

Supporting Information

Dynamic metal-ligand coordination enables hydrogel with rewritable dual-mode pattern display

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Experimental Section

Materials: Citric acid, formamide, acetone and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. Acrylic acid (AAc, 98%), Acrylamide (AAm), N,N'-Dimethylacrylamide (DMA), N,N'-methylenebisacrylamide (Bis), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), Sodium dodecyl sulfate (SDS) and 2-Hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (I₂₉₅₉) were purchased from Aladdin Chemical Co. All reagents were used without any

treatment or purification. Dodecylglyceryl itaconate (DGI) was synthesized according to the previous report¹.

Synthesis of solvatochromic carbon dots (CDs): Firstly, 5.60 g of citric acid was dissolved in 100 ml of formamide in a three-necked round-bottom flask and stirred until fully dissolved. The mixture was then stirred at 160 °C for 2 hours under a nitrogen atmosphere. After cooling to room temperature, the resulting crimson solution was settled by adding 500 mL of acetone and stored in a refrigerator at -20 °C for two days. The dark brown suspension was separated by vacuum filtration and washed with an acetone/methanol mixture (v:v=1:1). The pure carbon dots (CDs) were obtained by freeze-drying.

Fabrication of pDGI-PAAm hydrogel: Initially, 0.14 g of DGI, 0.71 g of AAm, 2 mg of BIS, 3 mg of TPO, and 0.1 mL of SDS water solution (1.6 mg/mL) were dissolved in 4.9 mL of deionized water. The mixed solution self-assembled at 55 °C for 24 hours to form stable lamellar bilayers. After purging with nitrogen to remove dissolved oxygen, the precursor solution was injected into a simple polymerization cell composed of two 8 cm × 8 cm glass sheets and a 0.5 mm thick PDMS mold. The oriented bilayer was then stabilized under UV irradiation (365 nm, 20 W) at 55°C for 3 hours. Subsequently, the hydrogel was soaked in deionized water for 1 week to reach swelling equilibrium and remove any remaining unreacted chemicals. Finally, the treated hydrogel was immersed in an ethanol solution for approximately 30 minutes and air-dried at room temperature.

Fabrication of pDGI-PAAm/P(AAc-CDs) hydrogel: First, a precursor solution for the double network hydrogel was prepared by combining 40 mL of water, 1.37 mL of AAc, 4 mg of BIS, and 6 mg of I₂₉₅₉. Air-dried pDGI-PAAm hydrogels were then immersed in this precursor solution and kept in the dark at 35°C for 24 hours to achieve full swelling. Subsequently, the swollen hydrogel was sandwiched between two pieces of

quartz glass to ensure there were no air bubbles, and irradiated with UV light (365 nm, 50 W) for 30 minutes. Finally, the prepared *pDGI-PAAm/P(AAc-CDs)* double network hydrogel (DN hydrogel) was immersed in water to remove any unreacted monomers.

Measurements

¹H NMR spectra were obtained from a Bruker Avance III 400 MHz spectrometer in D₂O. UV-Vis absorption and transmittance spectra were measured on an UV-Vis spectrophotometer (TU-1810, Purkinje General Instrument Co. Ltd.). ATR-FTIR spectra was recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The digital photos of the polymeric films were taken under a UV lamp (ZF-5, 5 W, 254 nm). All fluorescent photographs were taken using the same UV lamp. Steady-state fluorescence measurements, fluorescence lifetime of microgels with different water content were obtained from a HPRIBA FL3-111 fluorescence spectrofluorometer at room temperature with a 500 W Xenon lamp. Quantum efficiency of MG-derived systems with different water content were obtained from quantum efficiency tester (Otsuka Photal Electronics QE-2100). The excitation wavelength was 254 nm. The morphology of microgels were performed by a field-emission scanning electron microscopy (SEM, S-4800, Hitachi) with an accelerating voltage of 4.0 kV. The laser confocal pattern was conducted on a Biotype laser confocal microscope (LEICA) machine. The hydrodynamic diameters of the microgels in water at different temperatures and Zeta potential were measured by dynamic light scattering (Zetasizer Nano ZS, Malvern).

