

Supporting Information

Photo- and thermo-responsive supramolecular polymer networks *via in situ* polymerization using homoternary macrocyclic host with coumarin monomers in water

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1. Characterization of polymerizable coumarin monomer (MABC)

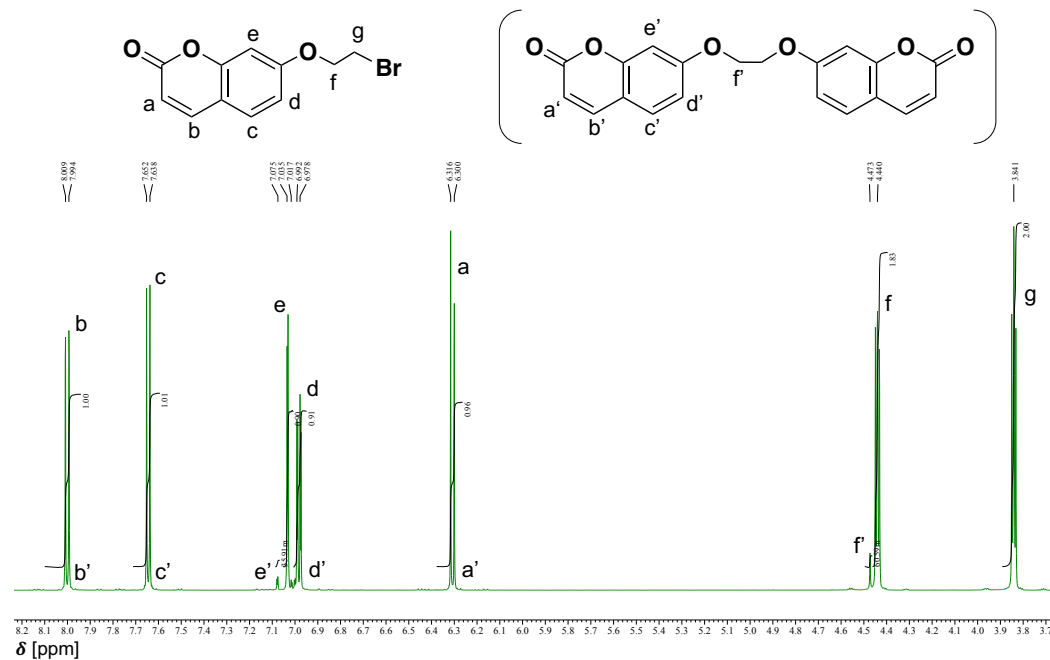


Fig. S1 ^1H NMR spectrum (600 MHz, $\text{DMSO-}d_6$) of Br-COU. A by-product (2.6%) was also present.

Br-COU (M_1 : $\text{C}_{11}\text{H}_9\text{O}_3\text{Br}$, exact mass 269.10)
 m/z 270.10, $[\text{M}_1 + \text{H}]^+$
 m/z 292.99, $[\text{M}_1 + \text{Na}]^+$

By-product: (M_2 : $\text{C}_{20}\text{H}_{14}\text{O}_6$, exact mass 350.34)
 m/z 351.09, $[\text{M}_2 + \text{H}]^+$
 m/z 373.07, $[\text{M}_2 + \text{Na}]^+$

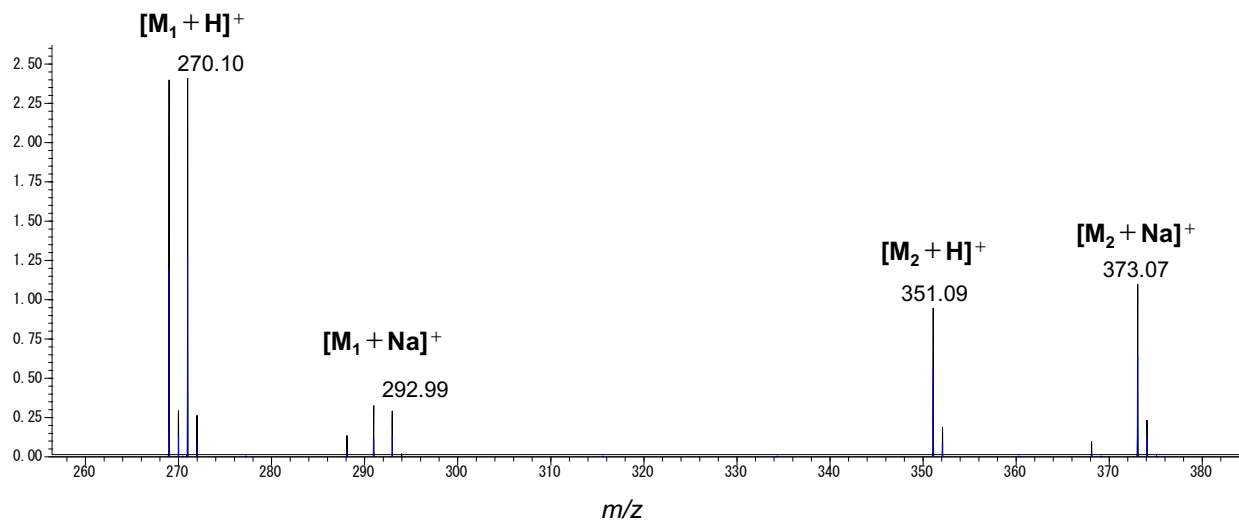


Fig. S2 Electrospray ionization mass (ESI-MS) spectrum (positive) of Br-COU. A by-product comprising a coumarin dimer linked by ethane-1,2-diol was detected.

