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Aqueous Phase Visible-Light-Excited Organic Room-Temperature Phosphorescence via Cucurbit[8]uril-Mediated Supramolecular Assembling

Jie Wang, Zizhao Huang, Xiang Ma* and He Tian

Abstract: Solid state materials with efficient room-temperature phosphorescence (RTP) emissions have found widespread applications in material science, while liquid or solution-phase pure organic RTP emission system has been rarely reported due to the non-radiative decay and quenchers from the liquid medium. Herein we propose the first example of visible-light excited pure organic RTP in aqueous solution via a supramolecular host-guest assembling strategy. The unique cucurbit[8]uril-mediated quaternary stacking structure allows tunable photoluminescence and visible-light excitation, enabling the fabrication of multi-color hydrogels and cell imaging. The present "assembling-induced emission" approach, as a proof of concept, contributes to the construction of novel metal-free RTP system with tunable photoluminescence in aqueous solution, providing broad opportunities for further applications in biological imaging, detection, optical sensors and so forth.

Developing new photoluminescence methodologies that give access to unprecedented photophysical properties or provide more efficient and environmentally sustainable alternatives to established approaches is the central goal of optical material science. Room-temperature phosphorescence (RTP) has been widely developed in organic light-emitting diodes,[1] detectors,[2] anti-counterfeiting materials[3] owing to its large Stokes shift, long lifetime and versatile responsiveness. Commonly used strategies for achieving pure organic RTP emission focus on the enhancement of intersystem crossing (ISC) process and restriction of non-radiative decay.[4] Based on the above two points, efficient pure organic RTP emission in solid phase can be feasibly acquired through polymer matrix,[5] crystallization,[6] halogen bonding,[7] self-assembly,[8] and H-aggregation[9]. At the same time, the development of time-resolved biological imaging and detection fields has promoted the demand for solution phase RTP materials. However, access to organic RTP emission in liquid or solution phase especially in aqueous phase is still limited, given that high dissolved oxygen concentration in water and the free molecular motions would largely bring the chromophores from the excited triplet state to non-radiative decay process rather than phosphorescence emission, leading to the quenching of RTP.

The aforementioned obstacles prompt us to adopt the supramolecular assembling strategies. Supramolecular assembling has been explored as a promising strategy in constructing materials owing to the spontaneously assembled structures with unique features fostered by non-covalent interactions. These non-covalent interactions, e.g. π-π interactions, hydrogen bonding, metal-coordination and host-guest interactions,[10] enable oriented and ordered structures of individual molecules, inducing synergetic effect on the electron distribution and promoting intriguing optical properties, which could be summarized as "Assembling-Induced Emission". Notably, host-guest interaction has been utilized to achieve RTP in both solid and solution phase.[11] Through the inclusion by host molecules, the designed guest molecules could locate or assemble in a rigid cavity, avoiding quenchers in the solution and suppressing the free molecular motions. Our previous work utilized cucurbit[7]uril (**CB[7]**) to provide a confined cavity for a quinoline derivative with encoded green RTP emission signals in aqueous media.[12] However, the short excitation wavelength and low RTP quantum yield limit the overall value of this approach for further applications in biology fields. Inspired by the tunability and responsiveness of supramolecular assembling system, we hypothesized using supramolecular host molecule cucurbit[8]uril (**CB[8]**) as a confined cavity to include heavy-atom modified molecule (triazine derivative, **TBP**) (Figure 1) to achieve RTP emission in aqueous solution. The cavity of **CB[8]** would allow two **TBP** molecules to reach a structure-restricted dimer with a new charge-transfer triplet state, which benefits performing yellow RTP emission in water under visible-light excitation. Additionally, multi-color photoluminescence emissions from blue to white and yellow could be realized by adding different molar ratios of **CB[8]** into the blue fluorescent **TBP** solution. Competitive guest could be utilized to break the host-guest inclusion apart and provide the system with reversible photoluminescence emission color. To the best of our knowledge, this tunable assembling-induced RTP emission under visible-light excitation in aqueous solution has rarely been reported. Furthermore, RTP hydrogels and cell imaging based on the **TBP-CB[8]** assembling systems were demonstrated to manifest appealing potentials for further applications such as biological sensors and time-resolved imaging.

