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Color-tunable luminescent materials *via* a CB[8]-based supramolecular assembly strategy†

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Fabricating color-tunable organic luminescent materials through a supramolecular host–guest strategy has attracted considerable attention recently. Herein, a series of color-tunable emissive materials consisting of small organic molecules, cucurbit[8]uril (CB[8]), and their host–guest complexes were developed. Fluorescent wavelength can be reversibly regulated by controlling the concentration of CB[8] in aqueous solution. Such properties exhibited promising applications for smart luminescent materials.

Color-tunable luminescent materials based on small organic molecules have attracted much attention due to their potential applications in sensors, probes, and electronic devices.^{1–3} Traditional strategies to design multi-color fluorescence materials mainly involve (i) chemical covalent modifications of the fluorophores to extend π systems, and introduce donor–acceptor (D–A) groups;⁴ (ii) strictly mixing multiple components with energy matching based on the principle of fluorescence resonance energy transfer (FRET) processes, which usually require a time-consuming synthesis and purification.^{2,5} In addition, fluorescence properties of such materials are difficult to regulate owing to their static structures, which are unfavorable to fabricate smart luminescent materials with wavelength tenability, stimuli-responsive and adaptive properties as their potential applications in light emitting devices as well as encryption materials.^{3,6} Therefore, developing intelligent multi-color luminescent materials in a controllable way remains a challenge.

Recently, supramolecular assembly based on non-covalent interactions has been proven to efficiently regulate fluorescence properties.^{7–11} In particular, supramolecular host–guest interactions based on macrocycles such as cyclodextrins,¹¹ cucurbit[*n*]uril (CB[*n*], *n* = 5–8, 10),^{10,12} crown ethers,⁸ box,¹³ and other molecular motifs¹⁴ have been widely used to fabricate intelligent multi-color fluorescent materials due to their specific recognition and dynamic properties. In particular,

cucurbit[*n*]uril (CB[*n*]) with high selectivity and affinity towards positively charged units have been incorporated to develop various host–guest systems.^{10,12,15} Cucurbit[8]uril (CB[8]), a promising molecule in the cucurbit[*n*]uril family, have been utilized to fabricate diverse emissive host–guest systems owing to its large cavity that can combine multiple guest molecules to regulate various intermolecular processes (*e.g.* charge transfer, excimer formation and so on), resulting in changes of the fluorescence.^{16–21} For example,²¹ Ni *et al.* fabricated color-tunable luminescent materials in aqueous solution through the CB[8]-based host–guest strategy. However, fabricating intelligent multi-color fluorescent materials with simple molecules through supramolecular host–guest interaction strategies remains a challenge.

Herein, we designed color-tunable fluorescent materials, based on simple small molecules *via* a CB[8]-based supramolecular assembly strategy that can be dynamically controlled. As shown in Fig. 1, small and rigid fluorescent molecules were constructed by the incorporation of fluorescent core thiazolothiazole between two positively charged pyridinium units. The

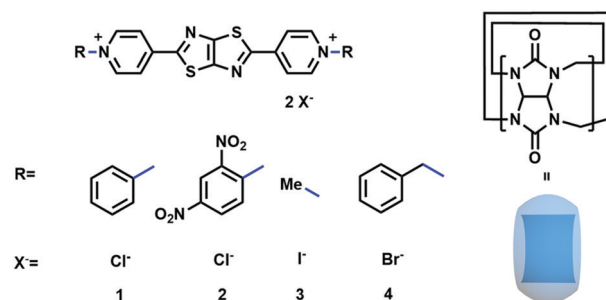


Fig. 1 A schematic presentation of the chemical structures for four compounds and macrocyclic cucurbit[8]uril.

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positive charges could provide water solubility as well as the binding sites of cucurbit[8]uril, allowing the formation of dynamic host-guest complexes that can couple the fluorophores together and prevent unpredictable aggregation. Resultantly, the fluorescence wavelength and intensity could be reversibly regulated. Significantly, the fluorescence of these complexes showed a response to humidity, displaying reversible emission color changes under both dry and wet conditions. Such humidity-dependent emissive properties exhibited great potential of applications for organic sensing materials with light-emitting and humidity properties.