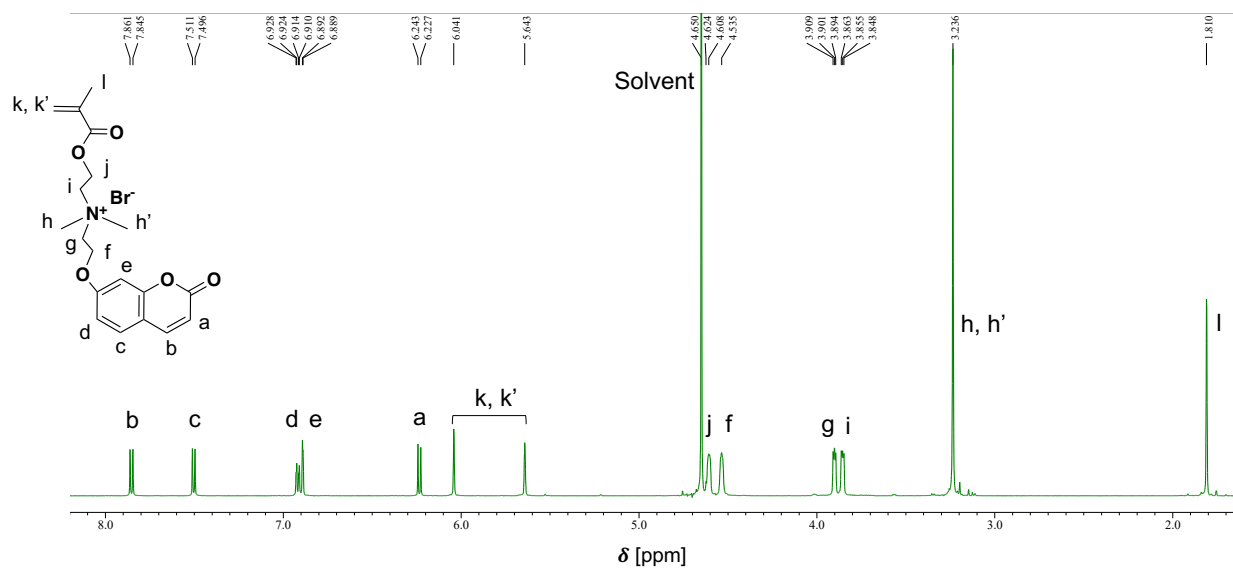


Fig. S3 ^1H NMR (600 MHz, D_2O) spectrum of MABC.

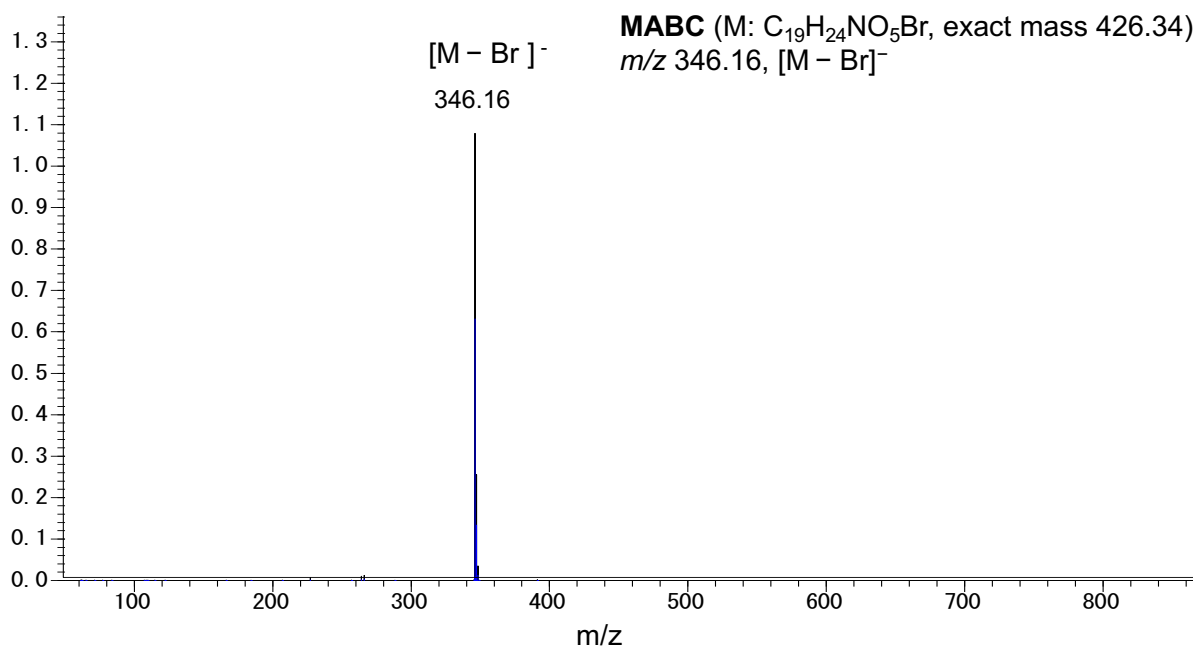


Fig. S4 ESI-MS spectrum (positive) of MABC.

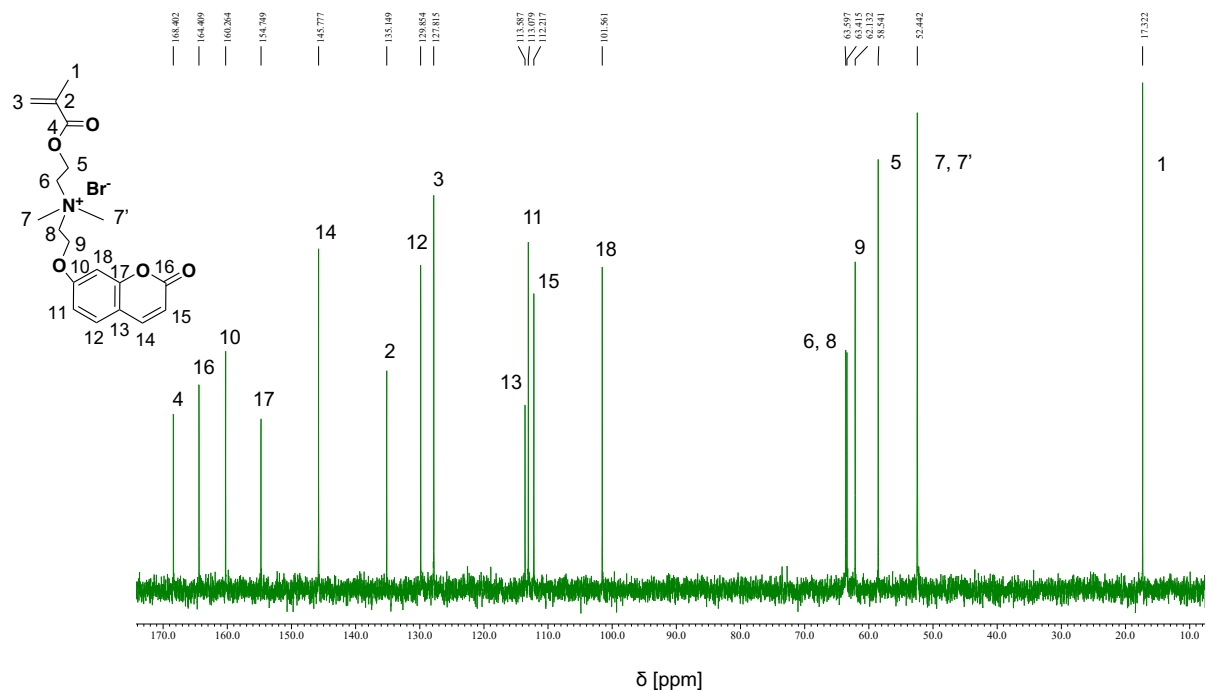


Fig. S5 ^{13}C NMR spectrum of MABC in D_2O .

