



# Construction of artificial light-harvesting system based on host-guest interactions of sulfobutylether- $\beta$ -cyclodextrin and its application in photocatalysis<sup>☆</sup>



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## ABSTRACT

Light-harvesting systems (LHSs) play an important role in natural photosynthesis for converting light energy into chemical energy, which paves a prospective way for the exploitation of renewable energy resources. In this work, two artificial light-harvesting systems with an efficient energy transfer were constructed successfully in the aqueous media based on sulfobutylether- $\beta$ -cyclodextrin ( $\beta$ -CD) and curcumin (Cur) through host-guest interactions, in which two different fluorescence dyes, sulforhodamine (SR101) and Nile blue (NiB) were employed as energy acceptors. The obtained artificial LHSs can achieve an efficient energy transfer process from  $\beta$ -CD + Cur to SR101 or NiB with energy transfer efficiencies of up to 16.3% and 15.8%, respectively. The energy harvested by the acceptors (SR101 and NiB) was used for photocatalysis in the aqueous phase dehalogenation of the  $\alpha$ -bromoacetophenone reaction with a yield of up to 80%.

## 1. Introduction

Green plants convert solar light into chemical energy through photosynthesis, which is the basis for living things to survive in nature [1–3]. Photosynthesis mainly depends on the absorption of photons by the contained LHSs, which effectively transfers excitation energy to the acceptor dye molecules in the reaction center through electron transfer or energy transfer, triggering a series of redox reactions [4]. This process has inspired many scientists, so the construction of various artificial LHSs by simulating the process of photosynthesis is gradually coming into people's view. After decades of development, various artificial LHSs based on non-covalent interactions including hydrogen bonding [5–9], coordination-induced self-assembly [10–14], supramolecular polymers [15–21], micelles [22–28] or vesicle [29,30], liquid crystal [31], electrostatic interaction [32–35] and host-guest interactions [36–41,49] have been constructed, in which the solar energy can be efficiently transferred. For example, Liu et al. reported an artificial light-harvesting

supramolecular assembly with the host-guest interaction by using poly-anionic  $\gamma$ -cyclodextrin (COONa- $\gamma$ -CD), pyrene derivative (PYC12), Nile red (NiR), and diarylethene derivative (DAE) in aqueous solution [42]. Then, in 2020, Liu et al. synthesized a novel triazole bridging cucurbituril (CB)-cyclodextrin (CD) dimer and constructed a stable supramolecular inclusion complex with high-efficiency fluorescence resonance energy transfer [43]. Subsequently, Liu et al. reported an efficient artificial light-harvesting system based on sulfato- $\beta$ -cyclodextrin, an oligo(phenylenevinylene) derivative (OPV-I), and a fluorescent dye, Nile red (NiR), via noncovalent interactions in the aqueous solution [36]. However, the mentioned above processes in the construction of artificial LHS all used strong fluorescent groups as energy donors or by other means, and the synthesis of fluorescent molecules required complex synthesis and separation processes. Therefore, it is a good strategy to construct artificial LHS through host-guest interaction and electrostatic interaction by using the hydrophobic cavity of sulfobutylether- $\beta$ -cyclodextrin ( $\beta$ -CD) to encapsulate hydrophobic dye as an energy donor.

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At the same time, based on constructing artificial LHSs for energy transfer, scientists have studied its application in the field of photocatalytic organic reactions, including dehalogenation of  $\alpha$ -bromoacetophenone [44–46], cross-dehydrogenation coupling (CDC) reaction [47], alkylation of C-H bonds [34,35], photooxidation reaction of sulfide [48] and so on. Therefore, it is a good research strategy to apply our constructed artificial LHSs based on fluorescent dyes to the photocatalytic reactions mentioned above.

Herein, the anionic highly water-soluble sulfobutylether- $\beta$ -cyclodextrin ( $\beta$ -CD) was utilized to construct high-efficiency artificial LHSs by reducing the distance between energy donors (Cur) and energy acceptors (SR101 and NiB) through host-guest interactions, which can also be successfully used in the photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone in the aqueous phase (Scheme 1). After a series of tests including the zeta potential test and steady-state spectra test,  $\beta$ -CD + Cur was used as energy donors with cooperative energy level matching fluorescent dyes (SR101 and NiB) to construct two  $\beta$ -CD + Cur-based artificial LHSs with the efficient energy transfer process. Then, the fluorescence quantum yields of the two  $\beta$ -CD + Cur-based artificial LHS ( $\beta$ -CD + Cur + SR101 and  $\beta$ -CD + Cur + NiB) were obtained respectively, which ensured the efficient transfer of light energy. Subsequently, to further use the energy harvested by the energy acceptors, we applied the  $\beta$ -CD + Cur-based artificial LHSs for photocatalysis dehalogenation of  $\alpha$ -bromoacetophenone in the aqueous solution.

