



Polyrotaxane in-situ copolymerization stretchable supramolecular hydrogels for photo-controlled cascade energy transfer

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ABSTRACT

Amphiphilic polysorbate (Tween 80) encapsulated hydrophobic methyl acrylate (MA), spiropyran (SP), nitrobenzoxadiazole (NBDAE) and cyanine 5 (Cy5) was mixed to form micelles, which in-situ copolymerized with acrylamide (AM) and polyrotaxane (PR) containing polyethylene glycol (PEG) threaded into vinyl modified α -cyclodextrin (α -CD) with amantadine end-capping to form stretchable supramolecular hydrogel. Benefiting from the sliding cross-linking points of PR, the hydrogel exhibited excellent mechanical properties (1300 % breaking strain and 0.26 MPa breaking stress). Meanwhile, photoreactive achievement of reversible SP acted as primary energy acceptor tuned cascade energy transfer from energy donor NBDAE to secondary acceptor Cy5 (energy transfer efficiency = 80 % for primary transfer, 65 % for secondary transfer). Therefore, this stretchable supramolecular hydrogel material can achieve phototunable multi-color emission and be applied in the field of time-resolved information anti-counterfeiting.

1. Introduction

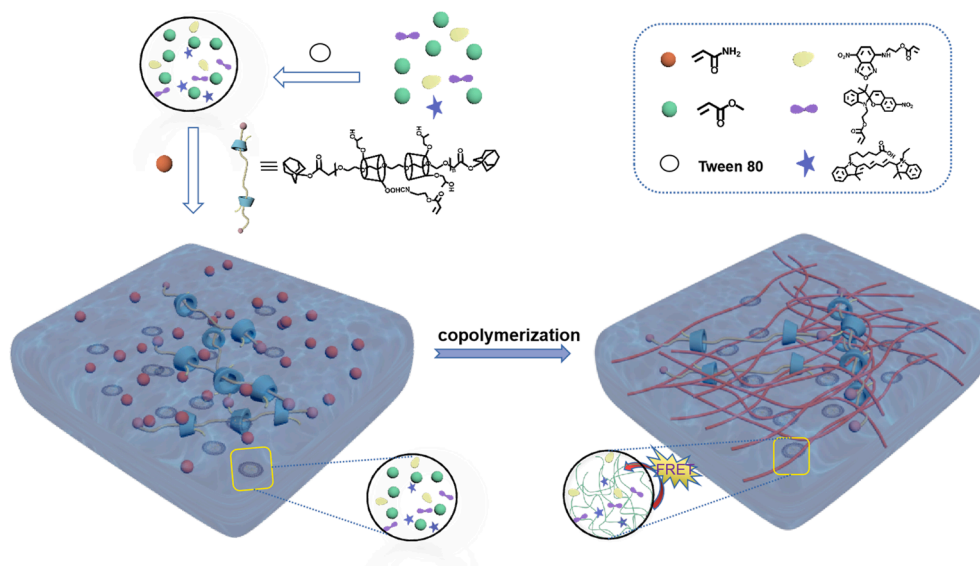
Polyrotaxane (PR), containing polyethylene glycol (PEG) threaded into α -cyclodextrin (α -CD) with amantadine end-capping, possesses unique advantages of free movement along with the chain of PEG under the external simulation [1,2]. Owing to the pulley effect of PR caused by sliding cross-links, PR can be widely used to construct slide-ring materials with good mechanical properties, including highly elastic chemically cross-linked gels [3,4], polymer elastomers [5], resins [6,7], and so on. Therefore, a lot of efforts have been devoted to studying the PR slide-ring materials. For example, Ito et al. [8] reported high strength PR slide-ring gels composed of PEG and hydroxypropyl- α -cyclodextrin by the strategy of strain induced crystallization, which can be used as coating materials because of their remarkable scratch resistance. Wang and co-workers [9] constructed a conductive polymer which was formed of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate films with PR and the polymer had high electrical conductivity and good mechanical strength and can be used as bioelectronic devices. Sakai et al. [10] reported *N*-isopropylacrylamide as monomer and PR as cross-agent were used to prepare extremely thermosensitive hydrogels with strong stretchability and good toughness by adding ionic liquids. We reported a slide-ring stretchable supramolecular hydrogel by in-situ

polymerization of PR and acrylamide, and the supramolecular hydrogel could be applied in wearable strain sensors because of 2540 % stretch strain under stress [11]. Although many studies have showed that PR can be used as a cross-linker to improve mechanical properties of slide-ring hydrogels, it is of significance to develop the stretchable supramolecular PR hydrogels loaded with dye molecular for photo-controlled cascade energy transfer.