The synthesis procedure of the four compounds (**1**, **2**, **3** and **4**) could be found in the supplementary material and the compound structures were confirmed by ^1H and ^{13}C NMR spectroscopies and mass spectrometry (Fig. S1–S16, ESI †). Compounds **1** and **2** were synthesized in an accessible route with different substitutions. Meanwhile, the control molecules, compounds **3** and **4**, bearing a methyl (compound **3**) and a benzyl substituent respectively (compound **4**), where their molecular structures are similar to **1** and **2**, were also synthesized for comparison.

To confirm the water solubility of compounds **1** and **2**, powders of the two compounds were directly dissolve in distilled water. Transparent solutions (>1 mM) of phenyl substituted (compound **1**) and 2,4-dinitrophenyl substituted pyridinium units (compound **2**) were observed (Fig. S17, ESI †), indicating the good solubility of the two compounds. Next, a macrocycle, cucurbit[8]uril, was introduced to the aqueous solutions to further regulate the fluorescence properties. Firstly, an optical spectrum study of compound **1** and CB[8] was performed (Fig. 2b, c and Fig. S18, ESI †). The maximum absorption peak at 410 nm gradually decreased and showed a considerable red-shift ($\Delta\lambda_m = 10$ nm) (Fig. 2b) owing to the addition of CB[8] to the solution of compound **1**. Four distinctive isosbestic points at 273, 325, 348 and 445 nm suggested the guest, compound **1**, was included into CB[8]. In addition, changes in the fluorescence emission peak at 478 nm (Fig. 2c) also suggested the supramolecular assembly of compound **1** and CB[8]. Two changes were observed when the addition of CB[8] was more than 0.5 equivalent: (i): shoulder absorption peaks at 445 nm increased; and (ii): a 34 nm red-shift of the fluorescence emission peaks (512 nm), suggesting a possible appearance of the multistep host-guest assembly states within this system (Fig. 2b, c and Fig. S19, S20, ESI †). Therefore, upon the addition of CB[8] solutions with an increasing concentration (0–1.0 eq.), multi-color fluorescence was observed (Fig. S21 and S22, ESI †). Based on these results, we hypothesized that two possible binding motifs between CB[8] and compound **1** could exist, *i.e.*, 1:2 and 2:2 complexes. To further confirm this, isothermal titration calorimetry (ITC) measurement was performed (Fig. S23, ESI †). A second transition was observed at a molar ratio of 2, indicating the formation of 1:2 complexes ($1_2@CB[8]$). A transition point with a large enthalpy change of approximately 100 kJ mol^{-1} was also observed at around 0.6, which may be attributed to the formation of the $1_2@CB[8]_3$ complex.¹⁶ In addition, ^1H NMR

