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Fluorescent Organohydrogel with Thermal-Induced Color Change for Anti-counterfeiting

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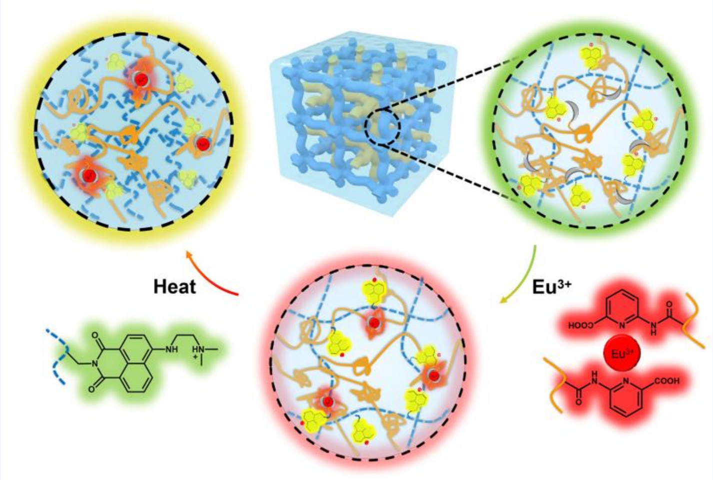
Comprehensive Summary

Smart fluorescent patterns enable dynamic color variation under external stimuli, showing a much higher security level in the field of anti-counterfeiting. However, there is still lacking of a simple and convenient way to achieve dynamic fluorescence changes. Herein, a fluorescent organohydrogel made up of a poly(*N*,*N*-dimethylacrylamide-*co*-isopropylacrylamide) (p(DMA-NIPAM)) hydrogel network and a poly(lauryl methacrylate) (PLMA) organogel network was fabricated via a two-step interpenetrating technique. The former network bears naphthalimide moieties (DEAN, green fluorescent monomer) and the later contains 6-acrylamidopicolinic acid (6APA, fluorescent ligand), leading to emitting green fluorescence. When Eu^{3+} was introduced and coordinated with 6APA, the organohydrogel displays red fluorescence, which can further emit yellow after applying thermal stimulus. Furthermore, by adjusting the proportion of comonomers, various organohydrogels can be obtained, which can be programmed and act as an effective platform for the encryption and decryption of secret information.



Thermal-induced fluorescence variation

Keywords

Dyes/pigments | Fluorescence | Gels | Information encryption | Stimuli responsiveness

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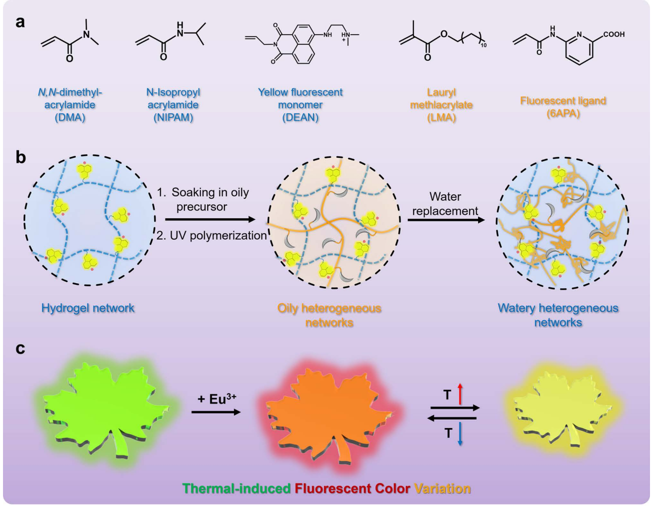
Background and Originality Content

Smart fluorescent patterns[1-3] exhibit dynamic color output in response to external stimuli, such as irradiation, chemical reagents, electricity, heat, *etc*., showing the highest security and thus gaining much attention. So far, much efforts have been devoted to developing novel emitting sources, including upcoversion nanoparticles,[4] lanthanide complexes,[5] carbon dots[6] and organic dyes.[7] In addition, through a combination of other security measures (structural color, dynamic wrinkle morphology and the like) with fluorescent color, security level has been further improved.[8-9]

As a new type of intelligent materials, stimulus-responsive gels have shown promising applications in various fields due to their unique characters of shape morphing and color changing under certain stimulus.[10-15] Recently, this kind of materials has already become a new candidate material for information storage. For example, Wu's group[16] has fabricated a shape memory hydrogel consisting of poly(1-vinylimidazole-*co*-methacrylic acid) network incorporating donor-acceptor chromophore units, in which tunable fluorescence and reconfigurable architecture can be achieved for dual-encryption. Xu *et al.*[17] presented a pH-responsive Chameleon luminescent sensor based on lanthanide doping hydrogel, which can repeatedly switch the emission color of encrypted information. Previously, our group[18] fabricated a urease-containing fluorescent hydrogel for transient information storage, which was based on the deprotonation process of fluorescent monomer DEAN as well as its dissociation with metal ions.

