Supporting Information

A Long-Wavelength Red-Light-Responsive Hydrogel with Tunable Optical Transparency for High-Resolution Information Display

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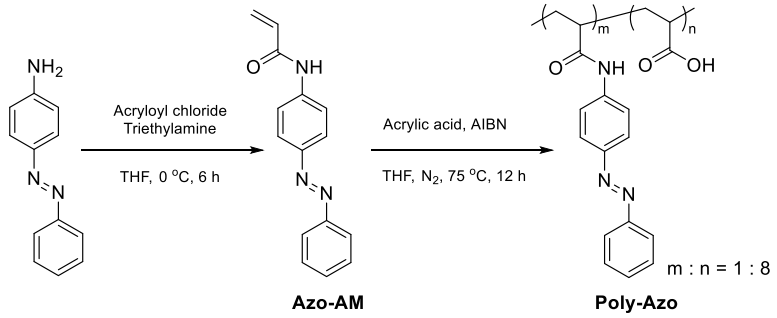
Supplementary Figures



Scheme S1. Synthesis route of the coumarin-based PPGs. The Azo-AM and Poly-Azo were synthesized according to the reported methods with modifications[1,2].

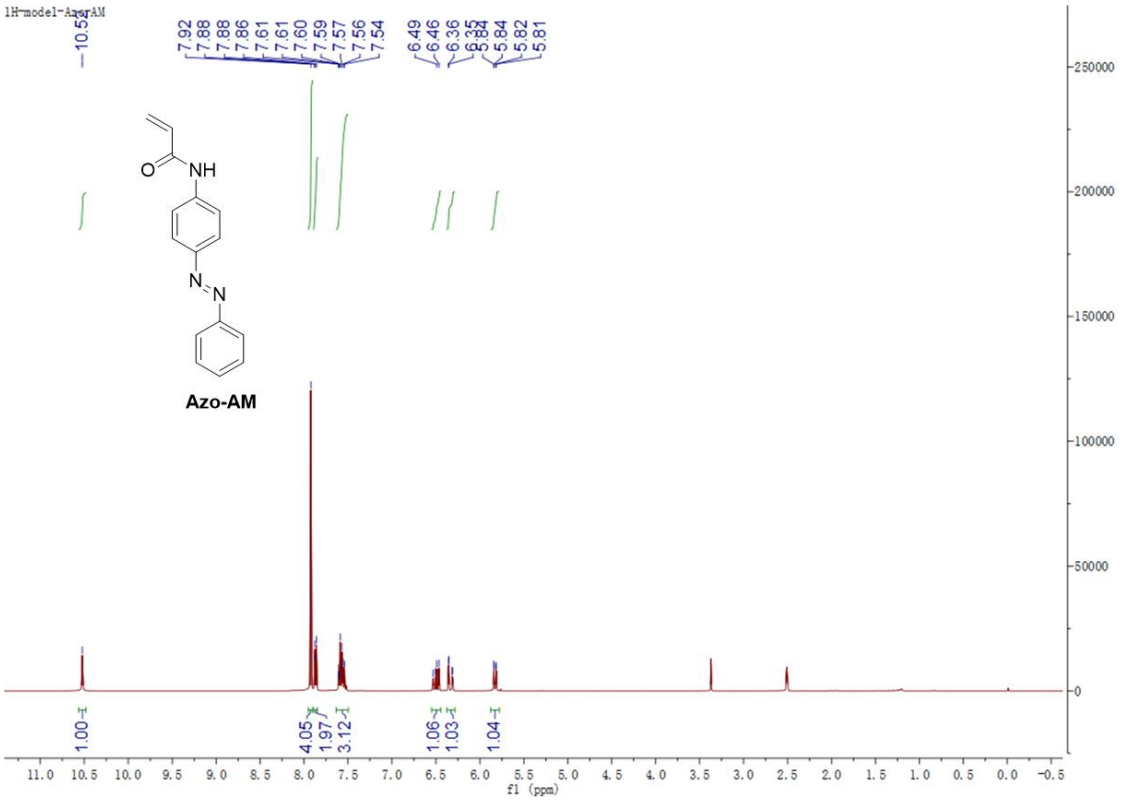


Figure S1. ^{1}H NMR spectra of Azo-AM monomer.