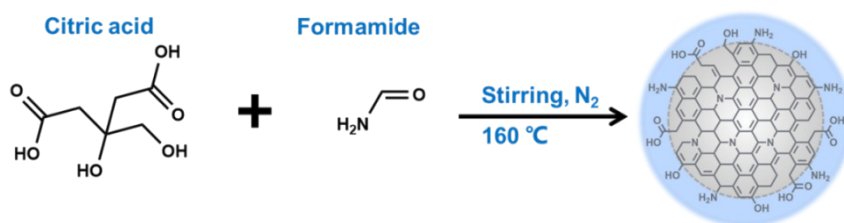


Figure S1. The synthetic route of CDs.

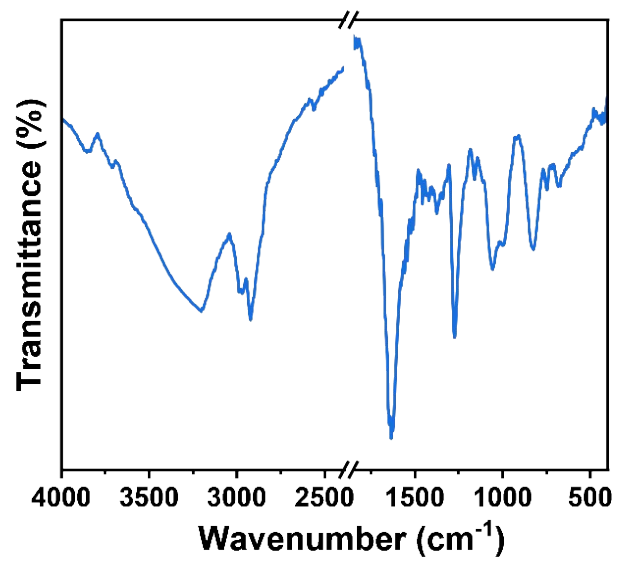


Figure S2. The FT-IR spectra of CDs.

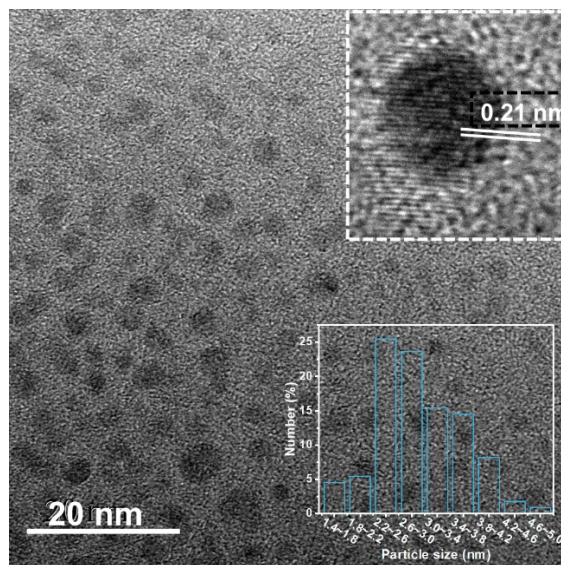


Figure S3. TEM image and particle size distribution of the prepared CDs.

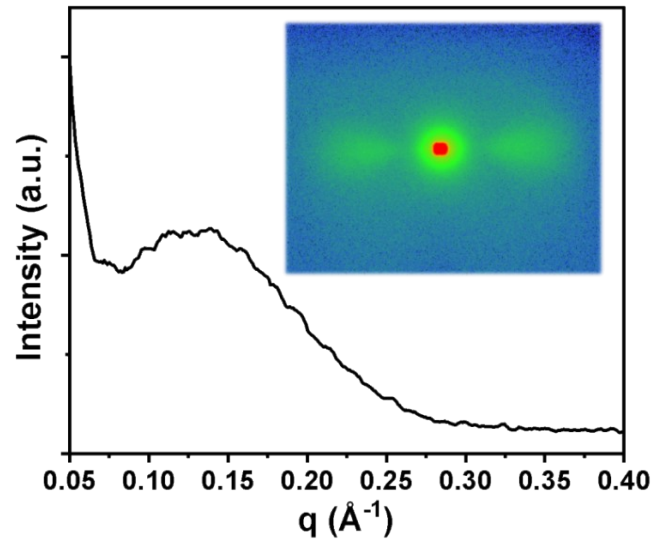


Figure S4. Scattering intensity versus the scattering vector q and 2D SAXS pattern (inset) for pDGI-PAAm/P(AAc-CDs) hydrogel.

