**Supporting Information *for***

# A quadruple-stimuli responsive supramolecular hydrogel constructed from poly(acrylic acid) derivative and *β*-cyclodextrin dimer

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## 1. Synthesis of 6-hydroxyhexyloxy-ferrocenecarboxylate (Fc-$C_6$-OH)

Ferrocenecarboxylic acid (2.30 g, 10 mmol), DMAP (1.22 g, 10 mmol), and EDC·HCl (2.80 g, 15 mmol) were dissolved in 100 mL of $CH_2Cl_2$ at 0 °C for 0.5 h. Then, 1,6-hexanediol (2.36 g, 20 mmol) in 50 mL $CH_2Cl_2$ was added and the mixture was stirred at 0 °C for 1 h. Finally, the reaction was kept at room temperature for 24 h. The solvent was evaporated under reduced pressure, and the residue was dried in the vacuum oven. The residue was purified by column chromatography using n-hexane/ethyl acetate (3/1, v/v) as eluent to give the product as a yellow powder. Yield: 50%. $^1$H-NMR ($CDCl_3$, 400 MHz) $\delta$ 4.83 (s, 2H), 4.42 (s, 2H), 4.29-4.17 (m, 7H), 3.69 (t, $J$ = 6.2 Hz, 2H), 1.82-1.71(m, 2H), 1.64 (d, $J$ = 5.8 Hz, 2H), 1.49 (d, $J$ = 2.6 Hz, 4H). HRE-TOF-MS (m/z): $[M+H]^+$ calcd for $C_{17}H_{22}FeO_3H^+$, 331.0952; found, 331.0890.

## 2. Synthesis of poly(acrylic acid) derivative (PAA-mAzo/Fc)

PAA-mAzo/Fc was prepared as following. PAA (0.288 g), DMAP (0.060 g, 0.48 mmol), and EDC·HCl (0.088 g, 0.48 mmol) were dissolved in 40 mL DMF at 0 °C for 0.5 h. Then, mAzo-$C_6$-OH (0.100 g, 0.24 mmol) and Fc-$C_6$-OH (0.079 g, 0.24 mmol) in 30 mL DMF were added and the mixture was stirred at 0 °C for 1 h. Finally, the reaction was kept at room temperature for 24 h. The product was purified using a dialysis bag for 7 d (cut-off molecular weight: 14 kDa).

## 3. Control release of Rhodamine B from supramolecular hydrogel

The loading capacity of the multi-stimuli supramolecular responsive hydrogel could

reach up to 30 wt% relative to the dry binary gelator. In brief, we prepared the hydrogel with rhodamine B solution in a little reagent bottle. The dye concentration in aqueous solution was 0.35 mg/mL. Then, the hydrogel was placed in the dark or irradiated by green light for 5 min. Afterward, 0.5 mL solution on the top was removed and a fresh 0.5 mL $H_2O$ was added immediately. Another 0.5 mL solution was collected after the hydrogel was installed in the dark or irradiated by green light for 5 min, and a fresh 0.5 mL $H_2O$ was added immediately again. This process was repeated for the total duration of 130 min. For the pH responsive experiment, the rhodamine B encapsulated hydrogels were prepared in aqueous solutions with different pH values. The experiment process was similar to that upon green light irradiation and in the presence of the oxidizing agent.