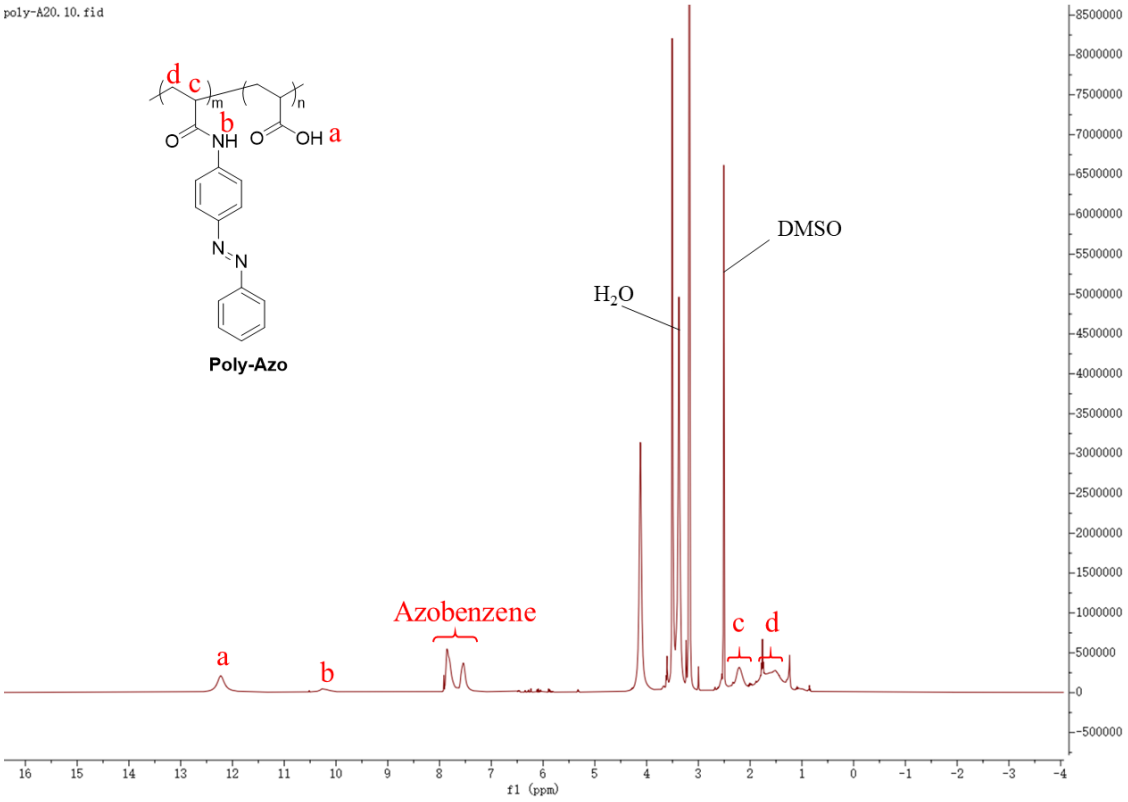


Figure S2. ^{1}H NMR spectra of Poly-Azo.

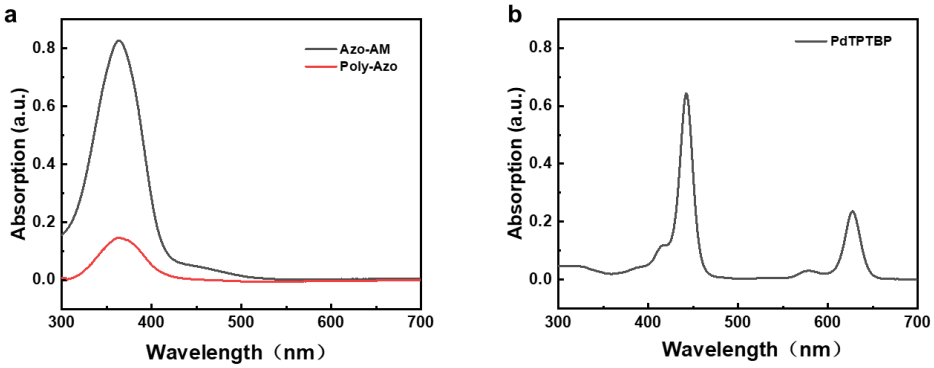


Figure S3. Absorption spectra of (a) Azo-AM (2×10^{-5} M), Poly-Azo (5×10^{-3} mg/mL), and (b) PdTPTBP (1×10^{-5} M) in dimethyl sulfoxide.

