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Tunable White-Light Emission by Supramolecular Self-sorting in Highly Swollen Hydrogel

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Fluorescence-tunable hydrogels especially emitting white-light were achieved by swelling hydrogels in the solutions containing two kinds of dyes. The fluorescence of 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 more attention due to their potential applications in chemosensors, light-emitting materials, etc[1]. Most of those gels are supramolecular gels, in which the small fluorescent molecules and polymers chelate as 3D networks through noncovalent interactions such as π-π interactions, hydrogen bondings, and metal coordinations (Fig 1a Strategy I).[2] But once gels were formed in 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 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-formed 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 macrocyclic host and guest moieties[3c, 5]. Different host-guest pairs usually show high binding affinity and selectivity for molecular recognitions which do not interact with each other. Those "self-sorting" behaviors[6] could make the supramolecular systems self-assemble in "orthogonal" way[7] at molecular levels, and even on 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 way for emitting different colors. Herein we reported a hydrogel-I containing two binding sites, i.e. the adamantyl (Ad) and the sulfonatocalix[4]arene (SC[4]A) moieties. The hydrogel-I exhibited excellent swelling property 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 and especially including white light.

Hydrogel-I was produced by 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'-

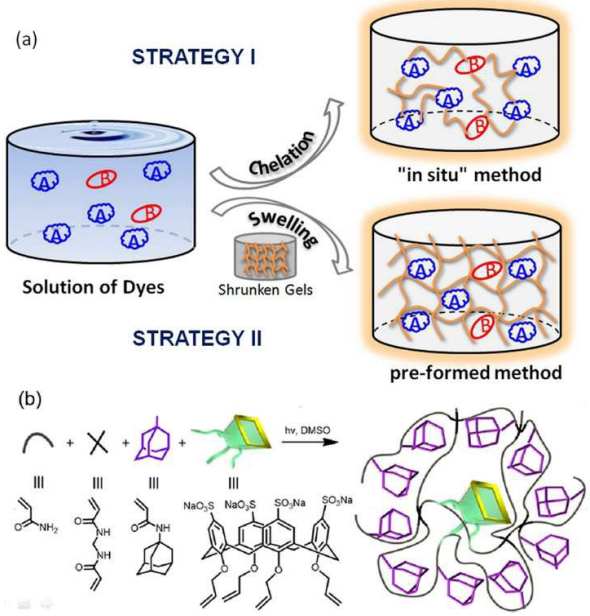

Fig. 1 a) Different strategies for fabricating multicolor fluorescent hydrogels (Strategy I: Sol-gel transformations, chelating fluorophores to gels; strategy II: swelling with fluorophores, self-sorting of fluorophores in gel phase). b) Synthesis of hydrogel-I by copolymerization.

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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 list in the Table 1. [b] Hydroxycyclohexylphenylketone was used as initiator.

methylenebisacrylamide (bisAAm) (mass ratio at 30:1:4:2) with hydroxycyclohexylphenylketone as photoinitiator (Fig 1b). After polymerization, the homogeneous solution yielded 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 excess amount of water. As shown in Tables 1 & S1, other referential hydrogels and polymers were prepared in the same way. As shown in the ^{1}H NMR spectrum of polymer-IV (Fig S5), 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 resulting hydrogels were transparent and colorless, with a water content ranging from 26% to 98%. Photographs of completely shrunken hydrogel-I, fully swollen hydrogel-I, -II and -III were presented in Fig S6. The weight of the fully swollen hydrogel-I was 11.5 g with a diameter of 4.2 cm, which was 46 folds higher than its shrinking state (diameter: 1.2 cm, weight: 0.25 g). That means, the hydrogel gelator ratio was eased from 74 % to 1.60 % when hydrogel-I fully swollen in the water. The scanning electron microscopy (SEM) images showed the morphology of fully swollen hydrogel-I as a porous structure (Fig S7), while the shrunk state as a dense structure (Fig S8). 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 undoubted attributed to the presence of SC4A. As shown in Fig S9, accompanied by the increased amounts of SC4AA (0, 5, 10, 15 mg/mL) in the polymers, the weight of fully swollen hydrogel was even up to 24.2 g with the water content as 99.2%.