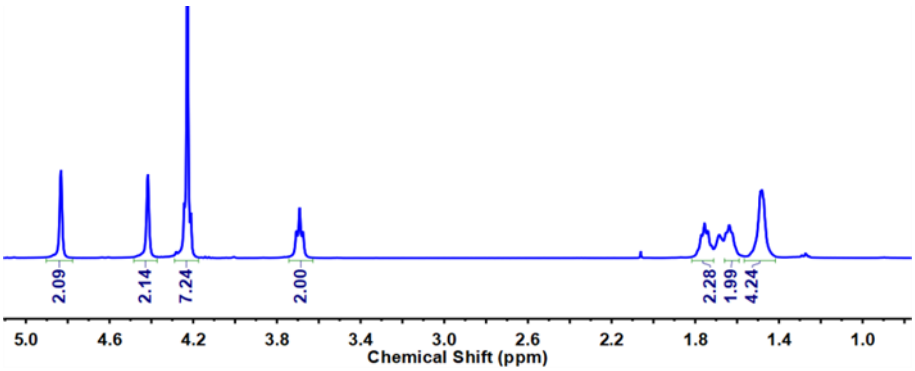


**Fig. S1**. $^1H$ NMR spectrum of Fc-$C_6$-OH in $CDCl_3$ at room temperature.

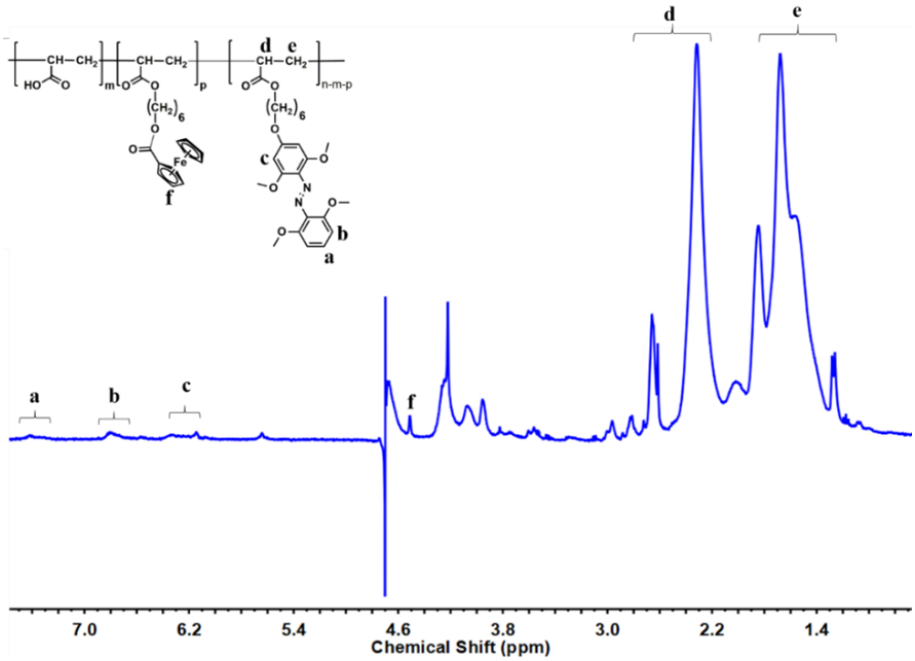


**Fig. S2**. $^{1}$H NMR spectrum of PAA-mAzo/Fc in $D_2O$ at room temperature.

## 4. Photo-responsive behavior of *cis* PAA-mAzo/Fc

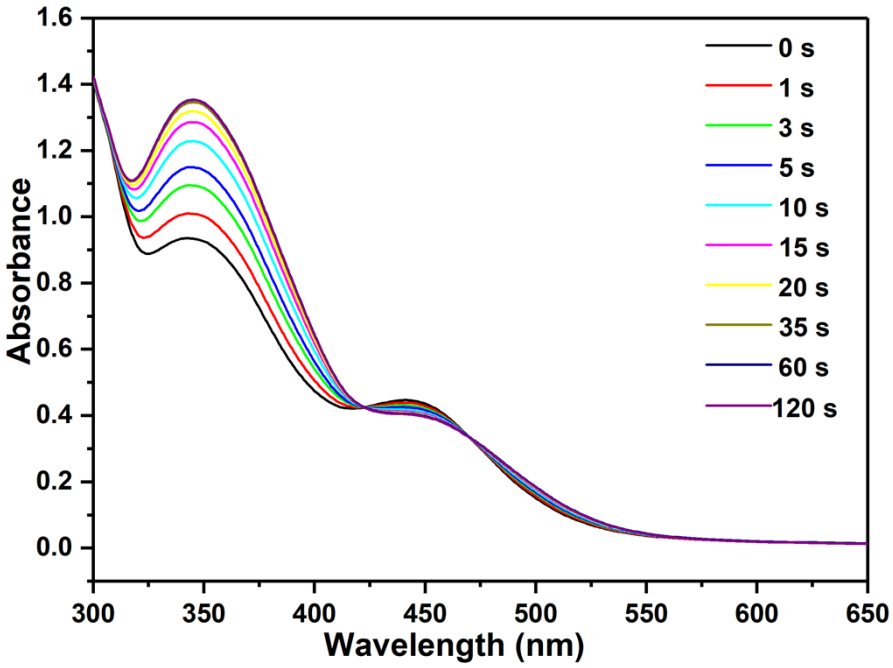


**Fig. S3**. UV−vis spectra of *cis* PAA-mAzo/Fc (0.1 mM) in aqueous solution upon blue light irradiation (450 nm, 20 mW/cm$^2$) for different times at room temperature. The *cis* PAA-mAzo/Fc was obtained upon green light irradiation (550 nm, 14 mW/cm$^2$) for 2 min.

