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Supramolecular hydrogel with tunable multi-color and white-light fluorescence from sulfato-β-cyclodextrin and aminoclay[†]

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A multi-color-tunable supramolecular hydrogel is constructed from aminoclay (AC), sulfato- β -cyclodextrin (SCD), and 4-methyl-styryl-pyridinium (SP), in which the SCD \supset SP complex emits monomer fluores-cence, and AC provides a restricted environment for excimer emission. The emission color of the supramolecular hydrogel can be tuned from yellow \rightarrow white \rightarrow blue by adjusting the SCD/SP molar ratio.

Luminescent hydrogels have attracted tremendous attention due to their special optical properties and potential application in materials science,^{1,2} chemical sensors,³⁻⁶ bioimaging,⁷ 3D printing,8 and tissue engineering.9,10 Among them, tunablelight-emission systems have attracted significant attention, in which the emission wavelength and intensity could be tuned *via* external stimuli^{11–15} or altering the constituent ratio.^{16–21} Traditionally, more than one kind of fluorophore should be incorporated to construct this kind of hydrogel, thus resulting in the complexity of the designed systems. The usage of one fluorophore to construct this type of functional material remains a challenge, in which the luminescent compounds should be designed to tune their structures or stacking manners.²²⁻²⁵ Tao and coworkers reported a color-tunable system based on the oligo(p-phenylenevinylene) (OPV) and cucurbit[8]uril, which provided a toolbox for producing cyan, yellow, green, and white fluorescent emissions by tuning the molar ratio of the OPV derivative and cucurbit[8]uril.²⁶ Besides this method, the emission behavior could also be tuned by changing their π - π stacking manners,²⁷ resulting in the change in the emission wavelength. For example, the emission behavior of neutral platinum(II) complexes mainly depends on their stacking manner. Their stacking manners have a vital effect on the d_{z^2} interaction, which could affect their metal-metal-to-ligand charge transfer (MMLCT)

states, thus resulting in their various emission wavelengths.²⁸ However, the study of multi-color emissive supramolecular hydrogels is still rare.

As is well-known, styrylpyridiniums and their derivatives, a kind of typical dipolar dye consisting of both electro-donor and electro-acceptor in one molecule, are easily accessible with various emission wavelengths and have strong binding affinities with specific macrocyclic hosts.^{29,30} Due to the dipolar nature of these dyes, they exhibit two kinds of stacking manners in solution, named as the syn-excimer ("head-to-head" pattern) and anti-excimer ("head-to-tail" pattern), which show different emission colors. For example, in the restricted cavity of cucurbit[8]uril, the excimer emission is dominant; therefore, the reversibly color-tunable luminescent supramolecular assembly can be successfully fabricated by tuning the ratio of monomer and excimer.^{27,31,32}

On the other hand, aminoclay (AC), referred to as magnesium (organo) phyllosilicate, was firstly reported by Mann and co-workers.33 Due to the trioctahedral sandwich-like structure with aminopropyl pendants on each side, AC has an excellent dispersibility in aqueous solution and presents as layered structures. Recently, several hybrid hydrogels have been fabricated from AC and organic anions via electrostatic interactions.³⁴⁻³⁶ Our previous research also showed that the AC could form a hybrid hydrogel with heptakis-[6-deoxy-6-(2-sulfanylethanesulfonic acid)]-\u03b3-cyclodextrin (SCD).37 Herein, we introduced 4-methyl-styrylpyridinium (SP), a kind of dipolar dye, to the SCD/AC supramolecular hydrogel. The inherent advantage of form the host-guest complex with SCD through electrostatic interactions and hydrophobic interactions,³⁸ thus enabling the monomer emission of SP, while the layer-like structure of AC in the hydrogel provided an environment for the excimer emission of the stacking SP (Fig. 1). Significantly, the formed hydrogel exhibited different emission colors that could be tuned from yellow to blue by altering the molar ratio of SP and SCD, and a white-light emission at the CIE coordinates (0.27, 0.34) was obtained at the SP/SCD ratio of 0.78.

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The negatively charged heptakis-[6-deoxy-6-(2-sulfanylethanesulfonic acid)]- β -CD (SCD) was synthesized by using β -CD as the starting material *via* a two-step reaction (Scheme S1, ESI†).³⁹ 4-Methyl-styrylpyridinium (SP) and aminoclay were synthesized according to the reported literature in a moderate yield (Scheme S3, ESI†).⁴⁰

The host-guest interaction between SCD and SP was investigated by ¹H NMR spectroscopy. After the addition of SCD to SP solution, the chemical shifts of the protons of SP exhibited a remarkable downfield shift, while those of the protons of SCD exhibited a little upfield shift (Fig. 2), probably due to the encapsulation of SP into the cavity of SCD. The 2D ROESY spectrum (Fig. S6, ESI⁺) presented obvious NOE correlation peaks between the H_b/H_c protons of SP and the $H_6/H_7/H_8$ protons of SCD, indicating that the pyridinium motif was surrounded by sulfonic groups. Moreover, the $H_d/H_e/H_f/H_g$ protons of SP exhibited obvious NOE correlation with H₃/H₅/H₆ protons of SCD. These results jointly indicated that SP was encapsulated in the cavity of SCD, and the pyridinium motif of SP was surrounded by the sulfonic groups of SCD. Such an inclusion complexation mode may result from the cooperation of hydrophobic interactions and electrostatic interactions with the host-guest association.