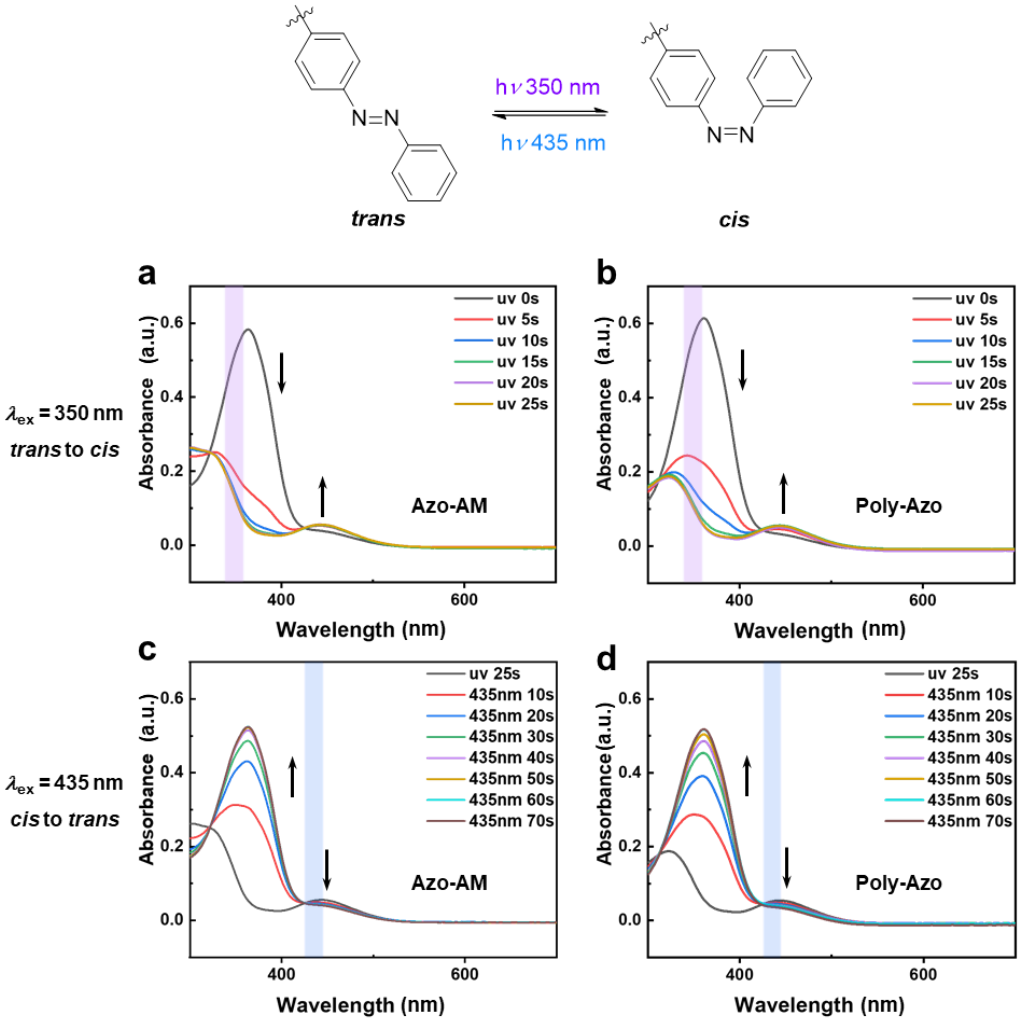


Figure S4. Absorption spectra of (a,c) Azo-AM and (b,d) Poly-Azo upon light exposure for different time periods at the same concentration of azobenzene moiety (1.5×10^{-5} M) in dimethyl sulfoxide. (a,b) For photoisomerization from *trans* to *cis* form, λ_{ex} = 350 nm, 2.2 mW/cm^2. (c,d) For photoisomerization from *cis* to *trans* form, λ_{ex} = 435 nm, 2.2 mW/cm^2.