Rheology experiments showed that the fully swollen hydro-gel-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), indicating that the hydrogel-I was stable and remained undamaged. The further increasing strain made G' decrease and G'' increase dramatically and came across at the strain of 900%, indicating the damage of the hydrogel-I.[12] The dynamic frequency sweep curves showed that G' kept larger than G" and did not change obviously with the fixed 1% strain (Fig S11), indicating the good stability of hydrogel towards the frequency oscillation.

To investigate the self-sorting assembly behaviors of hydrogels with two binding sites (Fig 3), corresponding dyes TPECD and DASPI were synthesized by reported methods[13, 14] and their structures were verified by NMR and HRMS (Fig S12-15). As a class of dyes with special fluorescent properties "aggregation-induced emission (AIE)", TPE derivatives gave stronger fluorescence emission when the "restriction of intramolecular rotation (RIR)" happened.[15] DASPI

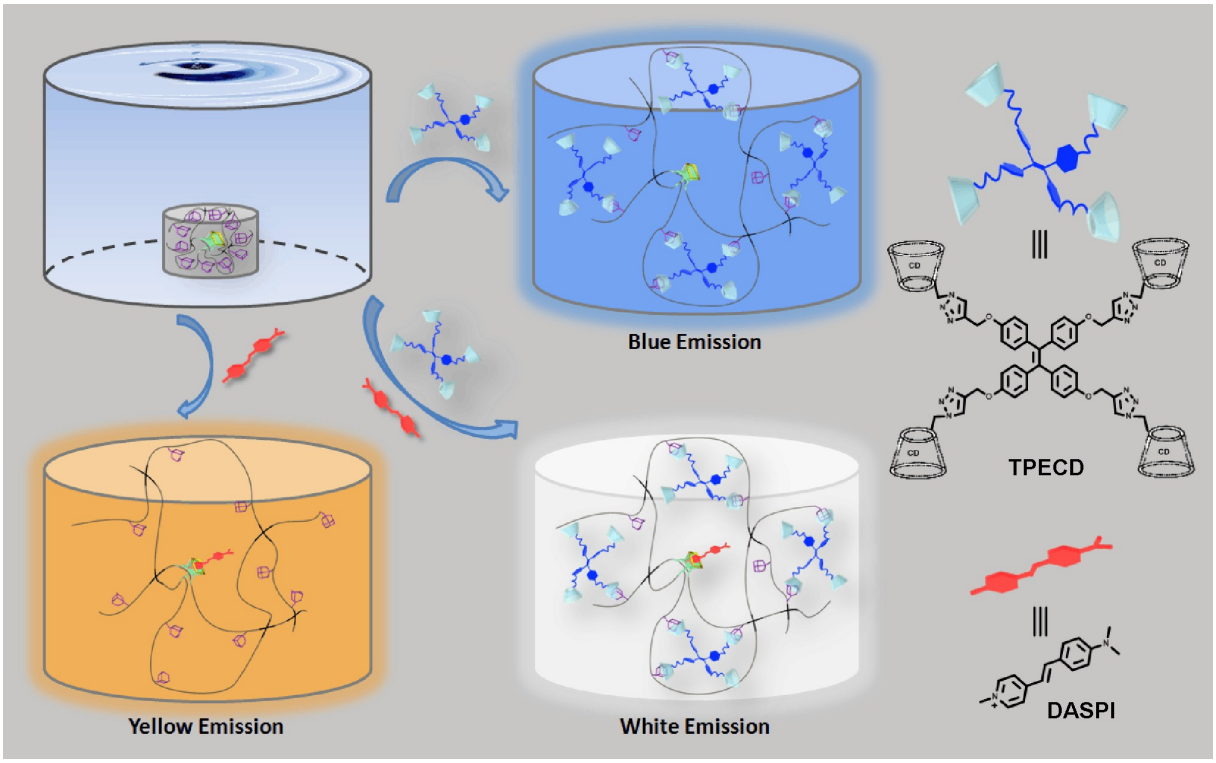

Fig 2. The schematic illustration of the orthogonal supramolecular recognition in the luminescent hydrogel during swelling process.

