Supporting Information for

Photochemically Driven One-Step Triple Dynamic Networks Formation in Printable Tough Hydrogel for Self-Healing Tubular Sensors

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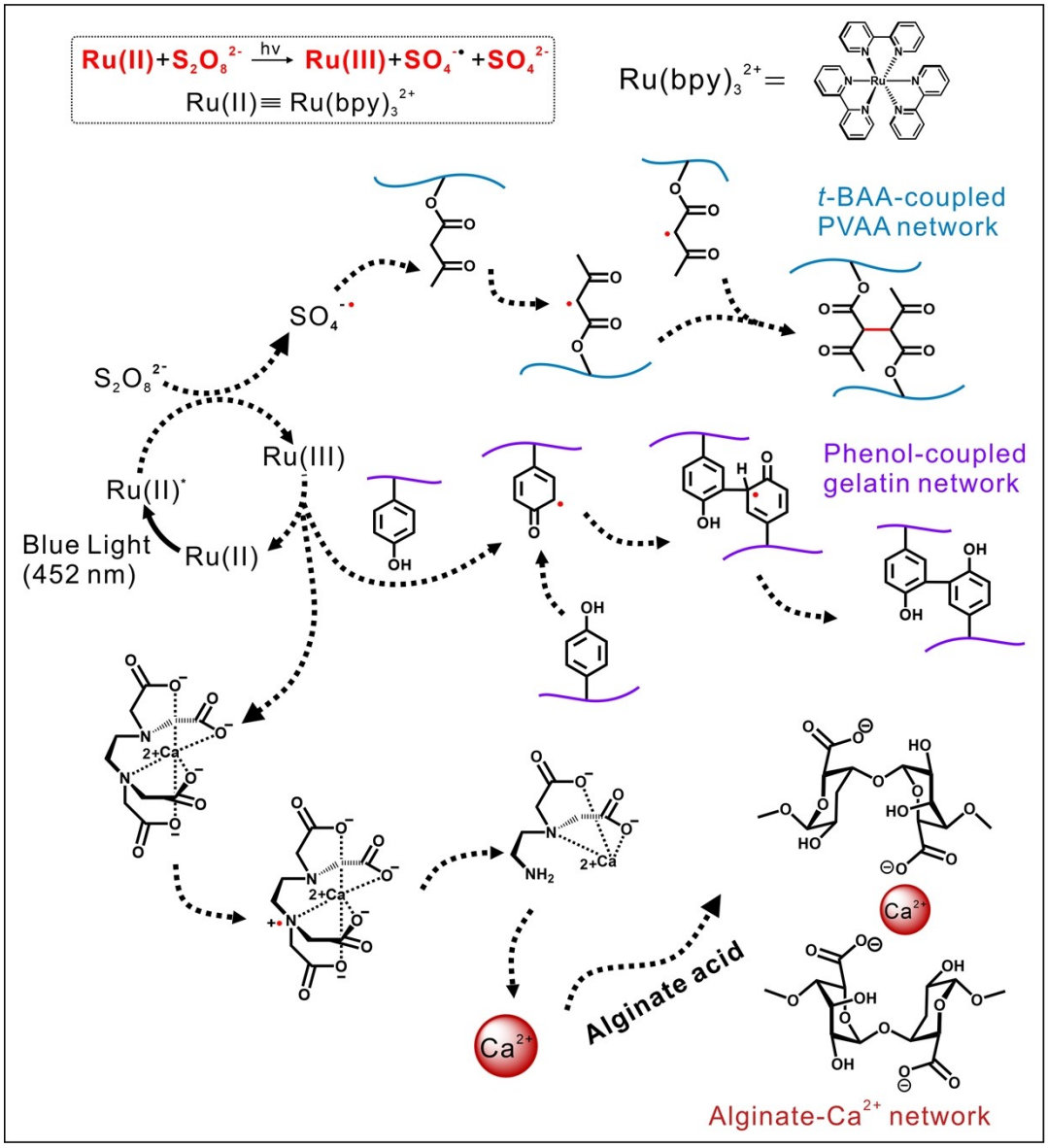

Figure S1. The proposed three orthogonal photoreactions in PSHTHs by the catalysis of ruthenium photochemistry [Ru(II)/$S_2O_8^{2-}$].