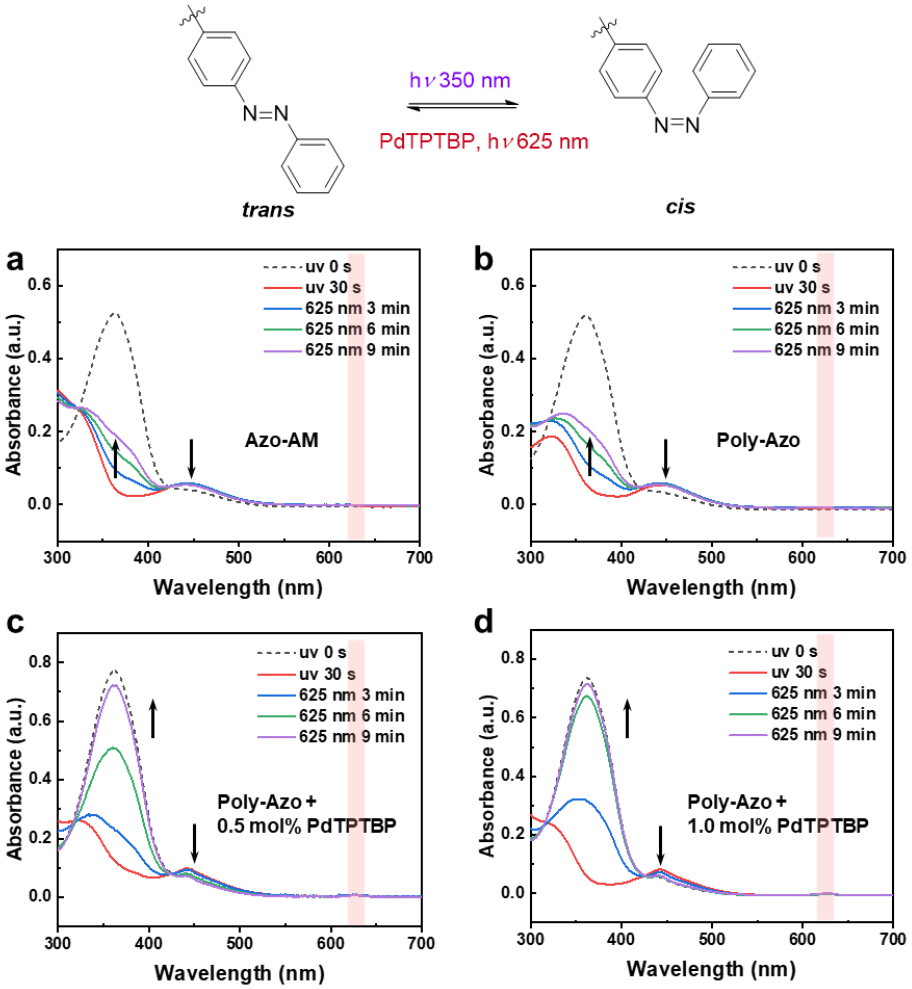


Figure S5. Absorption spectra of (a) Azo-AM, (b) Poly-Azo and (c,d) the mixture of Poly-Azo and PdTPTBP (0.5 or 1.0 mol% equiv. relative to azobenzene moiety) upon light exposure for different time periods at the same concentration of azobenzene moiety (1.5×10^{-5} M) in N_2 saturated dimethyl sulfoxide. The solutions are irradiated with 350 nm light for 30 s to get to photostationary state before 625 nm light exposure. λ_{ex} = 350 nm, 2.2 mW/cm^2. λ_{ex} = 625 nm, 2.2 mW/cm^2.

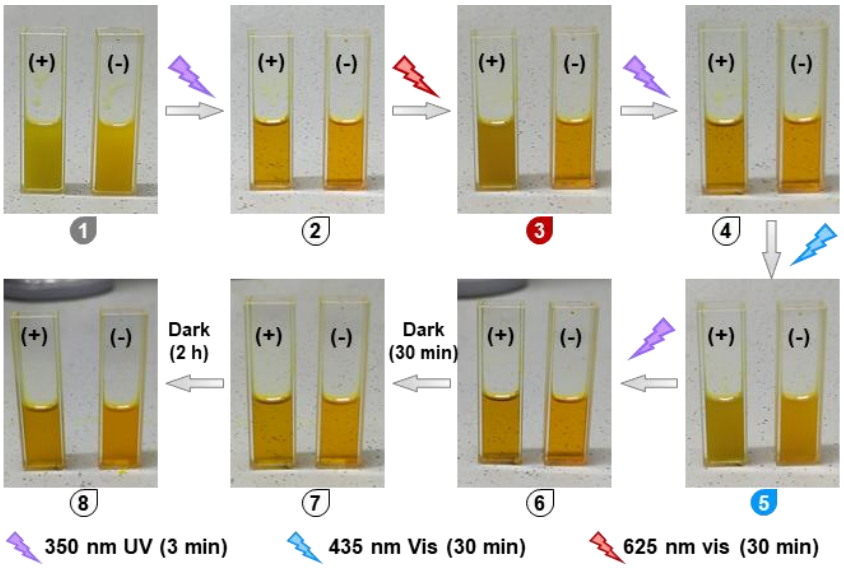


Figure S6. Photographs of Poly-Azo solution (10.4 mg/mL) at the presence of PdTPTBP (1 mol% equiv. relative to azobenzene moiety) or not after 350 nm, 435 nm or 625 nm light exposure. The Poly-Azo and PdTPTBP is dispersed in the mixed solvent of MeOH, DMSO and H_2O (v : v : v = 1 : 1 : 1.2). λ_{ex} = 350 nm, 40 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2. λ_{ex} = 625 nm, 20 mW/cm^2.

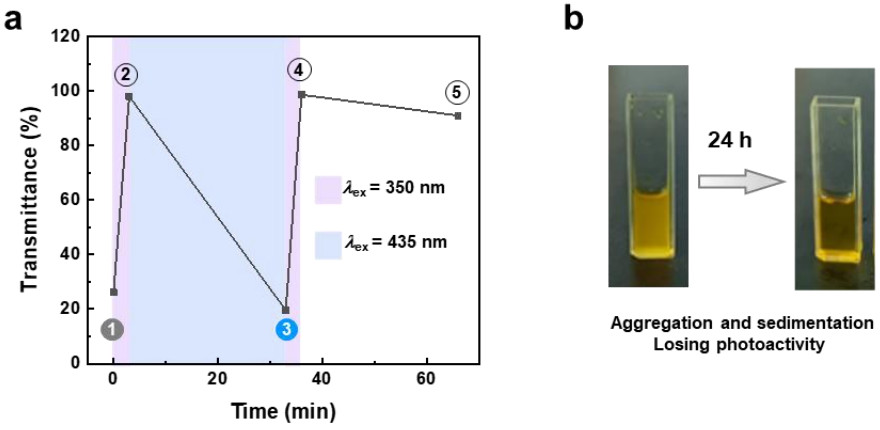


Figure S7. (a) Transmittance at 900 nm of Poly-Azo solution (10.4 mg/mL) after light exposure for different time periods. (b) Photographs of the Poly-Azo solution (10.4 mg/mL) freshly prepared and after 24 h of standing. The Poly-Azo is dispersed in the mixed solvent of MeOH, DMSO and H_2O (v : v : v = 1 : 1 : 1.2). λ_{ex} = 350 nm, 40 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2.

