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1. Introduction

Artificial light-harvesting systems with light-harvesting and energy transfer ability have received increasing attention due to their key role in photosynthesis and optoelectronic devices.¹ Since the fluorescent donor and acceptor molecules that construct the supramolecular organization are important parameters in these photophysical processes, a variety of multichromophoric scaffolds have been reported based on supramolecular chemistry in which fluorophore molecules are confined in a matrix.² Although effective excitation-energy transfer could be achieved through these systems, the application of organic fluorophores in light-harvesting systems is restricted due to their inherent narrow spectral window for light-collection and poor photostability.³

As highly prospective light harvesting materials, inorganic nanocrystals or quantum dots (QDs) have received tremendous

Embedding CsPbBr₃ quantum dots into a pillar[5] arene-based supramolecular self-assembly for an efficient photocatalytic cross-coupling hydrogen evolution reaction[†]

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Light-harvesting is a key step in photosynthesis, but it is still a challenge to create an efficient artificial light harvesting system in a broader solar spectrum to mimic natural processes. Here, we have fabricated, for the first time, a highly efficient artificial light-harvesting system through directly embedding CsPbBr₃ quantum dots (QDs) inside a supramolecular self-assembly of thymine functionalized-pillar[5]arene (PTY) and an eosin Y-based derivative (EYB). The donor CsPbBr₃ QDs exhibit a broad spectral absorption in the UV-visible range, and their emission shows good spectral overlap with the absorption of EYB, thus effective excitation energy is transferred from CsPbBr₃ to the acceptor EYB with an energy transfer efficiency of 96.5%. Importantly, the combination displayed excellent photocatalytic activity in cross-coupling hydrogen evolution reactions, and the product yield was more than 2.5 times that obtained using eosin Y alone. Our research opens up a new avenue for utilizing perovskite QDs with broad spectral absorption as the energy donor to construct efficient light-harvesting systems for solar energy conversion.

interest because they can absorb light across a wide spectral window.⁴ Among them, there is growing interest in the utilization of perovskite QDs as light harvesting materials due to their high extinction coefficient, high quantum yield, broad spectral absorption, and the potential for hot electron injection and multiple exciton generation, which can enhance the light capturing ability of organic dyes (the acceptor) through the fluorescence resonance energy transfer (FRET) process.⁵ However, using perovskite QDs as an energy donor to construct highly efficient artificial light harvesting systems to mimic chlorosomes is still a challenge.

Pillar[*n*]arenes, as a type of pillar-shaped macrocyclic hosts, have undergone a rapid development in the area of supramolecular chemistry because of their symmetrical architecture, unique rigid, and easily modified properties.6 The electron-rich cavity and different kinds of driving forces that lead to the formation of self-assemblies⁷⁻⁹ have enabled pillar[n]arenes to be successfully used in the construction of a variety of interesting supramolecular systems, such as nanotheranostics, chemosensors, molecular machines, and supramolecular polymers.10 More importantly, the various driving forces also provide good opportunities to construct a tunable supramolecular artificial light-harvesting system.11 We envisaged that rational introduction of perovskite QD donors and organic dye acceptors into pillar[n]arene-based supramolecular polymers could pave the way for the construction of a highly efficient artificial light-harvesting system.

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Fig. 1 Graphical representation of the self-assembly and photocatalytic hydrogen evolution reaction process of the supramolecular polymer $CsPbBr_3@PTY \supset EYB$.

In this study, we present a novel and efficient method to construct a highly efficient light-harvesting system by introducing lead-containing luminescent perovskite QDs into the supramolecular self-assembly of PTY and EYB for the crosscoupling hydrogen evolution reaction (Fig. 1). In such a system, EYB as a guest molecule could self-assemble with PTY through host-guest interaction. The supramolecular selfassembly of PTY⊃EYB contains a thymine moiety, which acts as a coordination site for Pb²⁺ ion to further form CsPbBr₃ QDs. The CsPbBr₃ QDs confined into the interlayer of PTY⊃EYB help overcome the daunting but long-term unsolved issue of selfquenching. In addition, the hydrophobic CsPbBr₃ QDs as good donors were loaded into the hydrophobic PTY⊃EYB assembly, thereby achieving an efficient energy transfer process from CsPbBr₃ QDs to the nearby receptor EYB. As a result, the resulting CsPbBr₃@PTY⊃EYB could be successfully applied in the photocatalytic cross-coupling hydrogen evolution reaction. To our knowledge, this is the first report on a light harvesting system based on luminescent perovskite QDs.

