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Tunable white-light emission by supramolecular self-sorting in highly swollen hydrogels†

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Fluorescence-tunable hydrogels especially emitting white-light were achieved by swelling hydrogels in solutions containing two kinds of dyes. The fluorescence of the dyes was enhanced by the orthogonal supramolecular complexation with different binding sites in the hydrogels.

Photo-luminescent gels with multicolor emissions, especially white light, have attracted much attention due to their potential applications in chemosensors, light-emitting materials, *etc.*[1] Most of these gels are supramolecular gels, in which small fluorescent molecules and polymers chelate as 3D networks through non-covalent interactions such as π–π interactions, hydrogen bonding, and metal coordination (Fig. 1a, strategy I).[2] But once gels are formed *via* these "*in situ*" ways, it is not easy to regulate the emission colors because the fluorophores have already been chelated in the gels. Considering networks of gels can swell and absorb some of the substances dissolved in the solvent,[3] making the hydrogels swell with two or more fluorophores might be a promising way for developing multifluorescent materials (Fig. 1a, strategy II).[4] This pre-forming method is more convenient to manipulate the emission colors by swelling different fluorophores in different ratios whenever necessary.

Macrocycle-based supramolecular hydrogels have been widely applied in stimuli-responsive and self-healing materials owing to distinct host–guest interactions between the macrocyclic host and guest moieties.[3c,5] Different host–guest pairs usually show high binding affinity and selectivity for molecular recognition and do not interact with each other. This "self-sorting" behavior[6] could make the supramolecular systems self-assemble in an "orthogonal" fashion[7] at the molecular level, and even on the macroscopic scale.[8] Our group has developed several self-sorting systems which showed potential applications in molecular machines, supramolecular polymers and biomedicines.[9] But it remains challenging to make a hydrogel swell with different fluorophores in an orthogonal fashion for emitting different colors. Herein we reported hydrogel-I containing two binding sites, *i.e.* adamantyl (Ad) and the sulfonatocalix[4]arene (SC[4]A) moieties. Hydrogel-I exhibited excellent swelling properties and orthogonal supramolecular recognition of β-cyclodextrin-modified tetraphenylethene (TPECD) and 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (DASPI). As a result, the regulation of the fluorescence emission was conveniently achieved, which was changed from blue to yellow, especially including white light.

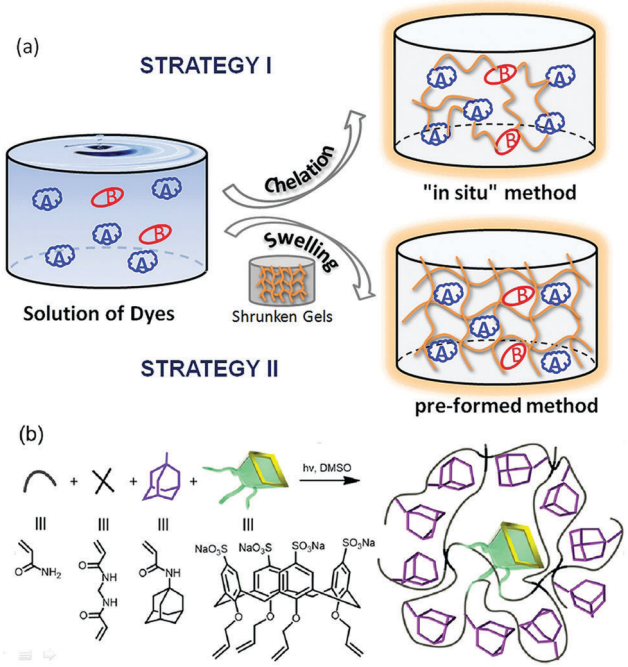

Fig. 1 (a) Different strategies for fabricating multicolor fluorescent hydrogels (strategy I: sol–gel transformations, chelating fluorophores to gels; strategy II: swelling with fluorophores, self-sorting of fluorophores in the gel phase). (b) Synthesis of hydrogel-I by copolymerization.