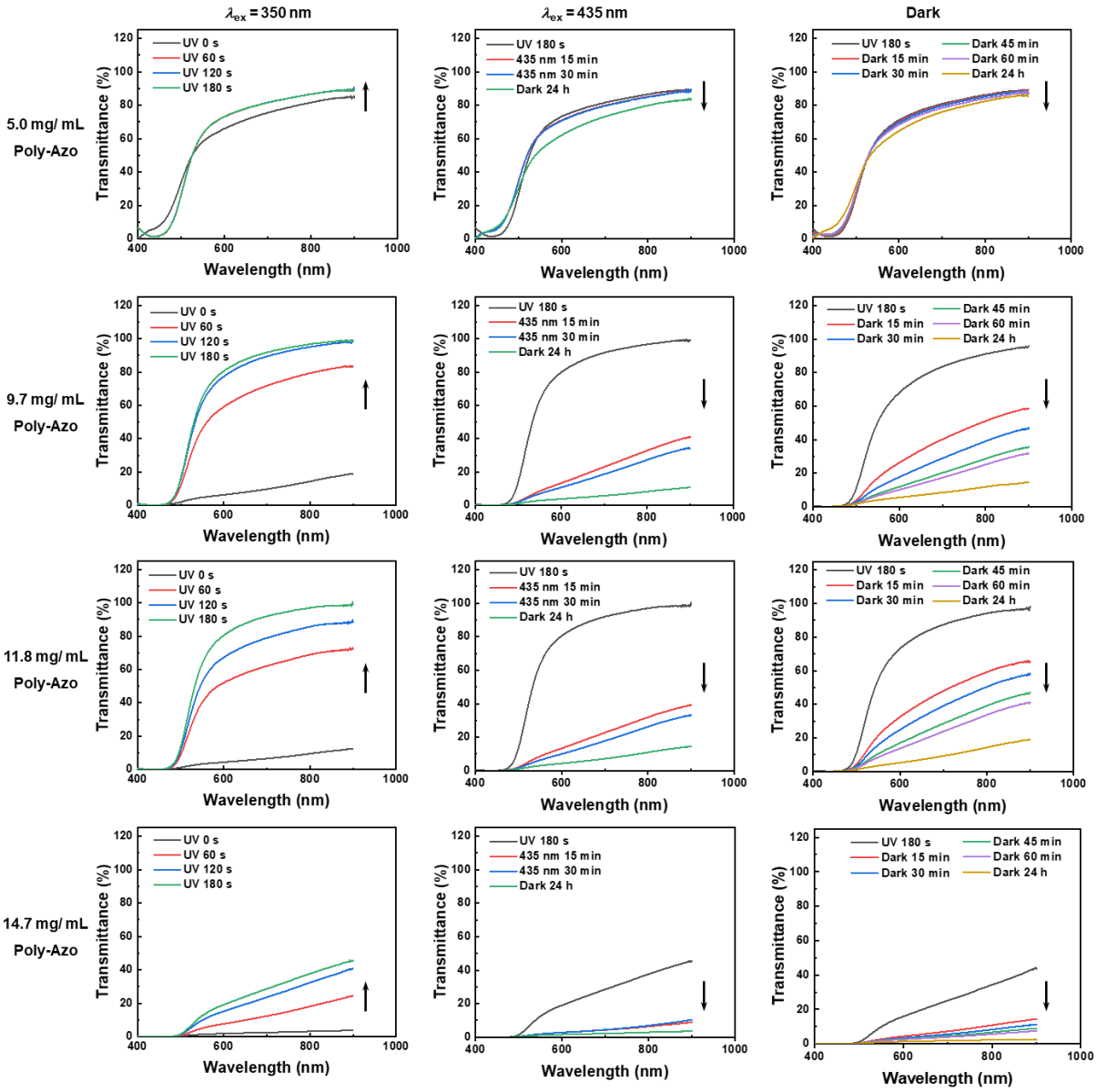


Figure S8. Transmittance spectra of Poly-Azo hydrogels upon 350 nm and 435 nm light exposure for different time periods. The hydrogels are prepared by varying the concentration of Poly-Azo (5.0, 9.7, 11.8 and 14.7 mg/mL) while maintaining a constant water content of 41.2 vol%. λ_{ex} = 350 nm, 60 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2.

