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Electronic Supplementary Information

Multiple Stimuli-Responsive Multicolor Luminescent Self-Healing Hydrogel and Application in Information Encryption and Bioinspired Camouflage

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2. Additional Data

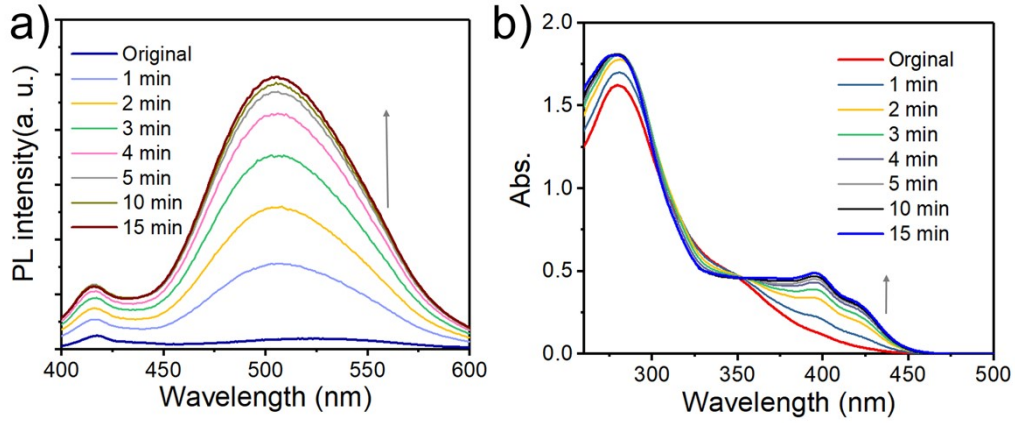

Figure S1 a) The emission spectra and b) Uv-vis absorption spectra of HCPB in aqueous solution under different UV irradiation time . These measurements were performed at 300 K with the concentration of HCPB 0.5×10^{-4} M.

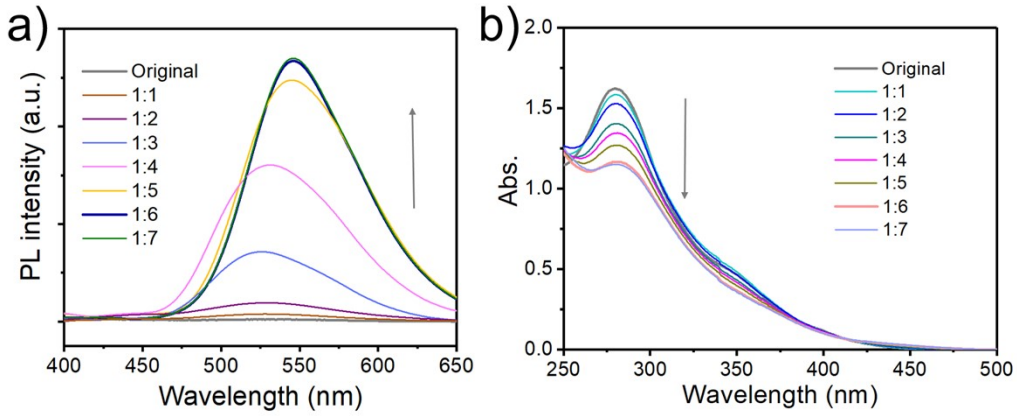

Figure S2 a) The emission spectra and b) Uv-vis absorption spectra of HCPB in aqueous solution with addition of HCl (the molar ratio of HCPB and H^+ changed from 1:1 to 1:7). These measurements were performed at 300 K with the concentration of HCPB 0.5×10^{-4} M,