The phosphor group 4-(4-bromophenyl)-pyridine was modified on the triazine core to obtain the two-branched molecule **TBP**.[13] Two positively charged pyridinium groups endow **TBP** with aqueous solubility and binding affinity with cucurbiturils. ^{1}H NMR titration spectroscopy was first carried out to study the assembling behavior of **TBP** and **CB[8]** in D_2O at 298 K (Figure 1a). Upon the addition of **CB[8]** to the solution of **TBP**, signals for the protons H_a and H_b of the pyridinium moieties showed slight upfield shifts of 0.20 ppm (H_a) and 0.54 ppm (H_b), demonstrating a location near the portal inside the **CB[8]** cavity. While H_c, H_d of the phenyl ring exhibited obviously upfield shifts from 8.08 to 6.97 ppm ($\Delta\delta$ = 1.11 ppm) and from 7.95 to 6.94 ppm ($\Delta\delta$ = 1.01 ppm) respectively, suggesting deeper inclusion

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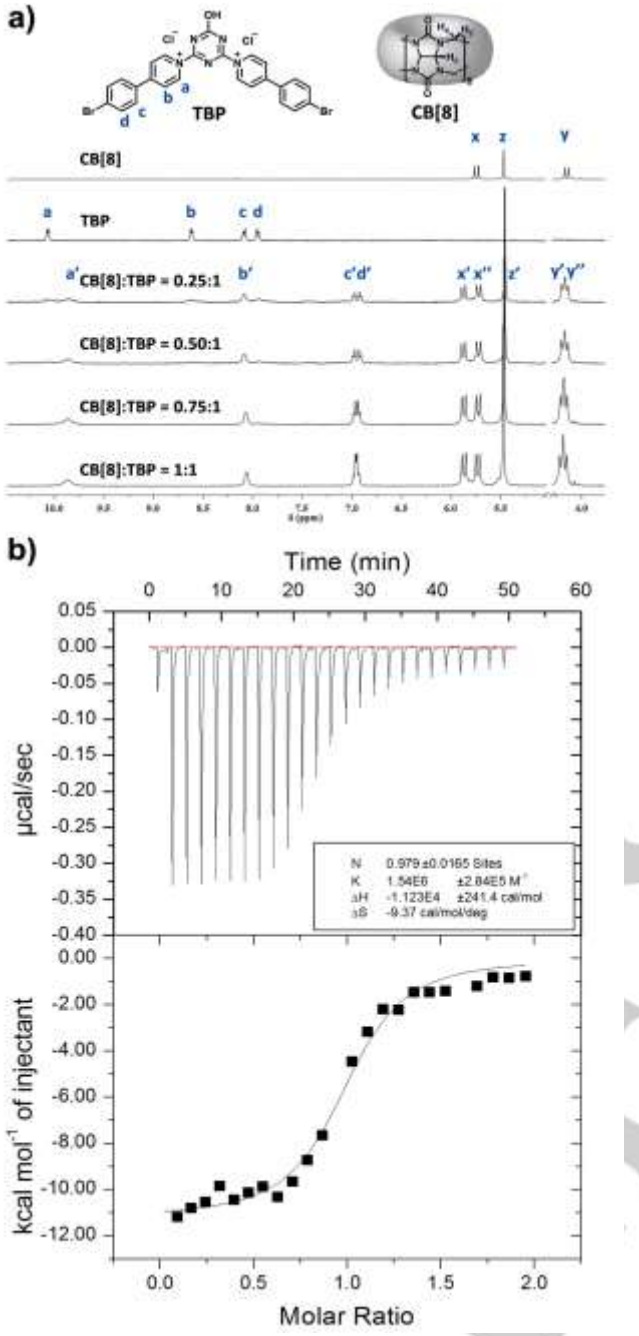