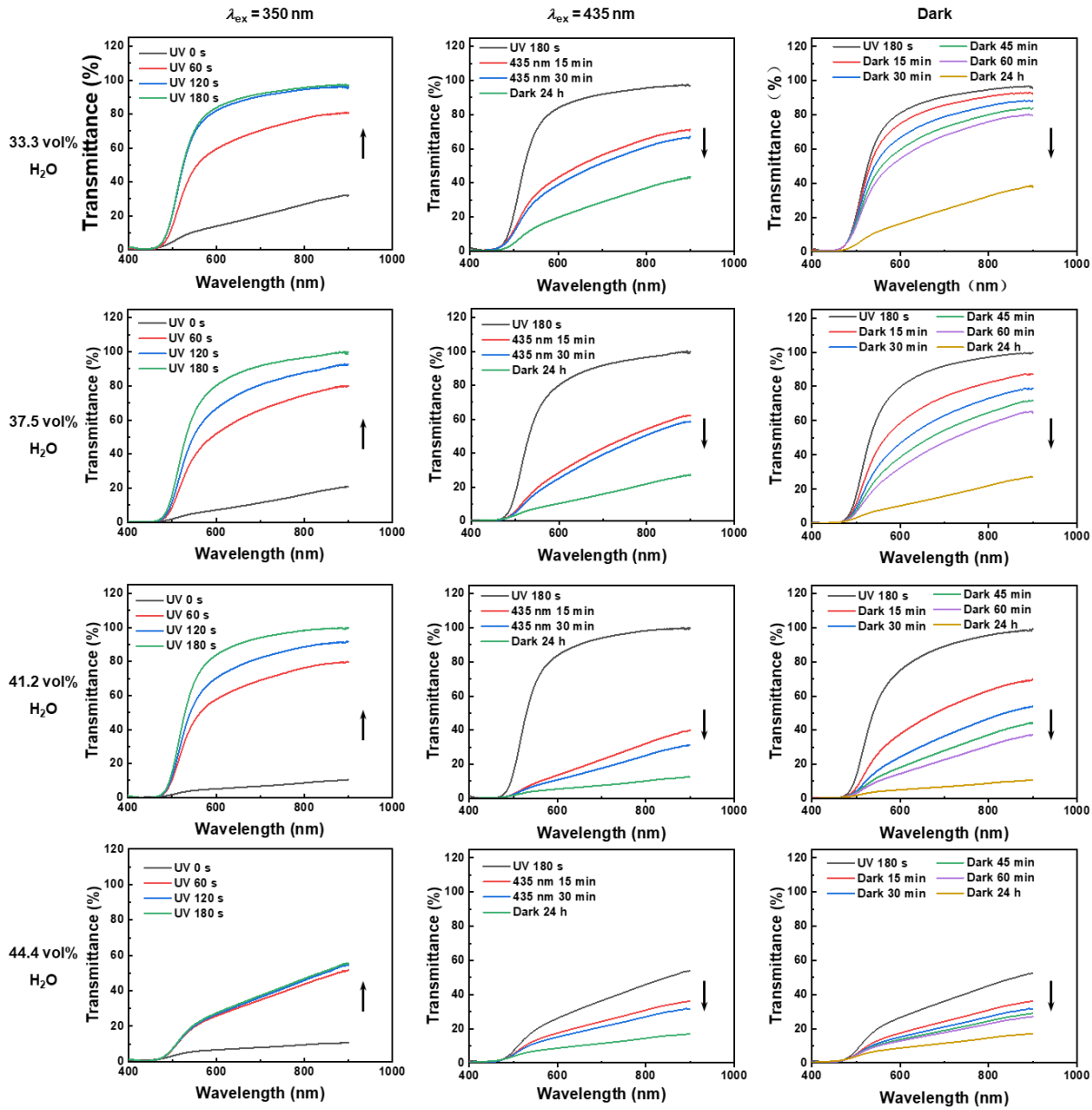


Figure S9. Transmittance spectra of Poly-Azo hydrogels upon 350 nm and 435 nm light exposure for different time periods. The hydrogels are prepared by varying the water content (33.3, 37.5, 41.2 and 44.4 vol%) while maintaining a constant Poly-Azo content of 9.7 mg/mL. λ_{ex} = 350 nm, 60 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2.

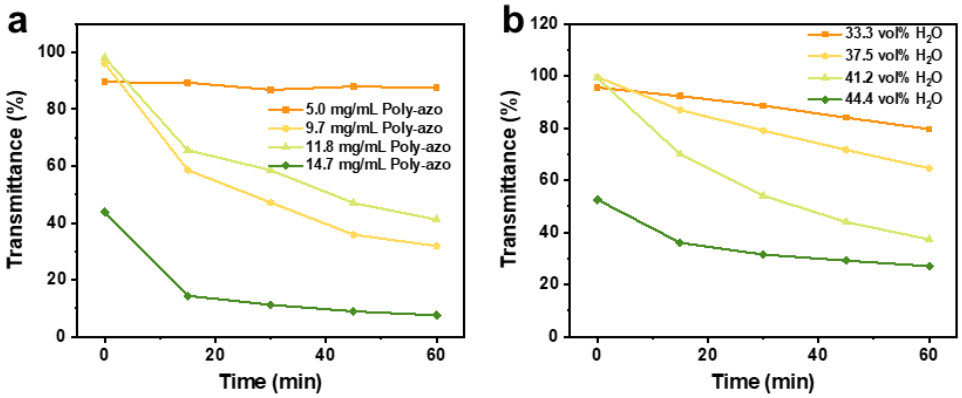


Figure S10. (a,b) Transmittance at 900 nm of Poly-Azo hydrogels in dark for different time periods after 350 nm light irradiation for 3 min with the power density of 60 mW/cm^2. (a) The hydrogels are prepared by varying the concentration of Poly-Azo (5.0, 9.7, 11.8 and 14.7 mg/mL) while maintaining a constant water content of 41.2 vol%. (b) The hydrogels are prepared by varying the water content (33.3, 37.5, 41.2 and 44.4 vol%) while maintaining a constant Poly-Azo content of 9.7 mg/mL.