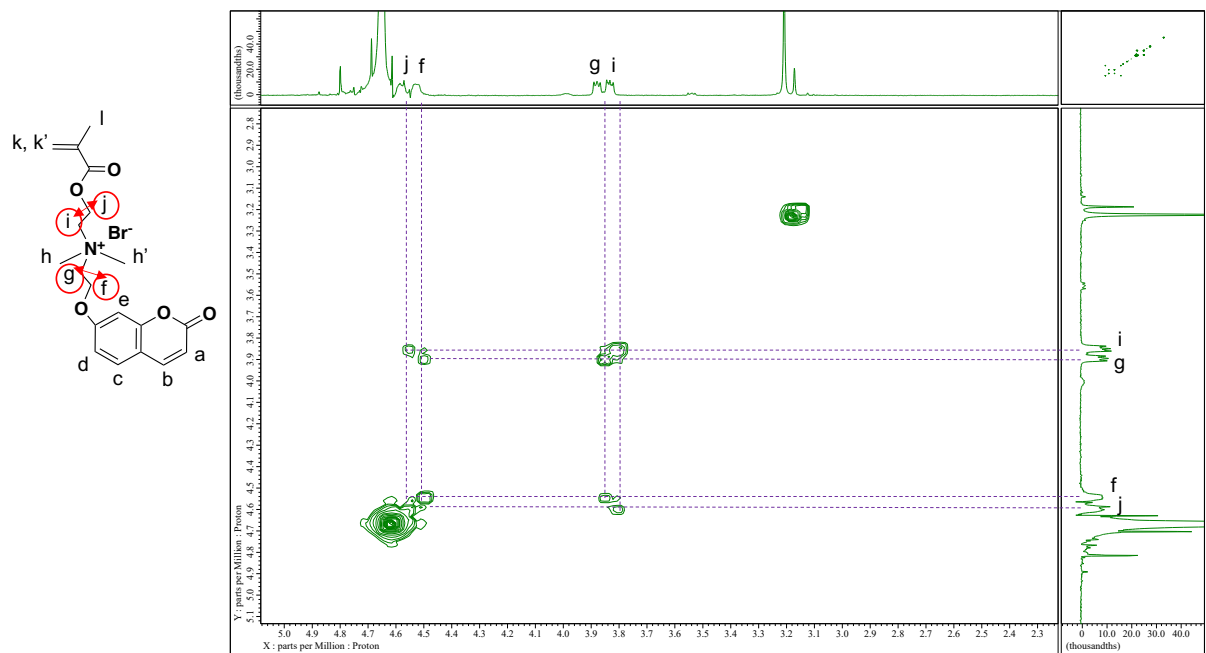


Fig. S6 H-H COSY spectrum of MABC in D_2O .

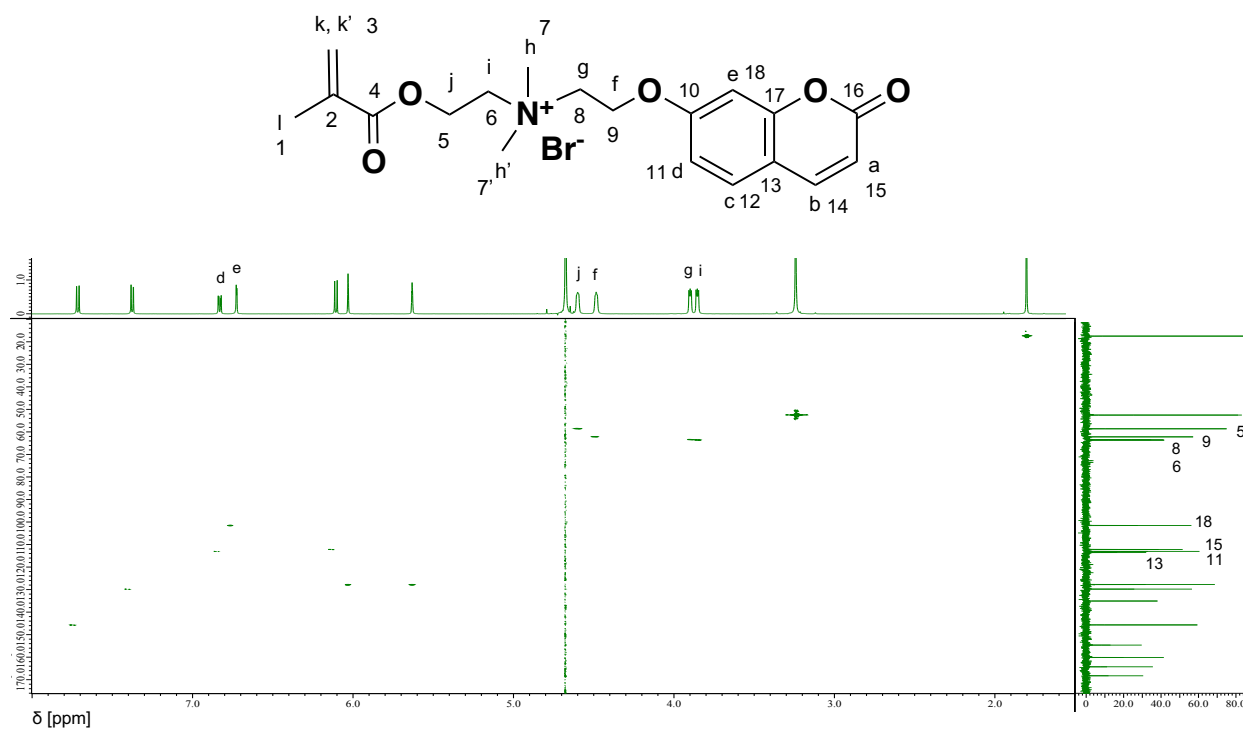


Fig. S7 HMQC spectrum of MABC in D₂O.