## 2. Experimental

### 2.1. Materials

Unless specifically mentioned, all chemicals are commercially available and were used as received.

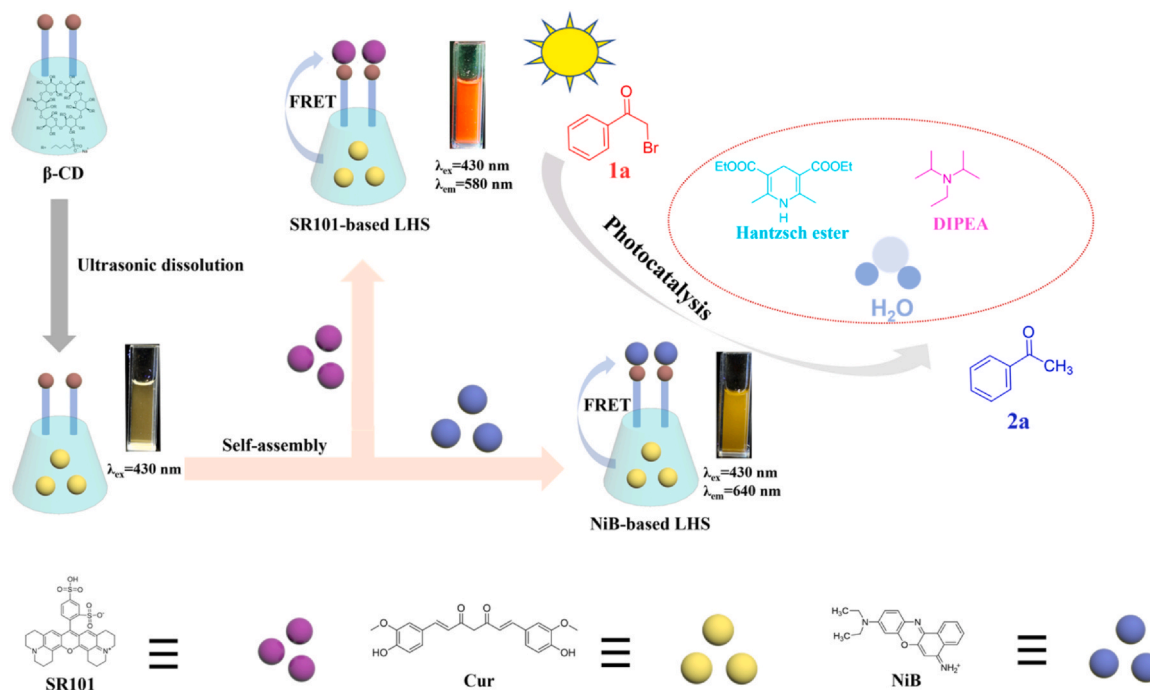
### 2.2. Characterizations

$^1\text{H}$  NMR was characterized by the Bruker Avance 400 NMR instrument. Shimadzu UV-2450 spectrophotometer characterized the UV–vis

absorption spectra. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. Dynamic light scattering (DLS) and Zeta potential tests were constructed on Malvern Zeta sizer Nano ZS90. Transmission electron microscopy (TEM) images were obtained on a JEM 2100 operating at 200 kV. Samples for TEM measurements were prepared by dropping the mixed ethanol solution on the microgrid (diameter: 3 nm) and drying by slow evaporation. Fluorescence decay curves were carried out on an FLS920 Edinburgh spectrometer. The fluorescence quantum yields were characterized by Hamamatsu absolute quantum yield measuring instrument Quantaury-QY.

