

Supporting Information

for

Photolysis of a Calixpyridinium-Based Supramolecular Amphiphilic Assembly and Its Selective Turn-on Fluorescence Recognition of Lysine in Water

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Experimental Section

Materials. 1-Methylpyridinium chloride, glutamic acid (Glu), and aspartic acid (Asp) were purchased from Tci. Proline (Pro) was purchased from Innochem. Lysine (Lys), tyrosine (Tyr), tryptophan (Trp), cysteine (Cys), serine (Ser), leucine (Leu), threonine (Thr) and isoleucine (Ile) were purchased from Adamas. Histidine (His) and phenylalanine (Phe) were purchased from Alfa. Arginine (Arg), alanine (Ala), methionine (Met), glycine (Gly) and valine (Val) were purchased from Ark. 2,2'-(4,4'-Biphenylylene)divinylene)di-benzenesulfonicacidisodiumsalt (CBS), asparagine (Asp), and glutamine (Gln) were purchased from Aladdin. All of these compounds were used without further purification. Calixpyridinium was synthesized and purified according to a previously reported procedure.¹ It was identified by ¹H (Figure S28) and ¹³C NMR spectroscopy (Figure S29) in D₂O, performed on a Bruker AV400 spectrometer, and by X-ray crystallographic analysis (Figure S30), performed on a Bruker APEX-II CCD diffractometer. Calixpyridinium–CBS supramolecular assembly was prepared by a simple mixture of calixpyridinium and CBS in aqueous solution and it would achieve balance over several minutes.

Measurements.

UV-Vis Spectra. UV-Vis spectra were measured in a quartz cell (light path 10 mm) on a Persee TU-1810 spectrophotometer.

Fluorescence Emission Spectra. Fluorescence emission spectra were recorded using a conventional quartz cell (light path 10 mm) on a Fluorolog-3 spectrometer from Horiba Jobin Yvon.

High-Resolution Transmission Electron Microscopy (TEM) Experiments. High-resolution TEM images were acquired using a Tecnai G² F20 high-resolution

TEM operating at an accelerating voltage of 200 kV.

Electrical Conductivity Measurements. Electrical conductivity was measured by a DDJ-A automatic electrical conductivity instrument.

NMR Spectroscopy. ^1H NMR spectra were recorded with a Bruker AV400 spectrometer.

Irradiation. The solution was irradiated using a Handhold UV Lamps (ZF-5) at 365 nm.

Results and Discussion

As can be seen from Figure S1, the addition of CBS could first lead to a linear increase in its electrical conductivity, and then the further addition of CBS would lead to a slower increase in its electrical conductivity because of the self-aggregation. A CAC value of 0.94 mM for free CBS could therefore be obtained by observing the inflection point on the plot of the electrical conductivity versus the concentration of CBS.

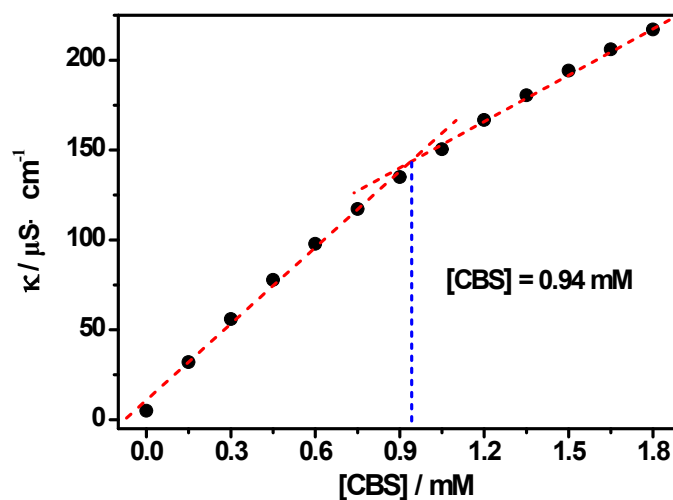


Figure S1. Dependence of the electrical conductivity on the CBS concentration.

As can be seen from Figure S2a, at first, the addition of CBS hardly affected its maximum emission wavelength. Upon the further addition of CBS, its maximum emission wavelength had an obvious red shift, indicating the self-aggregation of CBS. A CAC value of 0.77 mM for free CBS could therefore be obtained by observing the inflection point on the plot of the maximum emission wavelength of CBS versus its concentration (Figure S2b).

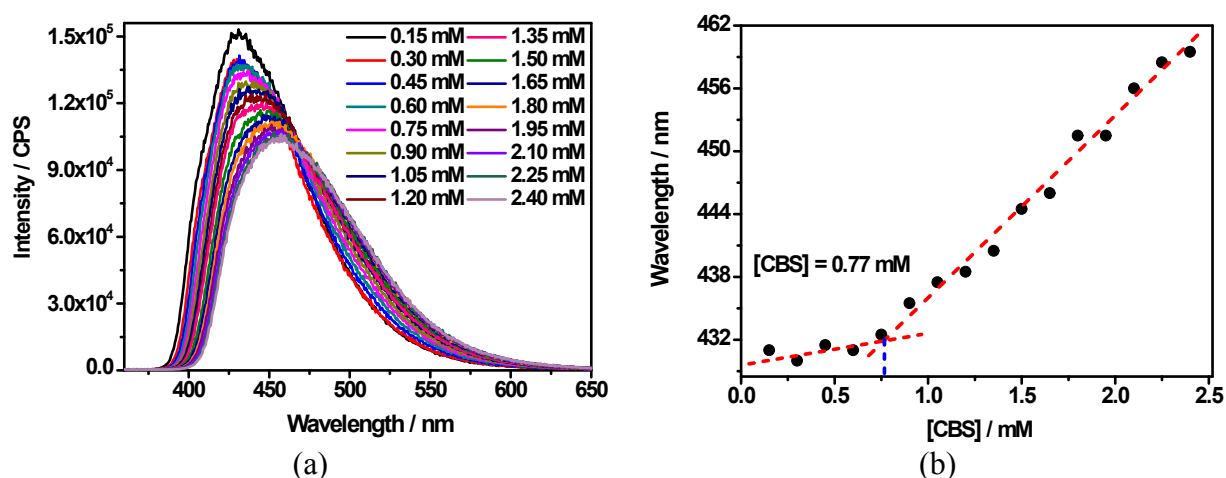


Figure S2. (a) Fluorescence emission spectra of different concentrations of CBS. (b)

Dependence of the maximum emission wavelength of CBS on its concentration, $\lambda_{\text{ex}} = 350 \text{ nm}$.