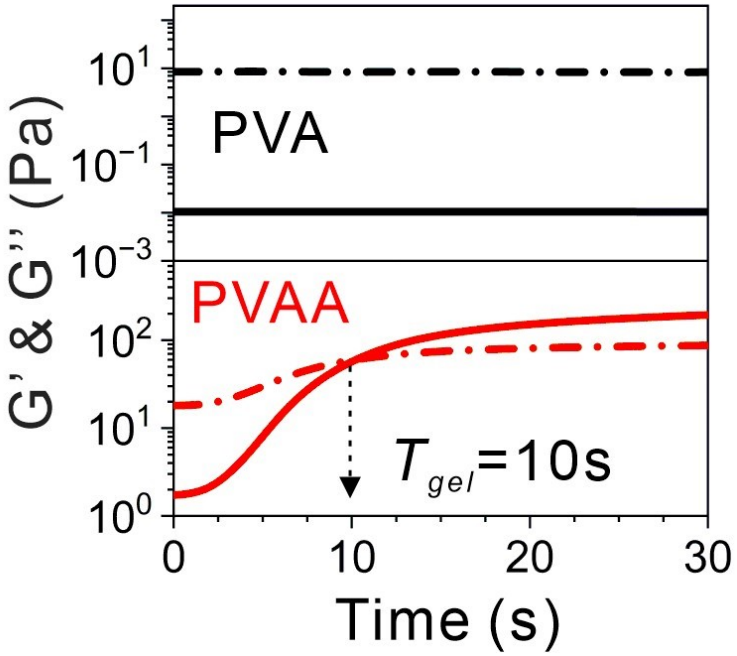

Figure S2. Rheology characterization of PVAA and PVA under blue light irradiation.

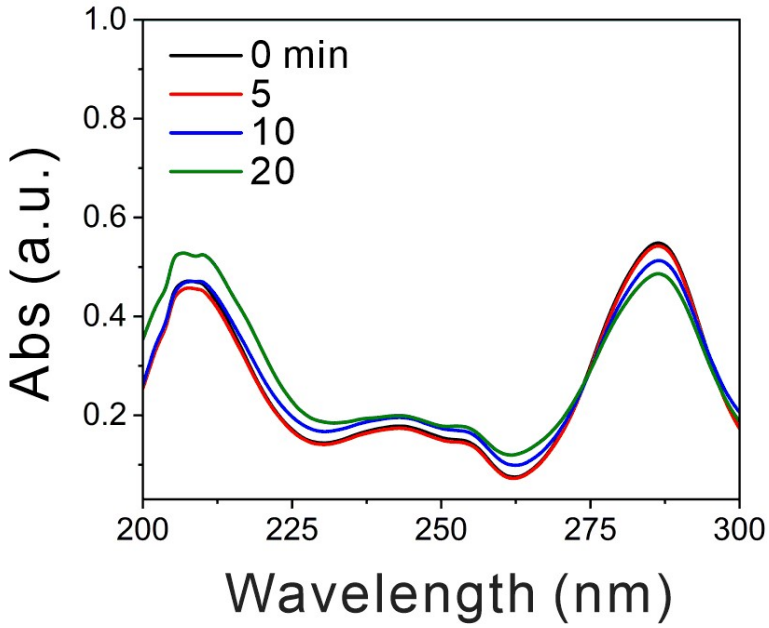

Figure S3. UV-vis characterization of Ru(II)/APS solution under different irradiation times. There was no obvious decrease in the UV-Vis absorption of this solution at 240 nm, indicating that the decrease in the precursor under light irradiation was assigned for the coupling reaction of *t*-BAA molecules.