## 3. Results and discussion

Sulfobutylether- $\beta$ -cyclodextrin ( $\beta$ -CD) has a hydrophobic cavity, which allows it to hold hydrophobic fluorescent dyes into the cavity to exhibit photophysical properties. Because  $\beta$ -CD has good water solubility, it can be dissolved in an aqueous solution with a negative potential of  $-23.9$  mV (Fig. 1a). Then, we selected a hydrophobic fluorescent dye curcumin (Cur), which can be transferred into the cavity of  $\beta$ -CD in the aqueous solution ( $5.0 \times 10^{-5}$  M) by ultrasound. The steady-state spectral property results of  $\beta$ -CD and  $\beta$ -CD + Cur solution showed that the  $\beta$ -CD solution alone did not have absorption and emission in the aqueous solution. However, after the addition of Cur, the  $\beta$ -CD + Cur showed an absorption peak at 440 nm and an emission peak with light-yellow fluorescence at 540 nm (Fig. S1), indicating that the Cur successfully entered into the hydrophobic cavity of  $\beta$ -CD. Meanwhile, the zeta potential changed from  $-23.9$  mV to  $-23.6$  mV after the addition of Cur (Fig. 1b). Moreover, dynamic light scattering (DLS) was employed to further investigate the self-assembly properties of  $\beta$ -CD and  $\beta$ -CD + Cur. It can be seen that  $\beta$ -CD exhibited an aggregate with a particle size at  $\sim 200$  nm (Fig. 1c). After the addition of Cur, the particle size increased to  $\sim 230$  nm (Fig. 1d), indicating that the Cur was entered into the hydrophobic cavity of  $\beta$ -CD. Meanwhile, under the irradiation of a laser lamp,  $\beta$ -CD and  $\beta$ -CD + Cur both showed an obvious Tyndall effect, indicating the formation of large aggregates.



Scheme 1. Schematic diagram of artificial LHSs with efficient energy transfer process based on  $\beta$ -CD and Cur.

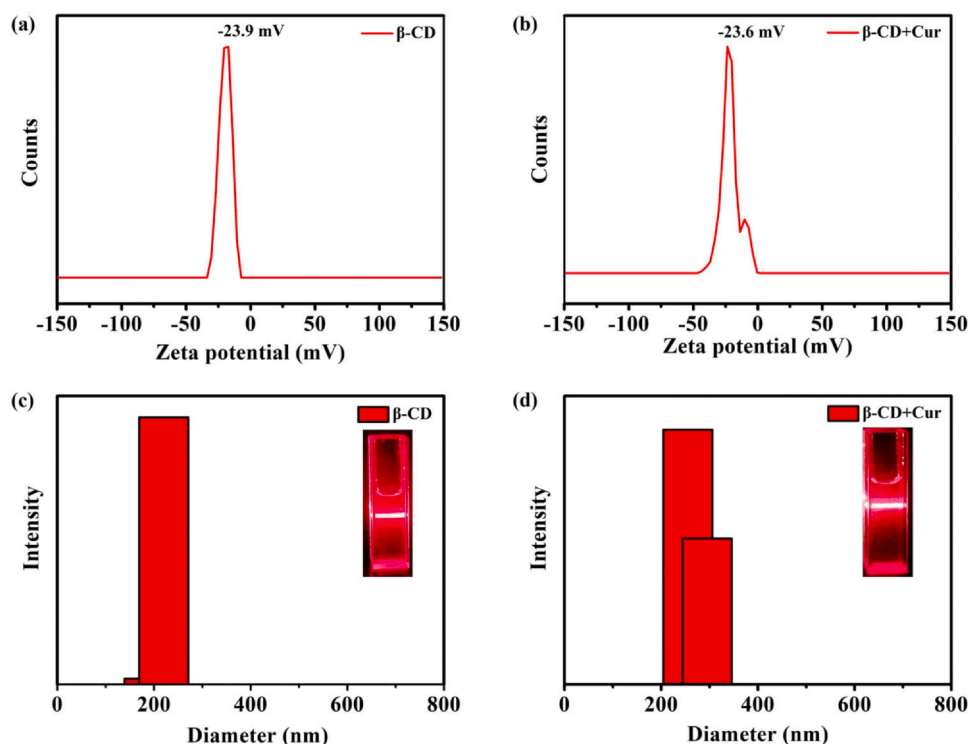


Fig. 1. Zeta potentials of  $\beta$ -CD (a) and  $\beta$ -CD + Cur (b); Particle size of  $\beta$ -CD (c) and  $\beta$ -CD + Cur (d). Inset: photographs of  $\beta$ -CD and  $\beta$ -CD + Cur.  $[\beta\text{-CD}] = 5.0 \times 10^{-5}$  M,  $[\text{SR101}] = 5.0 \times 10^{-5}$  M,  $[\text{NiB}] = 3.75 \times 10^{-5}$  M.