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Hydrogel-I was produced *via* one-pot UV-initiated free-radical copolymerization of acrylamide (AAm), 1-adamantyl acrylamide (AAmAd),[10] 4-(allyloxy)sulfonatocalix[4]arene (SC[4]AA)[11] and *N*,*N*′-methylenebisacrylamide (bisAAm) (mass ratio of 30 : 1 : 4 : 2) with hydroxycyclohexylphenylketone as the photoinitiator (Fig. 1b). After polymerization, the homogeneous solution yielded a gel, which was purified by washing with DMSO and water several times for removing unreacted monomers. Finally, hydrogel-I was easily obtained by solvent replacement in an excess amount of water. As shown in Tables 1 and S1 (ESI†), other reference hydrogels and polymers were prepared in the same way. As shown in the ^{1}H NMR spectrum of polymer-IV (Fig. S5, ESI†), the upfield shifted proton signals of phenyl rings and the disappearance of allyl proton signals suggested the copolymerization of SC4AA with acrylamide species.

All of the resulting hydrogels were transparent and colorless, with the water content ranging from 26% to 98%. Photographs of completely shrunken hydrogel-I, fully swollen hydrogel-I, -II and -III are presented in Fig. S6 (ESI†). The weight of the fully swollen hydrogel-I was 11.5 g with a diameter of 4.2 cm, which was 46-fold higher than that of its shrunken state (diameter: 1.2 cm, weight: 0.25 g). This means that the hydrogel gelator ratio was increased from 74% to 1.60% when hydrogel-I was fully swollen in water. Scanning electron microscopy (SEM) images showed the morphology of the fully swollen hydrogel-I as a porous structure (Fig. S7, ESI†), while the shrunken state had a dense structure (Fig. S8, ESI†). Compared to the fully swollen hydrogel-II (diameter: 2.6 cm, weight: 3.3 g), the better swelling properties of hydrogel-I and hydrogel-III (diameter: 3.6 cm, weight: 8.3 g) were undoubtedly attributed to the presence of SC4A. As shown in Fig. S9 (ESI†), with the increase in the amount of SC4AA (0, 5, 10, 15 mg mL^{-1}) in the polymers, the weight of the fully swollen hydrogel was increased even up to 24.2 g with the water content of 99.2%.

Rheology experiments showed that the fully swollen hydrogel-I has certain mechanical strength. The dynamic strain sweep curves showed that G' was always larger than G'' with the strain from 0.1% to 100% (Fig. S10, ESI†), indicating that hydrogel-I was stable and remained undamaged. A further increase in strain made G' decrease and G'' increase dramatically and intersect at the strain of 900%, indicating the damage of hydrogel-I.[12] The dynamic frequency sweep curves showed that G' remained larger than G'' and did not change obviously with the fixed 1% strain (Fig. S11, ESI†), indicating the good stability of the hydrogel towards frequency oscillation.

Table 1 Weight of substrates for I–VI[a]

	AAm	AAmAd	SC4AA	bisAAm	Initiator[b]
Hydrogel-I	150	20	10	5	5
Hydrogel-II	150	20	0	5	5
Hydrogel-III	150	0	10	5	5
Polymer-IV	150	20	10	0	5
Polymer-V	150	0	10	0	5
Polymer-VI	150	20	0	0	5

[a] Preparation of hydrogels and polymers with various substrates (mg) in 1 ml DMSO as listed in the table. [b] Hydroxycyclohexylphenylketone was used as an initiator.

To investigate the self-sorting assembly behaviors of hydrogels with two binding sites (Fig. 3), the corresponding dyes TPECD and DASPI were synthesized *via* reported methods[13,14] and their structures were verified using NMR and HRMS (Fig. S12–S15, ESI†). As a class of dyes with special fluorescent properties of "aggregation-induced emission (AIE)", TPE derivatives gave stronger fluorescence emission when the "restriction of intramolecular rotation (RIR)" happened.[15] DASPI is a typical twisted intramolecular charge transfer (TICT) molecule[16] which give strong fluorescence emission in confined region. The fluorescence properties of TPECD and DASPI based on molecular recognition with polymers were first investigated in aqueous solution. Upon the addition of an excess amount of polymer-VI (involving Ad), the fluorescence of TPECD enhanced 5 times (Fig. S18 and S19, ESI†), while the addition of polymer-V (without Ad) did not affect the intensity (Fig. S16, ESI†). So the fluorescence enhancement was attributed to the complexation of Ad with CD, which further restricted the intramolecular rotation of the TPE moiety for reducing the non-radiative relaxation.[13] As shown in Fig. S17 (ESI†), the fluorescence intensity of DASPI was greatly enhanced (34 times) in the presence of excess polymer-V (involving SC4A) due to the host–guest complexation between DASPI and SC4A,[16b] and changed slightly (4 times) with polymer-VI (without SC4A), which was attributed to the hydrophobic microenvironment aroused by polymers micelles (Fig. S20 and S21, ESI†).[17] These results indicated that the fluorescence enhancements for TPECD and DASPI were little interfered with each other in these systems.