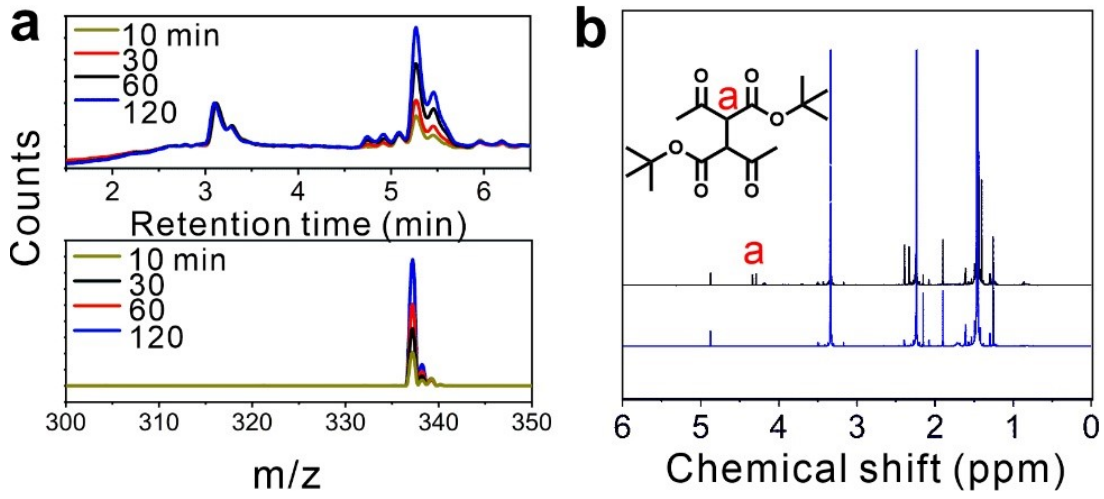

Figure S4. (a) HPLC-MS with different reaction times. (b) ^{1}H NMR spectra of *t*-BAA and dimer after 30min irradiation in $CDCl_3$ ([Ru(II)] = 0.316 mM, [APS] = 0.316 M, [t-BAA] = 0.316 M s:DMSO).

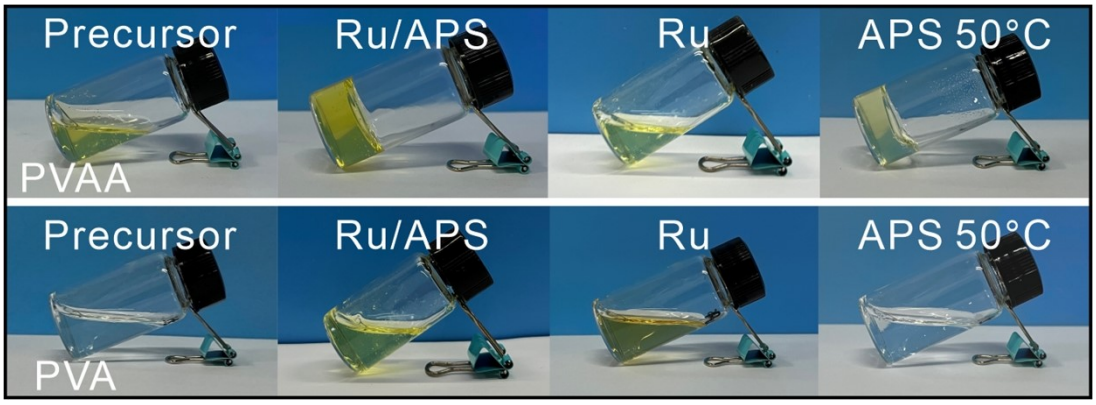

Figure S5. Digital images of PVAA and PVA with different initiation methods. PVAA can form gel in the presence of APS. All PVA samples were still in liquid states, indicating the sol-gel transition process was not observed in the *t*-BAA-free PVA precursors.

