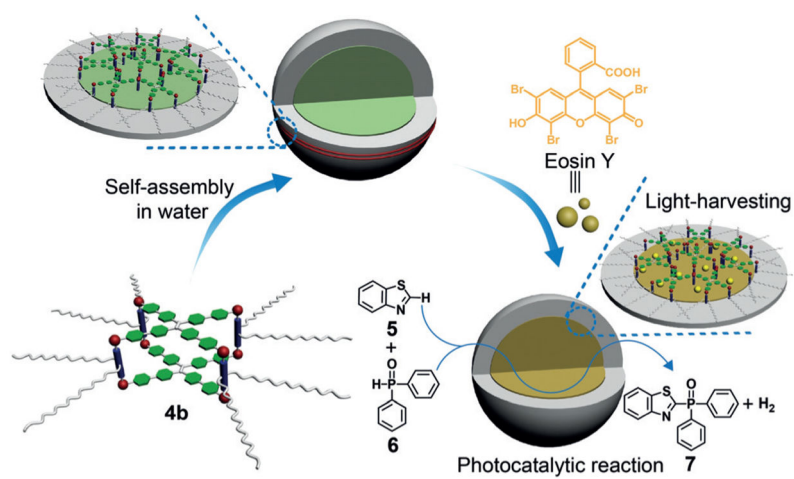([**4b**] = 30.0 μM, [eosin Y] = 1.6 μM).

Figure 4.
a) Conversions of **5** versus reaction time. b) Yields of **7** versus reaction time. c) Plausible mechanism of cross-coupling hydrogen evolution reaction using LHS as photocatalyst. LHS = light-harvesting system.

Scheme 1.
Self-assembly of the metallacages **4a** and **4b**. Tf = trifluoromethanesulfonyl.

Scheme 2.
Cartoon representations of the light-harvesting system and its application in a photocatalytic reaction.