It's well known that supramolecular systems have been one of the best choices for constructing cascaded energy transfer systems, in which the ordered aggregation structure helps the fluorophores pack tightly together and stay close to each other for better energy transfer [12–15]. Cascade energy transfer systems have broad applications in the development of fluorescent inks, bioimaging, information security and photoluminescent materials with color tenability [16–20], due to high energy transfer efficiency of long-range transfer, larger Stokes shift, more color variation [21,22]. However, there is no report on the dye-loaded stretchable supramolecular PR hydrogels for photo-controlled cascade energy transfer, to our best knowledge. Herein, we constructed a stretchable supramolecular hydrogel with both good mechanical properties and highly efficient cascade energy transfer property via the micellar-copolymerization method (Scheme 1). Hydrophobic methyl acrylate (MA), spiropyran (SP), nitrobenzoxadiazole (NBDAE)

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Scheme 1. The schematic diagram of stretchable supramolecular photo-controlled hydrogel and illustration of the FRET between NBDAE, SP and Cy5.

and cyanine 5 (Cy5) were encapsulated in amphiphilic polysorbate (Tween 80) to form micelles, and then in-situ copolymerized with acrylamide (AM) and PR to form stretchable supramolecular hydrogel in which PR was formed of PEG and α -CD with amantadine end-capping. The PR as a cross-linker can produce the pulley effect, which relieved the tension between the polymers to improve mechanical properties (1300 % breaking strain and 0.26 MPa breaking stress). Moreover, when fluorescent dyes NBDAE, SP and Cy5 were respectively used as energy donor, primary acceptor and secondary acceptor for cascade Förster resonance energy transfer (FRET) process, hydrogels showed photo-induced multicolor fluorescence due to photo-switchable property of primary acceptor SP. As a joint result, the stretchable supramolecular hydrogel achieved good mechanical properties and broad-spectrum photoluminescence, which may have great application potential in photoluminescent materials with color tunability.

2. Results and discussion

Stretchable supramolecular hydrogel based on vinyl-derived PR composed of α -CD and PEG was prepared with PR yield of 24 % (Fig. S1). In order to clearly characterize the structure of hydrogel, scanning electron microscopy (SEM) was performed, where the frozen-dried hydrogel clearly showed the three-dimensional porous network structure (Fig. 1a, b). Rheological tests were performed to study the hydrogels' mechanical properties. When strain (γ) varied between 0.1 % and 10 %, the storage modulus (G') and loss modulus (G'') of supramolecular hydrogel basically remained stable, and G' was higher than G'' , indicating that the system existed in a stable hydrogel state and wasn't easily destroyed (Fig. 1d). But when $\gamma > 80$ %, G'' was higher than G' , which indicated the breakdown of the hydrogel network. Therefore, the tests were fixed at 1 % frequency in the oscillating strain. As shown in Fig. 1c, in frequency sweep testing of three PR ratio hydrogels, the value of G' was larger than G'' as the frequency increased from 0.1 % to 100 %. Meanwhile, both G' and G'' were significantly improved and basically remained stable within the range of $\omega = 100$ –0.1 rad/s with the action of PR in the frequency sweep curve. These data indicated that the supramolecular system was stable gel state. Specifically, 0.25 wt% PR had the

highest G' and G'' (the mass fraction of PR relative to the sum of AM and MA was 0, 0.25 % and 0.5 %, respectively). The G' value of hydrogel with 0.25 wt% PR increased to 4.8×10^4 Pa compared with 2.5×10^4 Pa of the hydrogel without PR while the G' of hydrogel containing 0.5 wt% PR increased to 3.3×10^4 Pa. So 0.25 wt% PR hydrogel was chosen for photo-controlled experiment. This result demonstrated the mechanical properties of supramolecular hydrogels were improved after adding PR. Moreover, we tested the rheological properties of the 0.25 wt% PR supramolecular hydrogels before and after 365 nm ultraviolet irradiation, and the result showed that there was almost no difference in their rheological pattern, indicating that hydrogels had good stability with ultraviolet irradiation (Fig. S4).