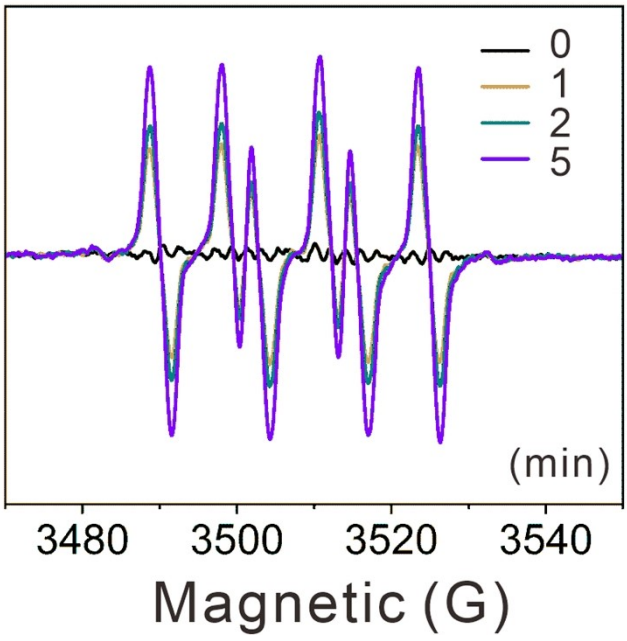

Figure S6. EPR spectra of the t-BAA solution with different irradiation times.

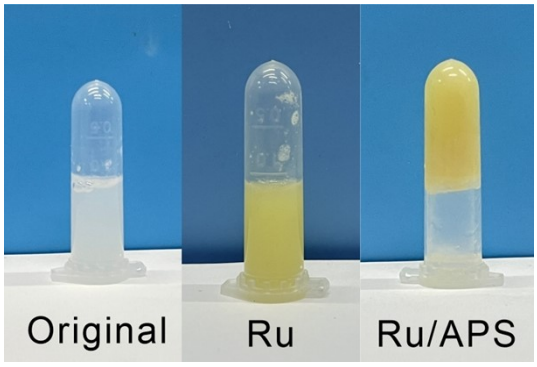

Figure S7. Digital images of Gel-UPy with different initiation methods. Gel-UPy can only form a cross-linking network in the presence of both Ru and APS after blue light irradiation.

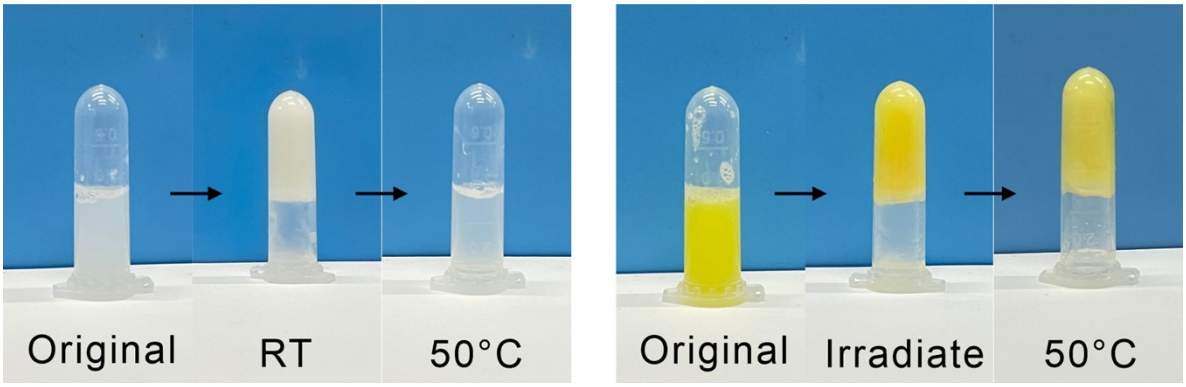

Figure S8. H-bonds crystallization and irradiated phenolic cross-linking of Gel-UPy. The phenol coupling forms a covalent network after blue light irradiation and does not break under heating.