Herein, we have demonstrated a heterogeneous organohydrogel enabling fluorescent color variation from red to yellowish-green via the stimulus of heat. As illustrated in Scheme 1a, the hydrogel network was made up of *N*,*N*-dimethylacrylamide (DMA), thermal-responsive isopropylacrylamide (NIPAM) and yellowish-green fluorescent monomer (DEAN). Meanwhile, the oily precursor solution, which was introduced to the hydrogel network through UV polymerization, contained lauryl methacrylate (LMA) and fluorescent ligand (6APA). The target watery heterogeneous networks can be obtained after successively immersing oily heterogeneous networks in ethanol and water for solvent replacement (Scheme 1b). As a result, the gels can go through a thermal-induced fluorescent color variation, which can be applied in the field of anti-counterfeiting with higher security level.

Scheme 1 Schematic illustration of the heterogeneous gels p(DMA-NIPAM-DEAN)/p(LMA-6APA) for thermal-induced fluorescent color variation. a) The monomers utilized for the preparation of heterogeneous gel, hydrogel network (blue) and organogel precursors (yellow). b) Preparation of the heterogeneous gels using hydrogel network as the scaffold to incorporate and organogel network via a two-step interpenetrating technique. c) After introducing Eu^{3+} ions, the heterogeneous gels can exhibit red-yellow fluorescent color transformation by the treatment of heat.



Results and Discussion

The method of preparing heterogeneous organohydrogels was according to previous works[19-20] based on the successful synthesis of fluorescent monomer (DEAN) (Scheme S1, Figure S1 and Figure S2) and fluorescent ligand (6APA) (Scheme S2, Figure S3 and Figure S4). Briefly, various hydrogels were firstly prepared by co-polymerization of *N*,*N*-dimethylacrylamide (DMA) and isopropylacrylamide (NIPAM) with different mass ratios as 1 : 1 (D1N1), 1 : 3 (D1N3), 1 : 5 (D1N5), 1 : 7 (D1N7) and 1 : 9 (D1N9) in the presence of DEAN monomer, ammonium persulfate (APS) as an initiator and *N*,*N*'-methylene bis(acrylamide) (BIS) as a crosslinker. After dehydration in acetone, the gels were soaked in an ethanol solution containing hydrophobic monomer lauryl methacrylate (LMA), fluorescent ligand 6APA in the presence of 2,2-diethoxyacetophenone (DEAP) as a photoinitiator and ethylene dimethacrylate (EGDMA) as a crosslinker. By UV polymerization, the organohydrogels with heterogeneous structure were obtained after being immersed in ethanol for removing residual monomers and placed in water for solvent replacement. As the D1N5 organohydrogel exhibits excellent color change performance in the follow-up study, it was therefore chosen for the following investigation of fundamental properties.

As shown in Figure 1a, the maple leaf-shaped D1N5 organohydrogel has an opaque and yellowish appearance due to the heterogeneous structure with DEAN moieties in hydrogel network. Scanning Electron Microscope (SEM) was applied for observing the morphologies of both the hydrogel (Figure S5) and organohydrogel (Figure 1b). Compared with D1N5 hydrogel with loose porous structure, the D1N5 organohydrogel had a denser network, which consisted of continuous hydrogel network and hydrophobic spherical structure caused by water-induced microphase separation. What's more, attenuated total reflection Fourier transformed infrared spectrometer (ATR-FTIR) was employed for analyzing chemical composition and structure of both D1N5 hydrogel and D1N5 organohydrogel. As presented in Figure 1c, hydrogel (black line) and organohydrogel (red line) possess a similar ATR-FTIR spectrum except for the peaks located at 2851.4 cm^{-1} and 2923.5 cm^{-1}, which are caused by the stretching vibrations of C—H bond corresponding to alkane chains of LMA. In addition, the newly emerging peak at 1728.6 cm^{-1} is attributed to the stretching vibrations of C=O bond belonging to ester bonds of LMA. The big difference of hydrogel and organohydrogel can also be obviously seen from the rheological property. In contrast, the latter one showed a twice storage modulus (*G*') of the former one and the loss modulus (*G*'') was increased by more than 10 times, which was ascribed to the introduction of organogel network as well as the formation of hydrophobic microzones that plays a key role in the enhancement.