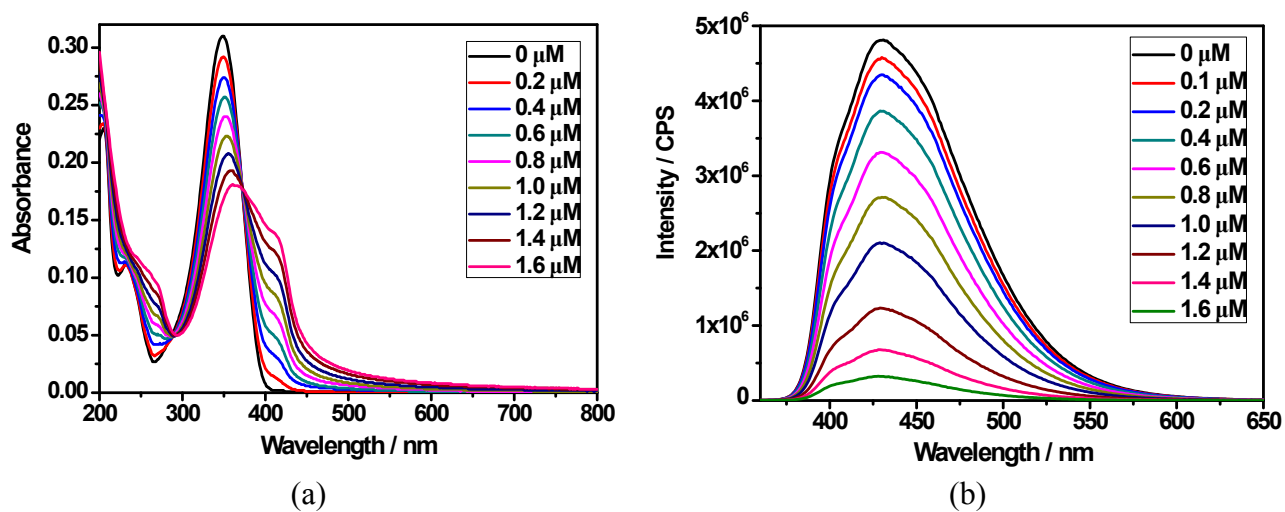


Figure S3. UV-Vis absorption (a) and fluorescence emission (b) spectra of 5 μM CBS by increasing the concentration of calixpyridinium from 0 to 1.6 μM , $\lambda_{\text{ex}} = 350 \text{ nm}$.

The calixpyridinium-complexation-induced CAC of CBS was further determined by measuring the electrical conductivity of a very dilute aqueous solution of calixpyridinium ($5\ \mu\text{M}$) in the presence of different concentrations of CBS. As shown in Figure S4, the addition of CBS could first lead to a linear increase in the electrical conductivity of the calixpyridinium solution, and then the further addition of CBS would lead to a slower increase in the electrical conductivity of the calixpyridinium solution because of the formation of large calixpyridinium–CBS supramolecular amphiphilic assembly. A calixpyridinium-complexation-induced CAC value of $0.94\ \mu\text{M}$ for CBS could therefore be obtained by observing the inflection point on the plot of the electrical conductivity versus the concentration of CBS.

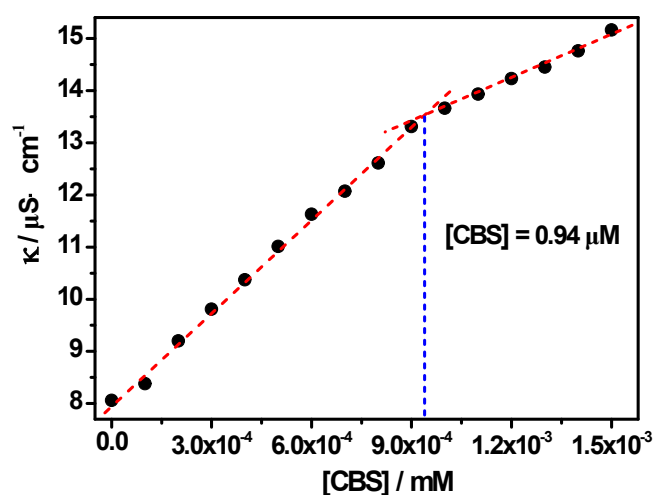


Figure S4. Dependence of the electrical conductivity on the CBS concentration in the presence of $5\ \mu\text{M}$ calixpyridinium.

As shown in Figure S5a, there was no obvious change in the absorbance of the calixpyridinium solution over 450 nm with the addition of a small amount of CBS. Further addition of CBS would lead to a gradual increase in the absorbance of the calixpyridinium solution over 450 nm because of calixpyridinium-induced aggregation of CBS. A calixpyridinium-complexation-induced CAC value of $0.41 \mu\text{M}$ for CBS could therefore be obtained by observing the inflection point on the plot of the absorbance at 500 nm versus the concentration of CBS (Figure S5b). The obtained value was in the same order of magnitude as that obtained by electrical conductivity.

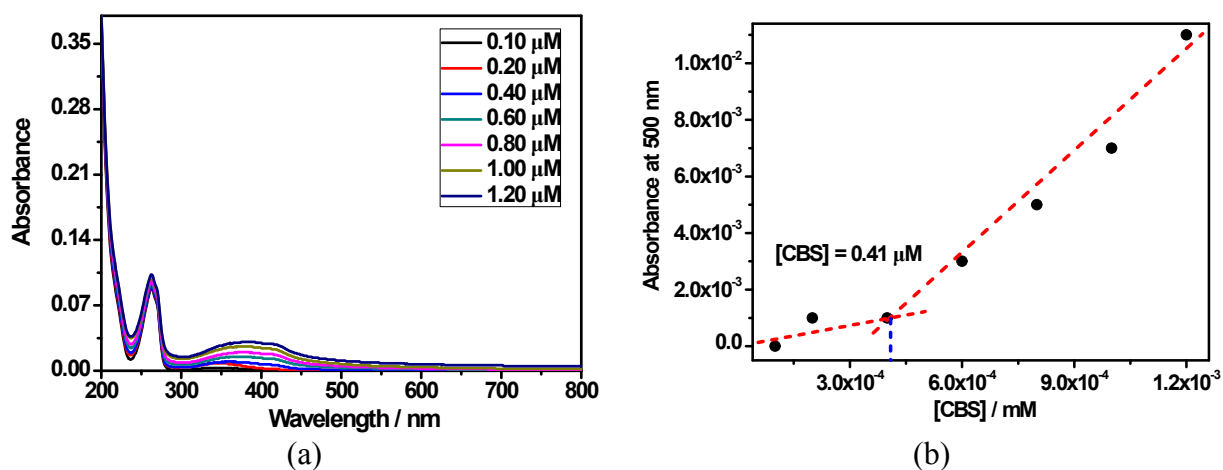


Figure S5. (a) UV-Vis absorption spectra of aqueous solutions of $5 \mu\text{M}$ calixpyridinium by increasing the concentration of CBS from 0.1 to $1.2 \mu\text{M}$. (b) Dependence of the absorbance at 500 nm on the concentration of CBS.

The continuous variation method was then used to determine the binding stoichiometry between calixpyridinium and CBS by observing the dependence of the absorbance at 500 nm on the molar ratio of CBS. As shown in Figure S6, a maximum was identified in the Job's plot for a 0.67 molar ratio of CBS, suggesting that the stoichiometry between CBS and calixpyridinium was 2n:n.