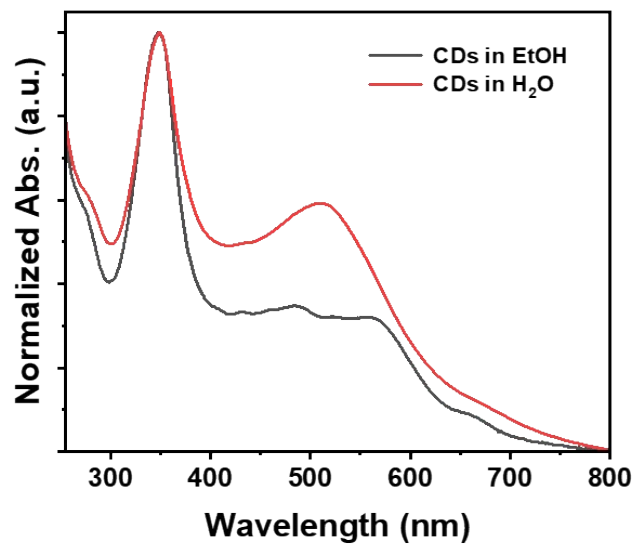


Figure S5. UV absorption spectra of CDs in H_2O (good solvent) and ethanol (poor solvent), respectively.

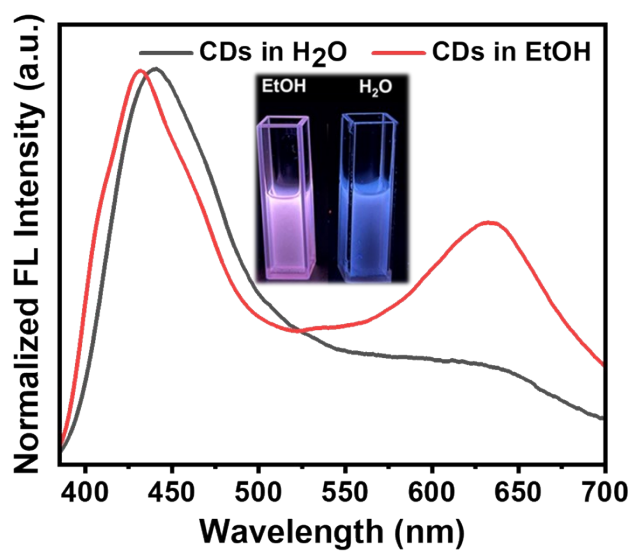


Figure S6. Fluorescent spectra of CDs in H₂O (good solvent) and ethanol (poor solvent), respectively.

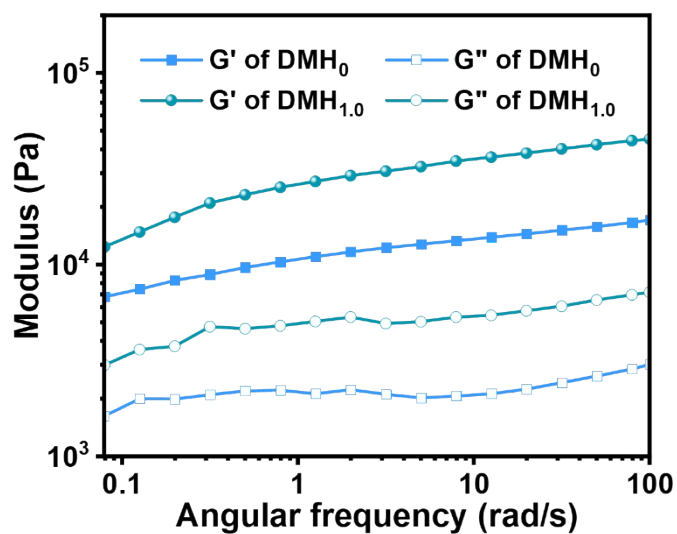


Figure S7. Storage modulus (G') and loss modulus (G'') of DMH₀ and DMH_{1,0}.