The continuous step strain measurements illustrated the viscoelastic recovery of hydrogels (Fig. 1e, f). Initially, the G' and G'' values remained constant and $G' > G''$ at room temperature. After the hydrogel was subjected to the strain of 500 %, both the G' value and G'' value decreased sharply, and G'' was larger than G' , indicating that the hydrogel network was broken. When the strain was restored to 0.1 %, the hydrogel healed itself and almost returned to the initial viscoelastic profile. The fracture and recovery behaviors could be repeated many times, and both G' and G'' maintained a steady trend, indicating that the hydrogel had excellent self-healing properties.

To further study the effect of PR's proportion on mechanical strength of hydrogels, the tensile tests were carried out. In a series of tensile tests, the maximum tensile length of hydrogel made of the 0.25 wt% PR could reach about 1300 %, while the original hydrogel with 0 wt% PR reached about 700 % (Fig. 2b). We speculate that the increased mechanical properties were due to the 'rings' of PR connected to the polymer chains could freely pass through the shaft, allowing good internal stress dispersion in the gel network. In addition, the reason why adding 0.5 wt % PR to the gel led to the decrease in tensile properties may be because too much PR caused increased cross-linking density and the fragility of the system. All of three gels had certain restorative properties. Besides, compared with 0 and 0.5 wt% PR, the gel of 0.25 wt% PR had not only good ductility but also better fracture energy tensile recovery, so the gel could recover more quickly after stretching (Fig. 2c, d), which reflected the important role of PR in improving the mechanical