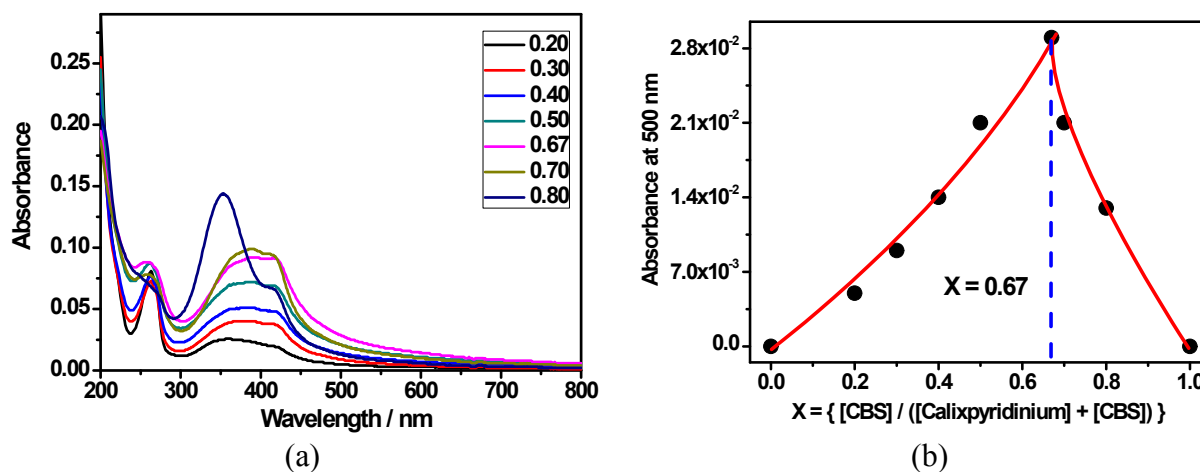


Figure S6. (a) UV-Vis absorption spectra of aqueous solutions of calixpyridinium and CBS with different mixing molar ratios. (b) Job's plot for calixpyridinium and CBS in water. $[\text{Calixpyridinium}] + [\text{CBS}] = 5 \mu\text{M}$.

Upon the addition of calixpyridinium, the maximum absorption wavelength of CBS had an obvious red shift accompanied with the appearance of a broad absorption over 450 nm (Figure S7). However, the addition of 1-methylpyridinium could hardly cause any change in the absorption spectrum of CBS, which proved undoubtedly the crucial role of the cyclic structure of calixpyridinium in the calixpyridinium-induced CBS aggregation.

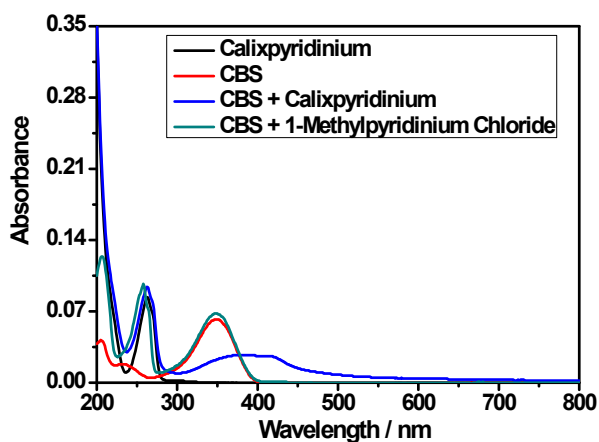


Figure S7. UV-Vis absorption spectra of calixpyridinium, CBS, CBS + calixpyridinium, and CBS + 1-methylpyridinium, [Calixpyridinium] = 5 μ M, [CBS] = 1 μ M, [1-Methylpyridinium Chloride] = 0.02 mM.

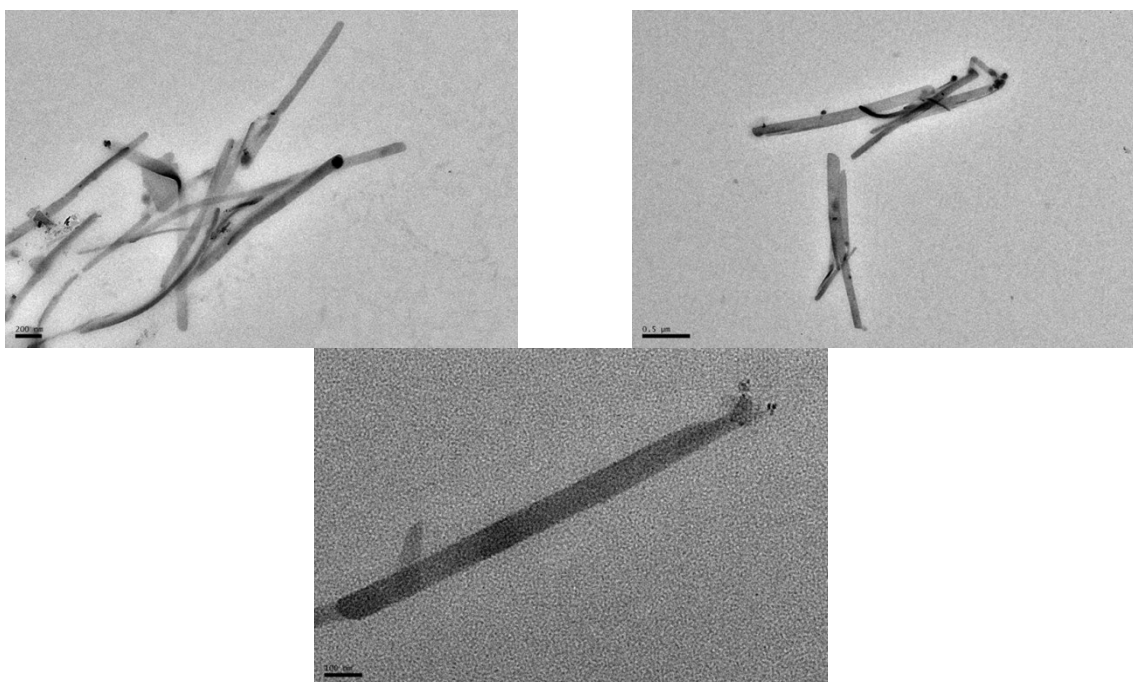


Figure S8. High-resolution TEM images of the calixpyridinium–CBS supramolecular amphiphilic assemblies. [Calixpyridinium] = 5 μM , and [CBS] = 1 μM .

Further studies on the stability of calixpyridinium–CBS supramolecular amphiphilic assembly were focused on their tolerance to time and temperature. As shown in Figure S9, there was no obvious change in the absorbance of the calixpyridinium–CBS solution over at least 6 h at room temperature, indicating that the assembly had sufficient stability at room temperature. As can be seen from Figure S10, there was also no obvious change in the absorbance of the calixpyridinium–CBS solution with temperature ascending from 28 to 40 °C or descending from 28 to 5 °C, implying that the calixpyridinium–CBS supramolecular amphiphilic assembly even had sufficient stability to a higher or a lower temperature.

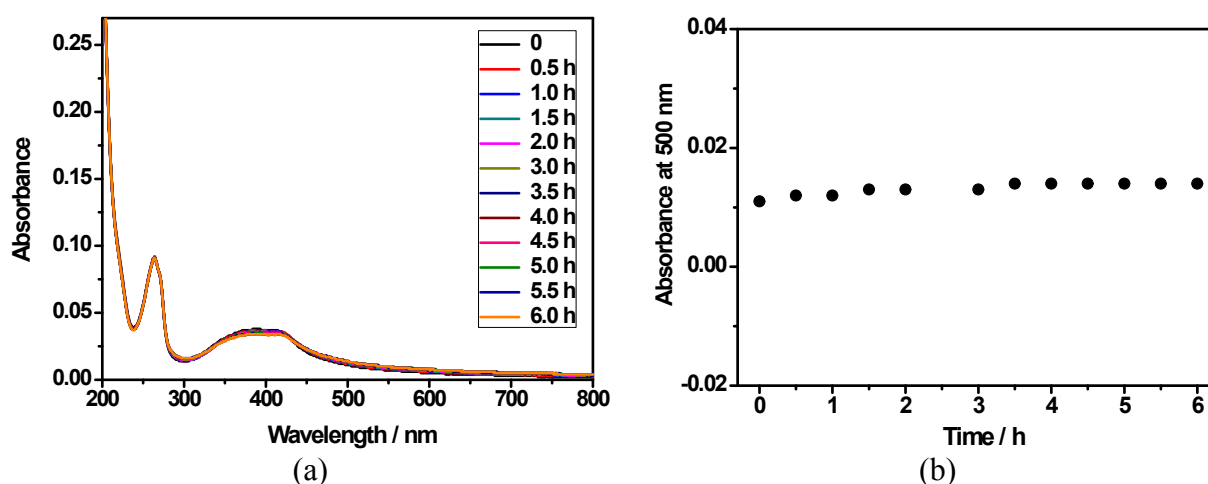


Figure S9. (a) UV-Vis absorption spectra of the calixpyridinium–CBS supramolecular amphiphilic assemblies at different time within 6 h at room temperature in water. (b) Dependence of the absorbance at 500 nm on time. [Calixpyridinium] = 5 μ M, and [CBS] = 1 μ M.