Since the pyridine carboxylic acid groups can coordinate with lanthanide ions[21-22] such as Eu^{3+} thus leading to a red fluorescence upon exposing to UV light (254 nm), the original green D1N5 organohydrogel displayed red fluorescence after introducing Eu^{3+} ions (Figure 2a). As illustrated in Figure 2b, the PL mapping spectrum of D1N5-Eu^{3+} organohydrogel revealed the existence of two emission centers in our system, which belong to green fluorescent moieties (DEAN, 524 nm) and red complex (6APA-Eu^{3+}, 617 nm), respectively. Once Eu^{3+} was introduced, the characteristic peaks of fluorescent intensity corresponding to 6APA-Eu^{3+} complex at around 617 nm showed up under the selective excitation of 254 nm (Figure 2c).

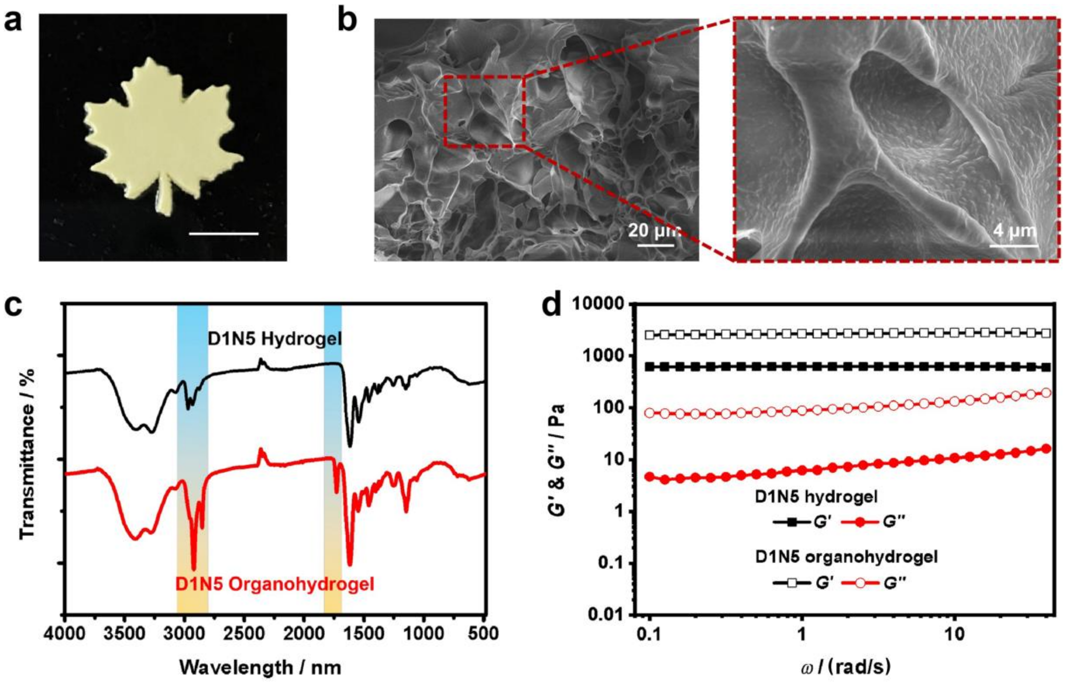


Figure 1 Characterization of D1N5 organohydrogel and D1N5 hydrogel. Photograph, scale bar: 1 cm a) and cross-section SEM images b) of D1N5 organohydrogel. FT-IR spectra c) and dynamic mechanical analysis (DMA) of D1N5 hydrogel as well as D1N5 organohydrogel.