Figure 1. a) Titration of **CB[8]** into **TBP** monitored by ^{1}H NMR in D_2O at 298 K. b) ITC data for **TBP** with **CB[8]** in H_2O, [**TBP**] (cell) = 25 µM, [**CB[8]**] (syringe) = 250 µM, 298 K.

of the 4-(4-bromophenyl)-pyridinium moiety inside the **CB[8]**. Notably, ^{1}H NMR spectra of **TBP-CB[8]** complexes revealed a significant splitting of **CB[8]** protons (H_x) into two sets of equivalent peaks, suggesting an asymmetric charge density environment for two **CB[8]** portals.[14] Figure S6 illustrates a 2D Diffusion Ordered Spectroscopy (DOSY) plot of **TBP** solution before and after the addition of 1.0 eq **CB[8]**. **TBP** molecule diffuses as a single molecular species (log D = -9.569 m^2s^{-1}). While upon the addition of 1.0 eq **CB[8]**, the signals of **TBP** and **CB[8]** share a single diffusion coefficient (log D = -9.752 m^2s^{-1}), which proves the existence of one species assembly in this host-guest system.

Additionally, the binding behavior between **TBP** and **CB[8]** were estimated through Isothermal Titration Calorimetry (ITC) experiments. As shown in Figure 1b, the ITC results indicated a stoichiometry of 1:1 for **TBP-CB[8]** assembly. The data were fitted to give the binding constant as 1.54×10^6 M^{-1}. Moreover, as shown in 2D Rotating Frame Overhauser Effect Spectroscopy (ROESY) NMR spectrum (Figure S7, SI), proton correlations of H_b-H_c and H_b-H_d was observed between two adjacent **TBP** molecules. This intermolecular correlation suggested that the pyridinium group in the complex should indeed be close to the phenyl group from the other **TBP** molecule, and the complexed **TBP** molecules could likely stack with each other in a parallel and partially overlapped manner. Based on these observations and previous reports for the host-guest complex structures based on **CB[8]**,[15] we propose a 2:2 quaternary model for the **TBP-CB[8]** complex, in which two partially overlapping **TBP** derivatives are held in place by two **CB[8]** macrocycles around the aryl moieties. This binding model satisfies a 1:1 stoichiometry with two **CB[8]** hosts complexed with two **TBP** guests. The confined quaternary structure coincides with the splitting peaks observed for the **CB[8]** proton signals during the NMR titration. Therefore, we could further exclude the formation of a head-to-tail linear supramolecular polymer.