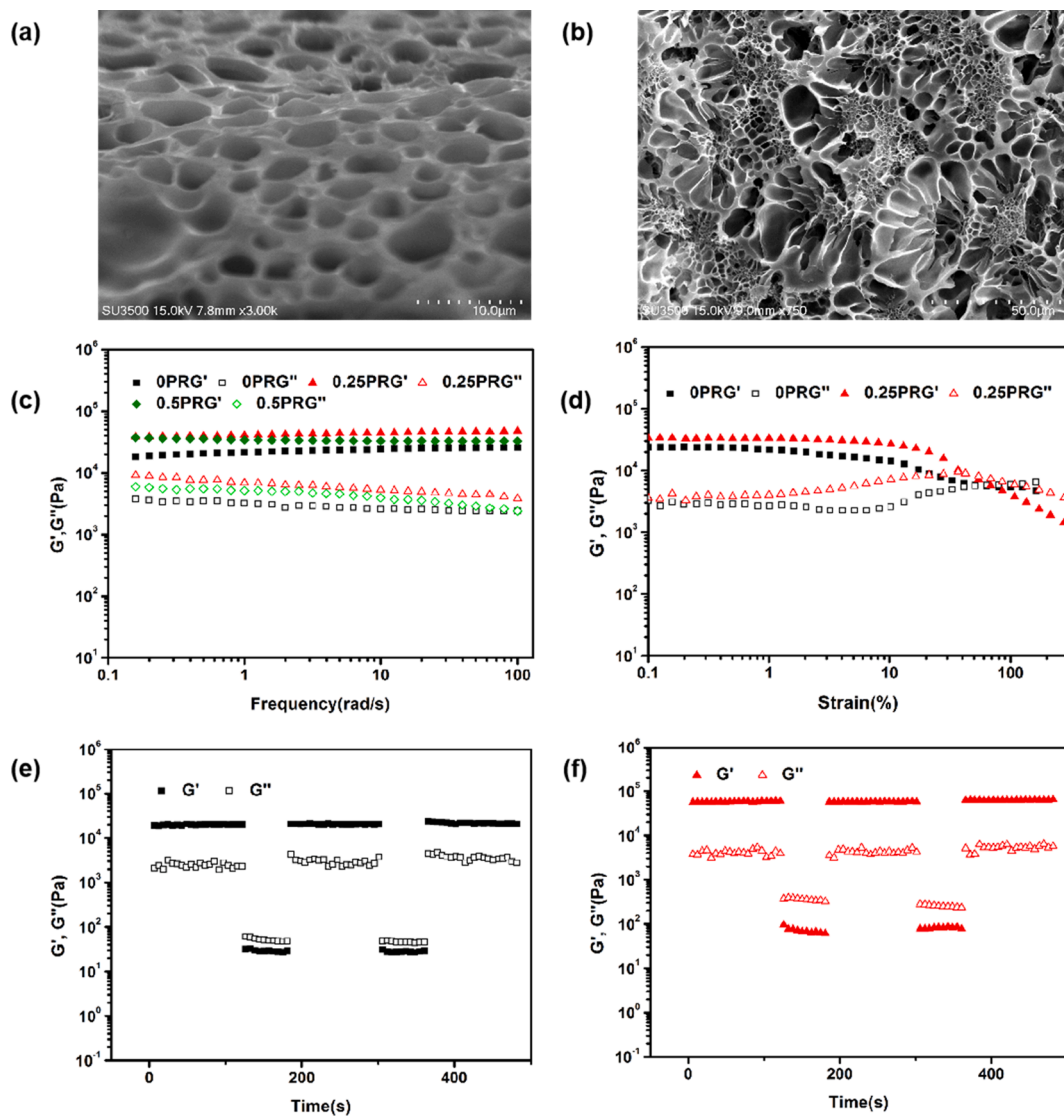


Fig. 1. (a-b) Surface SEM image of frozen-dried hydrogel with 0.25 wt% PR. (c) The oscillatory frequency sweep curves (the hydrogels with 0, 0.25 wt% PR and 0.5 wt% PR; $\gamma = 1\%$, $\omega = 0.1-100$ rad/s, 25 °C). (d) The strain sweep curves (the hydrogels with 0 and 0.25 wt% PR; $\gamma = 0.1\% - 500\%$, $\omega = 1.0$ Hz). (e) Continuous step strain curves of the 0 PR hydrogel at $\gamma = 0.1$ and 500% with $\omega = 1.0$ Hz. (f) Continuous step strain curves of the 0.25 wt% PR hydrogel at $\gamma = 0.1$ and 500% with $\omega = 1.0$ Hz.