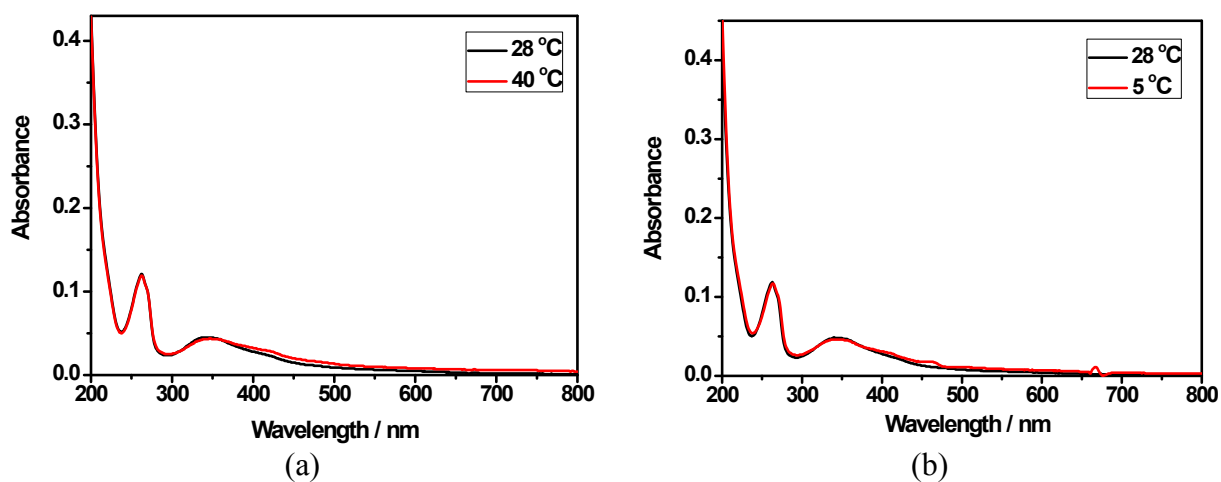


Figure S10. (a) UV-Vis absorption spectra of the calixpyridinium–CBS supramolecular amphiphilic assemblies at 28 and 40 °C in water. (b) UV-Vis absorption spectra of the calixpyridinium–CBS supramolecular amphiphilic assemblies at 28 and 5 °C in water. [Calixpyridinium] = 5 μ M, and [CBS] = 1 μ M.

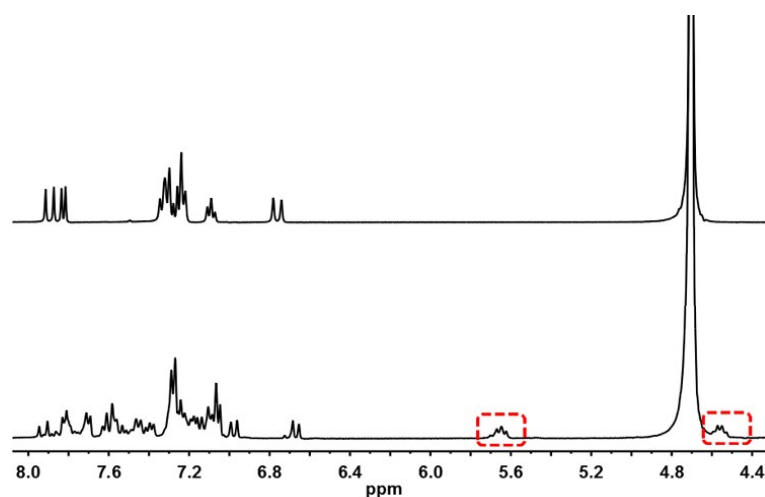


Figure S11. ^1H NMR spectra of CBS before (top) and after (bottom) irradiation (365 nm) for 6 h in D_2O , $[\text{CBS}] = 5 \text{ mM}$.

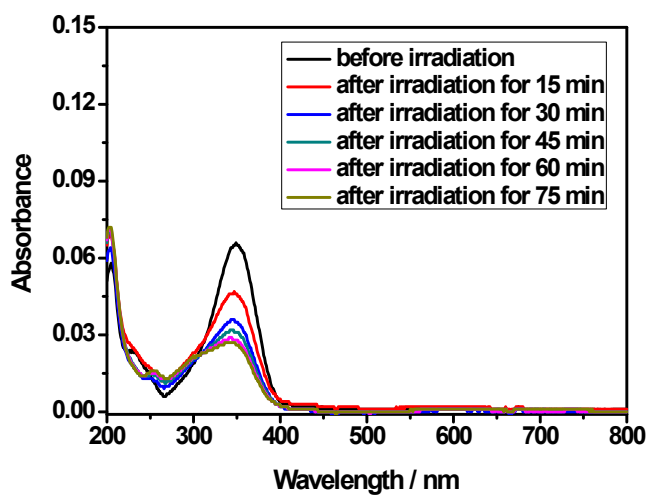


Figure S12. UV-Vis absorption spectra of CBS before and after irradiation (365 nm) for different times, $[\text{CBS}] = 1 \mu\text{M}$.

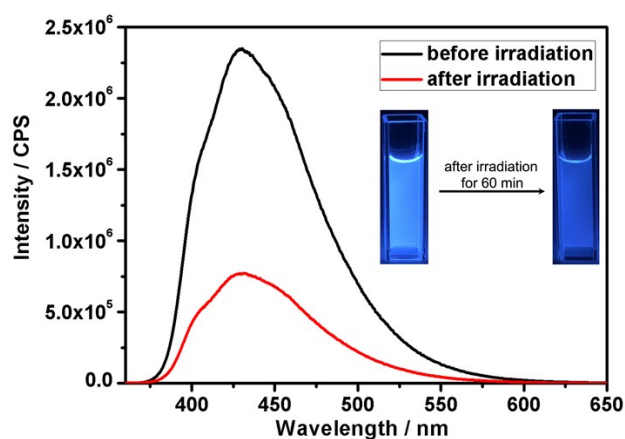


Figure S13. Fluorescence emission spectra of CBS before and after irradiation (365 nm) for 60 min ($\lambda_{\text{ex}} = 350$ nm). Inset: photograph showing the fluorescence of CBS before and after irradiation (365 nm) for 60 min. [CBS] = 1 μM .