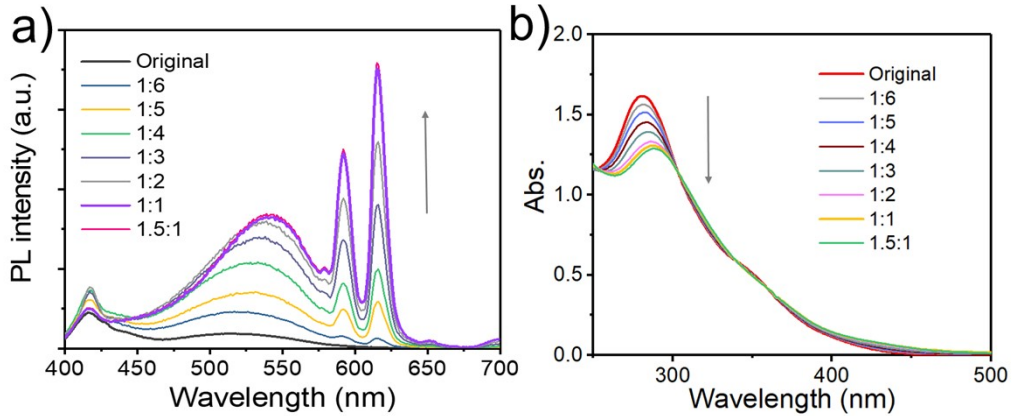

Figure S3 a) The emission spectra and b) Uv-vis absorption spectra of of HCPB in aqueous solution with addition of $EuCl_3$ gradully (the molar ratio of Eu^{3+} and HCPB changed from 1:6 to 1.5:1). These measurements were performed at room temperature 300 K with the concentration of HCPB 0.5×10^{-4} M.

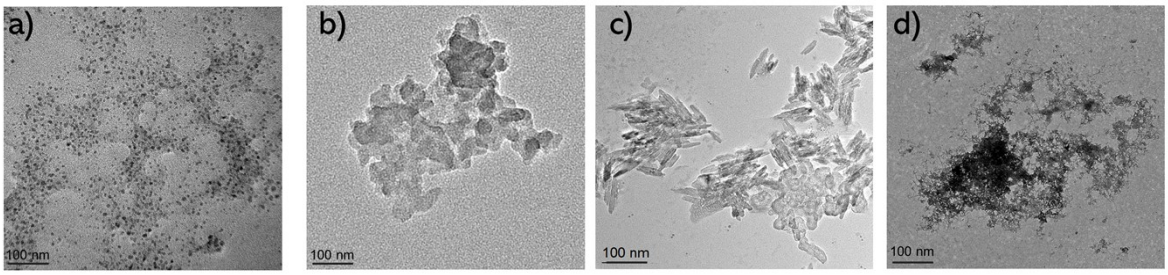

Figure S4 TEM images before and after different stimuli. a) prepared from solution without any stimuli, b) prepared from solution after UV irradiation for 5 min c) prepared from solution after H^+ added, the molar ratio of HCPB and H^+ was 1:6. d) prepared from solution after Eu^{3+} added, the molar ratio of HCPB and Eu^{3+} was 1:1.

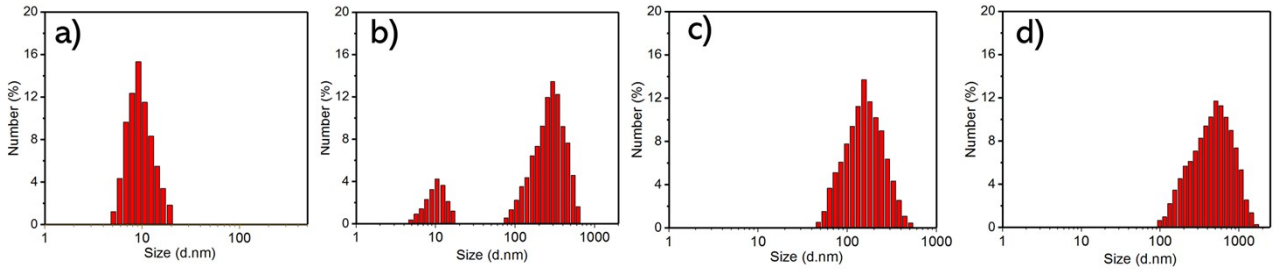

Figure S5 DLS data before and after different stimuli. a) solution without any stimuli, b) solution after UV irradiation for 5 min. c) solution after H^+ added, the molar ratio of HCPB and H^+ was 1:6. d) solution after Eu^{3+} added, the molar ratio of HCPB and Eu^{3+} was 1:1.