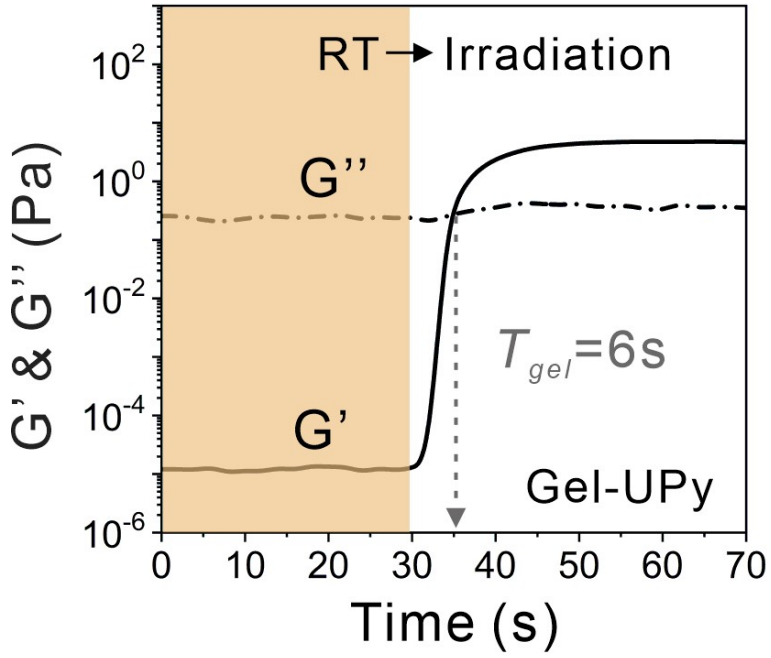

Figure S9. Rheology characterization of Gel-UPy solution at room temperature (RT) and upon blue light irradiation.

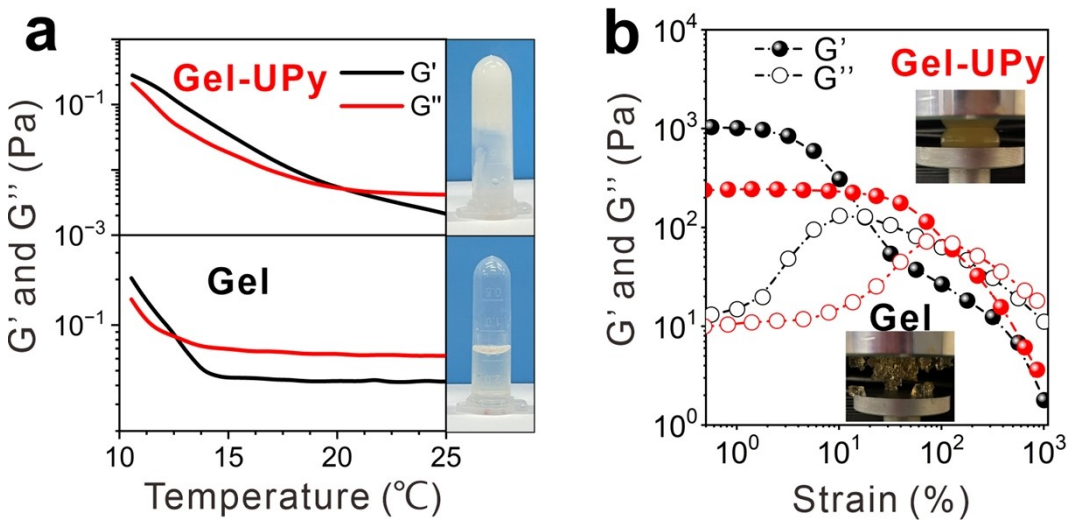

Figure S10. Rheology characterization of Gel and Gel-UPy. (a) Comparison of the low-temperature crystallization ability of 5% gel and 5% Gel-UPy. (b) Shear stress sweep tests of 5% Gel and 5% Gel-UPy. The photo is the state of 5% Gel and 5% Gel-UPy after the same load.