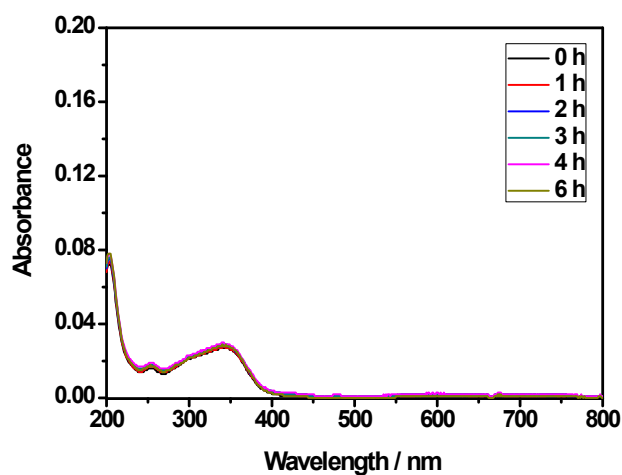


Figure S14. UV-Vis absorption spectra of the irradiated CBS at different time within 6 h at room temperature in water, [CBS] = 1 μM .

The CAC of CBS after UV irradiation was first studied by measuring its electrical conductivity. As can be seen from Figure S15, the addition of irradiated CBS could first lead to a linear increase in its electrical conductivity, and then the further addition of irradiated CBS would lead to a slower increase in its electrical conductivity. This indicated that the irradiated CBS also had the tendency towards self-aggregation. A CAC value of 0.69 mM for free irradiated CBS could therefore be obtained by observing the inflection point on the plot of the electrical conductivity versus the concentration of irradiated CBS. The CAC values of free CBS before and after UV irradiation were similar, indicating that free CBS before and after UV irradiation had the similar ability to self-aggregate.

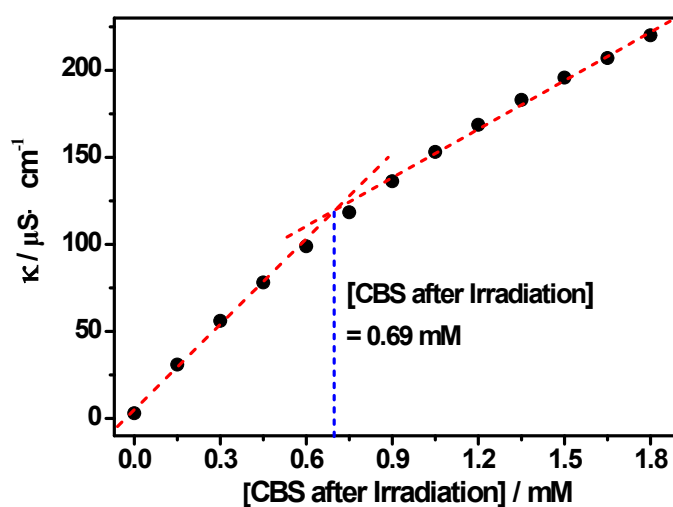


Figure S15. Dependence of the electrical conductivity on the irradiated CBS concentration. The mother liquor of CBS was 60 mM and irradiated for 4 h.

The fluorescent spectroscopy was used to confirm the CAC value of free irradiated CBS. As can be seen from Figure S16a, at first, the addition of irradiated CBS hardly affected its maximum emission wavelength. Upon the further addition of irradiated CBS, the maximum emission wavelength had an obvious red shift, indicating the self-aggregation of irradiated CBS. A CAC value of 0.81 mM for free irradiated CBS could therefore be obtained by observing the inflection point on the plot of the maximum emission wavelength of irradiated CBS versus its concentration (Figure S16b). The obtained value was in the same order of magnitude as that obtained by electrical conductivity.

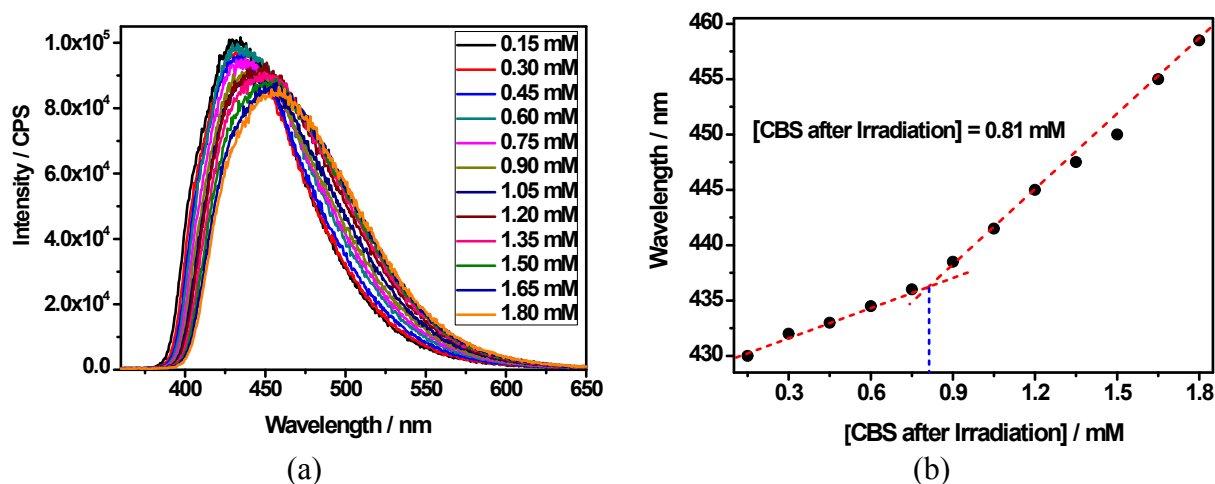


Figure S16. (a) Fluorescence emission spectra of different concentrations of the irradiated CBS. (b) Dependence of the maximum emission wavelength on the concentration of irradiated CBS, $\lambda_{\text{ex}} = 350$ nm. The mother liquor of CBS was 60 mM and irradiated for 4 h.

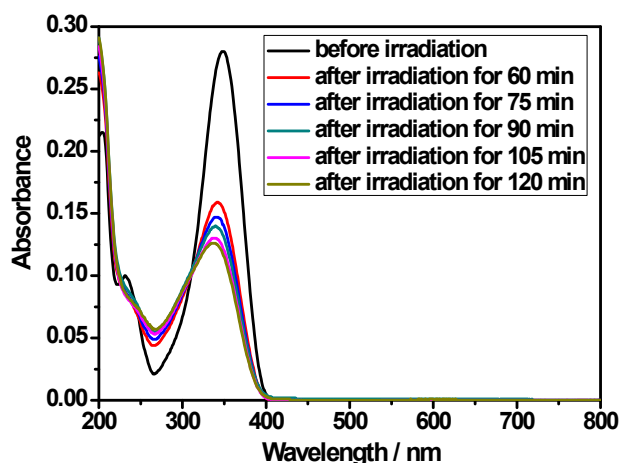


Figure S17. UV-Vis absorption spectra of CBS before and after irradiation (365 nm) for different times, [CBS] = 5 μM .