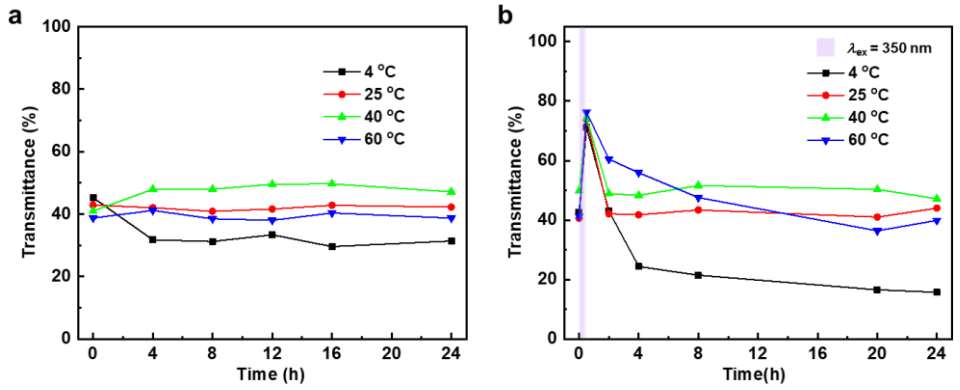


Figure S11. Transmittance at 900 nm of the (a) transparent and (b) opaque Poly-Azo hydrogels at different temperatures in 24 h. The opaque hydrogels were prepared with the condition of 41.2 vol% H_2O and 9.7 mg/mL Poly-Azo before polymerization reaction. The transparent hydrogel was obtained by irradiating the opaque hydrogel with 350 nm light (60 mW/cm^2) for 3 min.

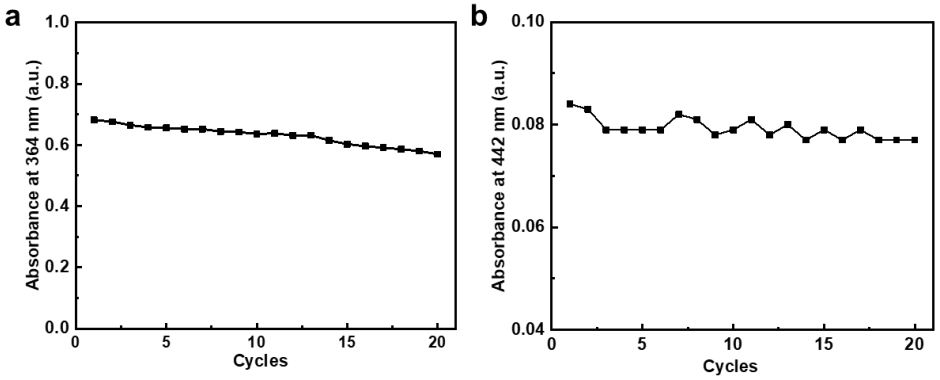


Figure S12. Absorbance of Azo-AM (1.5×10^{-5} M in DMSO) (a) at 364 nm after full exposure to 435 nm light, and (c) at 442 nm after full exposure to 350 nm light, during alternating 350 nm (⩾3 min) and 435 nm light (⩾15 min) exposure for 20 cycles. λ_{ex} = 350 nm, 60 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2.

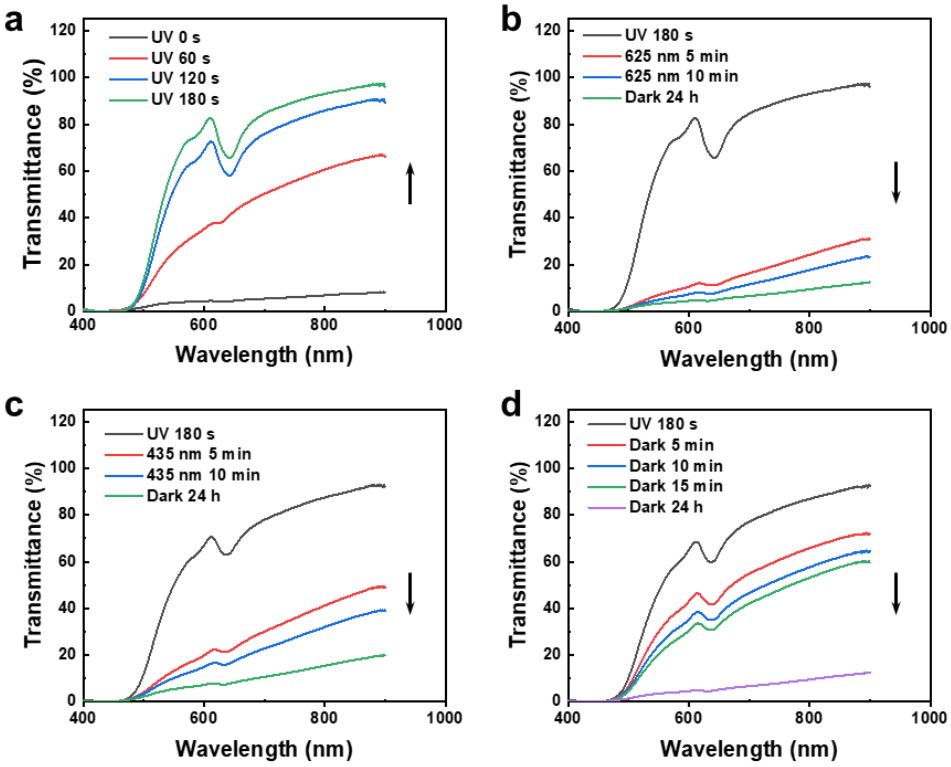


Figure S13. (a) Transmittance spectra of Poly-Azo hydrogel added with PdTPTBP (1 mol% equiv. relative to azobenzene moiety) after 350 nm light exposure for different time periods. (b-d) Then the hydrogel was exposed under 625 nm and 435 nm light irradiation or stood in dark for different time periods. The hydrogels were prepared with the condition of 41.2 vol% H_2O and 9.7 mg/mL Poly-Azo before polymerization reaction. λ_{ex} = 350 nm, 60 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2. λ_{ex} = 625 nm, 20 mW/cm^2.