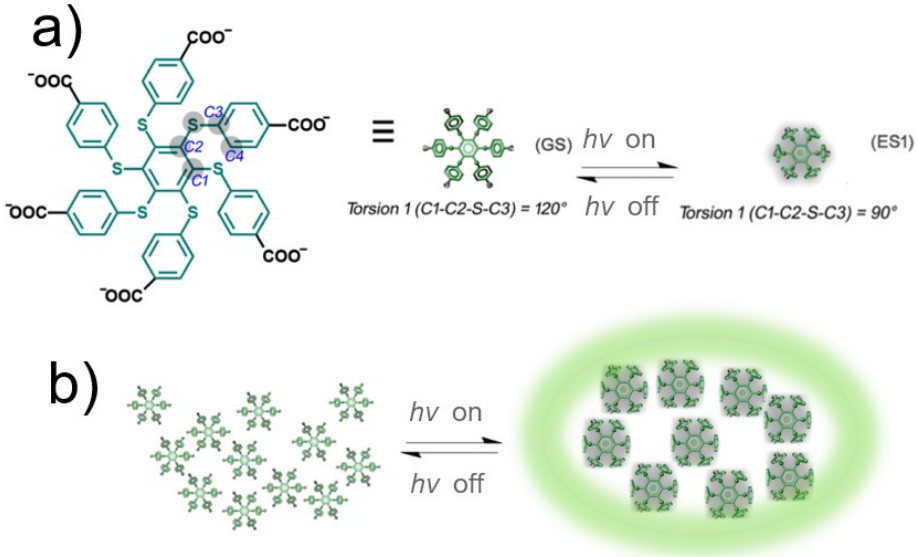

Figure S6 Illustration the formation of aggregates under UV irradiation. a) Schematic illustration of the Chemical structure under UV, b) photoexcitation-controlled aggregation process.

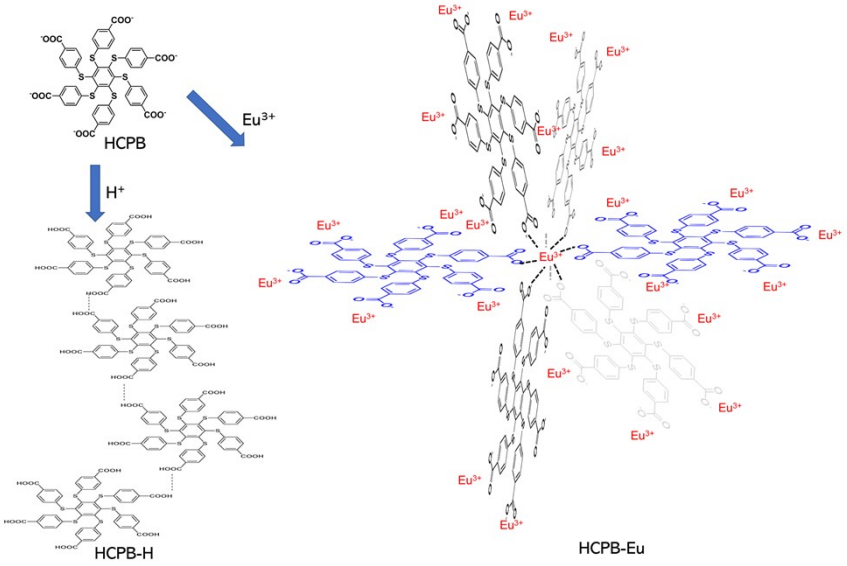

Figure S7 Illustration the formation of aggregates under different stimuli.