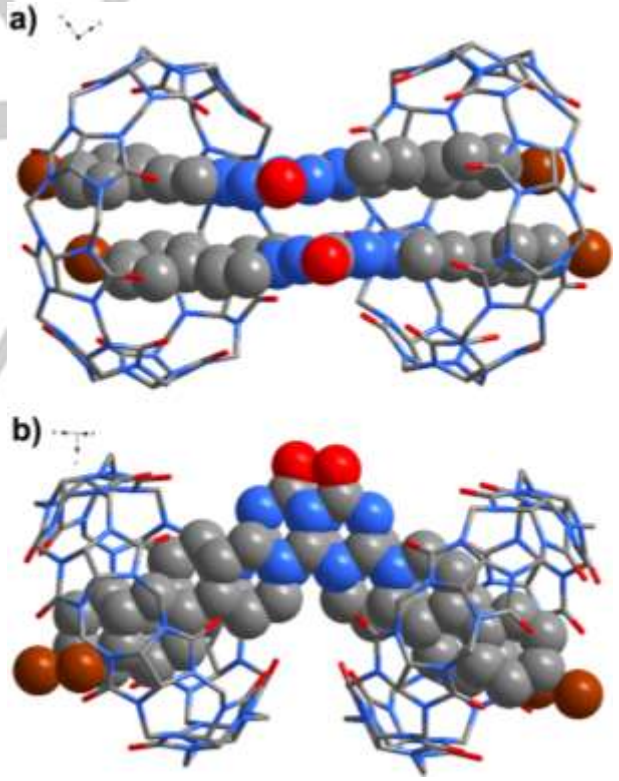

Figure 2. Side a) and top b) views of single X-ray crystal structure of **$(TBP)_2$·CB[8]$_2$** assembly. C, gray; N, blue; O, red; Br, brown.

Single crystal data provides direct and solid evidence for this 2:2 quaternary complex structure. In a 1:1 mixture of **TBP** and **CB[8]** in aqueous solution, the single crystal of **TBP-CB[8]** complex was formed under slow evaporation of water. The structure of the complex was determined by single X-ray crystallography (Table S2, SI). Figure 2 and S14 show the

molecular packing structure in the single crystal. Each unit cell consists of two **TBP** molecules and two **CB[8]**s. As anticipated, two branches of **TBP** located in the **CB[8]** cavity, leaving triazine cores outside and under multiple weak interactions. The aromatic and pyridinium rings of two molecules adopt co-facial parallel and staggered arrangement with centroid-to-centroid vertical distance of 3.27 Å, indicating the presence of π-π stacking interaction between them and the Coulomb repulsion of the charged pyridinium. The single crystal structure is consistent with the aforementioned NMR analysis, verifying the 2:2 quaternary structures.

We further studied the optical properties of the **TBP**-**CB[8]** system. The guest molecule **TBP** exhibited blue fluorescence emission located at around 445 nm upon 365 nm light irradiation in aqueous solution. As shown in Figure 3a, upon the addition of **CB[8]** into **TBP** aqueous solution, a new peak at 565 nm appeared with the decrease of 445 nm emission. The Commission International de l'Eclairage (CIE) coordinates were calculated to demonstrate the photoluminescence emission color change upon the addition of **CB[8]**. A transition from blue to yellow through white light zone was clearly shown in Figure 3b with photographs of representative samples under 365 nm UV light. To confirm the photophysical properties of the new emission peak at 565 nm, time-resolved luminescence spectra of **TBP** solution with 1.0 eq **CB[8]** were measured, and the result indicates a long lifetime of 0.190 ms for the yellow luminescence (Figure 4, Table S1). Compared with the PL spectra under ambient conditions, the intensity of 565 nm emission peak showed an obvious increase under N_2 atmosphere. Thus we could attribute the 565 nm emission as RTP emission in aqueous solution. From the UV-Visible absorption spectra (Figure S8, SI), an obvious bathochromic-shift of the maximum absorbance peak from 346 nm to 360 nm with broad structure could be observed with the addition of **CB[8]**. And the intensity of absorption peak at 346 nm decreased simultaneously, which could be attributed to the conformation of **TBP**-**CB[8]** complexes and the change in the polarity of the phosphor local environment upon migration of the guest from the water medium to the **CB[8]** cavity. The noteworthy red-shift in the absorption and the iso-photoluminescence emission point featuring the 1:1 model indicated the formed 2:2 quaternary complexes possessing a new **CB[8]**-stabled charge-transfer state.[16] We also studied the photophysical properties of the **$(TBP)_2$·$CB[8]_2$** assembly in single crystal phase. It is noteworthy to find almost the same yellow phosphorescence emission peak with 0.852 ms decay (Figure S9, SI), which is in consistence with the phenomenon in solution state.