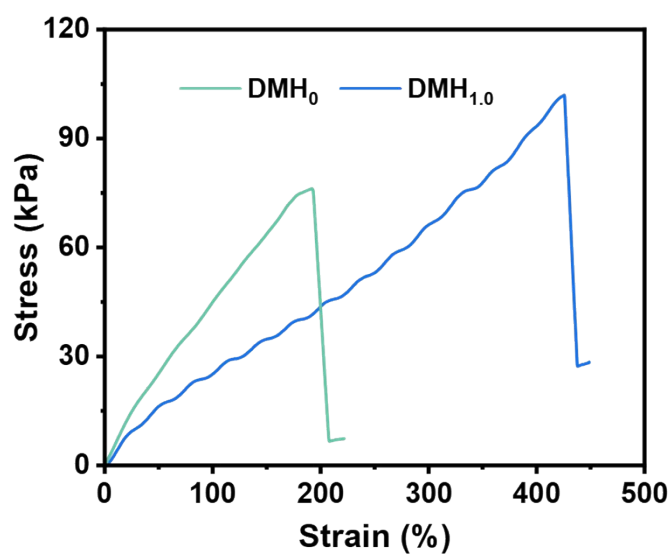


Figure S8. Stress-strain curves of DMH₀ and DMH_{1.0}.

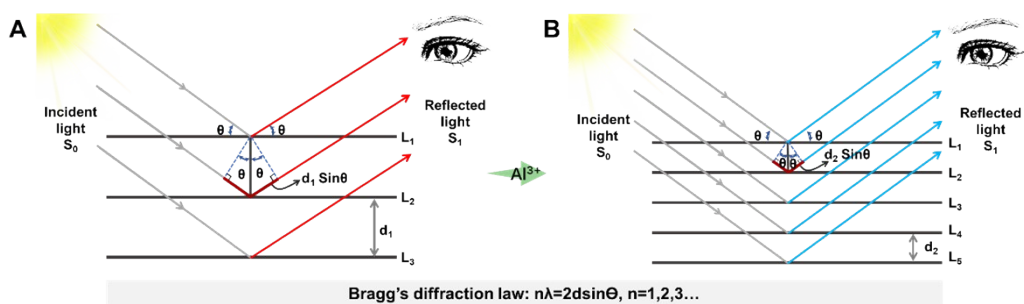


Figure S9. Based on Bragg's diffraction law, the changes of optical path and reflected light wavelength of different DMHs before and after Al³⁺ ions treatment.

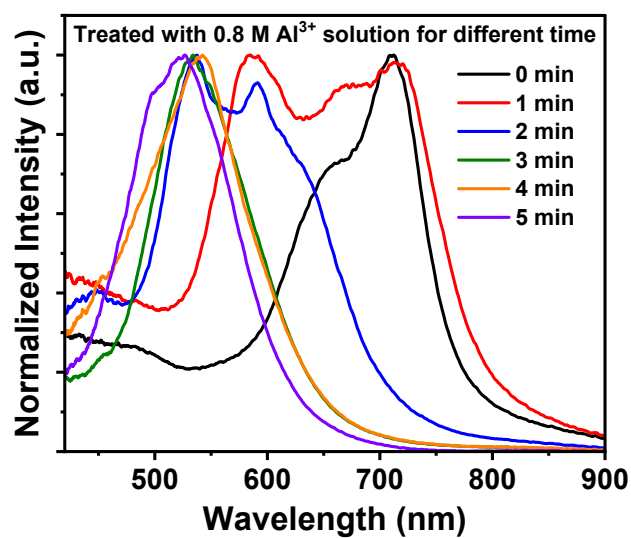


Figure S10. Reflection spectra of DMHs treated with Al^{3+} solution (1 M) for different time (0 min, 1 min, 2 min, 3 min, 4 min, 5 min).