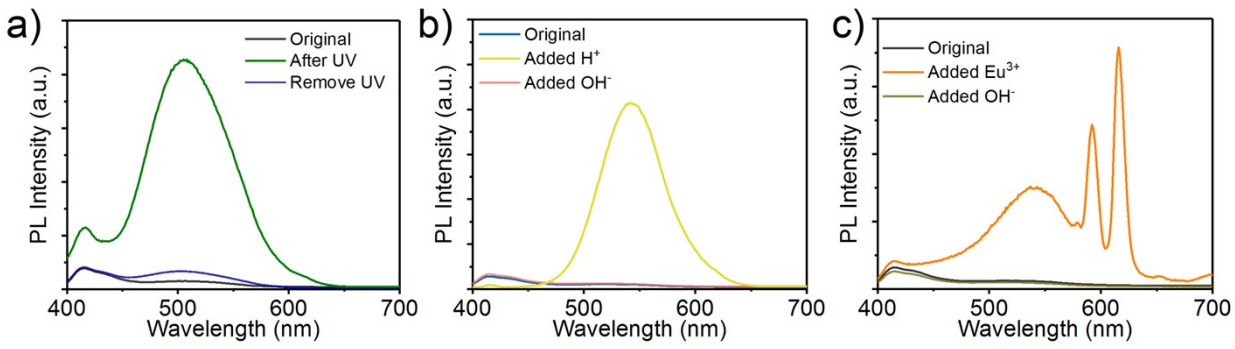

Figure S8 The emission spectra of HCPB in aqueous solution under different stimuli. a) After UV irradiation for 5 min and relax in dark for 1 h, b) After addition 6 μ L of HCl (0.5 M) and 6 μL $NH_3 \cdot H_2O$ (0.5 M), c) After addition 10 μ L of $EuCl_3$ (0.05 M) and 1 μL $NH_3 \cdot H_2O$ (0.5 M). These measurements were performed at 300 K with the concentration of HCPB 0.5×10^{-4} M.

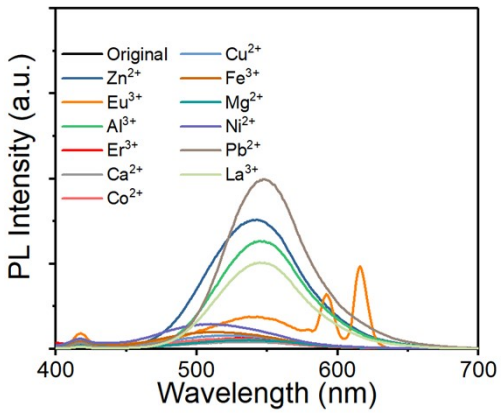

Figure S9 The emission spectra of HCPB in aqueous solution after different metal ions added. These measurements were performed at 300 K with the concentration of HCPB 0.5×10^{-4} M. The molar ratio of HCPB and metal ion was fixed at 1:1.