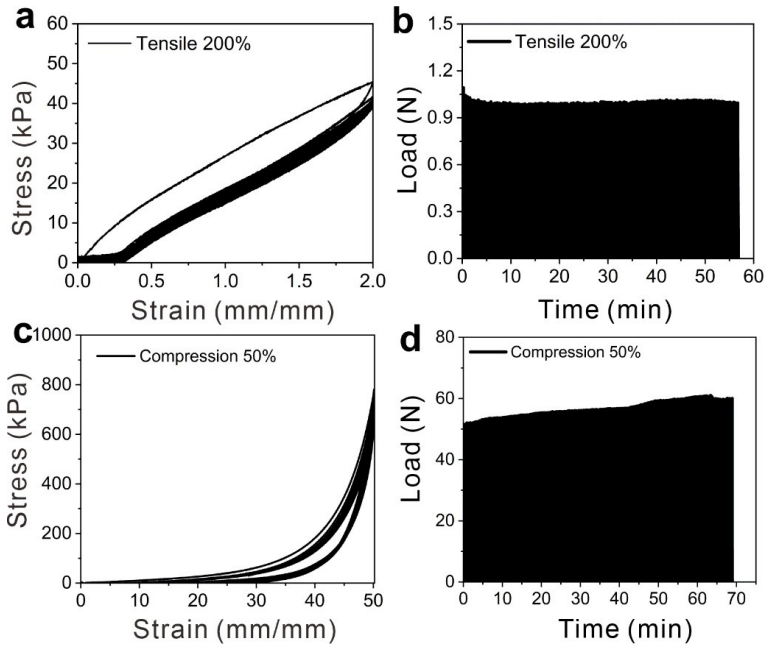

Figure S11. Mechanical tests of PSHTHs. (a) Tensile stress-strain curves of hydrogels and (b) loading force under continuous stretching to a strain of 200%. (c) Compression stress-strain curves and (d) loading force under continuous compressing to a strain of 50%.