2. Results and discussion

Schemes S1 and S2[†] show the detailed synthesis procedure of compounds PTY and EYB. PTY was synthesized by sensibly connecting a pillar[5]arene group and thymine group *via* an alkyl chain. EYB was obtained by the nucleophilic substitution reaction between eosin Y and 1,4-dibromobutane. The obtained products were characterized by ¹H NMR and ESI-MS (Fig. S1–S6[†]), respectively. The PTY⊃EYB assembly was formed by simply mixing equimolar PTY and EYB in DMF, and then PbBr₂

was added to the above PTY⊃EYB assembly to obtain Pb²⁺@PTY⊃EYB. A solution of Cs-oleate was added to the toluene dispersion containing Pb²⁺@PTY⊃EYB and vigorously stirred, resulting in the formation of CsPbBr₃@PTY⊃EYB. The self-assembly process of PTY⊃EYB was confirmed from the ¹H NMR spectrum. As shown in Fig. S7,† when equal amounts of PTY and EYB were mixed in CDCl₃ solution, the phenyl proton H_a from PTY shifted downfield (Fig. S7b†), while the peaks of the alkyl proton H₁ and H₂ in EYB shifted greatly towards the upfield region ($\Delta \delta = -0.53$ and -0.30 ppm, respectively), which was due to the shielding effect of the pillar[5]arene with



Fig. 2 Partial ¹H NMR spectra (400 MHz, 298 K) of Pb²⁺@PTY⊃EYB in DMSO-d₆ at various concentrations: (a) 10.0 mg mL⁻¹, (b) 20.0 mg mL⁻¹, (c) 40.0 mg mL⁻¹, and (d) 60.0 mg mL⁻¹ (e) 80.0 mg mL⁻¹.



Fig. 3 (a) XRD diagrams of CsPbBr₃@PTY \supset EYB, CsPbBr₃, and PTY \supset EYB; (b) FT-IR spectra and (c) XPS spectra, (d) TEM images of CsPbBr₃@PTY \supset EYB with different magnifications; (e) HAADF image and the corresponding STEM-EDS elemental mapping images of C, N, O, Br and Pb in CsPbBr₃@PTY \supset EYB.

electron-rich cavities.^{11a} The above observations indicated that there were interactions between the alkyl moieties in EYB and the cavities of PTY, which led to the formation of the pseudorotaxane PTY⊃EYB.¹¹ As shown in Fig. S8,† as the concentration of PTY \supset EYB increased, the signals of protons H_{1,2} on the alkyl chain and H_{5,6} on xanthene groups of EYB underwent substantial upfield shifts, indicating that host-guest interactions and π - π stacking interactions between the xanthene groups were enhanced during the self-assembly process.^{12a} Meanwhile, the signal of proton H_e also exhibited significant downfield shift, indicating the intermolecular hydrogen bond interactions. From the FT-IR spectra (Fig. S9[†]), the vibration absorption peaks of -NH and -C=O in PTY appeared at 3348 and 1674 cm⁻¹, respectively. However, after the formation of the PTY⊃EYB assembly, the vibration absorption peaks of -NH shifted to 3320 cm⁻¹, and the peak of -C=O split into two peaks at 1669 and 1772 cm⁻¹, respectively (Fig. S9[†]).¹² The above results indicated that there were stable intermolecular hydrogen bonds (-N-H···O=C-) on adjacent molecules.