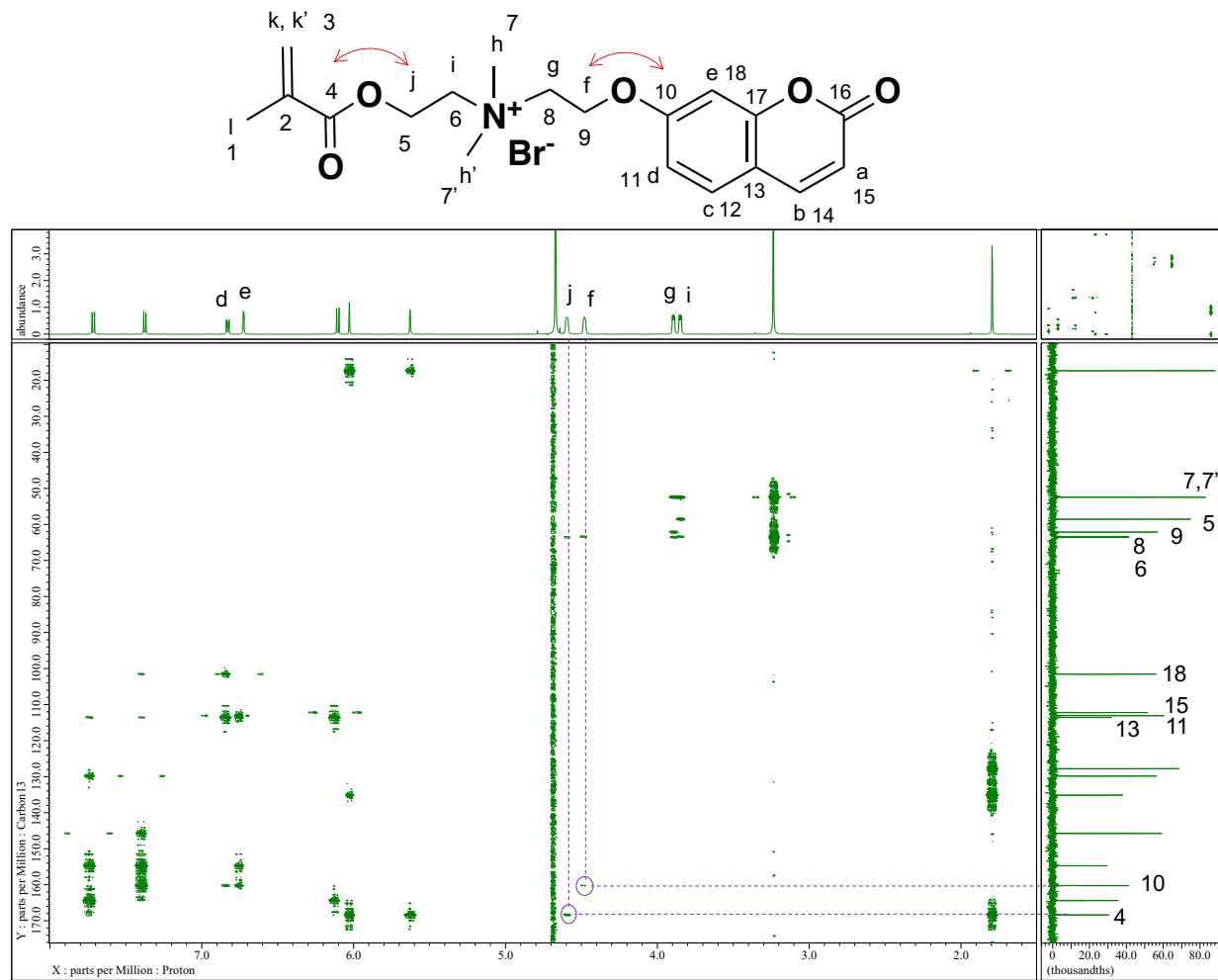


Fig. S8 HMBC spectrum of MABC in D₂O.

2. Characterization of host-guest complex

There was an upfield shift in the peak attributable to the H-3 and H-5 protons of γ -CD upon inclusion of MABC in γ -CD. The total concentration, $[\gamma\text{-CD}]_0 + [\text{MABC}]_0$ was 11.76 mM (constant). Each subtracted shift change from the original H-5 position was also recorded for each molar fraction of γ -CD. The plot reached a maximum at a ratio of 0.33 for the molar fraction of γ -CD ($[\gamma\text{-CD}]_0 / ([\text{MABC}]_0 + [\gamma\text{-CD}]_0)$), indicating the formation of a 1:2 host-guest complex between γ -CD and MABC in water.