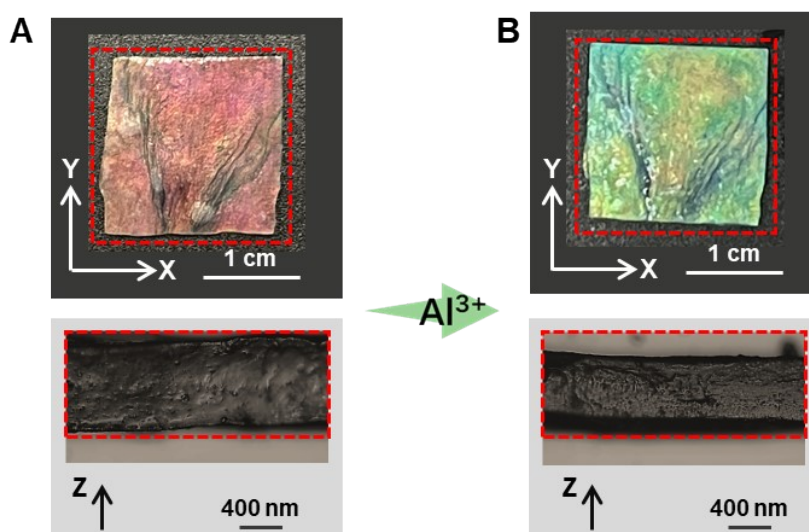


Figure S11. Top view optical pictures and optical microscope image in the Z-axis direction of DMHs before A) and after B) treated with Al^{3+} solution (1 M).

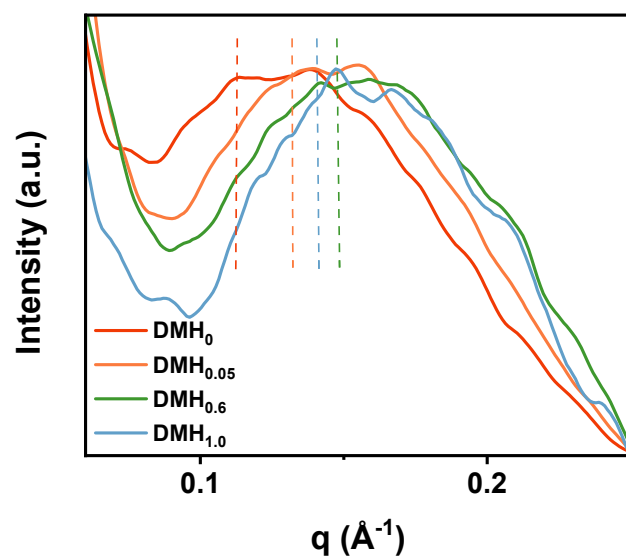


Figure S12. Scattering intensity versus the scattering vector q for DMH_0 , $\text{DMH}_{0.05}$, $\text{DMH}_{0.6}$ and $\text{DMH}_{1.0}$.

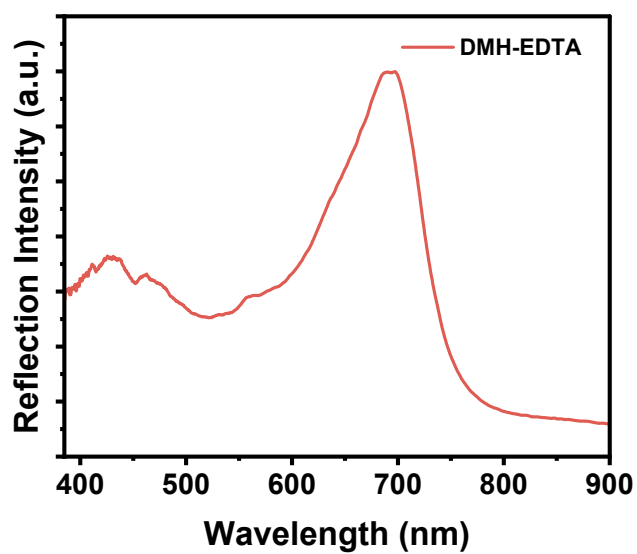


Figure S13. Reflection spectrum of DMH after conducting 10 cycles of coordination-decoordination with Al^{3+} ions.