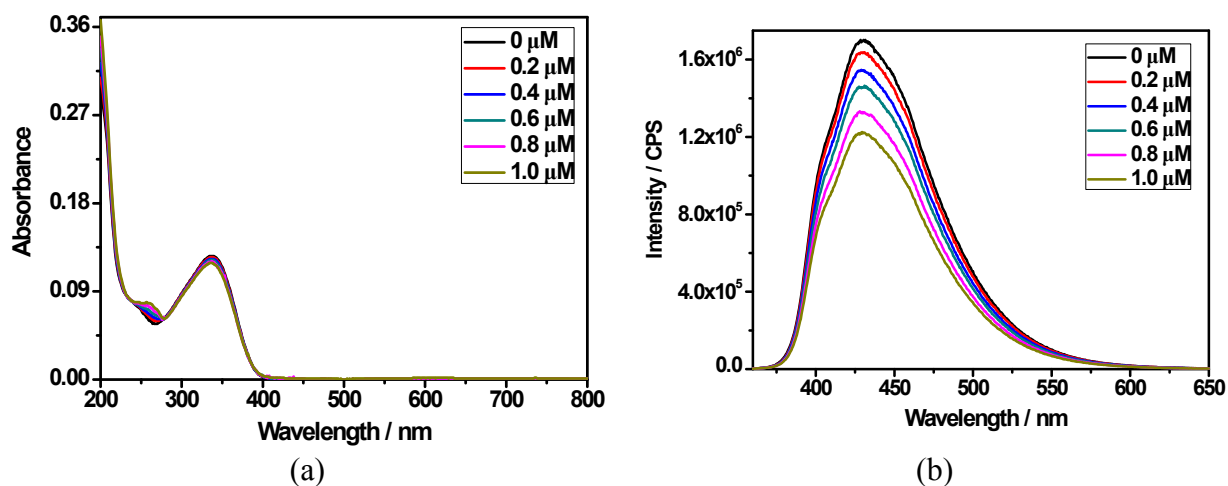


Figure S18. (a) UV-Vis absorption spectra of 5 μM irradiated CBS by increasing the concentration of calixpyridinium from 0 to 1.0 μM . (b) Fluorescence emission spectra of 5 μM irradiated CBS by increasing the concentration of calixpyridinium from 0 to 1.0 μM ($\lambda_{\text{ex}} = 350 \text{ nm}$).

The continuous variation method was used to determine the binding stoichiometry between calixpyridinium and the irradiated CBS by fluorescence spectroscopy (Figure S19). The total concentration of calixpyridinium and the irradiated CBS was kept constant at 5 μM , and the molar ratio was varied between 0 and 1. As shown in Figure S19c, a maximum was identified in the Job's plot for a 0.67 molar ratio of the irradiated CBS, suggesting that the binding stoichiometry between the irradiated CBS and calixpyridinium was also 2n:n.

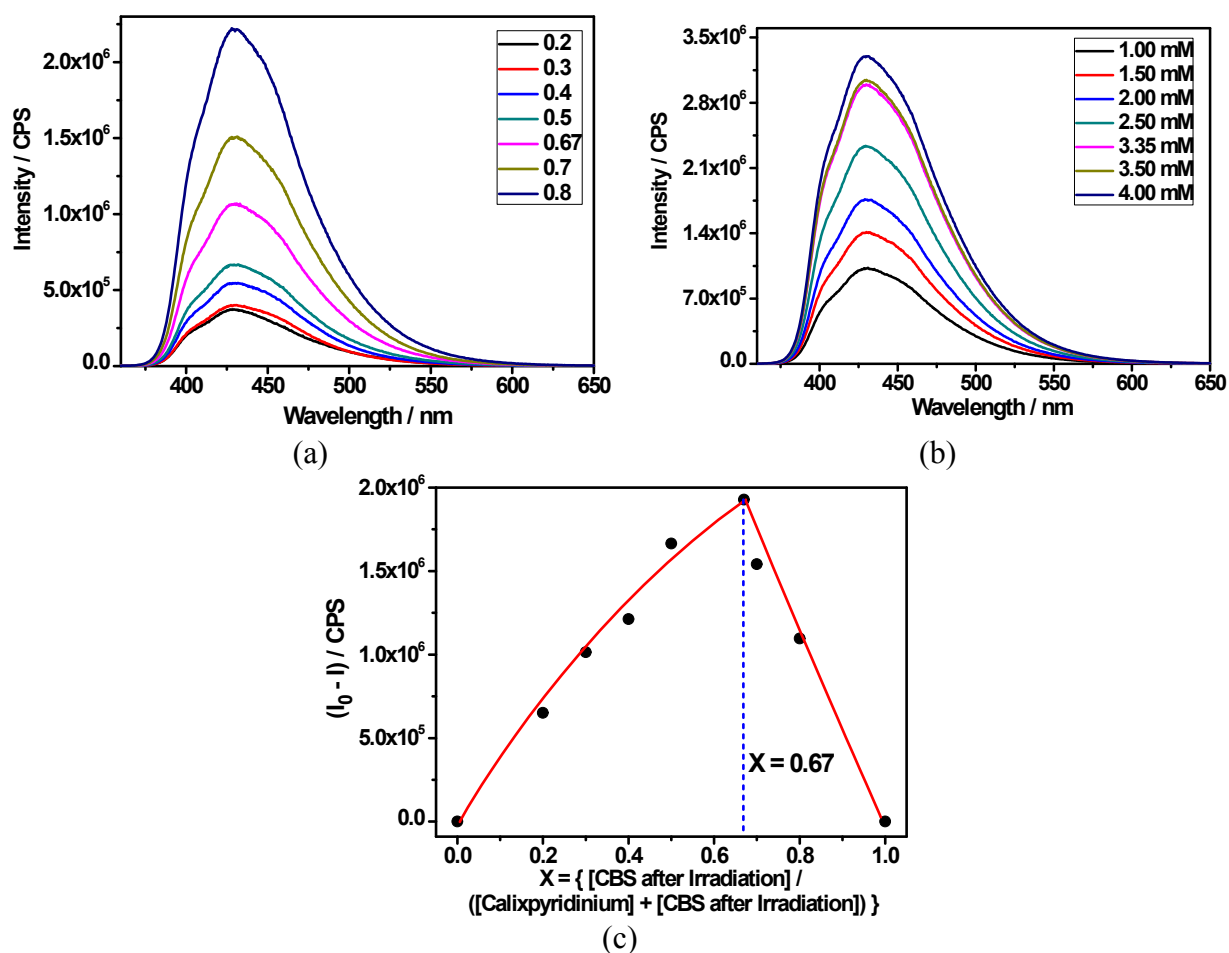


Figure S19. (a) Fluorescence emission spectra of calixpyridinium and the irradiated CBS with different mixing molar ratios. (b) Fluorescence emission spectra of the irradiated CBS with different concentrations. (c) Job's plot for calixpyridinium and the irradiated CBS in water. $[\text{Calixpyridinium}] + [\text{CBS}] = 5 \mu\text{M}$, $\lambda_{\text{ex}} = 350 \text{ nm}$.

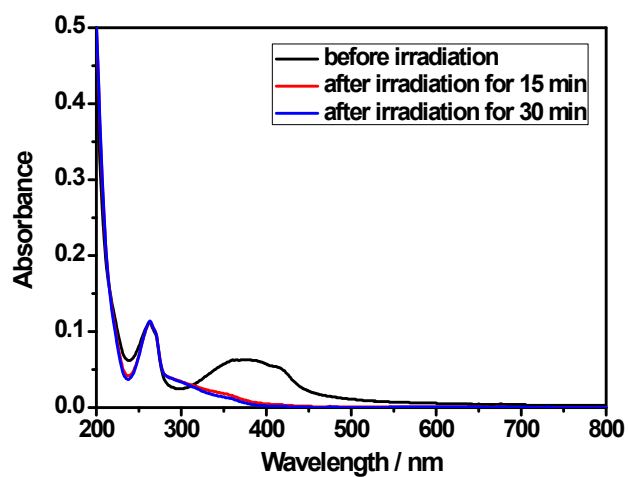


Figure S20. UV-Vis absorption spectra of CBS + calixpyridinium before and after irradiation (365 nm) for different times, [Calixpyridinium] = 5 μM , and [CBS] = 1 μM .