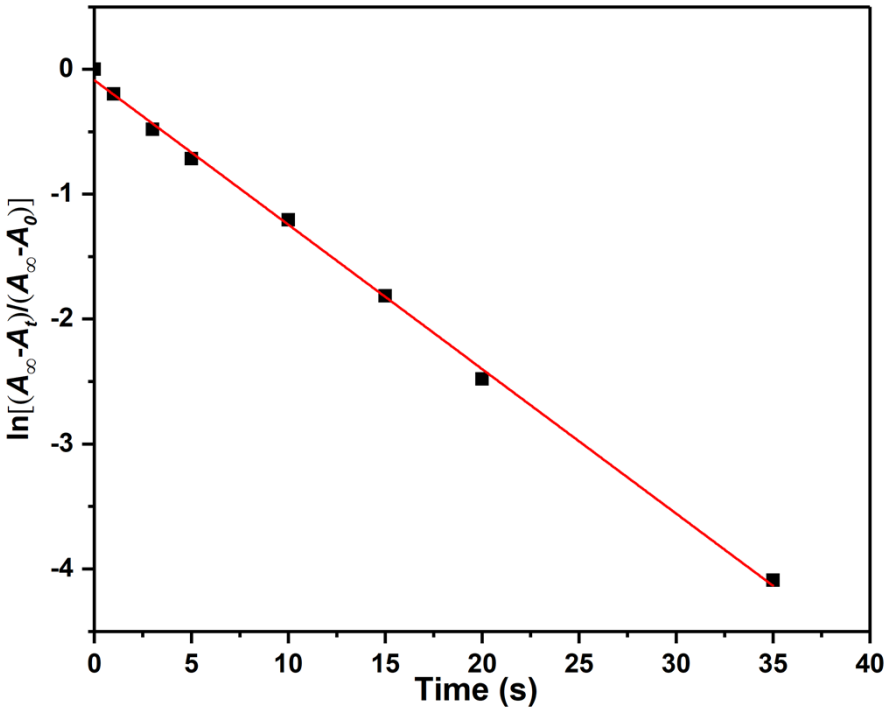


**Fig. S4**. First-order kinetic curve for *cis*-to-*trans* transition for PAA-mAzo/Fc.

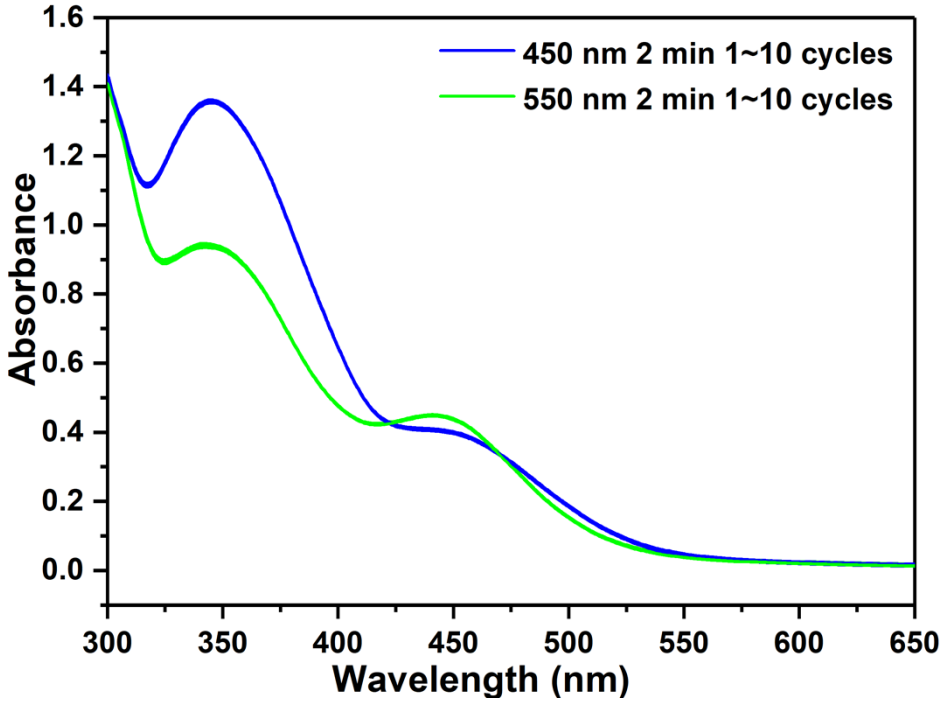


**Fig. S5**. UV–vis spectra of PAA-mAzo/Fc (0.1 mM) in aqueous solution upon alternate green light (550 nm, 14 mW/cm$^2$, green curve) and blue light (450 nm, 20 mW/cm$^2$, blue curve) irradiations. All irradiation times are 2 min. Both curves are almost overlapped for 10 cycles.

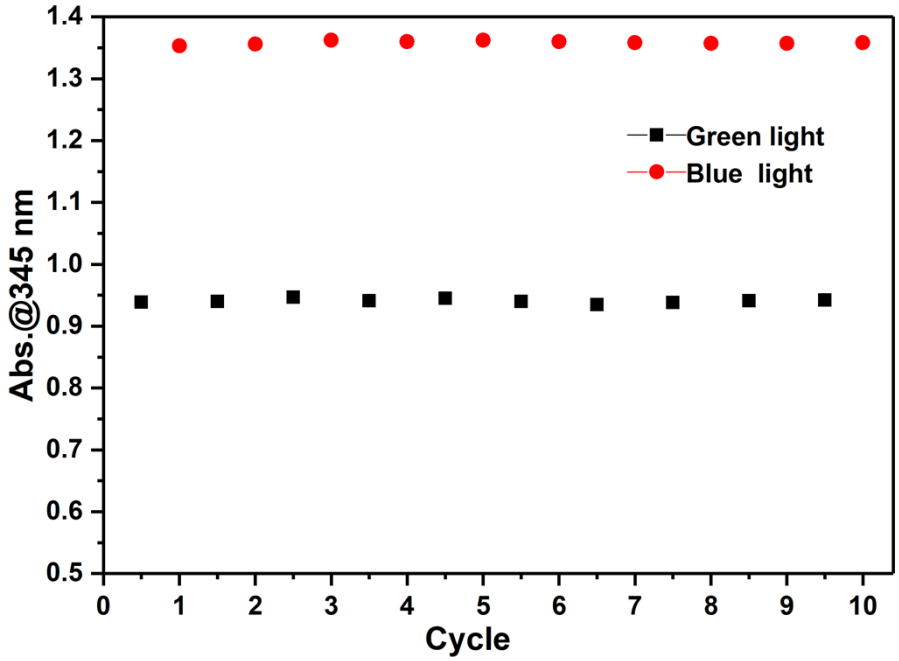


**Fig. S6**. Reversible absorbance changes of PAA-mAzo/Fc at the photo-stationary state under the alternate green light and blue light irradiations.