To gain a deeper insight into the unique optical properties originated from the host-guest assembly, we further conducted a set of control experiments. Cucurbit[7]uril (**CB[7]**) was utilized to obtain **TBP-CB[7]** complex. Based on the reported cavity size of **CB[7]**[17] and Job's plot from UV-Vis spectroscopic titrations (Figure S10, SI), only one branch of **TBP** could be included by **CB[7]** rather than two, excluding the same two-guest-packing mode as **$(TBP)_2$·$CB[8]_2$** assembly. With the addition of **CB[7]** into the **TBP** aqueous solution, the absorption peak did not show obvious shift, eliminating the formation of **TBP** dimer. Furthermore, the blue fluorescence emission intensity increased without shift upon the addition of **CB[7]** owing to the host-enhanced emission effect.[45] To be specific, the cavity of **CB[7]** shows similar rigidification on the included guest molecules as **CB[8]** and prevents the non-radiative decay and enhances the fluorescence performance of **TBP** molecules.

Thus we could conclude that upon the addition of **CB[8]** into **TBP** solution, **CB[8]** directionally contains two **TBP**

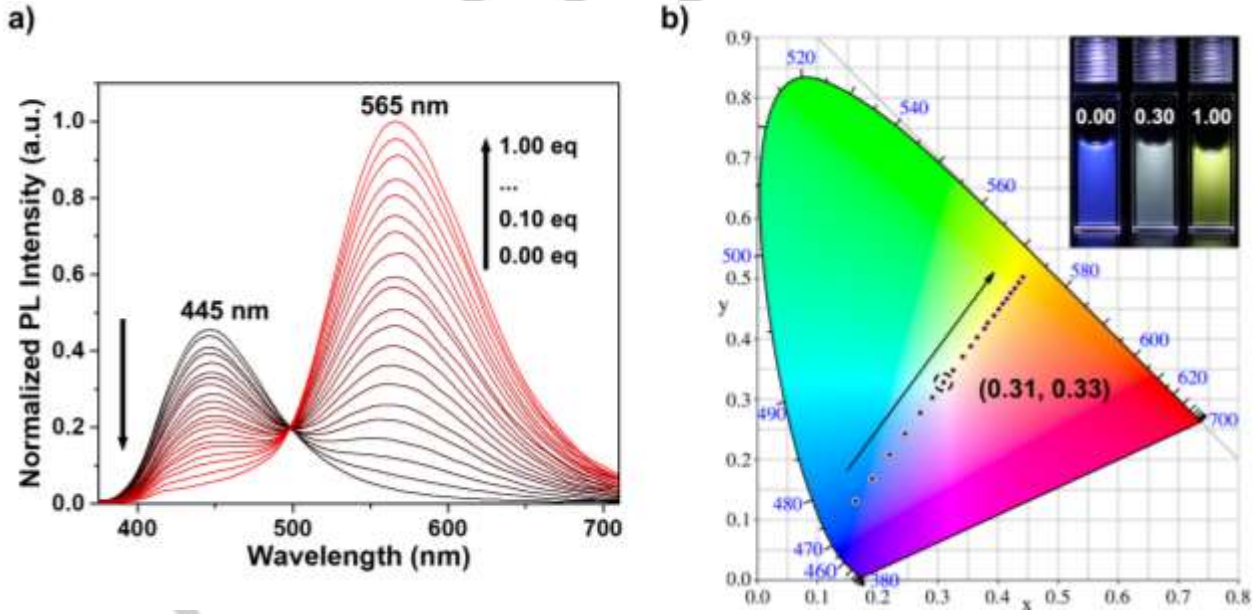

Figure 3. a) Photoluminescence emission spectra of **TBP** (50 μM) with different ratio of **CB[8]** (0.00 – 1.00 eq) in H_2O at 298 K (λ_{ex} = 365 nm). b) Chromaticity coordinate (CIE) of **TBP** with different **CB[8]** ratios in H_2O at 298 K in accordance with a). Inset: photographs of **TBP** with 0.00 (left), 0.30 (middle) and 1.00 (right) eq **CB[8]** in H_2O.