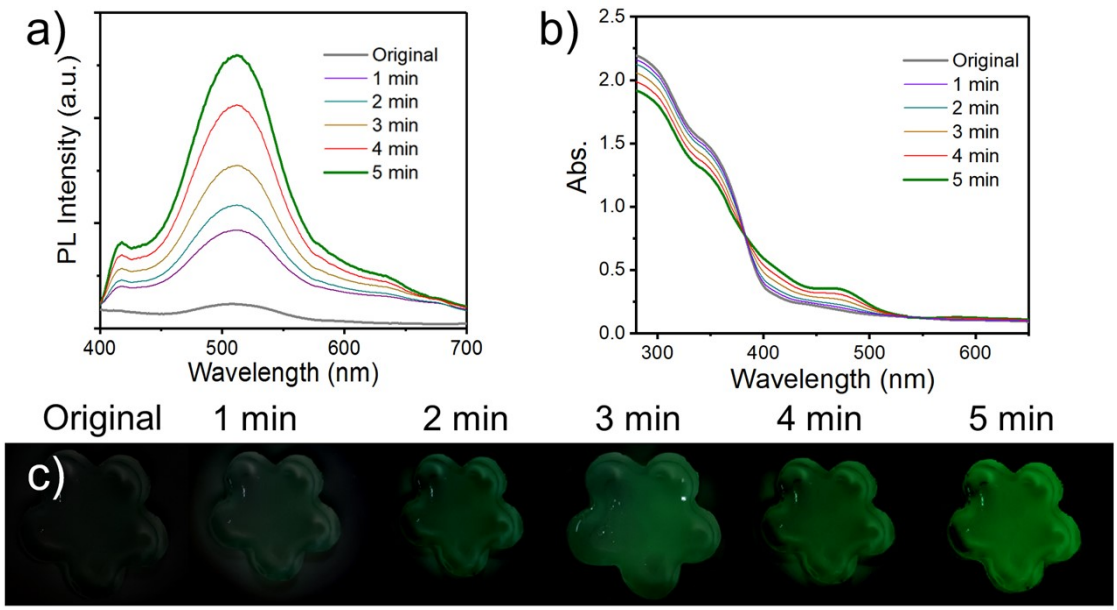

Figure S10 PVA-HCPB hydrogel under different irradiation time. a) Emission spectra of PVA-HCPB under different UV irradiation time, b) Uv-vis absorption spectra of PVA-HCPB under different UV irradiation time, c) Image of PVA-HCPB different UV irradiation time. These measurements were performed at 300 K with the amount of HCPB 0.8 mg.

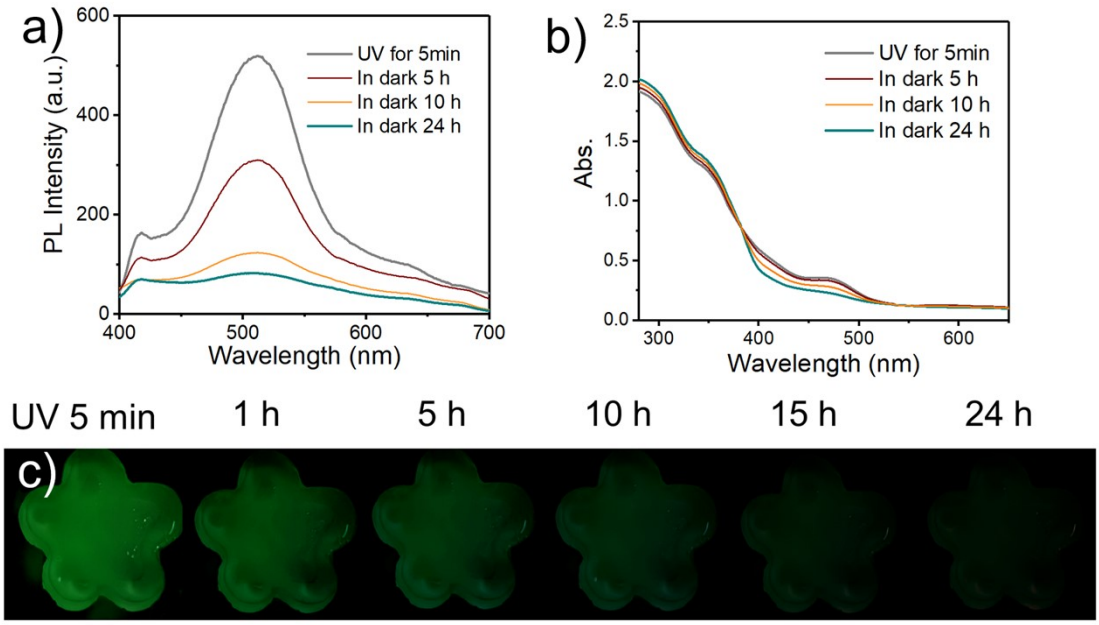

Figure S11 PVA-HCPB-UV hydrogel in dark for different time. a) emission spectra of PVA-HCPB-UV after UV irradiation for 5 min and relax in dark for 24 h, b)Uv-vis absorption spectra of PVA-HCPB-UV after UV irradiation for 5 min and relax in dark for 24 h, c) Image of PVA-HCPB-UV after UV irradiation for 5 min and relax in dark for 24 h. These measurements were performed at 300 K with the amount of HCPB 0.8 mg.