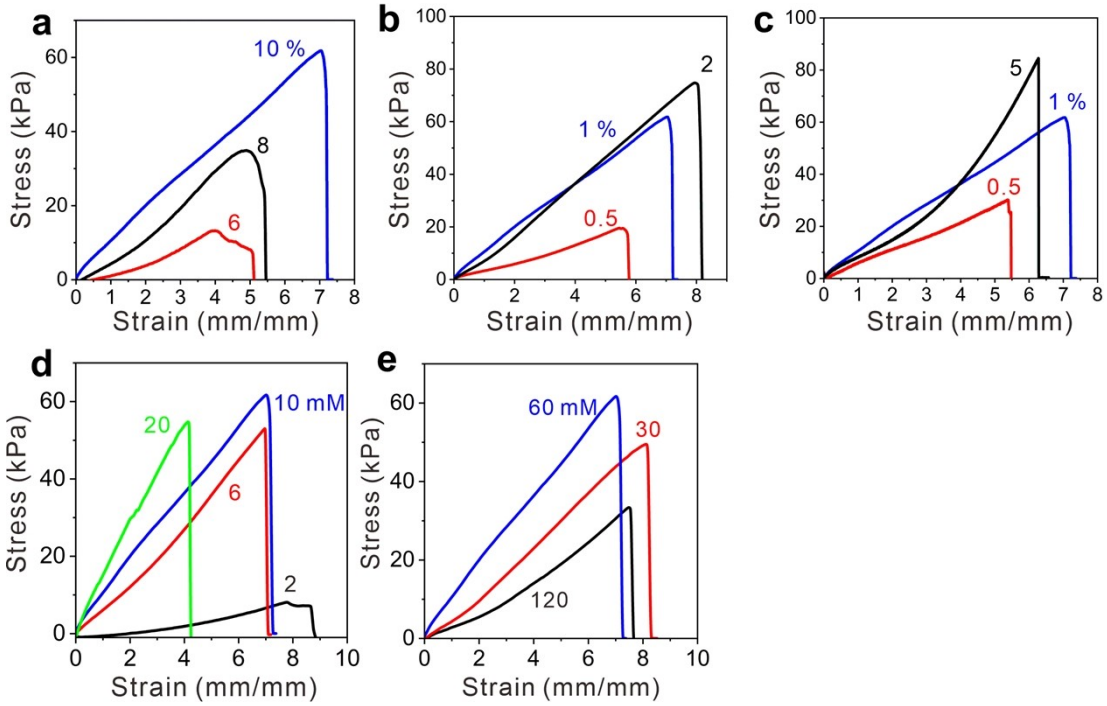

Figure S12. Stress-strain curves of different PSHTHs. (a-c) Different weight ratios of PVAA, ALG, and Gel-UPy. (d-e) Different concentrations of EDTA-Ca and APS, respectively. All tensile tests were performed at the stretching speed of 50 mm min^{-1}. Based on these tensile tests, the optimized preparation condition was fixed: [PVAA] = 10 wt%, [ALG] = 1 wt%, [Gel-UPy] = 1 wt%, [EDTA-Ca] = 10 mM, [Ru(II)] = 26.7 μM and [APS] = 60 mM. The irradiation intensity was 15 mW cm^{-2}, and the irradiation time was 240 s.

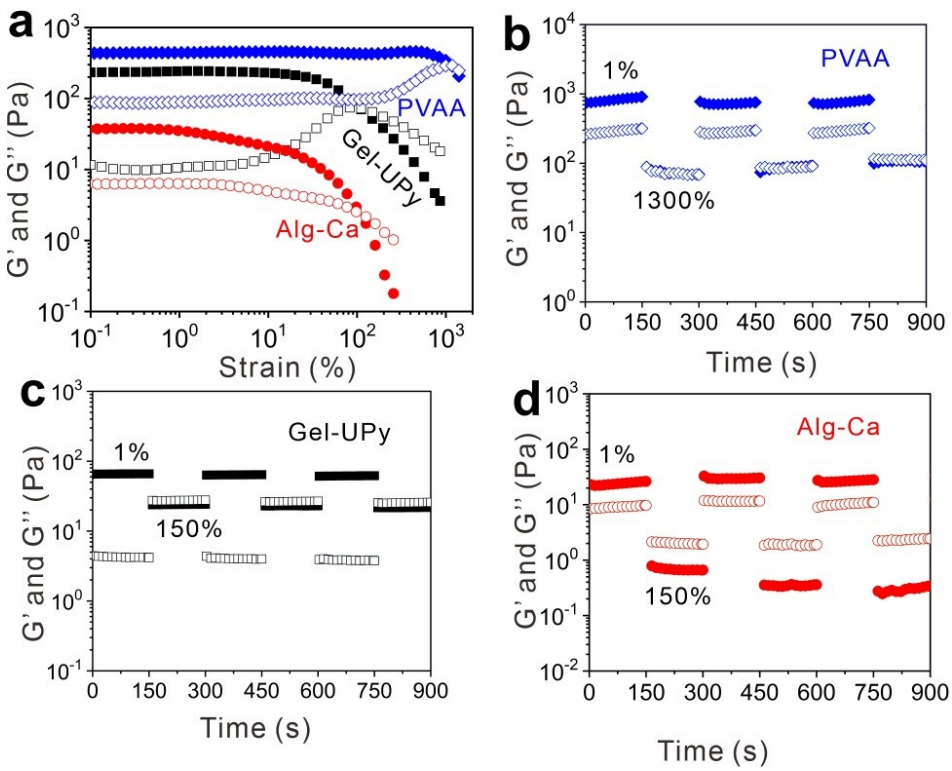

Figure S13. (a) Shear stress sweep tests of hydrogels with single networks at 25 °C. (b-d) The self-healing ability of each component was evaluated with an alternating strain at 25 °C.