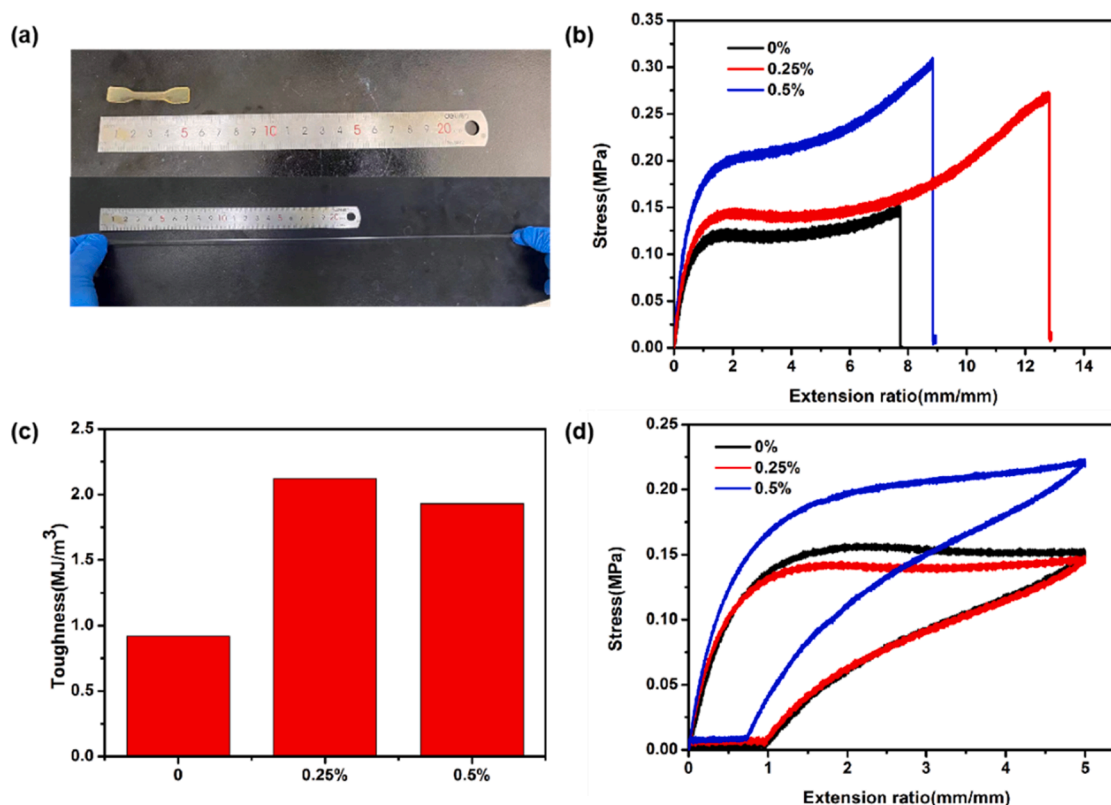


Fig. 2. (a) Visual photographs used to demonstrate the good ductility (0.25 wt% PR). (b) Tensile Stress–strain curves of hydrogels with different PR ratios added. (black, 0 % PR; red, 0.25 wt% PR; blue, 0.5 wt% PR). (c) Fracture energy of hydrogels with the PR ratio of 0, 0.25 wt% and 0.5 wt%. (d) Tensile loading–unloading curves of hydrogels with different PR ratios at 500 % strain (samples with different colors are shown in Fig. 2b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

properties of hydrogels.

Apart from excellent mechanical properties, due to the SP units' copolymerization, supramolecular PR hydrogels also possess good light-responsivity to switch energy transfer. Here, NBDAE (Fig. S2) and SP (Fig. S3) were synthesized from previously reported procedures [23,24]. The photophysical properties of NBDAE and SP were systematically studied by UV–vis and fluorescence spectroscopy (Fig. S5). According to the ¹H NMR spectrum (Fig. S6) and spectrum reported in the literature [25], we calculated that the conversion efficiency of SP is 52 %. The Fig. 3a illustrated that a significant spectral overlap occurred after the SP unit was converted to its isomeric MC state, indicating that the MC form was an ideal acceptor for energy transfer while the absorption spectrum of the SP form had no absorption between 450 and 600 nm (Fig. S7). Then, the photo-controlled energy transfer process of supramolecular hydrogels under different concentrations and ratios of FRET donor NBDAE and acceptor SP (1:5, 1:20, 1:50 and 1:100) was investigated (Fig. S5). The results showed that the FRET efficiency gradually increased with the increase of 365 nm illumination time. This was due to the fact that SP was converted to the fluorescent MC form under light illumination, which could effectively absorb the emission of the acceptor and emit fluorescence. As shown in Fig. 3b, when supramolecular hydrogels with donor NBDAE and acceptor SP 1:100 were irradiated with 365 nm UV light, the fluorescence intensity of NBDAE at 530 nm decreased gradually, while the emission of MC at 630 nm increased. Moreover, the photoresponse process was completed very quickly within 280 s, which benefited from the excellent photo-responsivity of SP. The 1931 Commission Internationale de l'Éclairage (CIE) chromaticity diagram showed the color coordinate variation from pale yellow to salmon-red area with the increase of 365 nm illumination time (Fig. 3c). Then we processed the supramolecular hydrogel into the

shape of the words “NKU”. The fluorescence color change of the words “NKU” under UV light over time and the color of the words under sunlight after the UV light were turned off (Fig. 3d). The results indicated that SP could rapidly change into the ring-opened amphoteric ion MC state under the irradiation of 365 nm UV light, which became the red luminescent acceptor in hydrogels. Time-resolved photoluminescence decay spectrum showed a decrease in NBDAE lifetime after illumination (Fig. S6), which indicated FRET from NBDAE to MC. In addition, the energy transfer efficiency was calculated as high as about 80 %.