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is a typical twisted intramolecular charge transfer (TICT) molecule,[16] which can shine brightly when falling down in a confined region. The fluorescence properties of TPECD and DASPI based on molecular recognitions 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, S19), while the addition of polymer-V (without Ad) did not affect the intensity (Fig S16). So the fluorescence enhancement was attributed to the complexation of Ad with CD, which further restricted the intramolecular rotation of TPE moiety for reducing the non-radiative relaxation.[13] As shown in Fig S17, the fluorescence intensity of DASPI 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 was less changed (4 times) with polymer-VI (without SC4A), which was attributed to the hydrophobic microenvironment aroused by penetrating into polymers micelles (Fig S20, S21).[17] Those results indicated that the enhanced fluorescence of TPECD and DASPI could little interfered each other in this systems.

Fortunately, multicolor hydrogel was easily obtained by swelling fluorophores based on the self-sorting assembly of TPECD-Ad and DASPI-SC4A pairs in hydrogel phase (Fig 3). Via soaking in the TPECD or DASPI solution, the shrunken hydrogel-I was expanded and gave blue (454 nm) or yellow (595 nm) emissions under 365 nm excitation (Fig 3b & 3c). Compared to the fluorescence spectrum of TPECD solution with the maxima peaked at 470 nm, a 16 nm blue shift suggested the efficient binding of TPECD-Ad rather than the free existing (Fig S22). The yellow emission also suggested the strong interaction of DASPI-SC4A in hydrogel phase. When the hydrogel-I was swelled in aqueous solution with different ratios of TPECD and DASPI, the fluorescence spectra of hydrogels exhibited two peaks around 454 and 595 nm which could be assigned to emissions of TPECD and DASPI respectively. The fluorescence emissions at 454 nm (TPECD) gradually decreased and around 595 nm (DASPI) increased slowly (Fig 3e). As shown in Fig S26, 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. Energy-transfer efficiency (ΦET) was calculated as 70.3%. To further confirm the self-sorting processes in hydrogel phase, similar swollen experiments were carried out for hydrogel-II and -III. When hydrogel-II (without Ad) was swelled in TPECD solution, the hydrogel did not give blue emission owing to no RIR effect on TPECD (Fig S23b). Analogously, when hydrogel-III (without SC4A) was swelled in DASPI solution, the yellow fluorescent hydrogel could not be obtained either because DASPI was not confined (Fig S23d).

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

The cationic pesticides, such as paraquat (PQ) and diquat (DQ), show high binding affinities with SC4A (binding constants are 9.33 x 10^4 M^{-1} and 7.95 x 10^5 M^{-1} respectively[18]), which are stronger than that of DASPI with SC4A (binding constant is 1.3 x 10^4 M^{-1}).[16b] So we could use the fluorescent hydrogel-I to detect PQ and DQ. As shown in figure 4a, the white light was quenched to the weak blue light when the thin layer of hydrogel-I was immersed with paraquat or diquat solution. But when the hydrogel-I emitting blue light was immersed with the pesticide solution, there was no obvious change in the fluorescence spectra (figure 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.