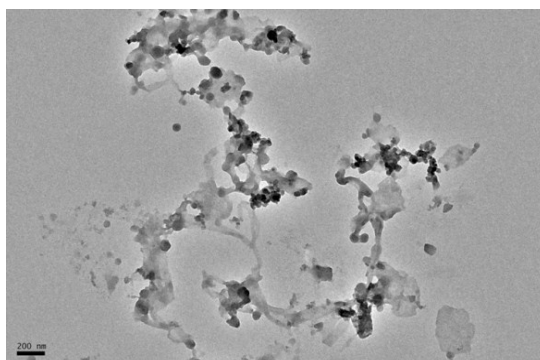


Figure S21. High-resolution TEM image of CBS + calixpyridinium after irradiation (365 nm) for 30 min. [Calixpyridinium] = 5 μM , and [CBS] = 1 μM .

The UV-Vis absorption and fluorescence emission spectra of the irradiated CBS in the absence and presence of calixpyridinium showed that the addition of calixpyridinium caused an obvious decrease of the maximum absorption peak of the irradiated CBS (Figure S22a) and a strong fluorescence quenching of the irradiated CBS (Figure S22b). This suggested that the photodegradable products of the calixpyridinium–CBS supramolecular amphiphilic assembly were calixpyridinium–irradiated CBS complexes rather than free irradiated CBS molecules.

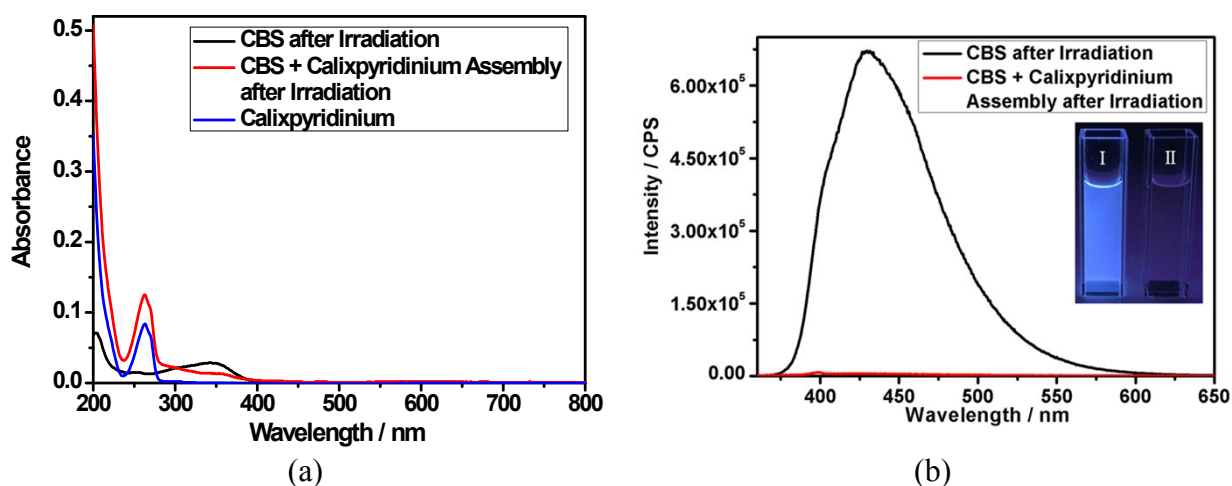


Figure S22. (a) UV-Vis absorption spectra of CBS after irradiation (365 nm) for 60 min, CBS + calixpyridinium assembly after irradiation (365 nm) for 15 min, and calixpyridinium. (b) Fluorescence emission spectra of CBS after irradiation (365 nm) for 60 min, and CBS + calixpyridinium assembly after irradiation (365 nm) for 15 min. Inset: photograph showing the fluorescence of CBS after irradiation (365 nm) for 60 min (I), and CBS + calixpyridinium assembly after irradiation (365 nm) for 15 min (II). [Calixpyridinium] = 5 μ M, and [CBS] = 1 μ M.

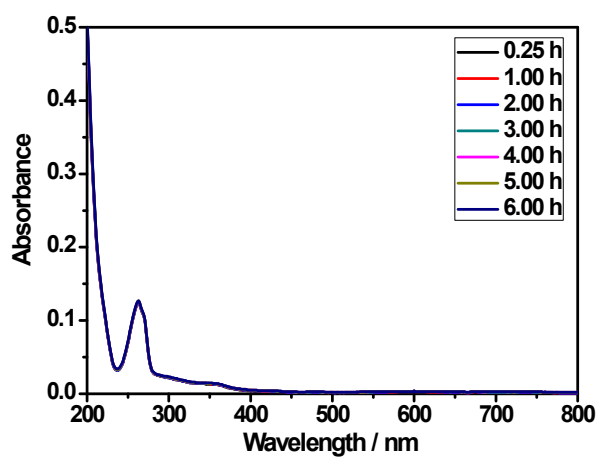


Figure S23. UV-Vis absorption spectra of CBS + calixpyridinium at different time within 6 h after irradiation (365 nm) for 15 min at room temperature in water. [Calixpyridinium] = 5 μ M, and [CBS] = 1 μ M.

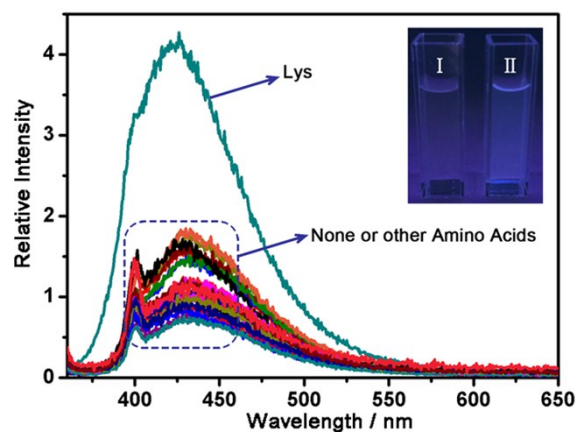


Figure S24. Fluorescence emission spectra of CBS + calixpyridinium and CBS + calixpyridinium + 20 native α -amino acids in aqueous solutions at pH 6.0 ($\lambda_{\text{ex}} = 350$ nm). Inset: photograph showing the fluorescence of CBS + calixpyridinium (I) and CBS + calixpyridinium + Lys (II). [Calixpyridinium] = 5 μM , [CBS] = 1 μM , and [Amino Acid] = 1 mM.