Because  $\beta$ -CD + Cur exhibits excellent fluorescence properties in the aqueous solution, which is expected to be used as a good energy donor to construct  $\beta$ -CD + Cur-based artificial LHS. Meanwhile,  $\beta$ -CD can self-assemble into negatively charged aggregate in the aqueous solution before and after the addition of Cur. Therefore, a cationic dye NiB and an amphoteric dye SR101 (Fig. S2) were selected to interact with  $\beta$ -CD + Cur to reduce the distance between the energy donors and energy acceptors. Moreover, in the process of constructing efficient artificial LHS, it is very important to select fluorescent dyes with matching energy levels. The amphoteric fluorescent dye SR101 (absorption band: 500–625 nm) (Fig. 2a) and NiB (absorption band: 500–675 nm) (Fig. 2b) were selected to construct artificial LHSs with  $\beta$ -CD + Cur through electrostatic interaction, which was well overlapped with the fluorescence emission spectra of  $\beta$ -CD + Cur.

UV–vis absorption and fluorescence emission spectra were carried out to investigate the energy transfer properties from  $\beta$ -CD + Cur to SR101 or NiB in the aqueous solution. The UV–vis absorption spectra results showed that the absorption at 430 nm decreased while the absorption at 580 nm increased gradually with the addition of SR101 (acceptor) to the aqueous solution of  $\beta$ -CD + Cur (donor) (Fig. 2c). Meanwhile, when  $\beta$ -CD + Cur was excited with a wavelength of 430 nm, the fluorescence emission at 540 nm decreased while the emission at 620 nm increased gradually with the addition of SR101 to the aqueous solution of  $\beta$ -CD + Cur (Fig. 2e). The energy transfer efficiency ( $\Phi_{\text{ET}}$ ) and antenna effect (AE) of this system were calculated as 16.3% (Fig. S3a) and 4.7 (Fig. S3b), while the fluorescence quantum yields increased from 0.2% to 5.6%. It can be observed in the CIE coordinate diagram that the color of the  $\beta$ -CD + Cur + SR101 mixed solution changed from light yellow to light red (Fig. S4a) compared with the  $\beta$ -CD + Cur. Meanwhile, the zeta potential of  $\beta$ -CD + Cur + SR101 was  $-27.5$  mV and the particle size increased to  $\sim 160$  nm in the aqueous solution (Figs. S5a and S6a). Meanwhile, transmission electron

microscopy (TEM) further confirmed the spherical structures with the size of  $\sim 150$  nm (Fig. S7a).

The UV–vis absorption spectra results showed that the absorption at 430 nm decreased while the absorption at 640 nm increased gradually with the addition of NiB (acceptor) to the aqueous solution of  $\beta$ -CD + Cur (donor) (Fig. 2d). Meanwhile, when  $\beta$ -CD + Cur was excited with a wavelength of 430 nm, the fluorescence emission at 540 nm decreased while the emission at 675 nm increased gradually with the addition of NiB to the aqueous solution of  $\beta$ -CD + Cur (Fig. 2f). The  $\Phi_{\text{ET}}$  and AE of the system reached 15.8% (Fig. S3c) and 6.5 (Fig. S3d), while the fluorescence quantum yields increased from 0.2% to 10.3%. More importantly, it can be observed in the CIE coordinate diagram that the colors of the  $\beta$ -CD + Cur + NiB mixed solution changed from light-yellow to bluish-yellow (Fig. S4b), indicating that there was an effective energy transfer between  $\beta$ -CD + Cur and NiB. Meanwhile, the zeta potential of  $\beta$ -CD + Cur + NiB was  $-19.6$  mV and the particle size increased to  $\sim 170$  nm in the aqueous solution (Figs. S5b and S6b). Meanwhile, transmission electron microscopy (TEM) further confirmed the spherical structures with the size of  $\sim 150$  nm (Fig. S7b).