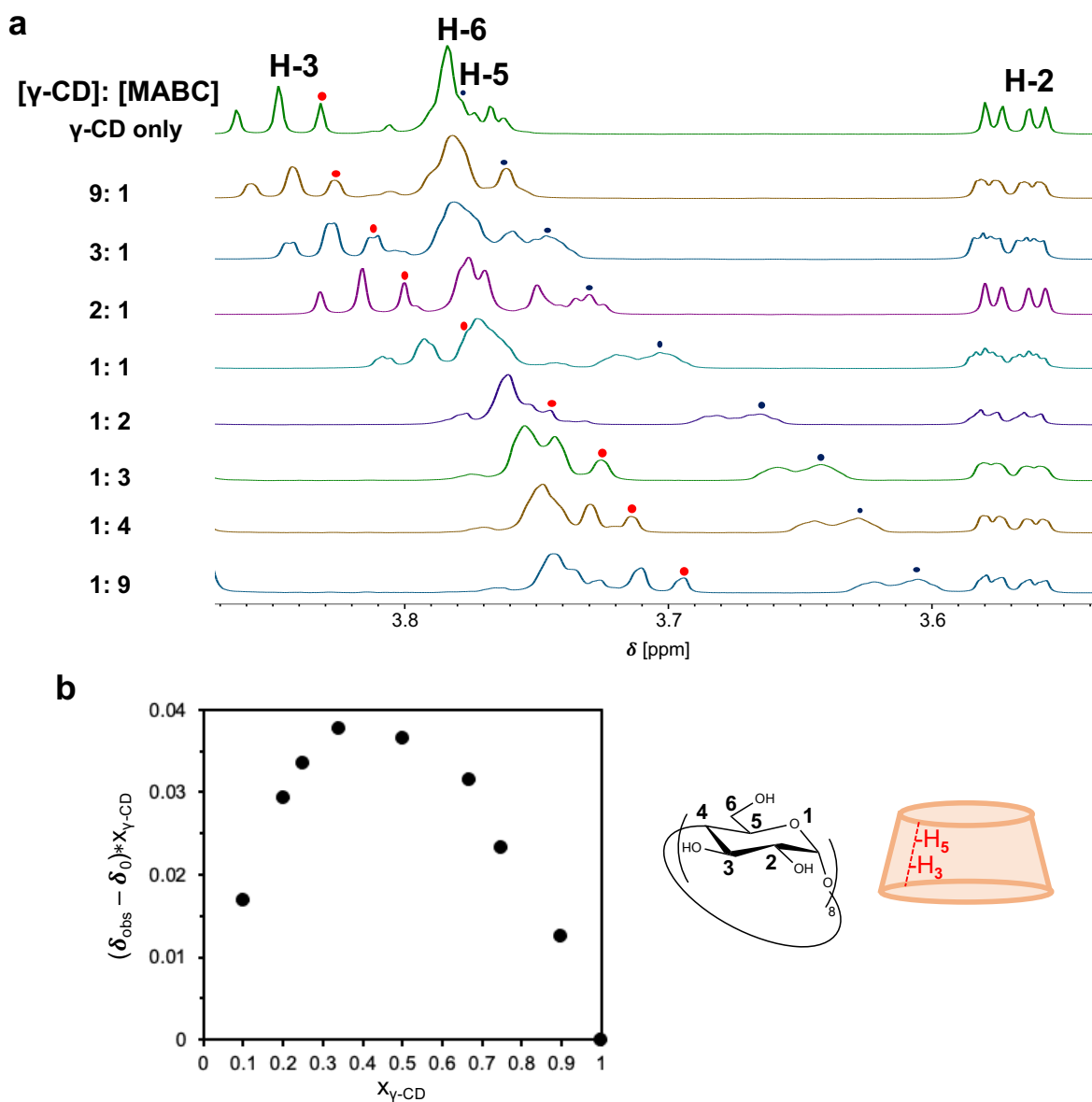


Fig. S9 Partial ^1H NMR (600 MHz, D_2O) (a) of MABC and γ -CD at different ratios for Job plot of MABC and γ -CD complex, where the shifts in the peak attributable to the H-3 and H-5 protons of γ -CD were assigned against each molar fraction, and Job plot (b) of MABC and γ -CD, where the H-5 proton was plotted against the molar fraction of γ -CD (Inset shows chemical structure of γ -CD).

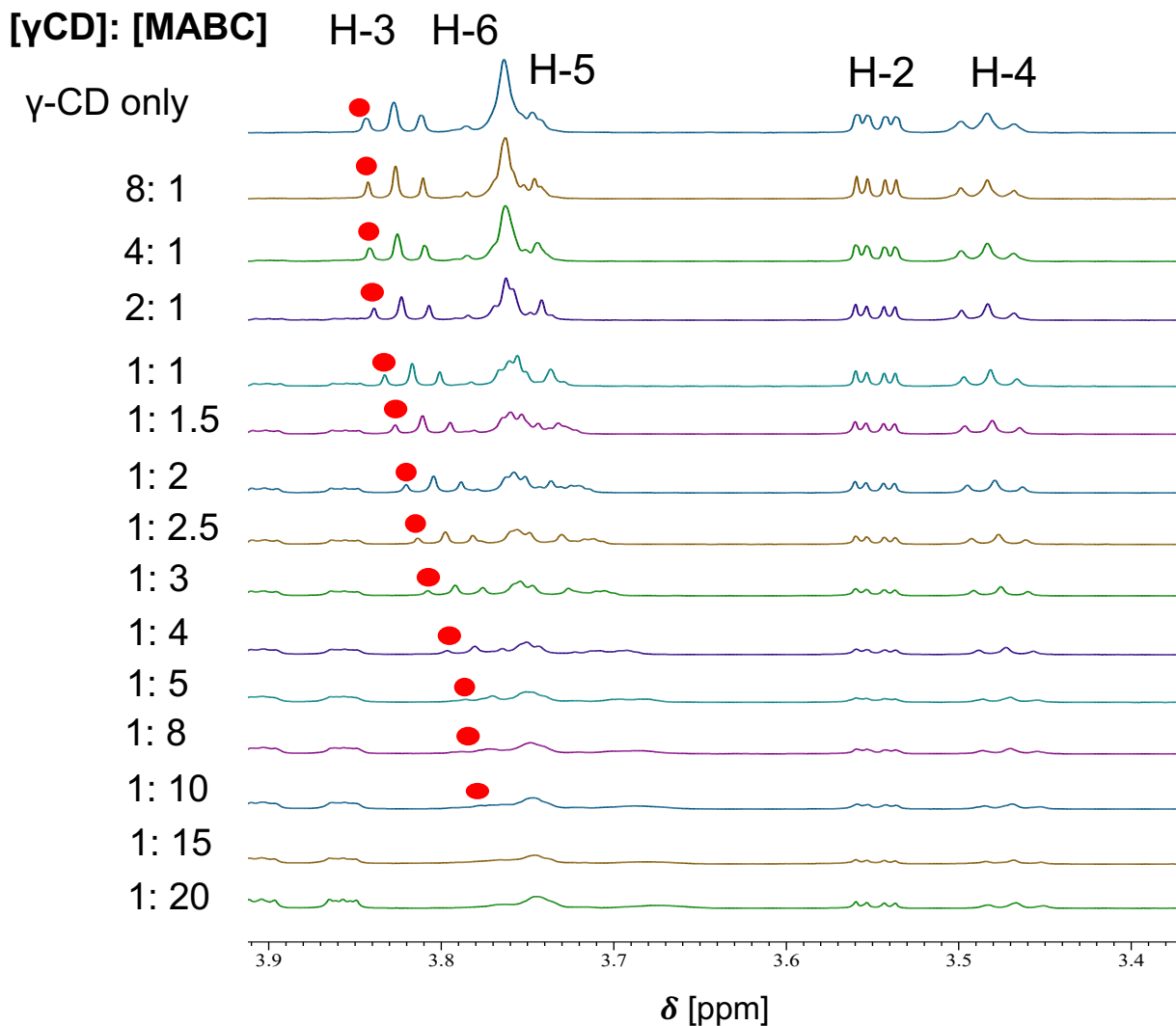


Fig. S10 Partial ¹H NMR (600 MHz, D₂O) of MABC and γ-CD at different ratios by NMR titration of γ-CD with added MABC, where the shift in the peak attributable to the H-3 proton of γ-CD was assigned against each molar fraction (The initial concentration of γ-CD, [γ-CD]₀ = 1.39 mM).

The titration results (shift changes vs. [guest]) of the host: guest complex were fit to equation [1] using non-linear least square fitting program.

$$\Delta\delta_{obs} = \frac{b[G]_0 (K_1\Delta\delta_1 [H] + K_1K_2\Delta\delta_2 [H]^2)}{1 + K_1 [H] + K_1K_2 [H]^2} \dots [1]$$

K_1 and K_2 are stepwise association constants for the 1:1 and 1:2 host–guest complexes, respectively.