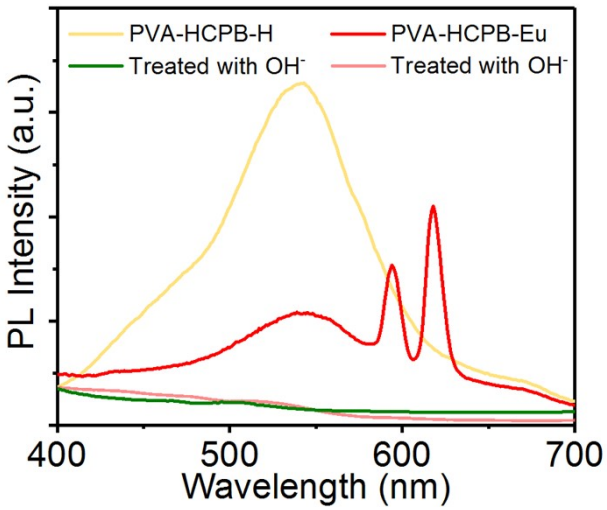

Figure S12 The emission spectra of PVA-HCPB-H and PVA-HCPB-Eu hydrogel after treated with 1 ml (10^{-2} M) $NH_3 \cdot H_2O$. These measurements were performed at 300 K with the amount of HCPB 0.8 mg.

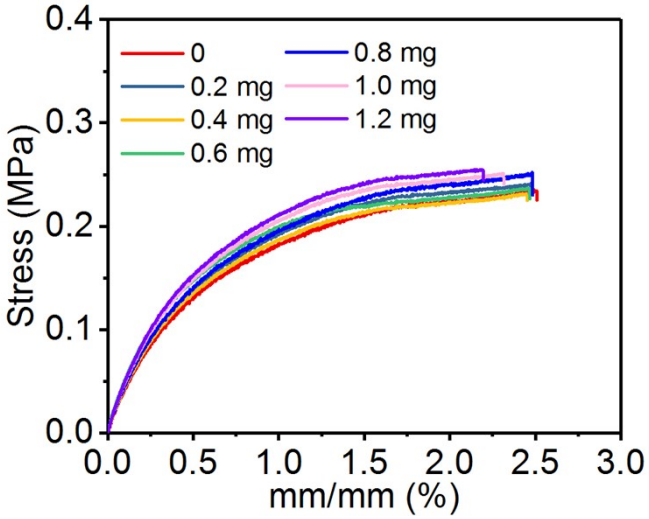

Figure S13 Stress−strain curves of PVA-HCPB with different amount of HCPB. Sample width: 6 mm; Thickness: 1 mm; Gage length: 3 mm; Loading speed: 5 mm min^{-1}.

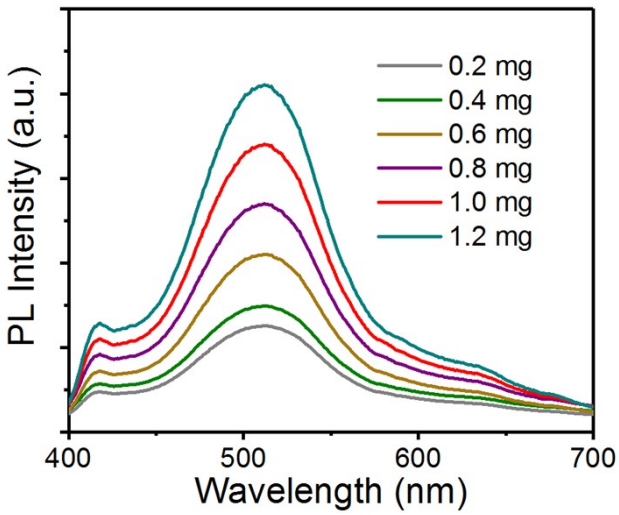

Figure S14 The emission spectra of PVA-HCPB with different amount of HCPB after UV irradiation for 5 min.