To make better use of the energy harvested from the energy acceptors (SR101 and NiB), we used two  $\beta$ -CD + Cur-based artificial LHSs ( $\beta$ -CD + Cur + SR101 and  $\beta$ -CD + Cur + NiB) to photocatalyze the dehalogenation of  $\alpha$ -bromoacetophenone in the aqueous solution. As shown in Table 1, in the presence of  $\beta$ -CD + Cur + SR101 ( $\beta$ -CD + Cur + 30  $\mu\text{L}$  SR101) and  $\beta$ -CD + Cur + NiB ( $\beta$ -CD + Cur + 100  $\mu\text{L}$  NiB), the yield can reach 80% and 75% after irradiation with white light for 8 h (Fig. S8). In contrast, it can be concluded by comparison experiments that  $\beta$ -CD (37%), SR101 (45%), NiB (45%),  $\beta$ -CD + Cur (67%), without photocatalyst (30%) or without light (no reaction) (3 mL, at the same concentration) all obtained lower reaction yields in water solution than that of  $\beta$ -CD + Cur + 30  $\mu\text{L}$  SR101 (3 mL) and  $\beta$ -CD + Cur + 100  $\mu\text{L}$  NiB (3 mL). Meanwhile, the  $\beta$ -CD + Cur + 30  $\mu\text{L}$  SR101 (3 mL) obtained a