Next, we examined the binding of Pb^{2+} with the thymine moieties of PTY through ¹H NMR titration experiments in DMSO-*d*₆. As shown in Fig. S10,† the signal of the imide proton gradually shifted upfield as the concentration of Pb^{2+} was increased. In addition, the ¹H NMR of Pb^{2+} @PTY \supset EYB also offered important evidence for its self-assembly behavior. Fig. 2 shows that the signals of protons H_d also exhibited significant upfield shifts with increasing concentration of Pb^{2+} @PTY, indicating that strong coordination occurred with increase of concentration.^{13a} At the same time, the signals of protons H₅ and H₆ on EYB groups underwent large field shifts, indicating π - π stacking interactions between the xanthene groups. In addition, a peak at $2\theta = 23.47^{\circ}$ corresponding to a *d*-spacing of 3.78 Å was observed in the XRD pattern of PTY⊃EYB (Fig. 3a and S11[†]), further confirming the existence of π - π stacking in xanthene groups.¹² The coordination between Pb²⁺ and the N atom of amide (-NH) was also confirmed by FT-IR spectra. As shown in Fig. 3b, when PTY coordinated with Pb²⁺, the stretching vibration absorption peaks of imide (-NH) shifted from 3348 to 3320 cm⁻¹, and a new absorption peak appeared at 415 cm⁻¹ (Fig. S12b^{\dagger}), further indicating that the N–Pb²⁺–N coordination bond was formed.5a Meanwhile, the XPS survey spectra in Fig. 3c reveal that Pb was present only in the $\text{Pb}^{2+}(\text{PTY} \supset \text{EYB} \text{ sample. The binding energy of Pb } 4f_{7/2} \text{ and Pb}$ 4f_{5/2} peaks appeared at 138.7 and 143.5 eV, respectively (Fig. S13b[†]), indicating the existence of Pb^{2+.5} In the N 2p XPS spectrum, the peak of N 2p moved from 399.4 eV in the case of PTY \supset EYB to 399.6 eV for Pb²⁺@PTY \supset EYB (Fig. S13a⁺), indicating that the N atom was coordinated with Pb²⁺.5b For the determination of the stoichiometry between PTY and Pb²⁺, Job's plot analysis was used. In this method, the total concentration of PTY and Pb^{2+} was kept at 10.0 μ M, and the molar ratio of Pb^{2+} $(X_M: X_M = [Pb^{2+}]/{[PTY] + [Pb^{2+}]})$ was changed from 0 to 1. Fig. S13[†] shows that the molar fraction of Pb²⁺ was 0.33, indicating the formation of a 2:1 complex between PTY and Pb²⁺ (Fig. S14[†]).^{13b}

Moreover, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that the morphology changed from a fibrous shape in the case of PTY⊃EYB to multilayer nanosheets in the case of the formed Pb²⁺@PTY⊃EYB (Fig. S15†). As we all know, the H bond energy in most systems is usually within 10–40 kJ mol⁻¹, which is much lower than that of the coordinate bond (90– 350 kJ mol⁻¹).¹⁴ Therefore, when a certain amount of Pb²⁺ ions are added to the PTY⊃EYB assembly, the metal coordination bond replaces the H bond interaction, forming a stable metal coordination polymer gel (Fig. S16†).

In situ confined growth of CsPbBr₃ QDs into the PTY⊃EYB assembly to form CsPbBr₃@PTY⊃EYB was carefully investigated via SEM, TEM, and XRD. As shown in Fig. S14c,† SEM image showed that the formed CsPbBr₃@PTY⊃EYB was a multilayer sheet structure, and the layer thickness of CsPbBr₃@PTY⊃EYB significantly increased compared with PTY \supset EYB (Fig. S15[†]). TEM image showed that the CsPbBr₃ QDs with an average diameter of 3 nm were inserted into the sheet structure (Fig. 3d and S15f[†]). HRTEM image (Fig. 3d) showed that interplanar distances of 0.29 nm matching the spacing of the CsPbBr₃ (200) crystal surface could be easily identified. The elemental mapping (Fig. 3e) showed that Pb, C, N, O, and Br were evenly distributed in the multilayer nanosheet, which was further confirmed by EDS analysis (Fig. S17[†]). The XRD data (Fig. 3a) showed that CsPbBr₃@PTY⊃EYB had both the diffraction peaks of PTY⊃EYB at 23.47° and the diffraction peaks of CsPbBr3 QDs at 14.9°, 30.1° and 33.9°, which confirmed the formation of CsPbBr₃@PTY⊃EYB.⁵