molecules with stacking patterns upon diode-diode interaction, hydrogen bonding and hydrophobic interaction, which further induced a **CB[8]**-stabilized charge-transfer state with red-shifted excitation wavelength and efficiently suppressed the molecular motion. Additionally, the cavity of **CB[8]** could prevent quenchers from solution, which also benefit the phosphorescence emission in aqueous phase. Therefore, the fluorescence-phosphorescence dual-emission could be feasibly obtained through assembling. And the multi-color emission could be attributed to the mixture of **TBP** monomer with blue fluorescence and **$(TBP)_2$·$CB[8]_2$** assembly with yellow phosphorescence. Since the non-covalent interaction could endow this assembling-induced phosphorescence system with reversibility upon the addition of a competitive guest, 1-Amino-3,5-dimethyladamantane hydrochloride (**Me-Ad**), which owns a larger binding constant with **CB[8]** ($K = 4.33\times10^{11}$ M^{-1}) compared with **TBP**,[18] was added to the **TBP-CB[8]** aqueous solution (Figure S11, SI). As anticipated, the phosphorescence intensity decreased with the recovery of the blue fluorescence. And this phenomenon could further demonstrate the host-guest inclusion structure and reversibility of this photoluminescence system.

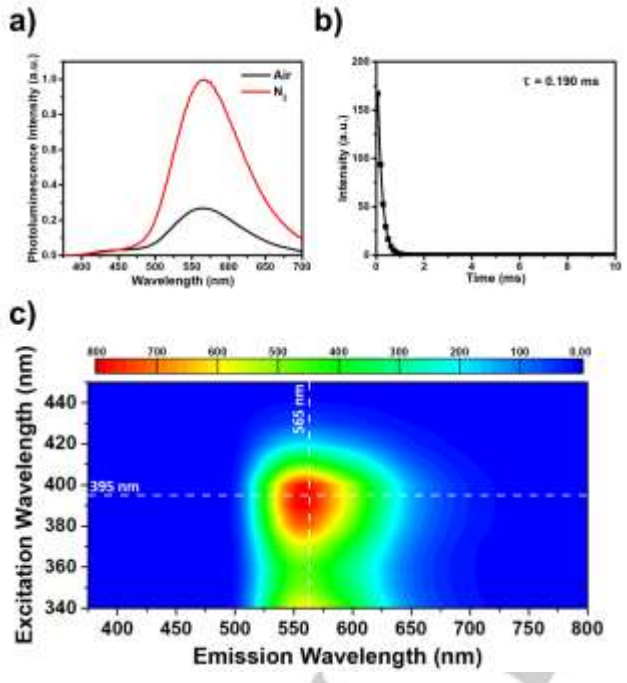

Figure 4. a) Steady-state photoluminescence spectra of **TBP** (50 μM) with 1.0 eq **CB[8]** recorded in air and N_2 atmosphere. b) Luminescent delay lifetimes of **TBP** (50 μM) with 1.0 eq **CB[8]** at 565 nm. c) Excitation-phosphorescence emission mapping of **TBP** (50 μM) with 1.0 eq **CB[8]**.

Hydrogels have been investigated as ideal matrices for biological applications.[19] Utilizing the multi-color emission property of the assembly, we could easily obtain multi-color emission hydrogel through simple dispersion of an agarose gelator in the **TBP** aqueous solution with different amounts of **CB[8]**. As shown in Figure 5a, three hydrogels were fabricated and their blue, white and yellow emission could be observed under naked eyes with 365 nm light irradiation. It should be pointed out that the yellow light emitting hydrogel is a pure organic RTP hydrogel. The resultant hydrogels could be a great impetus to construct novel fluorescence-phosphorescence dual-emitting soft materials.