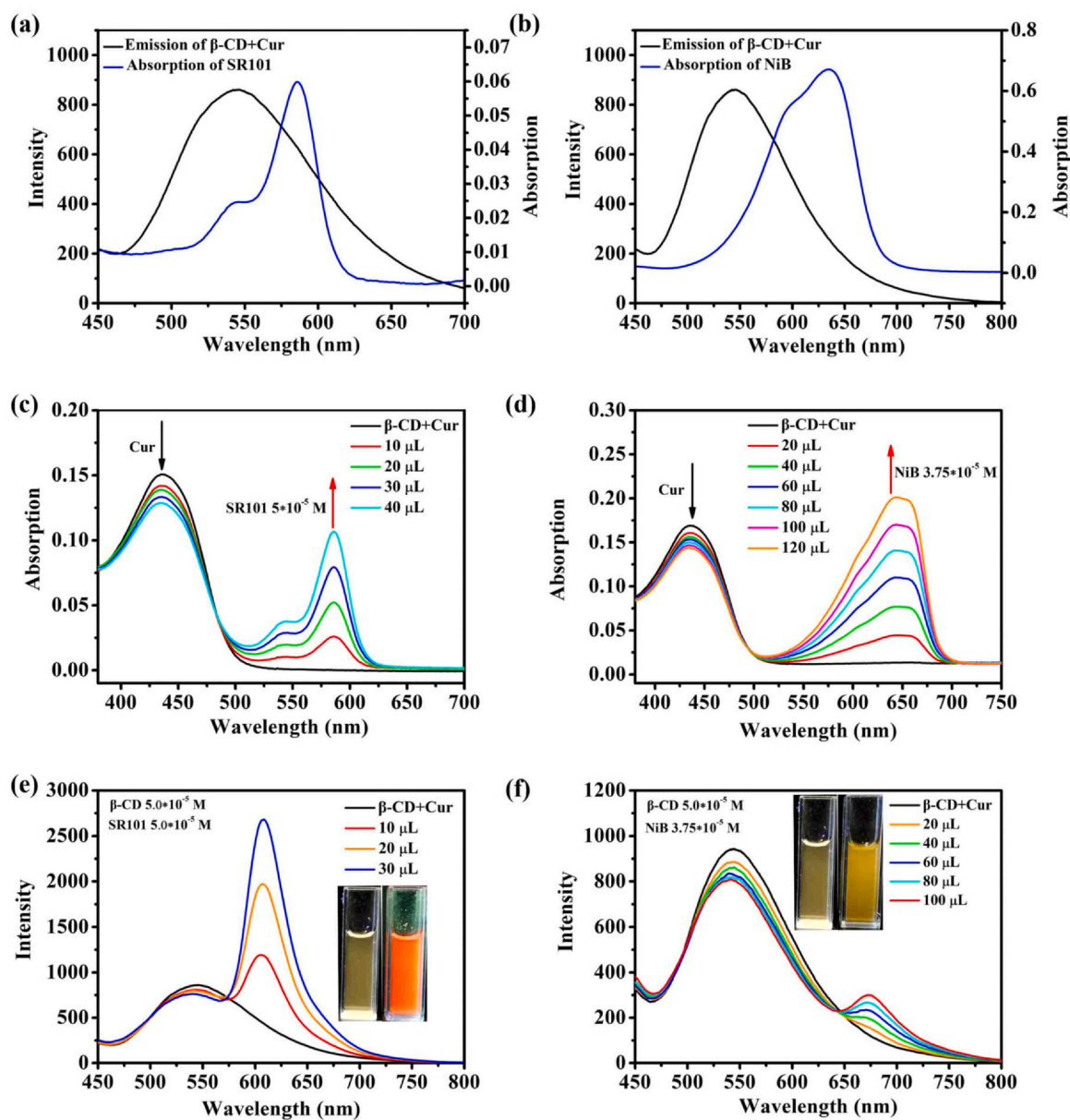


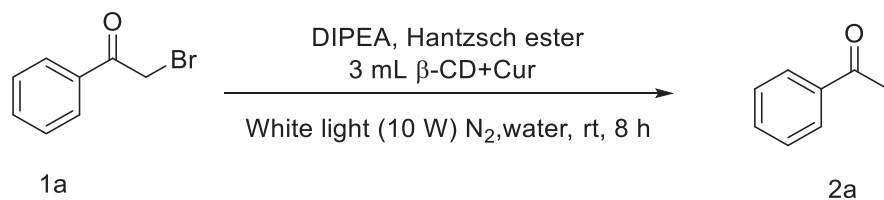
Fig. 2. UV-vis absorption spectra of SR101 (a) or NiB (b) and fluorescence emission spectra of  $\beta$ -CD + Cur. UV-vis absorption spectra of  $\beta$ -CD + Cur with the addition of different concentrations SR101 (c) and NiB (d); Fluorescence emission spectra of  $\beta$ -CD + Cur with different amounts of SR101 (e) and NiB (f) in the aqueous solution. Inset: Photographs of  $\beta$ -CD + Cur,  $\beta$ -CD + Cur + SR101 and  $\beta$ -CD + Cur + NiB. [ $\beta$ -CD] =  $5.0 \times 10^{-5}$  M, [SR101] =  $5.0 \times 10^{-5}$  M, [NiB] =  $3.75 \times 10^{-5}$  M.

higher yield than that of  $\beta$ -CD + Cur + 100  $\mu$ L NiB (3 mL). Therefore, we selected  $\beta$ -CD + Cur + 30  $\mu$ L SR101 (3 mL aqueous solution) as the optimal reaction condition for substrate expansion. The excellent catalytic effect of the  $\beta$ -CD + Cur + SR101 system and  $\beta$ -CD + Cur + NiB may be due to the fact that after the assembly of  $\beta$ -CD + Cur and SR101 (NiB) based on electrostatic interactions, SR101 or NiB molecules are arranged in a more orderly manner, and a higher energy transfer efficiency was obtained, indicating the best catalytic yield.

After establishing optimal reaction conditions (3 mL  $\beta$ -CD + Cur + 30  $\mu$ L SR101), the photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone derivatives was studied. As shown in Table 2, for methyl  $\alpha$ -bromoacetophenone derivatives (2b), the system achieved 82% yields, while for methoxyl derivatives, the yields were 75% (2c), 90% (2d) and 85% (2j), respectively. High yields of 2e (85%), 2f (83%), 2g (80%), and 2h (75%) were also found for the following  $\alpha$ -bromoacetophenone

derivatives with electron-withdrawing groups. In addition, the p-trifluoromethyl acetophenone can also be obtained with a 90% (2i) yield. These results indicated that  $\beta$ -CD + Cur + SR101 had universal applicability as a catalyst for photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone and its derivatives (Figs. S9–S17). More importantly, the above experimental process further proved the application of  $\beta$ -CD + Cur-based LHSs in the field of photocatalysis.