Fortunately, a multicolor hydrogel was easily obtained by swelling fluorophores based on the self-sorting assembly of TPECD–Ad and DASPI–SC4A pairs in the hydrogel phase (Fig. 2). By soaking in the TPECD or DASPI solution, the shrunken hydrogel-I expanded and gave blue (454 nm) or yellow (595 nm) emissions under 365 nm excitation (Fig. 3b and c). Compared to the fluorescence spectrum of the TPECD solution with the peak maximum at 470 nm, the 16 nm blue shift suggested the efficient binding of TPECD–Ad rather than the existence of free species (Fig. S22, ESI†). The yellow emission also suggested the strong interaction of DASPI–SC4A in the hydrogel phase. When hydrogel-I was swollen in aqueous solution with different ratios of TPECD and DASPI, the fluorescence spectra of the hydrogels exhibited two peaks around 454 and 595 nm, which could be assigned to the emissions of TPECD and DASPI, respectively. The fluorescence emission at 454 nm (TPECD) gradually decreased and that around 595 nm (DASPI) increased slowly (Fig. 3e). As shown in Fig. S26 (ESI†), the UV-Vis absorption band of DASPI shows a good overlap with the fluorescence band of TPECD, so a fluorescence resonance energy transfer (FRET) process could be involved in this hydrogel phase. The energy-transfer efficiency (Φ_{ET}) was calculated to be 70.3%. To further confirm the self-sorting processes in the hydrogel phase, similar swelling experiments were carried out for hydrogel-II and -III. When hydrogel-II (without Ad) was swollen in the TPECD solution, the hydrogel did not give blue emission owing to no RIR effect on TPECD (Fig. S23b, ESI†). Analogously, when hydrogel-III (without SC4A) was swollen in the DASPI solution, a yellow fluorescent hydrogel could not be obtained either because DASPI was not confined (Fig. S23d, ESI†).