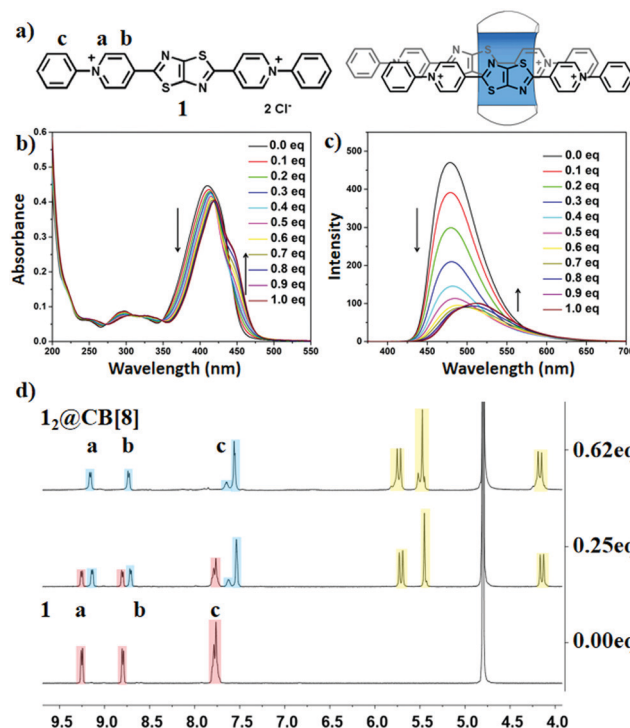


Fig. 2 (a) A schematic presentation of the chemical structures for **1** and the host-guest complex of CB[8] with **1**. Spectra of **1** in solution with an increasing concentration of CB[8]: (b) UV-vis absorption spectra (**1**, 10 μM), (c) fluorescence emission spectra (**1**, 10 μM), and (d) ^1H NMR (**1**, 10 mM).

spectroscopy has proven to be an accessible tool to probe the way of combining CB[8] with the guest, owing to the upfield (downfield) shifts of the proton signals when a guest molecule was located inside (outside) the CB cavity (Fig. 2d). Therefore, ^1H NMR analysis was carried out to further investigate the supramolecular assembly of compound **1** and CB[8]. Upon the addition of CB[8], significant upfield shifts for the $\text{H}^{\text{a,b,c}}$ suggested that the pyridinium and phenyl moieties resided inside of the host cavity and therefore formed stacking complexes. Moreover, the conformations of the host-guest complexes were confirmed by 2D NOESY spectrum (Fig. S24 and S25, ESI †). Such stacking conformations resulted in the red-shifts of the absorption and fluorescence spectra.

To understand the role for the incorporation of the phenyl substituent, two reference compounds, **3** and **4**, were utilized to replace the phenyl substituent with a methyl (compound **3**) and a benzyl substituent (compound **4**). When 0.5 equivalent of CB[8] solution was added to the solution of **3**, the fluorescence emission was close to quantitatively quenched, and no obvious change was observed when more CB[8] solution was added according to the UV/Vis and fluorescence spectra (Fig. S26 and S27, ESI †). These results showed the formation of host-guest complex induced fluorescence intensity quenching without any shift of the fluorescence wavelength (Fig. S28, ESI †). The host-guest combination between **3** and CB[8] was studied by Zhang, *et al.*¹⁹ The induced fluorescence quenching of **3** may be due to the π - π stacking between the electron-deficient pyridinium module and the thiazolothiazole module.¹⁹ Similar optical

changes were observed upon the addition of CB[8] to the compound **2** solution. Both the absorption and fluorescence intensity decreased when the amount of CB[8] was <0.5 eq (Fig. S29 and S30, ESI[†]). However, the increasing shoulder absorption peak at 425 nm and the rising fluorescence emission peak at 460 nm indicated that compound **2** and CB[8] possibly formed other types of host-guest complexes upon the addition of the CB[8] at >0.5 eq. Thus, ITC experiments and ^1H NMR spectra were performed (Fig. S31 and S32, ESI[†]). Two transition points at a molar ratio of 2.0 and 0.5 were observed in ITC experiments, suggesting two types of host-guest complexes. When a solution of compound **2** (1.0 mM) was added dropwise into the solution of CB[8] (0.1 mM), an abrupt change was observed at a molar ratio of 0.5 (Fig. S31, ESI[†]), suggesting the 1:2 complexes ($4\text{@CB}[8]_2$)²⁺ at the beginning of the titration when an excess of CB[8] appeared in the system (Fig. S31, ESI[†]). With continuing the addition of **2** into the CB[8] solution, a second transition appeared indicating that a 2:1 ($2_2\text{@CB}[8]$)⁴⁺ complex was formed. Such combination was also confirmed by ^1H NMR spectra (Fig. S32, ESI[†]).