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Generally, when there is an overlap between the absorption band of the acceptor and the emission band of the donor, energy transfer from the donor to the acceptor occurs in the light-harvesting system. Fig. 4a shows that there was a clear overlap between the absorption band of eosin Y and the emission band of CsPbBr₃ QDs. Under the excitation of 360 nm, only CsPbBr₃ QDs emitted strong fluorescence, while eosin Y almost did not give any fluorescence signal (Fig. S18a⁺) because there is no absorption centered at 360 nm (Fig. S18b[†]). When CsPbBr₃@PTY⊃EYB was formed, the emission peaks of both CsPbBr₃ QDs and EYB were simultaneously observed (Fig. S18c[†]). Since EYB itself has no detectable fluorescence signal under 360 nm excitation (Fig. 18c⁺), the fluorescence of EYB in CsPbBr₃@PTY⊃EYB must be due to the energy transfer of CsPbBr₃ QDs. This confirms that CsPbBr₃@PTY⊃EYB displays fluorescence through energy transfer from CsPbBr₃ QDs to EYB even at wavelengths where EYB has little or no absorption.15

As shown in Fig. 4b, when EYB was gradually added to the dispersion of CsPbBr₃@PTY in toluene, the CsPbBr₃@PTY

Fig. 4 (a) Normalized absorption spectrum of eosin Y and emission spectrum of CsPbBr₃; (b) fluorescence spectra of CsPbBr₃@PTY upon excitation at 360 nm before and after the addition of EYB. The inset photographs show the change in the fluorescence of CsPbBr₃@PTY and after the addition of EYB. (c) Fluorescence decay profiles of CsPbBr₃@PTY (blank line), CsPbBr₃@PTY \supset EYB (red line). (d) Yields of 6 *versus* reaction time. (e) Plausible mechanism of the cross-coupling hydrogen evolution reaction using CsPbBr₃@PTY \supset EYB as the photocatalyst.

(donor) emission at 504 nm decreases, and the EYB (acceptor) emission at 562 nm increases. The above result shows that the FRET occurred from the donor to the acceptor.^{1,2} At a donor/ acceptor ratio of 240 : 1, energy transfer efficiency was calculated to be 96.5% for EYB, showing that CsPbBr₃ QDs are an excellent light collecting antenna. In addition, the fluorescence lifetime decay curve of CsPbBr₃@PTY (Fig. 4c, black line) was fitted as a triple exponential decay with an average lifetime of τ = 8.43 ns (Table S1†). After the formation of CsPbBr₃@PTY⊃EYB (Fig. 4c, red line), the fluorescence lifetimes decreased to τ = 5.34 ns, confirming the energy transfer from the CsPbBr₃ donor to the EYB acceptor.¹⁶

Moreover, based on the fluorescence lifetime decay curve of EYB (Fig. S19†), the average lifetime (τ) of EYB ($\lambda_{ex} = 515 \text{ nm}$) was 0.57 ns (Table S2†). After the formation of CsPbBr₃@-PTY⊃EYB (Fig. S19b†), the fluorescence lifetimes increased to $\tau = 2.07$ ns. And compared with EYB alone, the average fluorescence lifetime of CsPbBr₃@PTY⊃EYB was significantly increased, providing more evidence for the energy transfer from the CsPbBr₃ donor to the EYB acceptor^{15,16e} Furthermore, as shown in Fig. S20,† when CsPbBr₃@PTY was gradually added to EYB in toluene, the emission intensity of CsPbBr₃@PTY at 504 nm increased, and the emission intensity of EYB at 562 nm also increased. These data further demonstrated that efficient FRET occurred from the donor to the acceptor.¹⁷

Recently, eosin Y has been applied as a photosensitizer to catalyze cross-coupling hydrogen evolution reactions and C-H arylation of heteroarenes.18 Since eosin Y has almost no absorption in the UV region (Fig. S18b[†]), visible light is usually used as the light source in photocatalytic reactions. However, for CsPbBr₃@PTY⊃EYB photocatalytic reactions, sunlight can be directly used as a light source due to the strong absorption of CsPbBr₃ QDs in the UV-vis region (Fig. S18d⁺), in which CsPbBr₃ QDs can act as an antenna to transfer energy from UV light to eosin Y. Therefore, in the photocatalytic cross-coupling reaction between benzothiazole 4a and diphenylphosphine oxide 5 catalyzed by CsPbBr₃@PTY⊃EYB, a Xe lamp simulating sunlight was used as the light source. Fig. 4d and S21[†] show that using CsPbBr₃@PTY⊃EYB could significantly increase the conversion rate of 4a and the yield of 6 compared to using eosin Y alone. After 12 hours of irradiation, the yield of the crosscoupled product 6a was 83% (Table S3[†]). In contrast, eosin Y alone achieved only 33% yield, and no product was detected for CsPbBr₃ (Fig. S22[†]). The H₂ generated in the reaction was detected by gas chromatography, which showed that CsPbBr₃@PTY \supset EYB displayed excellent photocatalytic activity, and the yield of H₂ was more than twice that obtained when eosin Y alone was used (Fig. S23 and S24[†]). However, no product was detected when CsPbBr₃ was used alone (Fig. S25[†]).^{18d}