Fig. 2 ¹H NMR (400 MHz, 298 K, D_2O) spectra of (a) SP, (b) SCD + SP, and (c) SCD. ([SCD] = [SP] = 3 mM).

Moreover, the inclusion complexation stoichiometry was further investigated by using UV-Vis spectroscopy. As shown in Fig. S7 (ESI†), the Job's plot showed a maximum value at 0.5, indicating the 1 : 1 binding stoichiometry between SCD and SP. Accordingly, the association constant for the SCD \supset SP complex was determined as $(1.08 \pm 0.41) \times 10^6 \text{ M}^{-1}$ via UV-Vis titrations with a constant concentration of SP and varying concentrations of SCD in water by a non-linear curve-fitting method (Fig. S8, ESI†). In addition, the zeta-potential of the SCD \supset SP complex was measured as -10.10 mV (Fig. S9, ESI†), indicating that the SCD \supset SP complex still had the possibility of interacting with the positively charged AC.

Possessing a layer-like structure and the positively charged surface, AC can form a hydrogel with anionic compounds *via* electrostatic interaction. Therefore, the AC/SCD \supset SP hydrogel was simply constructed by mixing the SCD \supset SP solution and the AC solution at room temperature (25 °C), which was further investigated by the invert-vial experiments and the rheological tests. In the oscillatory experiment (Fig. 3), AC/SCD \supset SP presented a stable hydrogel phase with the storage modulus *G'* larger than the loss modulus *G''* in the tested region ($\omega = 0.1-100$ rad s⁻¹). Upon fixing the strain amplitude sweep at 1 Hz, the hydrogel underwent a gel-to-sol phase transition at the critical strain region ($\gamma = 30\%$). In the SEM images, a number of talc-like assemblies with poriferous structures were observed, indicating the retention of the layer-like structure of AC in the hydrogel.

Furthermore, the fluorescence emission behavior of the hydrogel was investigated. As shown in Fig. S10 (ESI⁺), in the tested concentration range (1.0-100.0 µM), SP exhibited a single emission peak at 455 nm in aqueous solution, and its intensity changed with the increase of the concentration. However, when increased to higher concentration (4.0-9.0 mM), which corresponded to the concentration in the hydrogels, the emission peak exhibited a red-shift to around 465 nm (Fig. S11, ESI[†]). And the emission peak broadened in the range of 500 to 650 nm, indicating the occurrence of stacking between the SP moieties. After the complexation with SCD, this emission peak shifted to 445 nm (Fig. 4a) assigned to the more monomer emission of SP, resulting from the inclusion into the host cavity. Therefore, we could deduce that there existed two fluorescent species. One was the SCD \supset SP inclusion complex that emitted the monomer emission of SP. The other was the stacking complex, which emitted the excimer emission. The restricted



Fig. 3 (a) Oscillation frequency sweep of AC/SCD \supset SP (SP/SCD = 0.78) hydrogel at a constant strain of 1%, (b) strain sweep of the hydrogel at a constant frequency of 1 Hz (storage modulus G' (black, \blacksquare)), loss modulus G'' (red, \bullet , all the experiments were carried out at 20 °C), and (c) SEM image of the AC/SCD \supset SP hydrogel.



Fig. 4 (a) Fluorescence emission, and (b) the 1931 CIE chromaticity coordinates of SP ([SP] = 7.0×10^{-3} M), SCD \supset SP ([SP] = 7.0×10^{-3} M, and [SCD] = 9.0×10^{-3} M), and AC/SCD \supset SP (hydrogel, m_{AC} = 60 mg, V_{water} = 250 µL, [SP] = 7.0×10^{-3} M, and [SCD] = 9.0×10^{-3} M).

environment from the layer-like structure of AC in the hydrogel favored the formation of stacking excimers, resulting in the increase of stacking excimers as well as the enhancement of the emission intensity at the long wavelength range. As seen in Fig. 4a, the hydrogel showed a broad emission peak ranging from 400 to 700 nm, and the emission intensity ratio between $l_{\rm em} = 560$ nm and $l_{\rm em} = 438$ nm was much higher than that of the SCD \supset SP complex, indicating the increase of stacking excimers. Moreover, the fluorescence decay curves of the hydrogel (Fig. S12, ESI†) also gave two different fluorescence lifetimes at 0.41 ns and 0.56 ns. Significantly, the AC/SCD \supset SP hydrogel showed a nearwhite emission in the 1931 CIE chromaticity coordinate at the CIE coordinates (0.27, 0.34) a SP/SCD ratio of 0.78 (Fig. 4b).