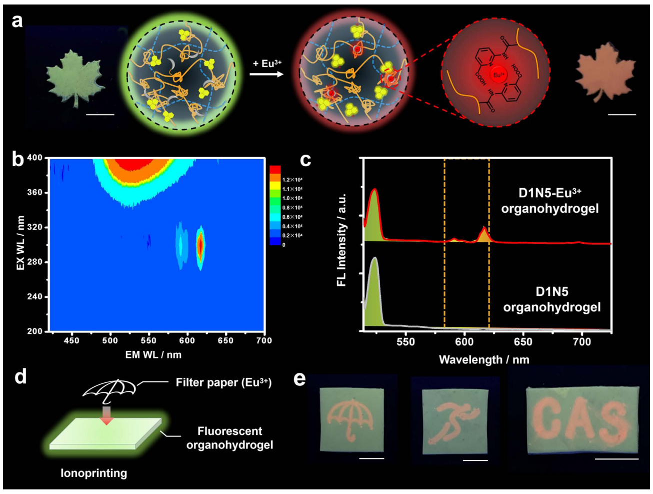


Figure 2 a) Illustration of the mechanism of fluorescence changes and images of maple leaf-shaped D1N5 organohydrogel and D1N5-Eu^{3+} organohydrogel upon exposing to UV light (254 nm), scale bar: 1 cm. b) PL mapping spectra of D1N5-Eu^{3+} organohydrogel. c) Fluorescence spectra of D1N5 organohydrogel and D1N5-Eu^{3+} organohydrogel (λ_{ex} = 254 nm). d) Schematic illustration of ionoprinting technique. e) Photos of ionoprinted patterns, including umbrella, running man and English letters “CAS”, scale bar: 1 cm.

Due to the big difference of fluorescent colors depending on the presence and absence of Eu^{3+} ions, information storage has been achieved via ionoprinting technique.[23-24] As shown in Figure 2d, the target pattern can be obtained by simply contacting a filter paper, which was firstly cut into certain shape and then immersed in Eu^{3+} solution, with the D1N5 organohydrogel for a few seconds. Once the filter paper was contacted with organohydrogel, Eu^{3+} ions spread from the former to the latter and then the pattern would be located. The patterns, including umbrella, running man and English letters “CAS”, have been successfully imprinted onto the surface of organohydrogels by this mature information loading technology.

As one of the typical thermal-responsive hydrogels, PNIPAM-based hydrogels possess an appealing feature that volume phase transition occurs above the lower critical solution temperature (LCST).[25-27] Given that fluorescent monomers were copolymerized on the smart polymer backbone, we were encouraged to explore the fluorescence variation associated with conformation changes of polymer chains (Figure 3a). As a proof-of-concept, the D1N5-Eu^{3+} organohydrogel was firstly tailored into maple leaf shape by laser cutting machine. As shown in Figure 3b and Movie S1, an obvious color change can be monitored with the increase of temperature, which can be also measured by the fluorescence spectra (Figure 3c). It is worth mentioning that though the fluorescence intensities at 524 nm and 617 nm both showed a decrease compared with organohydrogel without Eu^{3+} (Figure S6), the fluorescence intensity at 617 nm showed a larger drop when the temperature was raised, indicating the red-green transition. The Commission Internationale de L’ Eclairage (CIE) coordinates of the D1N5-Eu^{3+} organohydrogel are (0.49, 0.5), (0.45, 0.54) and (0.37, 0.60) during the heating process, respectively, corresponding to red, yellow and green. What’s more, the fluorescence color variation can be repeated at least 3 times in the process of temperature switching (Figure S7).

It is well known that the LCST can be regulated by the copolymerization of NIPAM with hydrophilic or hydrophobic monomers, corresponding to the increase or decrease of LCST.[28] As shown in Figure S8, the deswelling ratio of D1N5 exactly showed an obvious change at about 40 °C, which just corresponds to the LCST. In combination with above part of study that the fluorescence color does change with the conformation of polymer chains, we assumed that a completely different color changing behavior occurs when different ratios of monomers (DMA/NIPAM) were fed. As shown in Figure 4a and Figure S9, organohydrogels (D1N1-Eu^{3+}, D1N3-Eu^{3+}, D1N5-Eu^{3+}, D1N7-Eu^{3+}, D1N9-Eu^{3+}) exhibited big differences in both discoloration degree and discoloration point during the process of heating, which were obviously different from organohydrogels without Eu^{3+} (Figure S10). Herein, D1N1-Eu^{3+} organohydrogel and D1N5-Eu^{3+} organohydrogel were picked