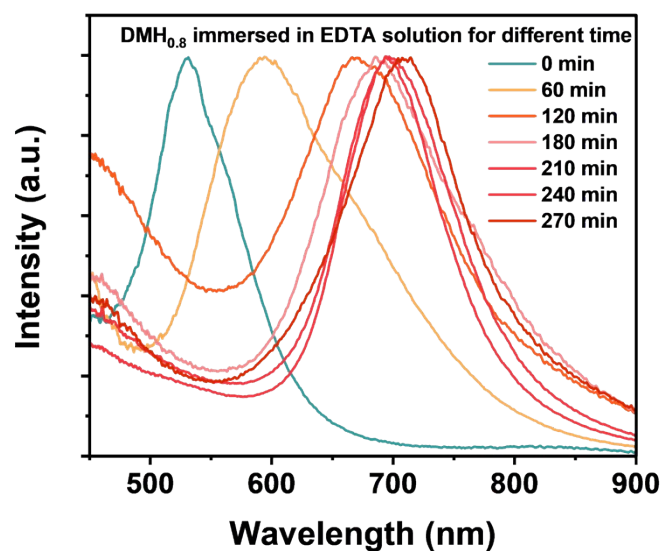


Figure S14. Reflection spectrum of DMH_{0.8} immersed in saturated EDTA solution for different time (0 min, 60 min, 120 min, 180 min, 210 min, 240 min, 270 min).

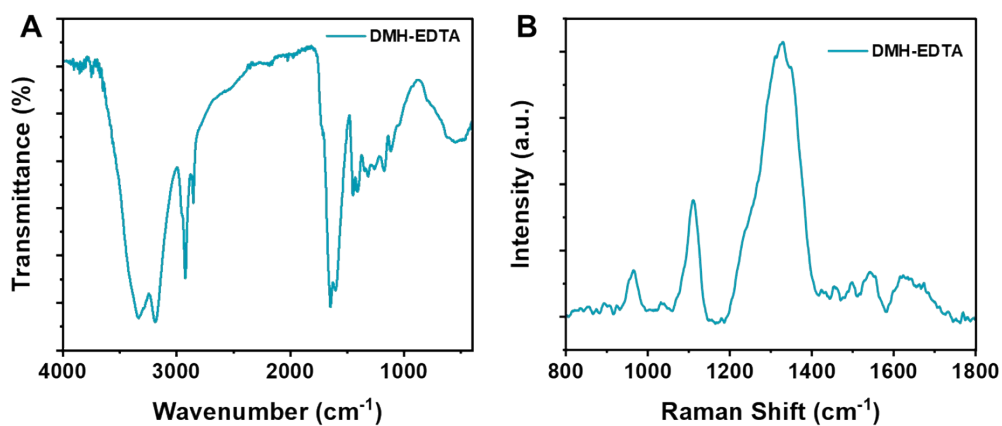


Figure S15. ATR-FTIR spectra A) and Raman spectra B) of DMH after conducting 10 cycles of coordination-decoordination with Al³⁺ ions .

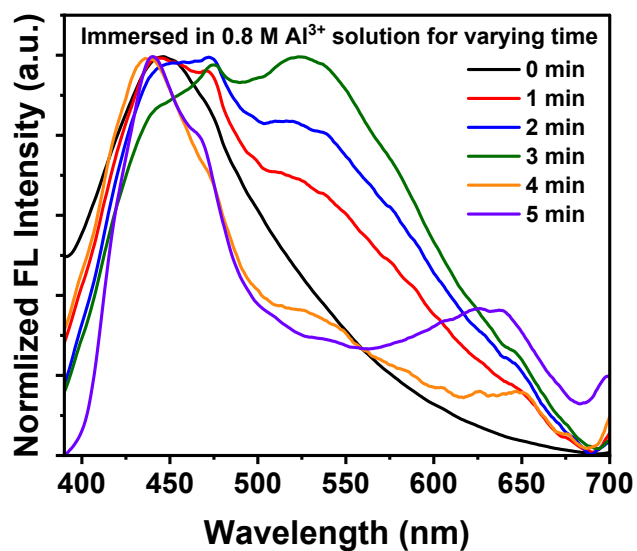


Figure S16. Fluorescence spectra of DMHs treated with Al^{3+} solution (0.8 M) for different time (0 min, 1 min, 2 min, 3 min, 4 min, 5 min).