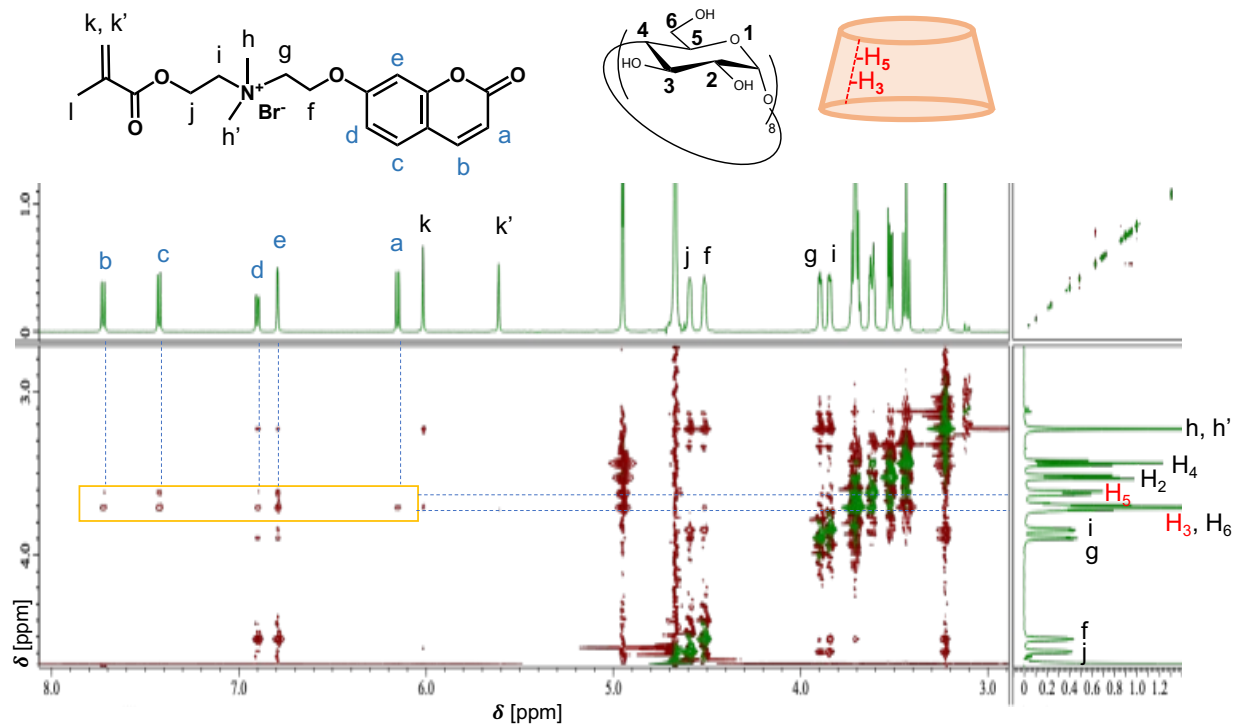


Fig. S11 Partial ROESY spectrum (D_2O , 25 °C) of MABC and γ -CD inclusion complex ($[\text{MABC}]_0: [\gamma\text{-CD}]_0 = 2:1$, fixed at 11.76 mM).

3. Photodimerization of guest monomer with or without γ -CD host

The dilute MABC monomer (1.0×10^{-4} M) with or without the γ -CD (0.5 equiv.) host in aqueous solution was irradiated with UVA light, centred around 365 nm in a UV crosslinker chamber for a given time to evaluate the photo-dimerization behaviour by tracing the decrease in the intensity of the absorbance peak corresponding to the coumarin moiety at 321 nm.

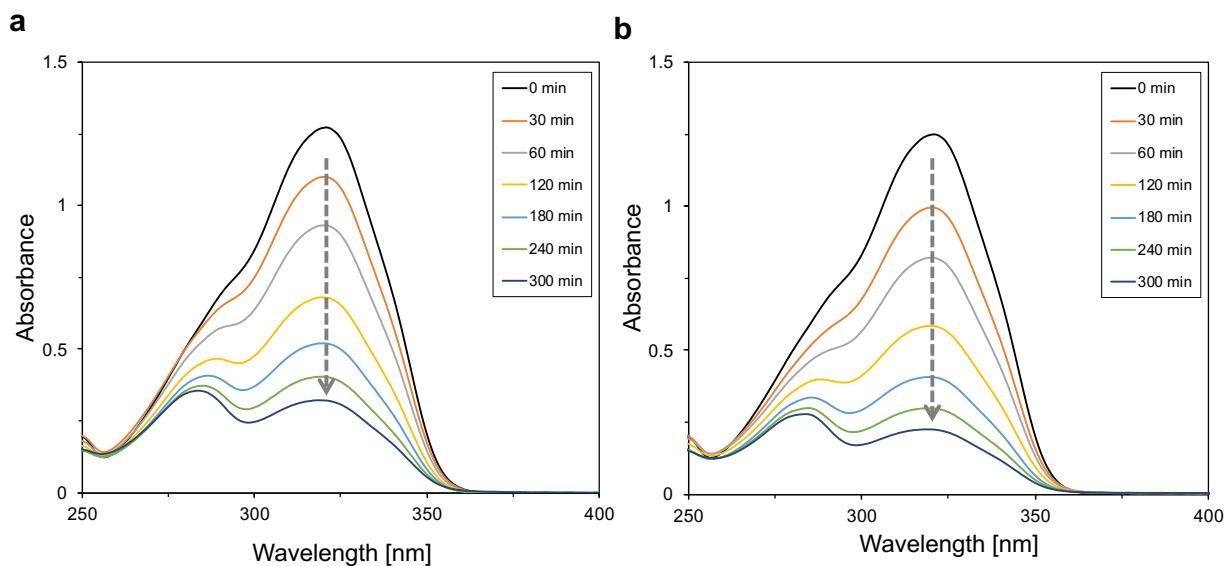


Fig. S12 Changes in the absorption spectra of (a) MABC and (b) the MABC/ γ -CD (molar ratio = 2:1) complex in aqueous solution following photo-irradiation at 365 nm; $[MABC]_0 = 1.0 \times 10^{-5}$ M, 25 °C.

4. Photographs of polymerization products

In a control experiment comprising the polymerization of DMAEMA-MABC comonomers without γ -CD and only DMAEMA monomer, the inversion methods revealed that fluid sol products were formed, resulting from the formation of a linear copolymer. In all cases, bulk hydrogels comprising crosslinked 3D networks were not formed, although their viscosities increased during polymerizations.