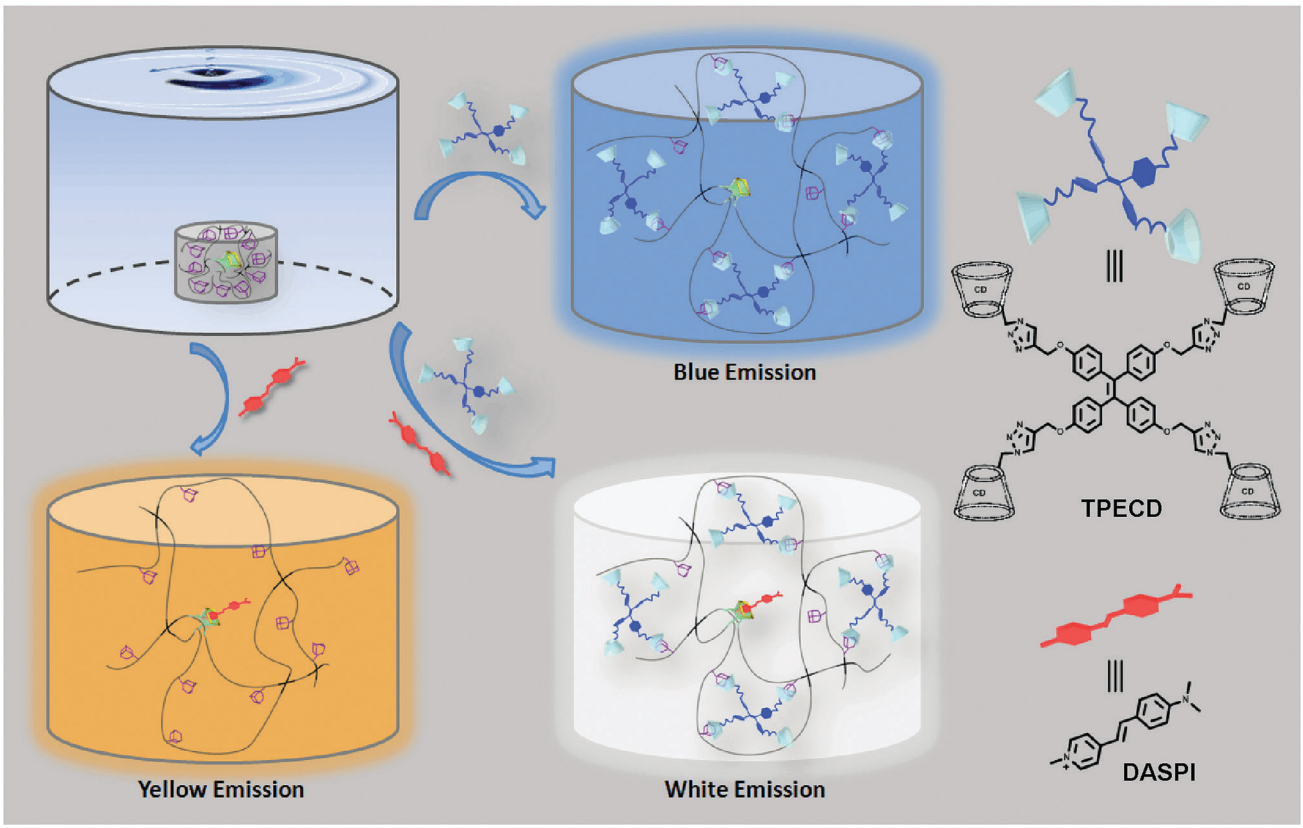

Fig. 2 The schematic illustration of the orthogonal supramolecular recognition in the luminescent hydrogel during the swelling process.

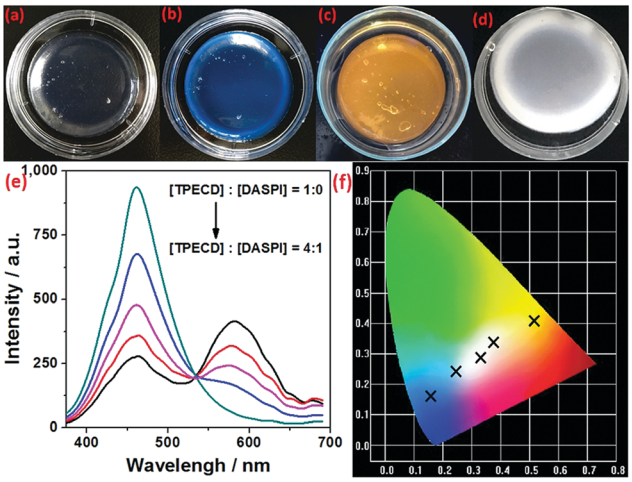

Fig. 3 Photos of hydrogels I swollen with (a) water, (b) TPECD (1×10^{-4} mol L^{-1}), (c) DASPI (1.25×10^{-5} mol L^{-1}) and (d) a mixture of TPECD (1×10^{-4} mol L^{-1}) and DASPI (1.25×10^{-5} mol L^{-1}) taken under 365 nm light; (e) fluorescence emission spectra of hydrogels swollen with TPECD and DASPI at different molar ratios (top–down: 1 : 0, 32 : 1, 16 : 1, 8 : 1, 4 : 1); (f) CIE diagram showing the trajectory of the color changes based on the fluorescence emission spectra.