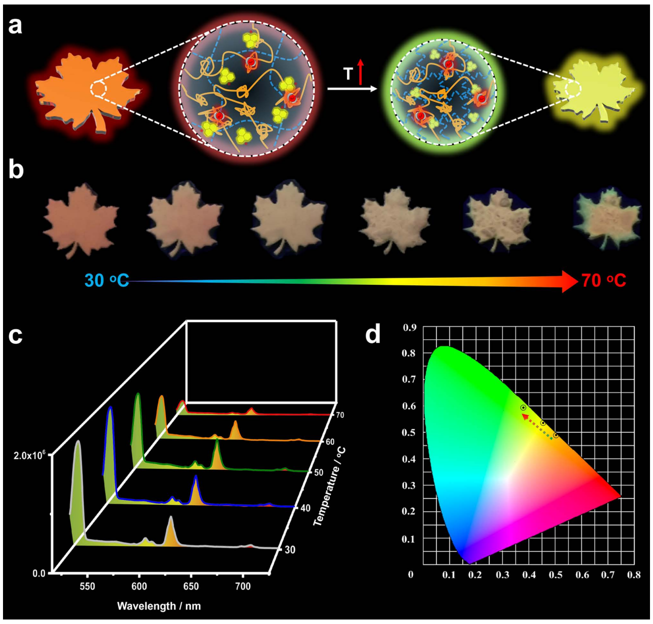


Figure 3 Realization of thermal-induced fluorescent color variation. a) Illustration of the mechanism of fluorescence changes and images of maple leaf-shaped D1N5-Eu^{3+} organohydrogel before and after the treatment of heat. b) Photographs of maple leaf-shaped D1N5-Eu^{3+} organohydrogel as the temperature increases from 30 °C to 70 °C. c) Fluorescence spectra of D1N5-Eu^{3+} organohydrogel at different temperature (30 °C, 40 °C, 50 °C, 60 °C, 70 °C). d) Fluorescnece color change of D1N5-Eu^{3+} organohydrogel with the increment of temperature at CIE (1931) chromaticity diagram.

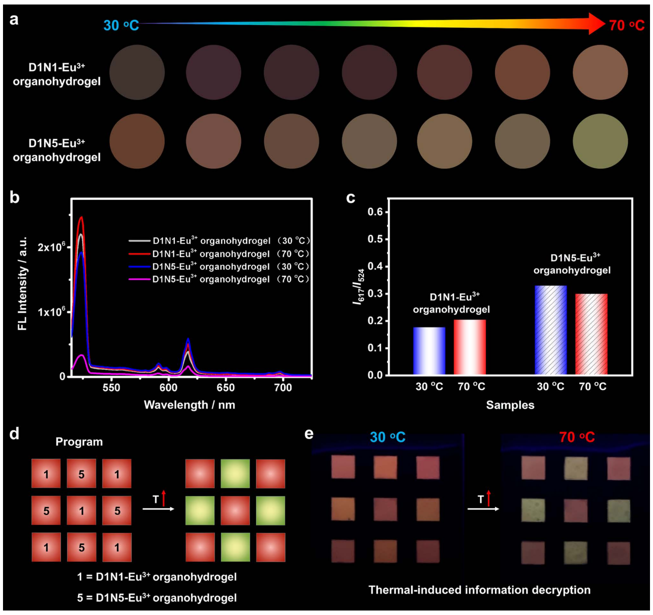


Figure 4 a) The fluorescence variations of D1N1-Eu^{3+} organohydrogel and D1N5-Eu^{3+} organohydrogel when temperature was increased from 30 °C to 70 °C. b) Fluorescence spectra of D1N1-Eu^{3+} organohydrogel and D1N5-Eu^{3+} organohydrogel at 30 °C and 70 °C, respectively. c) The fluorescent intensity ratios at 617 nm and 524 nm (I_{617}/I_{524}) with temperature of 30 °C and 70 °C. The design d) and photos e) of fluorescent 2D code made up of two different organohydrogels (D1N1-Eu^{3+} and D1N5-Eu^{3+}) before and after treating with heat.

up for constructing fluorescent 2D code due to the greatest differences in the color change procedure. Compared with D1N1-Eu^{3+} organohydrogel, D1N5-Eu^{3+} organohydrogel showed an obvious decrease in fluorescence intensity at 524 nm as well as at 617 nm when the temperature rises from 30 °C to 70 °C (Figure 4b). Correspondingly, there was a little increase in the fluorescence intensity ratios at 617 nm and 524 nm (I_{617}/I_{524}) of D1N1-Eu^{3+} organohydrogel before and after treating with heat (Figure 4c). Meanwhile, the related ratios of D1N5-Eu^{3+} organohydrogel behaved in the opposite way. Taking advantages of the difference in the above two organohydrogels in response to temperature, a fluorescent 2D code has been designed for thermal-induced information decryption and anti-counterfeiting. As an example, the useful codes (red square with 1) were made up of D1N1-Eu^{3+} organohydrogels while the fake codes (red square with 5) were composed of D1N5-Eu^{3+} organohydrogels (Figure 4d). Once stimulated by heat, the useful codes remained unchanged and the fake codes underwent fluorescence color changes from red to yellow, leading to the decryption of hidden information “X” (Figure 4e and Movie S2). Due to the stability of the system, this color changing performance can be conducted repeatedly (Figure S11).