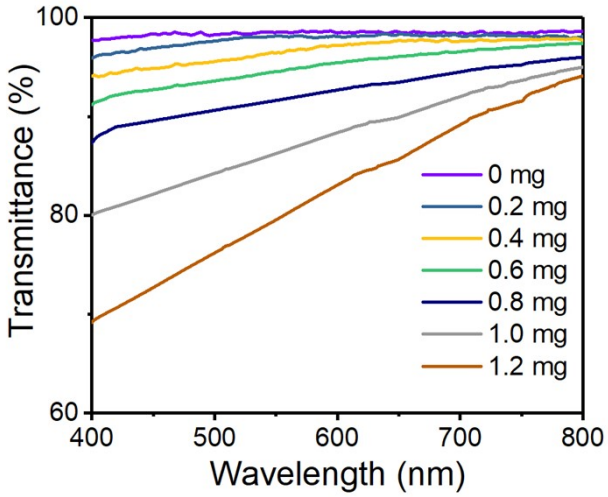

Figure S15 UV–vis spectra (transmittance mode) of PVA-HCPB with different amount of HCPB.

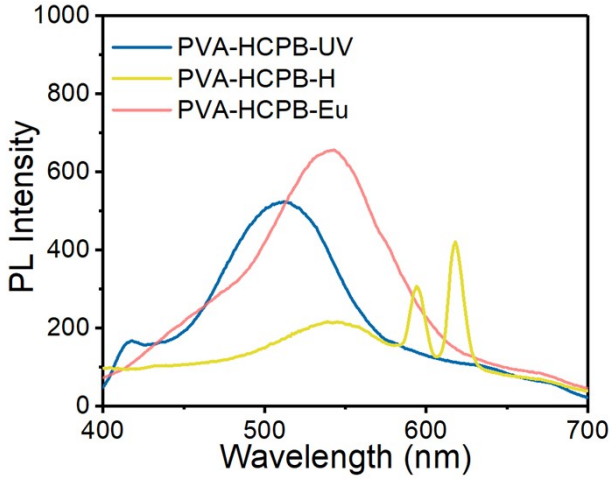

Figure S16 The emission spectra of PVA-HCPB -UV hydrogel after treated with treated with 0.5 mL of 10^{-2} M HCl and 0.8 mL of 10^{-3} M $EuCl_3$.

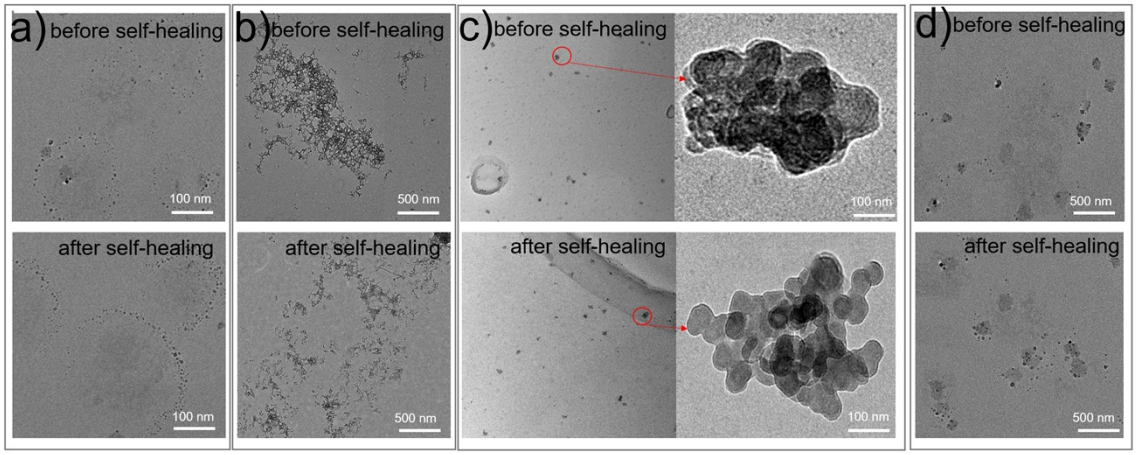

Figure S17 TEM images of different hydrogel before and after self-healing. a) PVA-HCPB hydrogel, b) PVA-HCPB-Eu hydrogel, c) PVA-HCPB-Eu hydrogel, d) PVA-HCPB-UV hydrogel.