To illustrate how the SCD and AC affected the emission behavior of SP, sodium alginate (SA), a natural polysaccharide, was used to replace SCD in the hydrogel, and the formed hydrogel was named as AC/SA-SP. In this AC/SA-SP hydrogel, the contents of SP and AC were the same with those in the AC/SCD \supset SP hydrogel, and the only difference was that the hostguest inclusion was eliminated. In the fluorescence spectrum of AC/SA-SP hydrogel (Fig. S13, ESI⁺), the emission intensity at 438 nm decreased, which was assigned to the emission of the SP monomer, while the emission at the range of 500 to 600 nm increased, which was assigned to the excimer emission, whose CIE coordinates were (0.29, 0.38). In another control experiment, AC was replaced by polyvinyl alcohol (PVA) to form $PVA/SCD \supset SP$ hydrogel that exhibited a blue emission similar to that of the SP monomer (Fig. S14, ESI⁺) but quite different from the white fluorescence of the AC/SCD \supset SP hydrogel. A possible reason may be that SP could not stack in the PVA/SCD⊃SP hydrogel due to the loose structure of PVA compared with the layer-like structure of AC. These results jointly indicated that both the host-guest complexation and the AC's positively charged layered structure played important roles in the white-light emission of the $AC/SCD \supset SP$ hydrogel.

Based on previous research, a strategy to tune the emission behavior of the AC/SCD \supset SP hydrogel was developed. Herein, hydrogels containing the same amount of AC (60 mg) and SCD (9.0 × 10⁻³ M × 0.25 mL) but different amounts of SP were prepared, where the molar ratios of SP/SCD were 0.94, 0.78, 0.63, and 0.47, respectively. The rheology results indicated that the change in content of SP had little influence in their



Fig. 5 (a) Florescence emission and (b) the 1931 CIE chromaticity coordinates of AC/SCD \supset SP hydrogels with different SP/SCD molar ratios of 0.94, 0.78, 0.63, and 0.47 under 365 nm light; inset: images of hydrogels under 365 nm light.

Table 1 CIE coordination data of the tested hydrogels

CIE (color)	m _{AC} / mg	V _{water} / μL	[SCD]/M	[SP]/M	[SP]/ [SCD]
1 0.28, 0.37 (yellow) 2 0.27, 0.34 (white) 3 0.26, 0.33 (light blue) 4 0.24, 0.29 (blue)	60 60 60 60	250 250 250 250	$\begin{array}{l} 9.0 \times 10^{-3} \\ 9.0 \times 10^{-3} \\ 9.0 \times 10^{-3} \\ 9.0 \times 10^{-3} \end{array}$	$\begin{array}{l} 8.4 \times 10^{-3} \\ 7.0 \times 10^{-3} \\ 5.6 \times 10^{-3} \\ 4.2 \times 10^{-3} \end{array}$	0.94 0.78 0.63 0.47

rheology properties. Moreover, the SEM images indicated that their aggregation structures had no obvious changes compared with the previous AC/SCD \supset SP hydrogel (Fig. S15–S17, ESI†). As shown in Fig. 5, the emission of the hydrogel exhibited an obvious blue shift with the decrease in the SP amount. These phenomena resulted from the tendency of the formation of the host-guest complex, and in this way, the monomer emission and stacking emission of SP would be changed. The photo images also provided visible evidence for this transformation, exhibiting the emission color changes from blue to white. The CIE chromaticity coordinate revealed a gradual change from the blue light region to the yellow light region (Table 1). The above-mentioned change could also be observed in the other two sets, in which the AC contents were changed to 50 mg (Fig. S18, ESI[†]) and 40 mg (Fig. S19, ESI[†]). These observations provided solid evidence for the successful construction of emission-tunable hydrogels by means of tuning the molar ratio of the host and guest molecules.

Conclusions

In summary, a kind of tunable multicolor hydrogel was successfully constructed from a single dipolar fluorophore that was noncovalently associated with sulfato- β -cyclodextrin and aminoclay *via* electrostatic and hydrophobic interactions. Interestingly, the formed hydrogel showed not only an obvious multicolor emission varying from yellow to blue but also a near white-light emission with CIE coordinates (0.27, 0.34). In this system, SCD played a vital role in maintaining the emission behavior of the SP monomer, and the AC provided a layer-like environment for the stacking of SP. That is, in hydrogels, except for the monomer emission of the SCD \supset SP complex, there is also the excimer emission owing to the AC-induced SP stacking. Moreover, the emission color of the obtained hydrogel could be simply tuned by adjusting the molar ratio of SP and SCD.

Conflicts of interest

There are no conflicts to declare.

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