Conclusions

In conclusion, we presented a series of heterogeneous organohydrogels consisting of a hydrophilic p(DMA-NIPAM-DEAN) network and a hydrophobic p(LMA-6APA) network. As DEAN moieties emit green fluorescence and 6APA can coordinate with Eu^{3+} leading to the red emission, the original p(DMA-NIPAM-DEAN)/p(LMA-6APA) organohydrogel (green fluorescence) can be endowed with red fluorescence by introducing Eu^{3+} ions. Furthermore, the conformation transition of PNIPAM polymer chains above LCST can cause the changes in aggregation state of fluorescent moieties, switching the fluorescent color from red to green. Given the differences in thermal-responsive capacity of organohydrogels with various composition, fluorescent 2D code can be constructed and utilized for anti-counterfeiting. In a word, our strategy provides a simple and convenient method for designing and fabricating gel-based anti-counterfeiting materials that are capable of fluorescence variation.

Experimental

Materials

N,*N*-Dimethylacrylamide (DMA), *N*,*N'*-methylene bis(acrylamide) (BIS), ammonium persulfate (APS), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TEMED), 2,2-diethoxyacetophenone (DEAP), and ethylene dimethacrylate (EGDMA) were commercially provided by Aladdin. *N*-Isopropylacrylamide (NIPAM) was purchased from TCI (Shanghai) Reagent Co., Ltd. Lauryl methacrylate (LMA) was purchased from Shanghai Macklin Biochemical Co., Ltd. HCl, NaHCO$_3$, ethanol, acetone, and anhydrous magnesium sulfate were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous dichloromethane (DCM) was bought from J&K Chemical Co., Ltd. Eu(NO$_3$)$_3$·6H$_2$O (99.9%) was supplied by Energy Chemical. DEAN as a fluorescent co-monomer and 6APA as fluorescent ligands were synthesized according to our previous reports. All other solvents and reagents were commercially obtained at extra-pure grade and were used as received.

Fabrication of organohydrogel

Taking D1N5 organohydrogel for example: 0.33 g DMA, 1.67 g NIPAM, 6.6 mg DEAN, 20 mg APS (initiator, 1 wt% of monomer), 2 mg Bis (crosslinker, 0.1 wt% of monomer) were firstly dissolved in 10 mL H$_2$O. Then, 10 μL TEMED was added before the mixed solution was oscillated rapidly and transferred into home-made modes. 24 h later, the hydrogels were put into acetone for dehydration and removing residual monomers. After completely drying, the gels were soaked into oily precursor solution overnight, which was made up of 20 g LMA, 20 mg EGDMA (crosslinker), 200 mg DEAP (photo-initiator), 30 mg 6APA and 20 g ethanol. After polymerization under UV light for 20 min, the target heterogeneous gels were obtained when the solvent was replaced by water.

^{1}H NMR measurement

^{1}H NMR spectra of DEAN and 6APA were recorded on a Bruker Avance III 400 MHz spectrometer in DMSO-d_6 and $CDCl_3$, respectively.

SEM characterization

The cross-section morphology of the organohydrogel was performed by a field-emission scanning electron microscopy (SEM, S-4800, Hitachi).

UV-Vis absorption tests

UV-Vis absorption was measured on a UV-Vis spectrophotometer (TU-1810, Purkinje General Instrument Co., Ltd.).

Fluorescence measurements

Steady-state fluorescence spectra were obtained by a fluorescence spectrofluorometer (FL3-111, Horiba).

ATR-FTIR characterization

Fourier transform infrared spectra were obtained through an attenuated total reflection Fourier transformed infrared spectrometer (FT-IR, Thermo Scientific Nicolet 6700).

Rheological tests

Rheological characterization was carried out on a stress-controlled rheometer (TA-dhr2) with a parallel plate (25 mm) in frequency sweep mode (from 0.1 to 100 rad/s) at a constant shear strain of 1%.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202100668.

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