The trajectory of color changes based on the fluorescence spectra of hydrogel-I swollen with different ratios of TPECD and DASPI solutions was marked out using a CIE program (Fig. 3f). When the TPECD : DASPI ratio was 8 : 1, the hydrogel gave dual emission colors under 365 nm excitation which could merge to produce white light (Fig. 3d). The same phenomena were also observed in the laser scanning confocal microscopy (LSCM) images. The lyophilized hydrogel-I swollen with TPECD gave blue emission signals at 435–475 nm, and that with DASPI gave yellow emission signals at 570–610 nm (Fig. S24, ESI†). However, the white-light emitting hydrogel-I showed strong signals both at 435–475 nm (Fig. S25a, ESI†) and 570–610 nm (Fig. S25b, ESI†) in the dark field, which can be assigned to the luminescence of TPECD and DASPI, respectively, and the merged image exhibited strong white light (Fig. S25d, ESI†). In addition, the porous morphology was also observed in the LSCM images, which coincided well with the SEM image.

Cationic pesticides, such as paraquat (PQ) and diquat (DQ), show high binding affinities with SC4A (binding constants are 9.33×10^4 M^{-1} and 7.95×10^5 M^{-1}, respectively[18]), which are stronger than that of DASPI with SC4A (binding constant is 1.3×10^4 M^{-1}).[16b] So we could use the fluorescent hydrogel-I to detect PQ and DQ. As shown in Fig. 4a, the white light was quenched to weak blue light when a thin layer of hydrogel-I was immersed in a paraquat or diquat solution. But when the hydrogel-I emitting blue light was immersed in the pesticide solution, there was no obvious change in the fluorescence spectra (Fig. 4b), indicating that PQ and DQ could not affect the fluorescence of TPECD. So the quenching of the white light was mainly attributed to the energy transfer from TPECD to the free DASPI as a result of the competitive binding of SC4A⊃DASPI with pesticides.

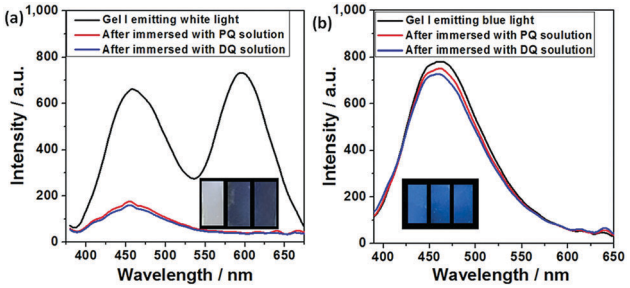

Fig. 4 (a) Fluorescence emission spectra and photos taken at 365 nm light (inset) of the thin layer of hydrogel-I emitting white light (black) and after immersing in PQ (red) or DQ (blue) solution (1×10^{-5} mol L^{-1}). (b) Fluorescence emission spectra and photos taken at 365 nm light (inset) of hydrogel-I emitting blue light (black) and after immersing in PQ (red) or DQ (blue) solution.

In summary, hydrogel-I was prepared from AAm, AAmAd and SC4AA with bisAAm as a cross-linker and showed good swelling properties and certain mechanical strength. Owing to orthogonal supramolecular recognitions of TPECD–Ad and DASPI–SC4A pairs in hydrogel-I, the multi-color fluorescence emissions including white light were achieved by swelling hydrogel-I in an aqueous solution of TPECD and DASPI with different ratios. This integrative self-sorting system in the hydrogels made the different fluorophores emit light efficiently due to the fluorescence enhancement and FRET induced by host–guest complexation. Compared with the well-known method of pre-gelation modification of luminescent species for gels, our post-gelation modification method was more convenient for fabricating tunable fluorescent hydrogels with multi-color emissions. We do believe that this post-modification method based on the integrative self-sorting concept would greatly promote the preparation of multi-color fluorescent gels which have potential applications in organic luminescent displayers or optical devices.

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Conflicts of interest

The authors have no conflicts of interest to declare for this communication.

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11 SC[4]AA was obtained *via* an efficient substitution reaction of sulfonatocalix[4]arene with allyl bromide (Scheme S2, ESI[1]), and its "cone" conformation was confirmed by the appearance of the single resonance peak of the methylene hydrogen signal in the ^{1}H NMR spectrum (Fig. S2, ESI[1]), which suggested the reservation of the hydrophobic cavity of the calix[4]arene. ^{13}C NMR (Fig. S3, ESI[1]) and mass spectroscopy (Fig. S4, ESI[1]) were also performed to verify the structure of SC[4]AA.

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