In summary, a copolymer hydrogel-I of AAm, AAmAd and SC4AA

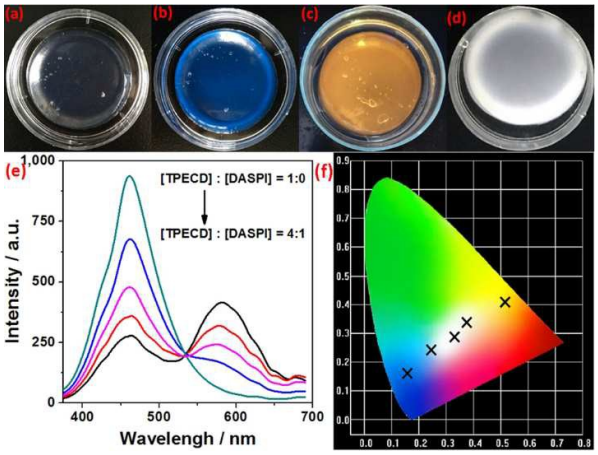

Fig. 3 Photos of hydrogels I swollen with (a) water, (b) TPECD (1x10^{-4} mol L^{-1}), (c) DASPI (1.25x10^{-5} mol L^{-1}) (d) mixture of TPECD (1x10^{-4} mol L^{-1}) and DASPI (1.25x10^{-5} mol L^{-1}) taken under 365 nm light; (e) fluorescence emission spectra of hydrogel swollen with TPECD and DASPI at different molar ratios (top-down are 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.

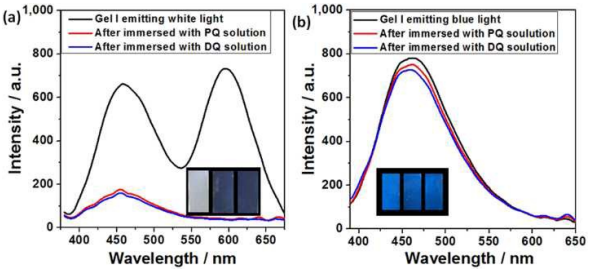

Fig. 4 (a) Fluorescence emission spectra and photos taken at 365 nm light (insert) of the thin layer of hydrogel-I emitting white light (black) and after immersing with PQ (red) or DQ (blue) solution (1x10^{-5} mol L^{-1}). (b) Fluorescence emission spectra and photos taken at 365 nm light (insert) of hydrogel-I emitting blue light (black) and after immersing with PQ (red) or DQ (blue) solution.

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with bisAAm as cross-linker was prepared and showed good swelling property 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 hydro-gel-I in aqueous solution of TPECD and DASPI with different ratios. This integrative self-sorting system in hydrogels made different fluorophores emit light efficiently due to the fluorescence enhancement and FRET induced by host-guest complexations. Comparing 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 this post-modification method based on integrative self-sorting concept would greatly promote the preparation of multicolor 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 efficient substitution reaction of sulfonatocalix[4]arene with allyl bromide (Scheme S2), and its "cone" conformation was confirmed by the appearance of single resonance peak of the methylene hydrogen signal in the 1H NMR spectrum (Fig S2), which suggested the reservation of hydrophobic cavity of the calix[4]arene. 13C NMR (Fig S3) and mass spectra (Fig S4) also performed to verify the structure of SC[4]AA.

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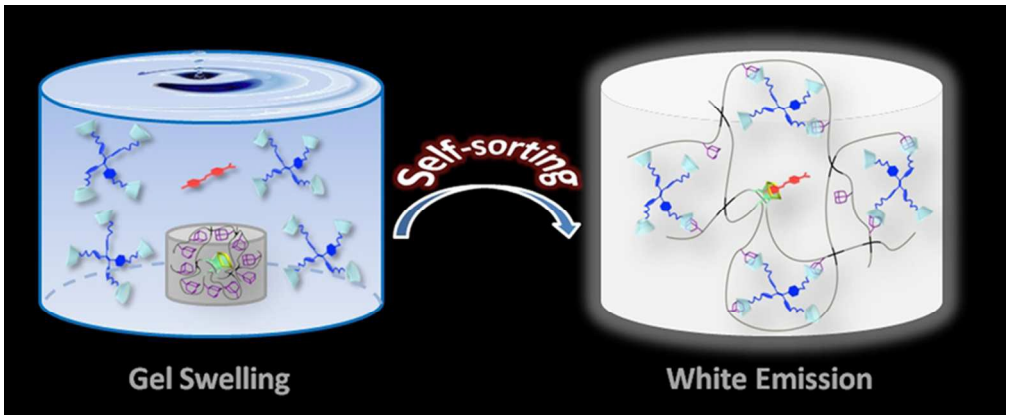

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