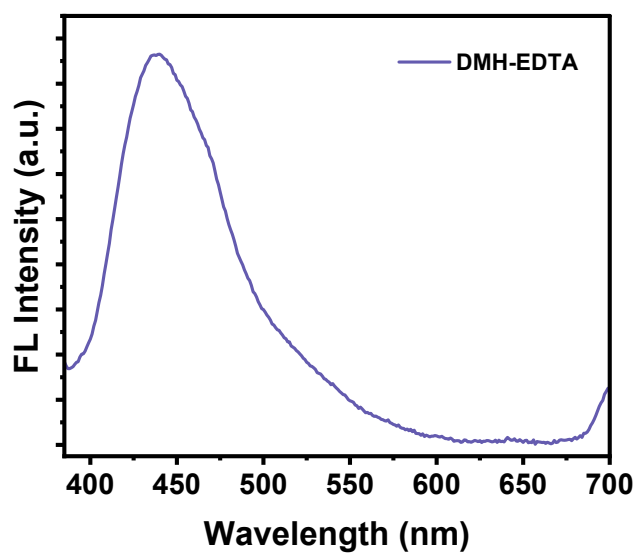


Figure S17. Fluorescent spectra of DMH after conducting 10 cycles of coordination-decoordination with Al^{3+} ions .

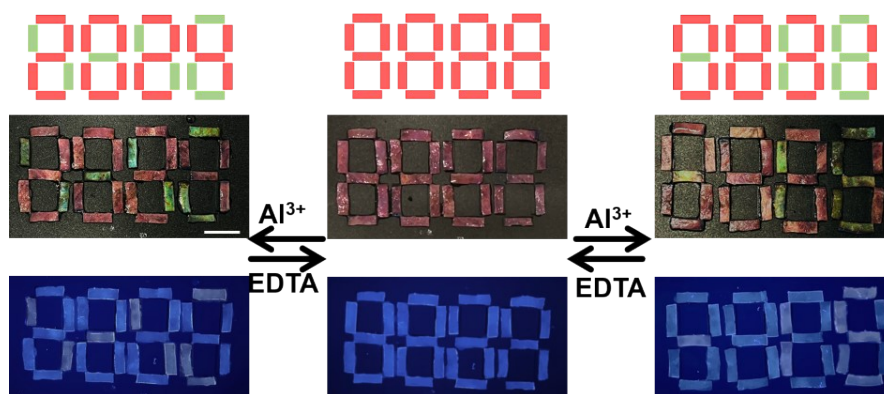


Figure S18. Different numerical information can be obtained by encoding with Al^{3+} ions and erasing with EDTA.

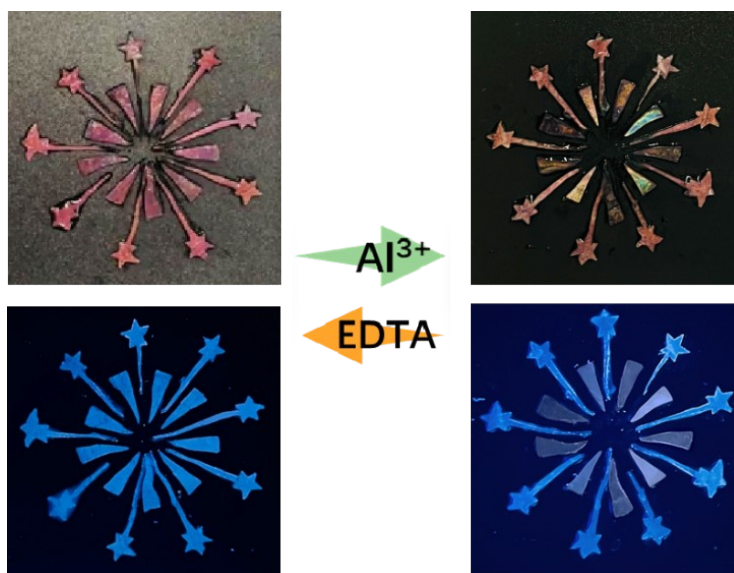


Figure S19. Colorful fireworks can be seen through different treatments (Al^{3+} ions or EDTA solution).

Notes and references

1. Y. Sun, X. Le, H. Shang, Y. Shen, Y. Wu, Q. Liu, P. Théato and T. Chen, *Adv. Mater.*, 2024, **36**.