The cross-coupling reaction between diphenylphosphine oxide **5** and benzothiazole with electron-donating or electron-withdrawing groups was also examined by using CsPbBr₃@-PTY⊃EYB as the photocatalyst. As shown in Table S3,† the yields of the cross-coupled products **6b**, **6c**, and **6d** were 76%, 78%, and 81%, respectively. The high photocatalytic activity of CsPbBr₃@PTY⊃EYB is due to the increased the number of excited photocatalysts (EYB) during FRET process. Meanwhile,



the increased hydrogen yield provides an effective way for the conversion and storage of solar energy in the cross-coupling reaction. In addition, the stability of CsPbBr₃@PTY⊃EYB was studied by XRD and TEM, which is essential for improving the photocatalytic activity of dye photosensitizers. As shown in Fig. S26,† after the photocatalyst reaction was complete, the morphology of CsPbBr₃@PTY⊃EYB was basically maintained, and the frame and composition of CsPbBr₃@PTY⊃EYB were also well maintained. All these results indicate that the CsPbBr₃@PTY⊃EYB light-harvesting system exhibits high efficiency light-harvesting and light-conversion performance.

3. Conclusions

In summary, the first example of a highly efficient artificial light-harvesting system was successfully fabricated based on the in situ confined growth of CsPbBr₃ QDs in the PTY⊃EYB assembly. The donor CsPbBr₃ QDs are used to harvest photons in a broad spectral region, in which EYB has almost no absorption. Therefore, such a combination can transfer energy from CsPbBr₃ QDs with much broader absorption spectra to EYB through an efficient FRET process, and an energy transfer efficiency of 96.5% was achieved. More importantly, in the cross-coupled hydrogen evolution reaction, CsPbBr₃@-PTY > EYB showed excellent photocatalytic activity, and the yield of the product was more than 2.5 times that obtained when eosin Y alone was used. This study not only paves the way for utilizing perovskite QDs as an energy donor to construct efficient light-harvesting systems with greater coverage of the solar spectrum but also offers one interesting possibility for the utilization of perovskite QDs to synthesize useful chemical products and chemical fuels.

4. Experimental section

4.1 Synthesis of PTY

Synthesis of PTY: 3 (300 mg, 0.29 mmol), thymidine derivative (81 mg, 0.44 mmol), 1-(3-dimethylaminopropyl)-3ethylcarbodiimide hydrochloride (84 mg, 0.44 mmol), and 4dimethylaminopyridine (3 mg) were added into dichloromethane (50 mL). Then, the resulting solution was stirred at room temperature for 24 h. The mixture was concentrated at reduced pressure. The crude product was purified by silica column chromatography (dichloromethane/methanol = 30 : 1) to give a white solid (0.24 g, yield: 68%).

4.2 Preparation of supramolecular assembly solutions

The blank PTY \supset EYB assembly solution was prepared as follows: EYB (10 mg) was dissolved in CHCl₃ (10 mL). Subsequently, the above solution was added to the PTY solution (10 mg mL⁻¹) during ultrasonication within 30 s to generate the assembly solutions in CHCl₃.

4.3 Preparation of CsPbBr₃@PTY⊃EYB

A mixture of PTY (100 $\mu L,$ 0.1 m mol), EYB (100 $\mu L,$ 0.1 m mol), and PbBr_2 (10 $\mu L,$ 0.1 m mol) was added to a 7 mL centrifuge

tube under vigorous stirring. Next, 10 μ L Cs-oleate (0.1 mmol, DMF) was slowly added dropwise to the above system to obtain the CsPbBr₃@PTY⊃EYB precursor. Then, a fixed amount of precursor solution was dropped into toluene under vigorous stirring. After that, a yellow-red colloidal solution was formed, indicating that CsPbBr₃@PTY⊃EYB was successfully obtained.

Conflicts of interest

There are no conflicts to declare.

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