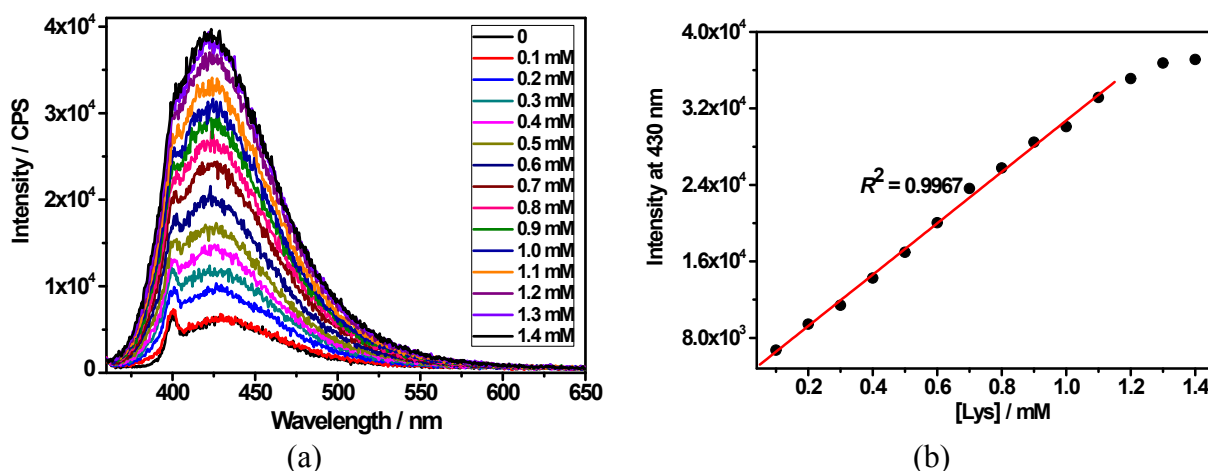


Figure S25. (a) Fluorescence emission spectra of CBS + calixpyridinium in the absence and presence of different concentrations of Lys in aqueous solutions at pH 6.0 ($\lambda_{\text{ex}} = 350$ nm). (b) Linear relationship between the fluorescence emission intensity at 430 nm and the concentration of Lys. [Calixpyridinium] = 5 μM , and [CBS] = 1 μM .

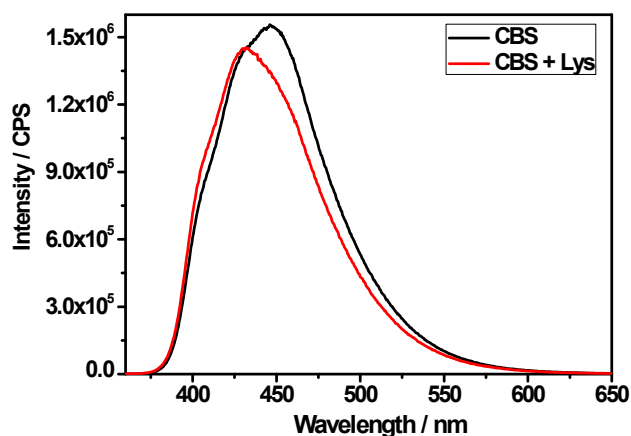


Figure S26. Fluorescence emission spectra of CBS and CBS + Lys ($\lambda_{\text{ex}} = 350$ nm), [CBS] = 1 μM , and [Lys] = 1 mM.

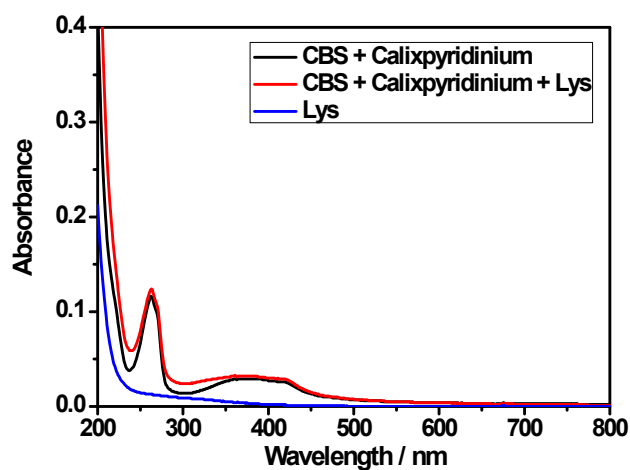


Figure S27. UV-Vis absorption spectra of CBS + calixpyridinium, CBS + calixpyridinium + Lys, and Lys. [Calixpyridinium] = 5 μ M, [CBS] = 1 μ M, and [Lys] = 1 mM.

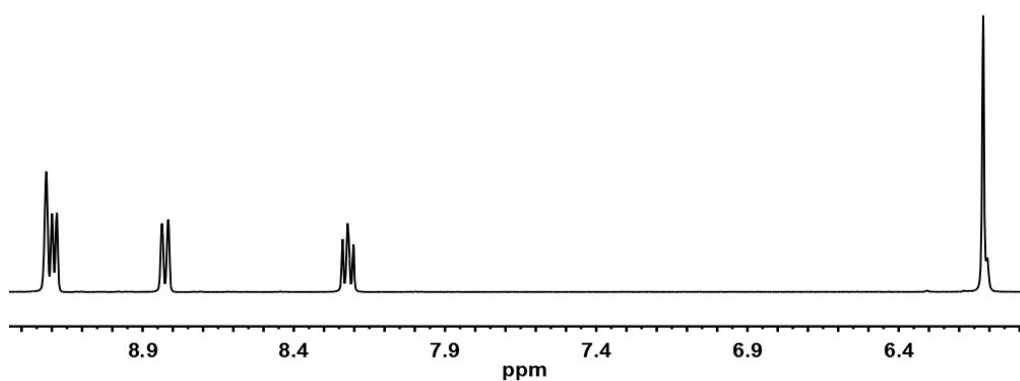


Figure S28. ^1H NMR spectrum of calixpyridinium in D_2O .

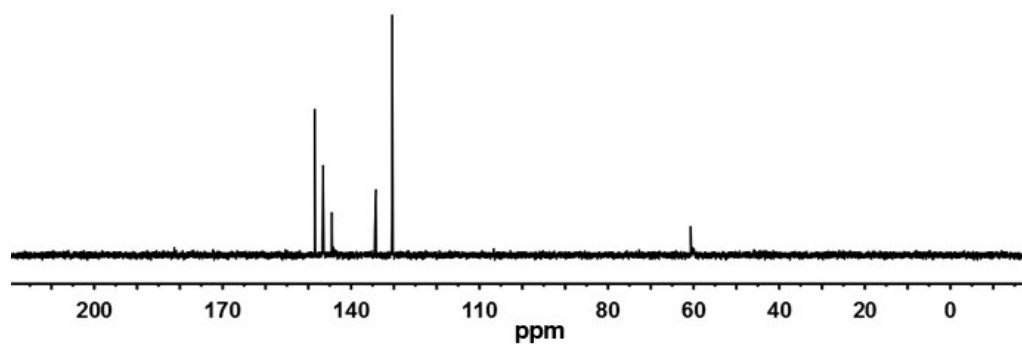


Figure S29. ¹³C NMR spectrum of calixpyridinium in D₂O.

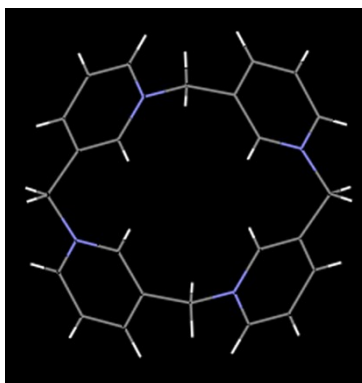


Figure S30. Crystal structure of calixpyridinium. It is in accordance with the previous reported crystal structure of calixpyridinium.¹

1. S. Shinoda, M. Tadokoro, H. Tsukube and R. Arakawa, *Chem. Commun.*, 1998, 181–182.