Furthermore, we investigated photo-controlled cascaded energy transfer in supramolecular hydrogels with Cy5 as the secondary receptor. The absorption spectrum of MC well overlapped with the emission spectrum of NBDAE, while its emission spectrum well overlapped with the absorption spectrum of Cy5, making it a suitable choice as an intermediate acceptor/donor to realize funneling of energy between NBDAE and Cy5 (Fig. 4a). Therefore, under light irradiation, the non-emitting SP unit could be transformed into the red-emitting MC state in an efficient reversible photoisomerization form, in which MC could be a pure energy relay dye in the cascade process to facilitate energy transfer of NBDAE-MC-Cy5. As shown in Fig. 4b, the fluorescence intensity of NBDAE at 530 nm gradually decreased with the increase of 365 nm UV irradiation time, while the emission fluorescence intensity of MC at 630 nm and Cy5 at 675 nm increased. The CIE chromaticity diagram showed the color coordinate changed from pale yellow to orange to red area as the irradiation duration at 365 nm increased (Fig. 4c). The occurrence of FRET could be further confirmed by time-resolved fluorescence experiments. In the presence of MC ($\lambda_{ex} = 470$ nm), the lifetime of Cy5 (Fig. S10) increased significantly while that of NBDAE (Fig. S13) decreased. Within the FRET system, the energy transfer from NBDAE to Cy5 was significantly enhanced due to the introduction of MC as a