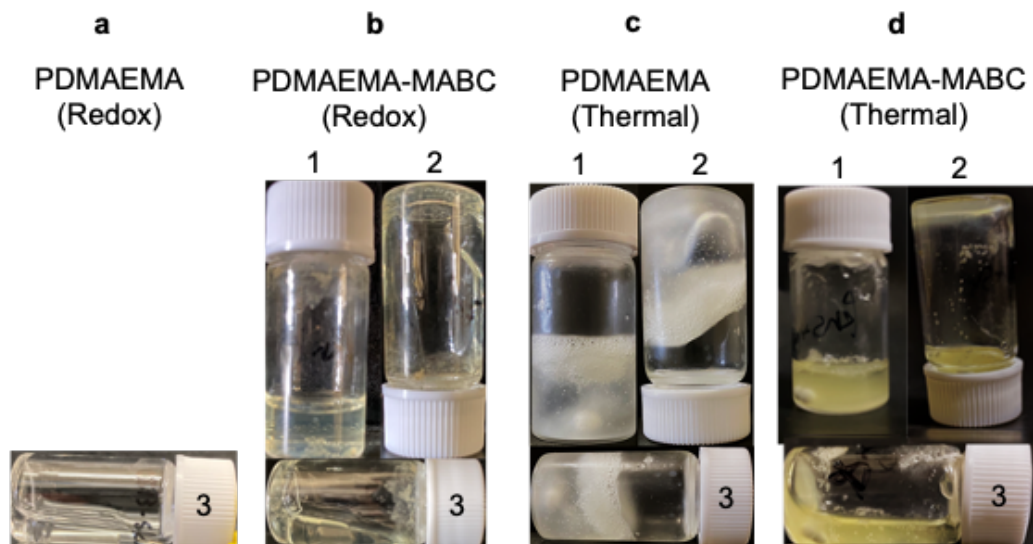


Fig. S13 Photographs of polymer products prepared by redox (a, b) and thermal (c, d) polymerizations of DMAEMA (a, c) or DMAEMA-MABC (b, d) comonomer (**1**: standing vertically, **2**: invert **1** to 180°, **3**: invert **1** to 90°).

5. FT-IR spectroscopy

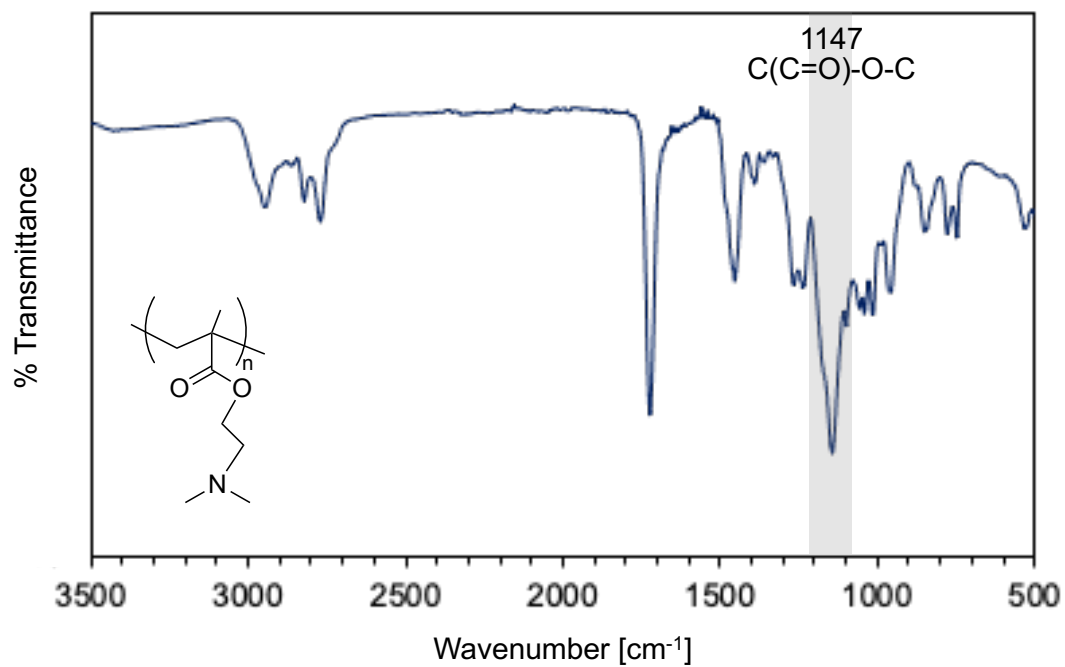


Fig. S14 FT-IR transmittance spectra of PDMAEMA (Inset shows chemical structure of PDMAEMA).

6. Characterization of PDMAEMA-MABC by redox polymerization

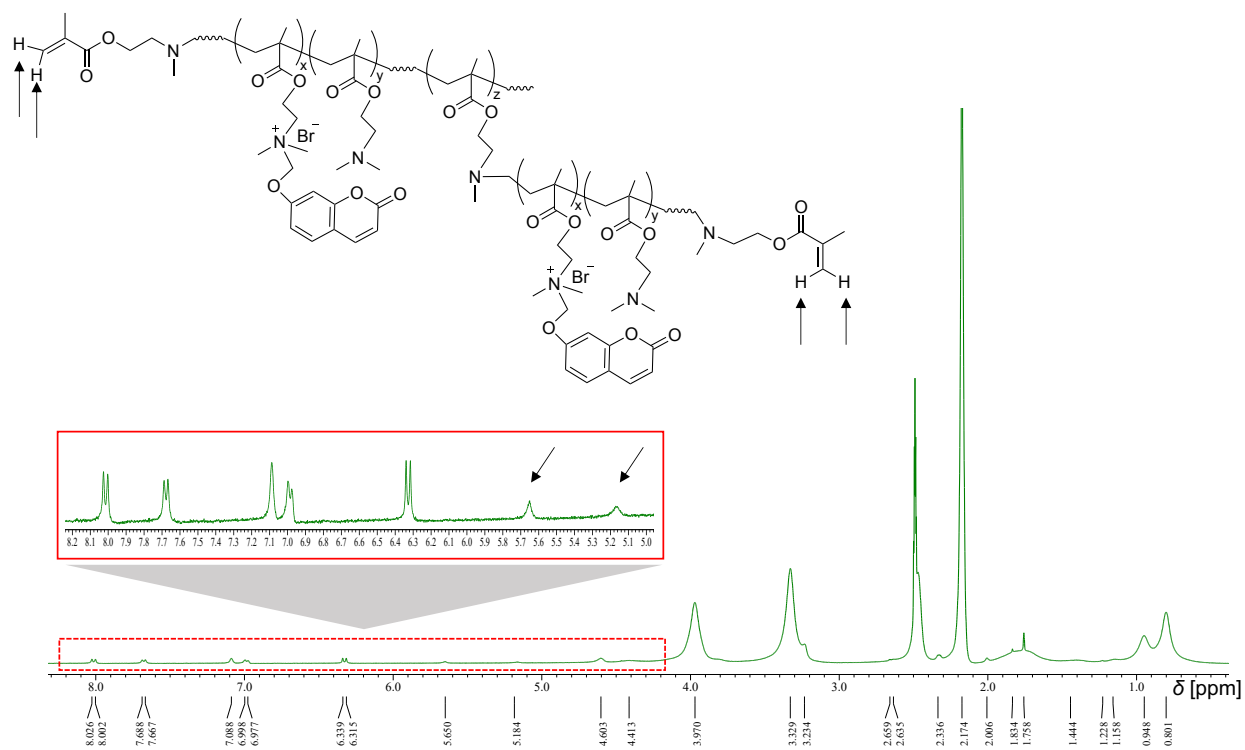


Fig. S15 ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of PDMAEMA-MABC formed by redox polymerization with an APS-DMAEMA initiating system: the inset is the possible branching structure. The inset arrows show polymer chain residues corresponding to the C=C double bonds.