We have also proposed a mechanism of photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone (2a) (Scheme 2). First, the ground state  $\beta$ -CD + Cur changed to the excited state of [ $\beta$ -CD + Cur] $^*$  after harvesting energy under white light irradiation. Then, the energy acceptor SR101/NiB in the excited state transferred to the excited state [SR101/NiB] $^*$  after gaining energy from [ $\beta$ -CD + Cur] $^*$ . The excited SR101 $^*$ /NiB $^*$  was converted to SR101 $\cdot^-$ /NiB $\cdot^-$  by the electrons donated from N, N-diisopropylethylamine (DIPEA) and meanwhile, DIPEA

**Table 1**  
Photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone under different conditions.<sup>a</sup>

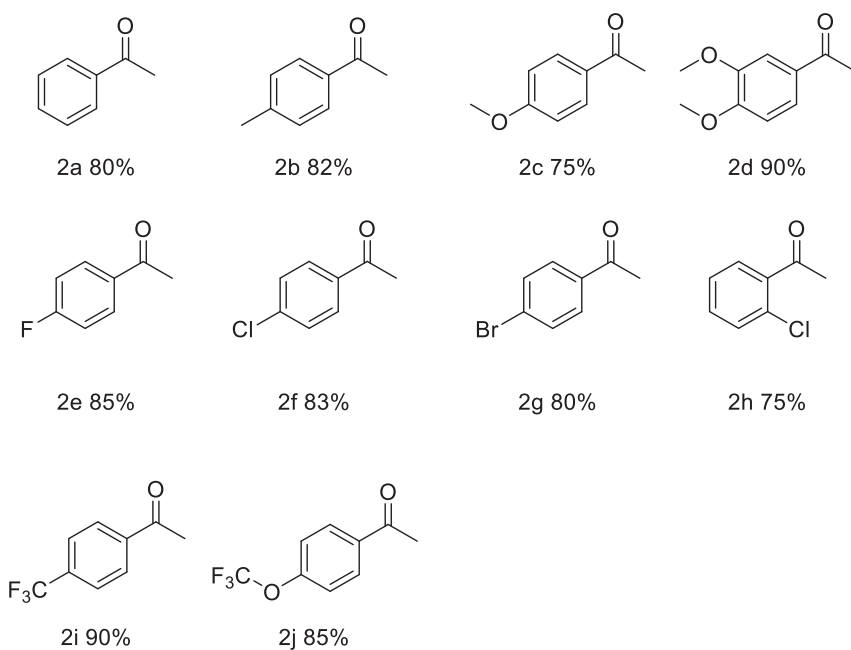
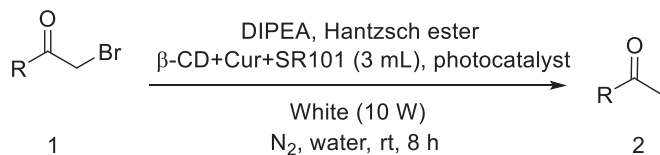
Entry	Conditions	Light irradiation	Yield <sup>b</sup> [%]
1	None	Yes	30
2	$\beta$ -CD	Yes	37
3	SR101	Yes	45
4	$\beta$ -CD + Cur	Yes	67
5	$\beta$ -CD + Cur + SR101	Yes	80
6	NiB	Yes	45
7	$\beta$ -CD + Cur + NiB	Yes	75
8c	$\beta$ -CD + Cur + NiB	No	no reaction
9c	$\beta$ -CD + Cur + SR101	No	no reaction

<sup>a</sup> Reaction conditions: Bromoacetone (40 mg, 0.2 mmol), Hantzsch ester (56 mg, 0.22 mmol), N, N-diisopropylethylamine (DIPEA) (70  $\mu$ L, 0.4 mmol),  $\beta$ -CD + Cur + SR101 (3 mL) aqueous solution (5 mL), 10 W UV light, room temperature, nitrogen, 16 h.