Considering the connection of the molecular structure and material function, *i.e.*, the fluorescence emission wavelength could be influenced by the guest structure and the conformation of the host-guest complexes, another electron poor substituent group, 2,4-dinitrophenyl, was introduced to investigate whether it will cause a red-shift of the fluorescence emission. The optical study was thus performed. A yellow solution was observed for the 10 μM aqueous solution while other solutions were colorless (Fig. S33, ESI[†]). Detailed absorption spectral analysis indicated that the molar extinction coefficient (ϵ_2) was larger than other compounds (Fig. S34, ESI[†]), and the maximum absorption peak red shifted about 9 nm (relative to compound **1**). In addition, a fluorescence emission peak at 500 nm was observed and the 1931 CIE chromaticity coordinate was located at 0.23, 0.47 (Fig. 3c and Fig. S35, S36, ESI[†]). To further regulate its fluorescence emission, CB[8] was introduced. Upon the addition of CB[8], the absorption gradually decreased with the appearance of the shoulder absorption peak at 434 nm, suggesting the formation of the supramolecular host-guest complexes. In addition, as the amount of CB[8] was >0.5 eq, the absorption spectra reached equilibrium, suggesting that the binding mode of the host-guest system between compound **2** and CB[8] was the 1:2 type. Meanwhile, remarkable changes were observed in fluorescence spectra upon the titration of the CB[8]: (i) the red-shift of the fluorescence emission peak (from 500 nm to 532 nm, Fig. S37, ESI[†]); (ii) the appearance of the maximum fluorescence intensity at 0.6 eq, the quantum yield of **2** increased significantly (Fig. 3c and Fig. S38, ESI[†]). These results also suggested that compound **2** and CB[8] formed 1:2 type supramolecular host-guest complexes. Moreover, the fluorescence wavelength blue shifted when the amount of CB[8] was >0.6 eq. (Fig. 3c and Fig. S37, ESI[†]) and the emission peak blue shifted to 504 nm with a continuous addition of the CB[8] (from 0.6 to 5 eq.), suggesting other host-guest complexes were formed. Therefore, we hypothesized that compound **2** and CB[8] formed 2:1 type

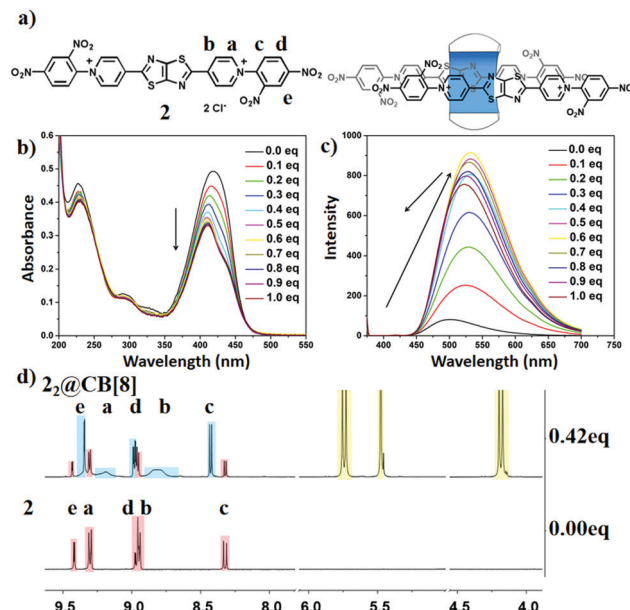


Fig. 3 (a) A schematic presentation of the chemical structures for **2** and the host-guest complex of CB[8] with **2**. Spectra of **2** solutions with an increasing concentration of CB[8]: (b) UV-vis absorption spectra (**2**, 10 μM), (c) fluorescence emission spectra (**2**, 10 μM), and (d) ^1H NMR (**2**, 2.6 mM).

of host-guest complexes due to the occurrence of two binding sites of compound **2**. Such a binding molar ratio was also confirmed by the ITC titration (Fig. S39, ESI[†]).