Since the assembled charge-transfer state enables a red-shift of the absorption peak to visible light zone (Figure S8), a longer excitation wavelength can be utilized and endows the assembling system with potential to be applied in cell imaging. Excitation-phosphorescence emission mapping of the **TBP**-**CB[8]** assembly (Figure 4c) also demonstrates an optimum excitation wavelength up to 395 nm. Considering the **TBP**-**CB[8]** complex could exhibit yellow phosphorescence emission under 405 nm visible light (Figure S12, SI), Hela cells was utilized for incubation with 10 μM **TBP-CB[8]** for 2 h, showing bright yellow phosphorescence under confocal microscopy (405 nm laser, Figure 5b). In addition, no obvious PL emission signal was observed for the control (Figure S13, SI). Furthermore, the imaging picture demonstrated that the complexes prefer aggregating in endosomes of cells, which is consistent with previous **CB[8]**-based endocytosis research.[20]

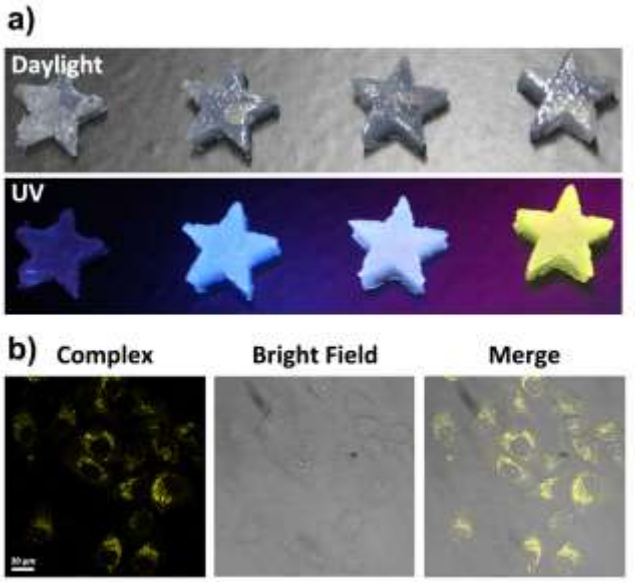

Figure 5. a) Photographs of multi-color hydrogels under daylight and 365 nm UV light. From left to right: blank agarose hydrogel, agarose hydrogels mixed with **TBP** adding 0.00 eq **CB[8]**, 0.30 eq **CB[8]** and 1.00 eq **CB[8]**. b) **TBP-CB[8]** complex (left), bright field (middle) and merge (right) confocal microscopic images of Hela cells cultured with a mixture of **TBP** with 1.0 eq **CB[8]** (10 μM).

We have developed a novel tunable photoluminescence supramolecular assembling system in aqueous solution based on a peculiar 2:2 quaternary structure, which could be further implemented into fabricating multi-color hydrogels. The findings show that the confined space of **CB[8]** promotes dimer assembling of **TBP** molecules, promoting a **CB[8]**-stabilized charge-transfer state with decent yellow RTP emission under visible-light excitation, which could be utilized in cell imaging. We believe that this approach to achieving aqueous RTP via "assembling-induced emission", as a combination of supramolecular assembling with photochemistry, will undoubtedly open up design strategies for novel RTP materials in liquid/solution phase.

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Keywords: room-temperature phosphorescence • assembling-induced emission • host-guest systems • self-assembly • supramolecular chemistry

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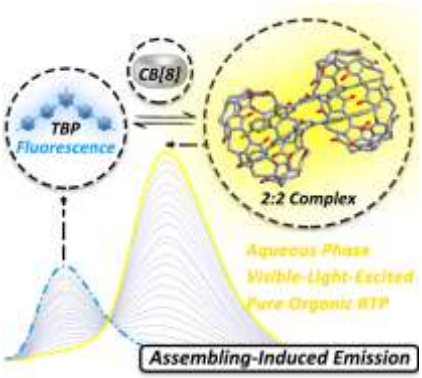

An “Assembling-Induced Emission” strategy was utilized to lighten a simple dye molecule with room-temperature phosphorescence and tunable photoluminescence in aqueous solution. The obtained peculiar supramolecular assembly structure endows the system with intriguing photophysical properties and enabling fabrication of multi-color hydrogel and cell imaging.