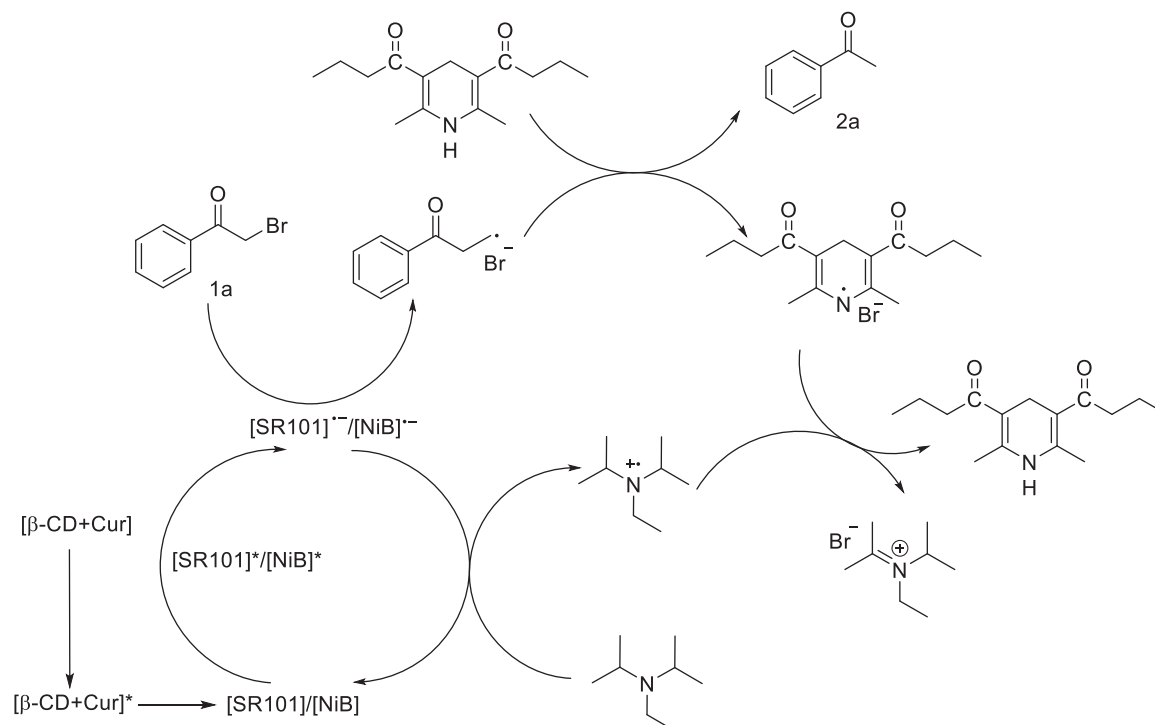
<sup>b</sup> Isolated yields. <sup>c</sup> Without a UV light.

transferred  $\text{DIPEA}^{\cdot-}$ . The  $\alpha$ -bromoacetophenone was reduced by  $[\text{SR101}/\text{NiB}]^{\cdot-}$  to produce phenylketone free radicals, while SR101/NiB was regenerated. The phenylketone radical can extract a hydrogen

atom from the Hantzsch ester to obtain the product acetophenone (2a). The dehydrogenated Hantzsch ester cation reacts with  $[\text{DIPEA}]^{\cdot-}$  to give pyridine ester as a byproduct (Scheme 2).

**Table 2**  
Expanded experiments on substrates for photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone derivatives.<sup>a</sup>

<sup>a</sup> isolated yields.



**Scheme 2.** A plausible mechanism for photocatalytic dehalogenation of  $\alpha$ -bromoacetophenone using the  $\beta$ -CD + Cur + SR101/ $\beta$ -CD + Cur + NiB system as a photocatalyst.

#### 4. Conclusions

In the present work, we have constructed a new supramolecular assembly based on the anionic highly water-soluble sulfobutylether- $\beta$ -cyclodextrin ( $\beta$ -CD) and hydrophobic dye curcumin (Cur) through host-guest interactions in the aqueous solution, which exhibited light yellow fluorescence.  $\beta$ -CD + Cur can be used to construct artificial light-harvesting systems (LHSs) with an efficient energy transfer process by attracting fluorescent dyes sulforhodamine 101 (SR101) and Nile blue (NiB) with matching energy levels through electrostatic interaction. It was proved that the two artificial LHSs ( $\beta$ -CD + Cur + SR101 and  $\beta$ -CD + Cur + NiB) were successfully constructed. More importantly, the harvested energy from the  $\beta$ -CD + Cur + SR101 and  $\beta$ -CD + Cur + NiB systems can be used to promote the dehalogenation of  $\alpha$ -bromoacetophenone with yields of 80% and 75% in the aqueous solution, which provides a new idea for the application of molecular assemblies based on host-guest interactions in light-harvesting systems and photocatalysis.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.esi.2023.07.001](https://doi.org/10.1016/j.esi.2023.07.001).

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