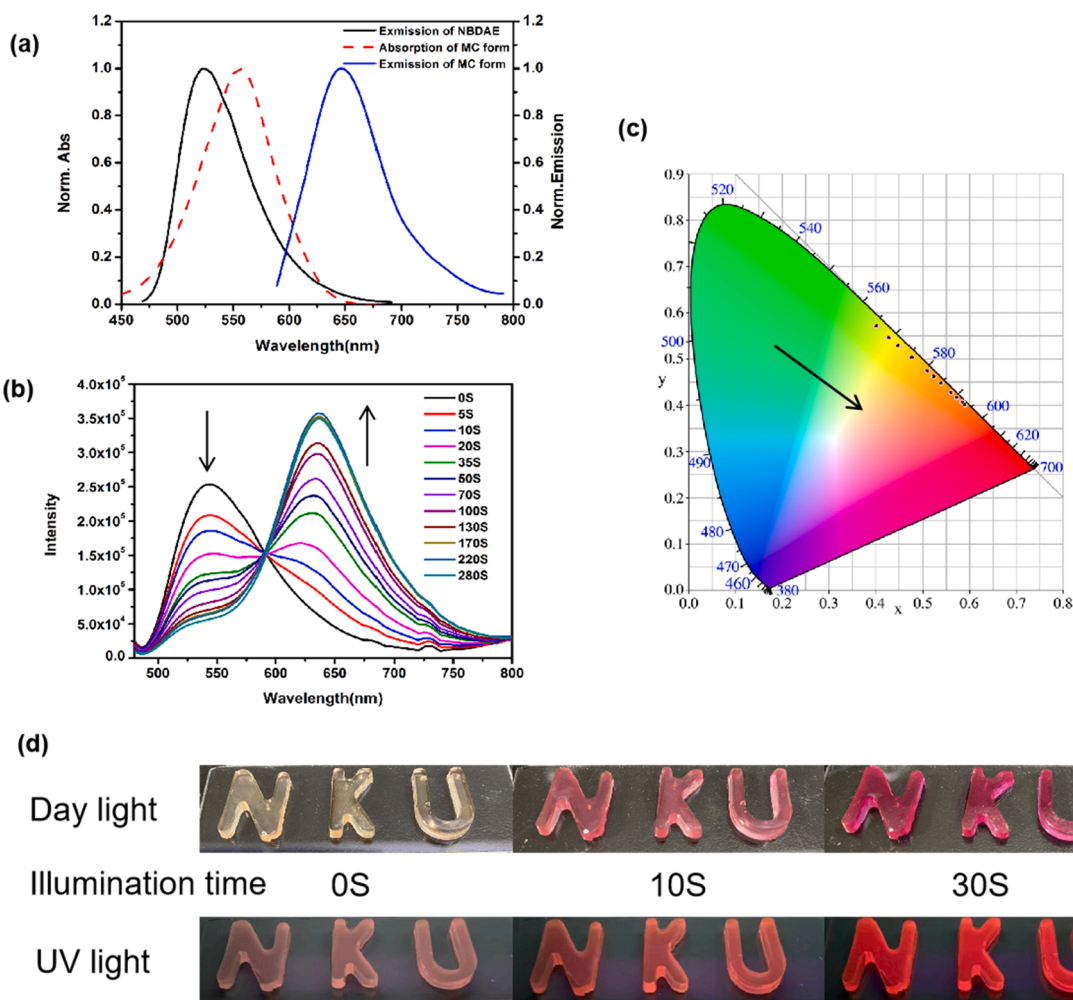


Fig. 3. (a) Normalized absorption spectra of SP and fluorescence emission of NBD and SP. (b) Fluorescence spectra of fluorescent hydrogel loaded with UV light (365 nm) ($\lambda_{ex} = 470$ nm, NBD = 4×10^{-5} M, SP = 4×10^{-3} M). (c) The CIE chromaticity diagram depicting the color changes under continuous UV irradiation, corresponding to Fig. 3b. (d) Photographs of fluorescent hydrogel over time under daylight and 365 nm light.

central fluorophore. To better confirm whether the long-distance energy transfer from NBD to Cy5 could be carried out in the absence of MC, we made the hydrogel with only NBD and Cy5, which proved to be unable to carry out energy transfer (Fig. S11). All these results demonstrated that the stretchable supramolecular fluorescent hydrogels exhibited good photo-controlled cascade energy transfer capability for multi-color luminescence.

Benefiting from the light-controlled cascade energy transfer property of supramolecular PR hydrogel system, we could apply it to the construction of photo stimulation-responsive materials. In this case, the spatiotemporal light switching behavior of hydrogel was further studied. Fig. 5a-c showed photos of a fluorescent hydrogel when UV-vis light was irradiated through two photomasks made of black opaque paper. The pattern was clearly recorded on the hydrogel when it was irradiated with UV light through a “cat” mask for 2 min (Fig. 5a). After irradiation with Vis light for 3 min, the “cat” pattern was removed (Fig. 5b). Then the same hydrogel was illuminated with UV light from the other “dolphin” photomask, and a “dolphin” pattern could be created on the hydrogel clearly (Fig. 5c). This result indicates that the supramolecular hydrogel has good reproducible photo-writing properties, which is due to the photo-responsiveness of the intermediate dye SP in cascade energy transfer. The light-responsive supramolecular hydrogels may have promising applications in intelligent display devices.

Given that the fluorescence patterns of photo-responsive

supramolecular hydrogels showed unique color changes under external stimulation, they were quite significant for anti-counterfeiting applications. Here, we used hydrogels with different NBD: SP: Cy5 ratios to achieve different color changes with increasing UV irradiation time for the purpose of dynamic anti-counterfeiting. The “sun” pattern cut out with hydrogels of different NBD: SP ratios increased the fluorescence intensity and deepened the luminescence color within 3 min of UV illumination, changing from orange yellow to bright red (Fig. 5d). Similarly, the letters “I” and “D” in the words “I DO” with NBD: SP: Cy5 ratio of 1: 50: 15 changed color with increasing UV exposure time while the “O” with only NBD emitting green fluorescence (Fig. 5e). The reason for this phenomenon was that SP rings opened under UV light, and FRET processes occurred in fluorescent hydrogels leading to luminescence intensity and color changes. The dynamic photo-controlled properties of the luminescent image are very easy to be detected with a portable lamp and cannot be faked by any substitute at this stage. Thus, cascade energy transfer rotaxane hydrogels may have great potential for dynamic anti-counterfeiting.

3. Conclusion

In summary, we constructed photo-controlled cascade energy transfer stretchable supramolecular hydrogel by in-situ copolymerization. The resultant supramolecular hydrogel exhibited high