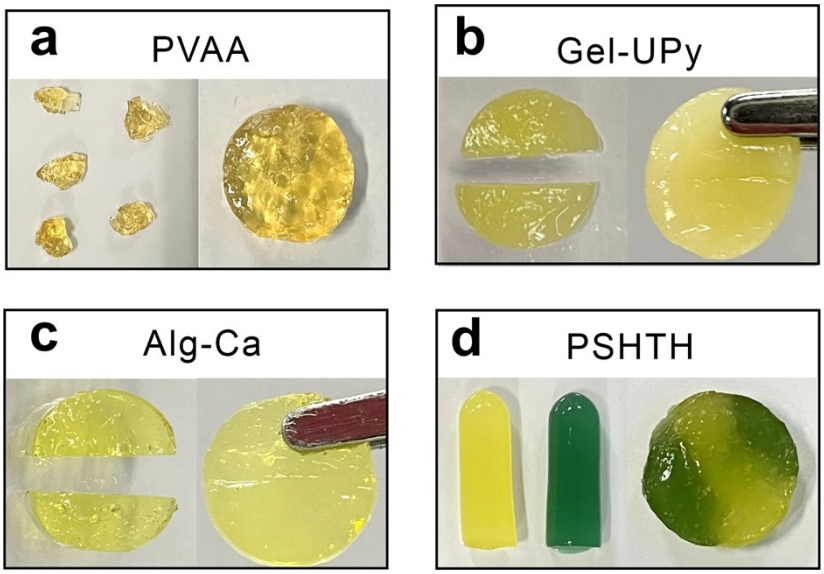

Figure S14. Self-healing pictures of each component. (a) [PVAA] = 10 wt%. (b) [Gel-UPy] = 5 wt%. (c) [ALG] = 2 wt%, [EDTA-Ca] = 20 mM. (d) [PVAA] = 10 wt%, [ALG] = 1 wt%, [Gel-UPy] = 1 wt%, [EDTA-Ca] = 10 mM, [Ru(II)] = 26.7 μM and [APS] = 60 mM.

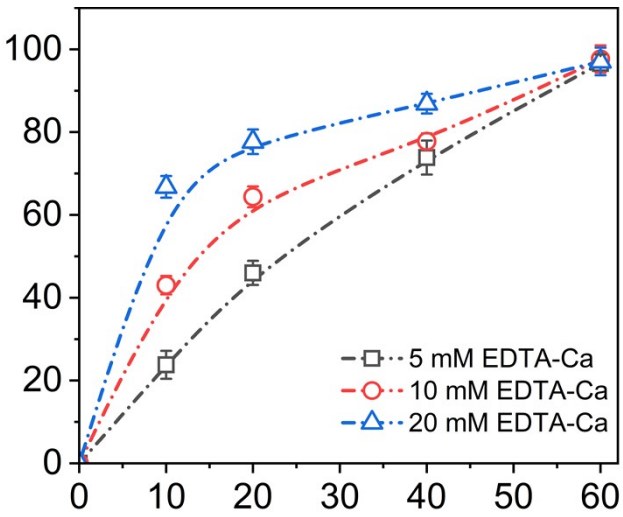

Figure S15. The self-healing efficiency of different concentrations of EDTA-Ca increased with repair time.

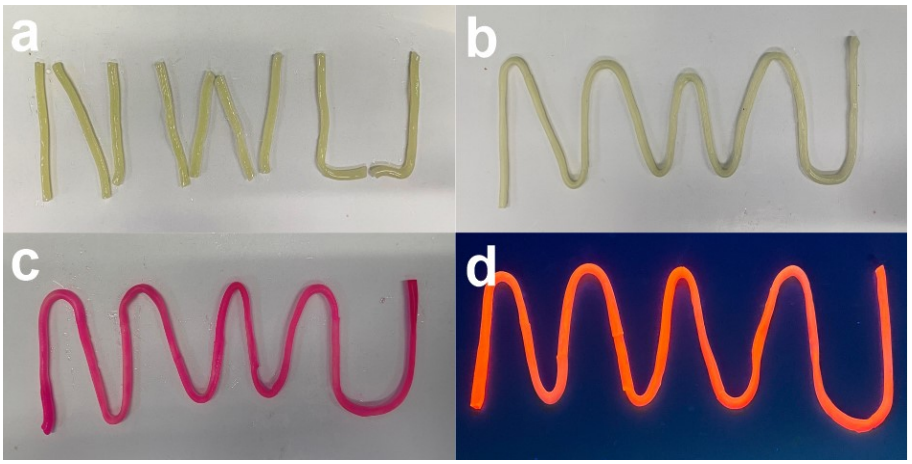

Figure S16. Digital images of (a) cut tubes, (b) healing tubes (c-d) healing tubes load fluorescent liquid under visible-/UV-light irradiation.