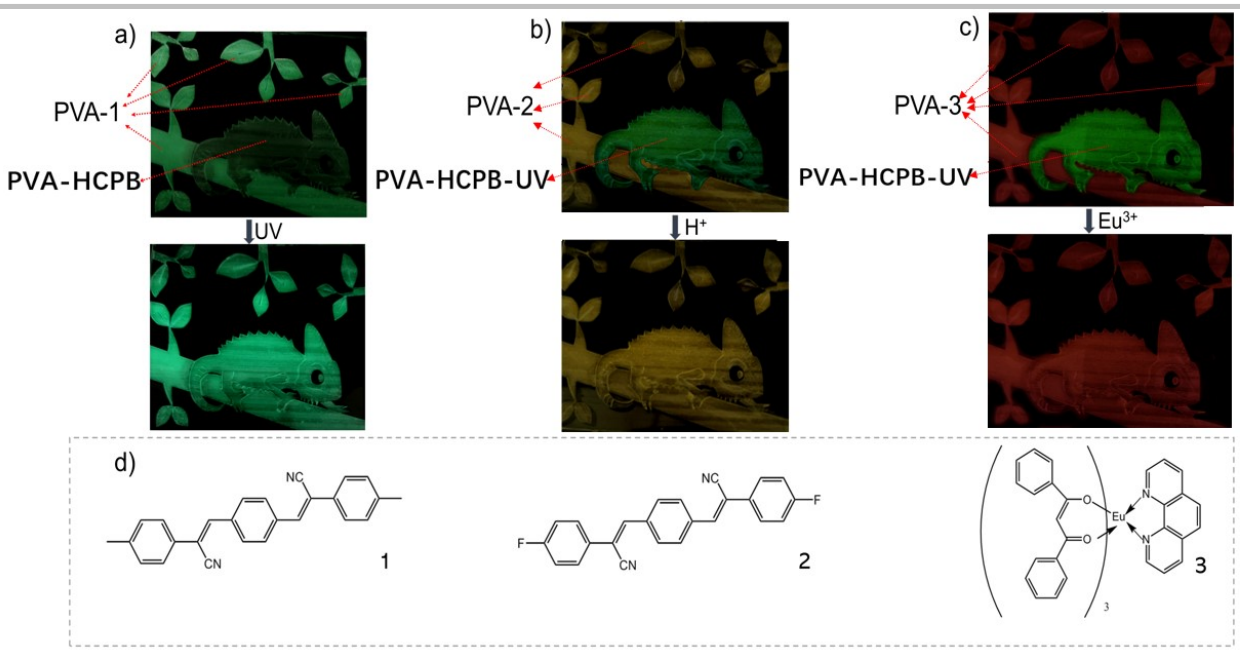

Figure S18 Chameleon-shaped PVA-HCPB hydrogel switches luminescence under different stimuli. a) Images showing the chameleon-shaped PVA-HCPB hydrogel that switches luminescence from colorless to green under UV. b) Chameleon-shaped PVA-HCPB hydrogel switches luminescence from green to yellow under H^+. c) Chameleon-shaped PVA-HCPB hydrogel switches luminescence from green to red under Eu^{3+}. d) Molecular structural of three compounds with different luminescent colors.

Fabrication process of these bioinspired chameleon-shaped hydrogel:
(1) PVA and compound 1, 2,and 3 can form green (PVA-1), yellow (PVA-2), and red (PVA-3) luminescence hygrogel, respectively. Fabrication process of these the surrounding environment hydrogels are as follow: The DMF solution of 1 (10 mg/mL, 0.1 mL) was added into 10 g of PVA solution. Then, the aqueous solution of $Na_2B_4O_7$ (0.1 M, 1 mL) was added in and green luminescence hydrogel formed. Finally, placed this hydrogel into the mold to form leaves and branches with green luminescence. Fabrication process of leaves and branches with yellow or red luminescence is similar to this by replacing compound 2 or 3 with 1.
(2) The chameleon-shaped hydrogel was made from PVA-HCPB and PVA-HCPB-UV hydrogel by placing PVA-HCPB hydrogel into chameleon-shaped mold, while the surrounding environment was made from PVA-1 hydrogel with green luminescence (a), PVA-2 hydrogel with yellow luminescence (b) and PVA-3 hydrogel with red luminescence (c).