7. Characterization of rheological property of PDMAEMA-MABC

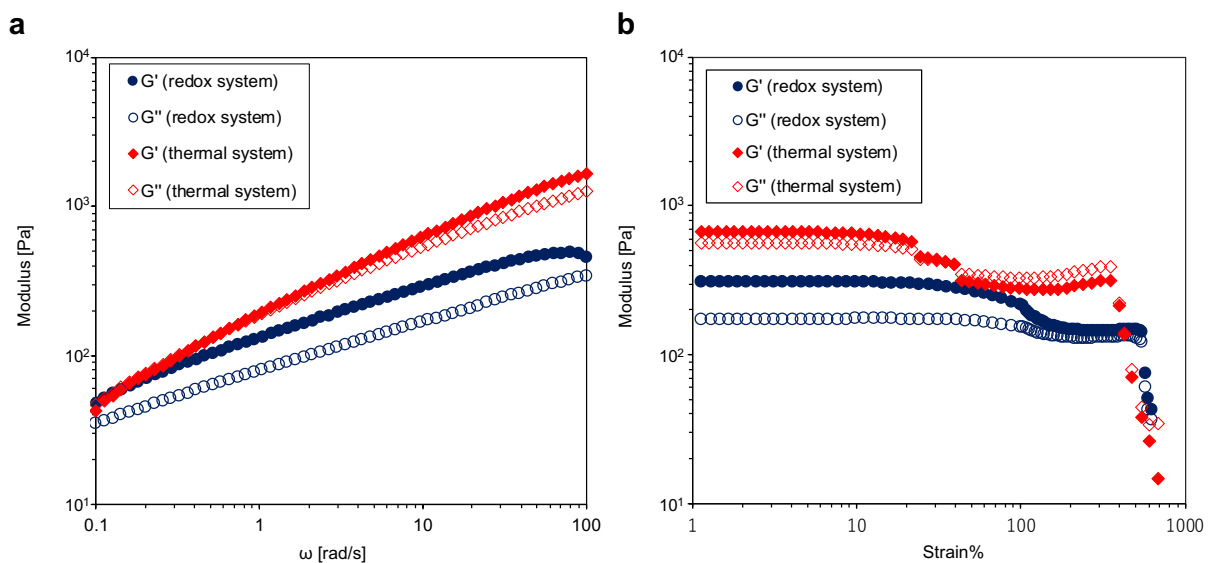


Fig. S16 Frequency (a) and strain sweep (b) measurements for PDMAEMA-MABC obtained by redox or thermal polymerization followed by irradiation with UV (365 nm).

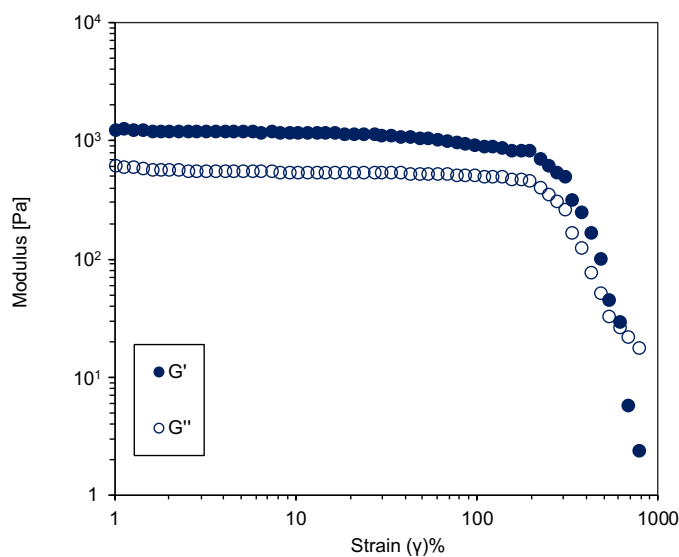


Fig. S17 Strain sweep measurements of non-covalent PDMAEMA-MABC/ γ -CD hydrogel obtained by thermal polymerization (strain (γ) = 1% to 1000%, ω = 10 rad/s).

8. Characterization of thermo-responsive property of PDMAEMA-MABC/ γ -CD hydrogel

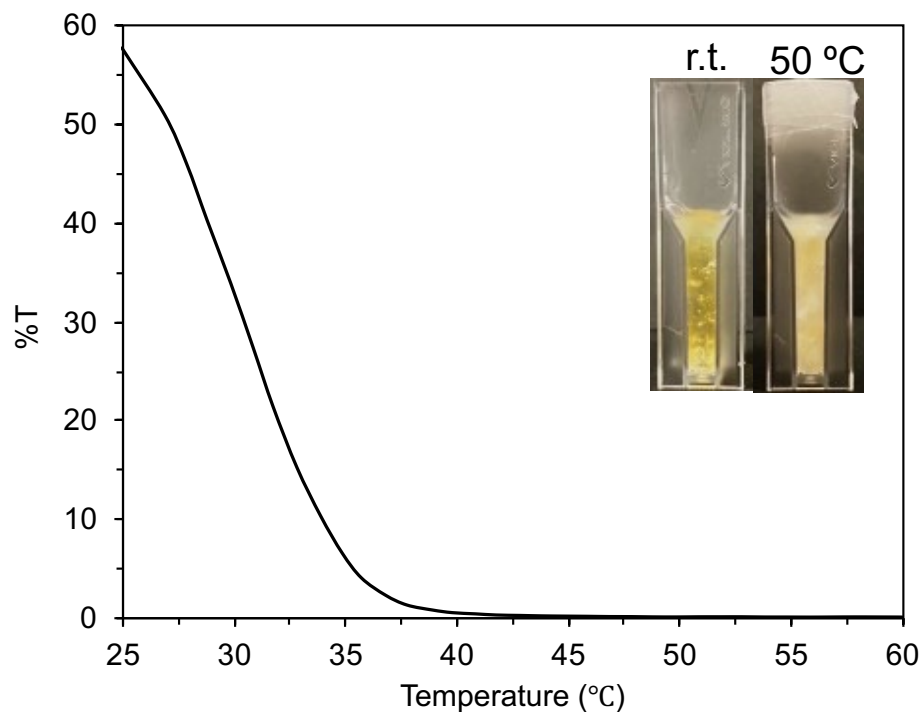


Fig. S18 Temperature-%T curves of covalent PDMAEMA-MABC/ γ -CD hydrogel after photo-dimerization of the coumarin moiety: the insets are photo images of the hydrogels at room temperature and 50 °C.