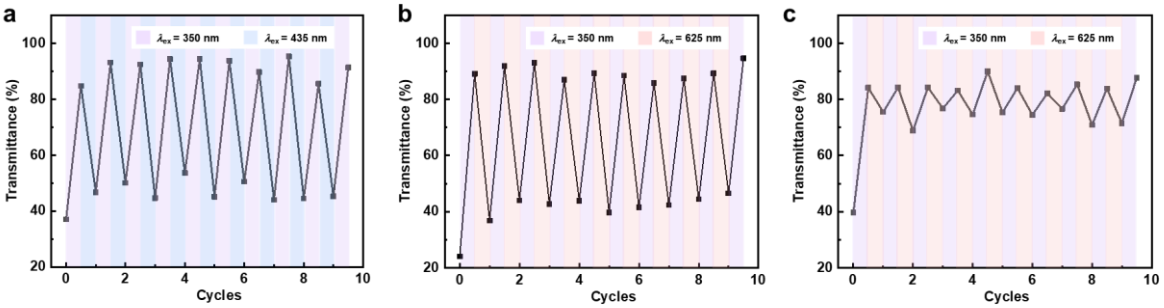


Figure S14. (a,b) Reversible photo response of the Poly-Azo hydrogel added with PdTPTBP (1 mol% equiv. relative to azobenzene moiety) upon (a) alternating 350 nm (3 min) and 435 nm light (15 min) exposure for 10 cycles and (b) alternating 350 nm (3 min) and 625 nm light (15 min) exposure for 10 cycles. (c) Reversible photo response of the Poly-Azo hydrogel upon alternating 350 nm (3 min) and 625 nm light (15 min) exposure for 10 cycles. λ_{ex} = 350 nm, 60 mW/cm^2. λ_{ex} = 435 nm, 20 mW/cm^2. λ_{ex} = 625 nm, 20 mW/cm^2.

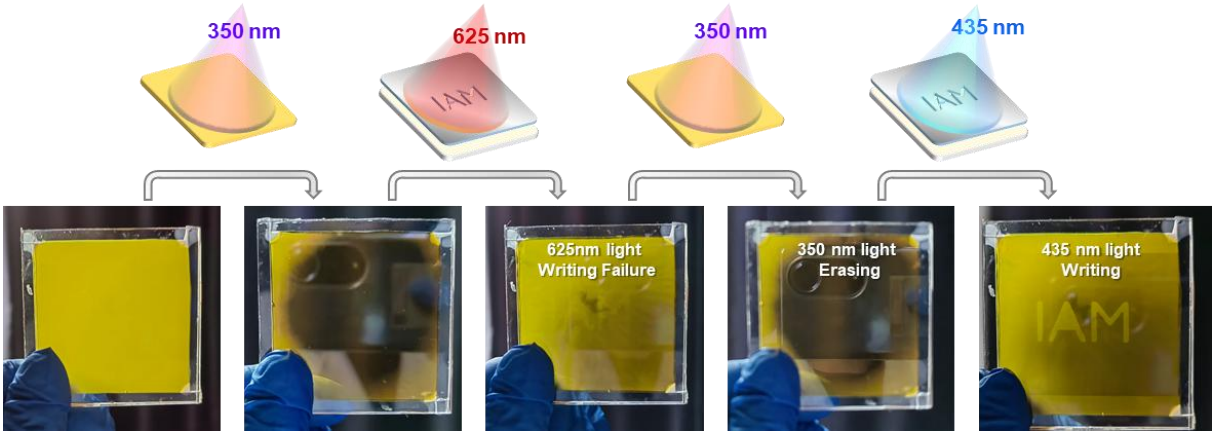


Figure S15. Schematic diagram and photographs illustrating information writing and erasing on Poly-Azo hydrogel without addition of PdTPTBP upon irradiation with 350 nm, 435 nm and 625 nm light. The hydrogels were prepared with the condition of 41.2 vol% H_2O and 9.7 mg/mL Poly-Azo before polymerization reaction. λ_{ex} = 350 nm, 60 mW/cm^2, 15 min. λ_{ex} = 435 nm, 20 mW/cm^2, 5 min. λ_{ex} = 625 nm, 20 mW/cm^2, 5 min.

Reference

1 H. Yamaguchi, Y. Kobayashi, R. Kobayashi, et al., *Nature Communications*, 2012, **3**, 603.

2 We.Lv, H. Xia, K. Y. Zhang, et al., *Materials Horizons*, 2017, **4**, 1185-1189.