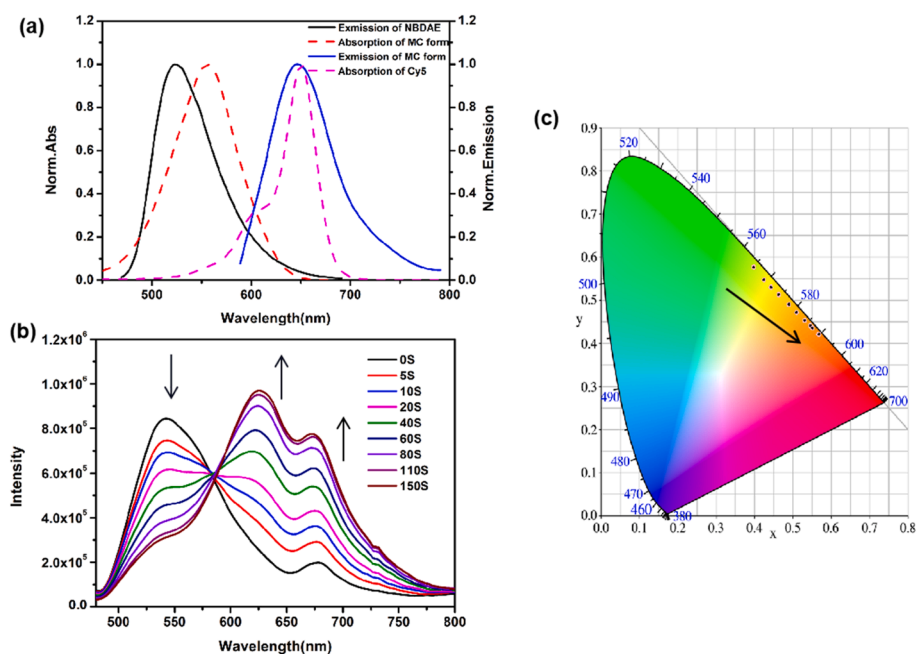


Fig. 4. (a) Normalized emission spectra of NBDAE, absorption spectra of Cy5, and absorption and emission spectra of SP. (b) Fluorescence spectra of fluorescent hydrogel with UV light (365 nm) ($\lambda_{\text{ex}} = 470$ nm, NBD = 4×10^{-5} M, SP = 4×10^{-3} M, Cy5 = 6×10^{-4} M). (c) The CIE chromaticity diagram depicting the color changes under continuous UV irradiation, corresponding to Fig. 4(b).

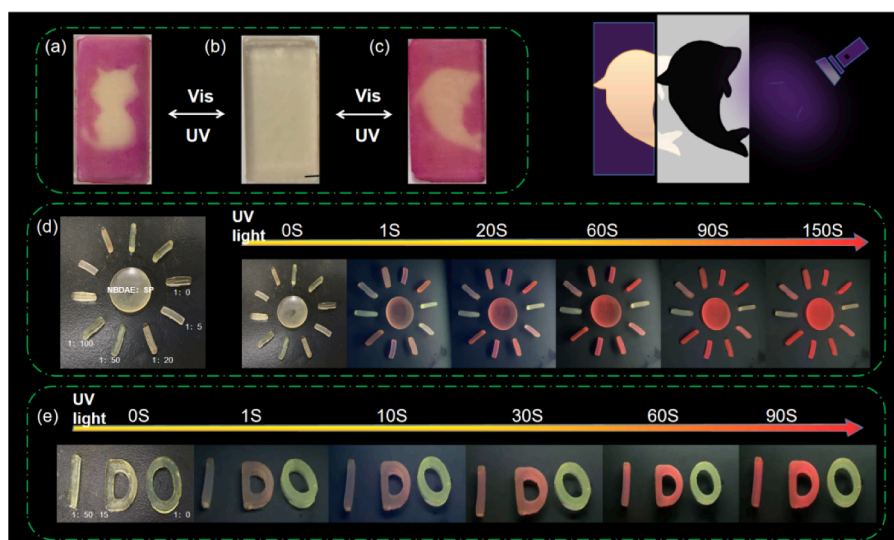


Fig. 5. (a)-(c) Photo-switchable hydrogel patterns under UV light with photomask. (d) The solar pattern with different ratios of NBDAE: SP changed color with increasing UV exposure time. (e) The "I DO" words with different ratios of NBDAE: SP: Cy5 changed color with increasing UV exposure time.

stretchability and good fatigue resistance because PR acted as a cross-linking agent and the slip of α -CD on the PEG chain can disperse the stress. Meanwhile, the hydrogels possessed tunable multi-color luminescence in which SP as an optical switch unit could control the secondary energy transfer. Benefitted from the excellent mechanical strength and multi-color luminescence, the hydrogels were successfully applied for fluorescence dynamic anti-counterfeiting. This supramolecular co-assembly strategy would provide a sight for the construction of smart materials with mechanical properties and photo-controlled cascade energy transfer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2023.112070>.

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