The conformations were also analysed by ^1H NMR spectra. According to the ^1H NMR spectra, after adding CB[8] into the D_2O solution of **2** (Fig. 3d), the changes in proton signals for the pyridine ($\text{H}^{\text{a,b}}$) suggested a host-guest combination between **2** and CB[8]. The binding mode was well demonstrated by carefully analyzing the ^1H NMR spectra. The proton H^{c} shifted downfield (8.3 to 8.4 ppm), indicating that the 2,4-dinitrophenyl groups were outside the CB[8] cavity.¹⁶ As shown in the NOESY spectrum (Fig. S40, ESI[†]) of **2** (2.6 mM) with CB[8] (1.1 mM), H^{a} was positioned close to proton H^{d} and H^{b} was close to $\text{H}^{\text{c,d,e}}$, indicating the stacking between the pyridinium and 2,4-dinitrophenyl moieties. On the other hand (Fig. S40, ESI[†]), this also suggested that the other two pyridinium moieties were stacked with the fluorescent core, thiazolothiazole, which is strongly related with the red-shift that appeared in the fluorescence spectra leading to an emission change from blue to yellow (Fig. S41, ESI[†]).

According to the previous demonstrations, the multi-color fluorescence could be generated by a simple small compound through the supramolecular assembly strategy. Such assembly behaviours were influenced by the structure of the substituted components, *i.e.*, different substituent molecules (phenyl, 2,4-dinitrophenyl, methyl, benzyl) led to different supramolecular complexes being formed in water with the increasing concentrations of CB[8], resulting in an intrinsic change of the fluorescence emission. In particular, compounds **1** and **2** solutions exhibited multi-colour luminescence with the addition of CB[8]. Such property allows us to raise an important question here: whether it is possible to transfer multi-color luminescence from the solution phase to the solid

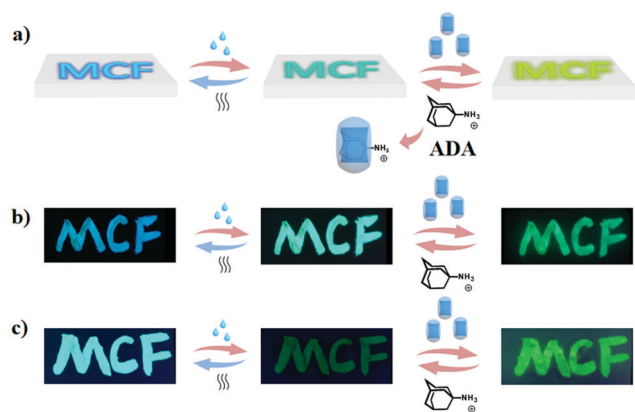


Fig. 4 (a) A schematic presentation of the intelligent fluorescent materials. Images of **1** (b) and **2** (c) supported on silica gel under UV light at 365 nm.

phase. It is well known that the later is more efficient for constructing intelligent fluorescent materials with diverse applications of smart materials with stimuli-responsive, adaptive and dynamic properties in recent years.²² Our strategy was to support **1** or **2** on silica gel by simply daubing the solution, dried by airing or heating. Compounds **1** and **2** exhibited green and blue luminescence on dry silica gel, respectively (Fig. 4b and c). As shown in Fig. 4, the blue luminescence could turn into green luminescence after dropping water onto it, reversed back after evaporation. Moreover, introducing CB[8] resulted in the red-shift of the fluorescence, *i.e.*, green luminescence transferred into green-yellow luminescence after adding CB[8] solution on the silica gel. Such change may be attributed to the formation of the host-guest complexes and such complexes could be reversibly regulated by Amantadine hydrochloride (ADA) (Fig. S42–S46, ESI†). Similar changes were observed in compound **2** (Fig. 4c). Fluorescence was reversibly changed between green (dry) and yellow (wet) when the wetness of the materials was altered. Further red-shift could be observed by adding CB[8] solutions and reversed with the addition of ADA solutions. Such water-dependent fluorescence properties have provided the studied molecular system with great practical potential in developing organic light-emitting and humidity sensing materials.

Conclusions

A color-tunable molecular system based on host-guest recognition has been successfully developed. Different substituent groups were discovered to influence the emission of the fluorescent compounds remarkably when interacting with CB[8]. The results could be potentially utilized to develop intelligent fluorescent materials with response to humidity. This study has given a clear demonstration of designing smart luminescent materials based on supramolecular fluorescent systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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