Supporting Information for

Multiresponsive Reversible Gels Based on a Carboxylic Azo Polymer

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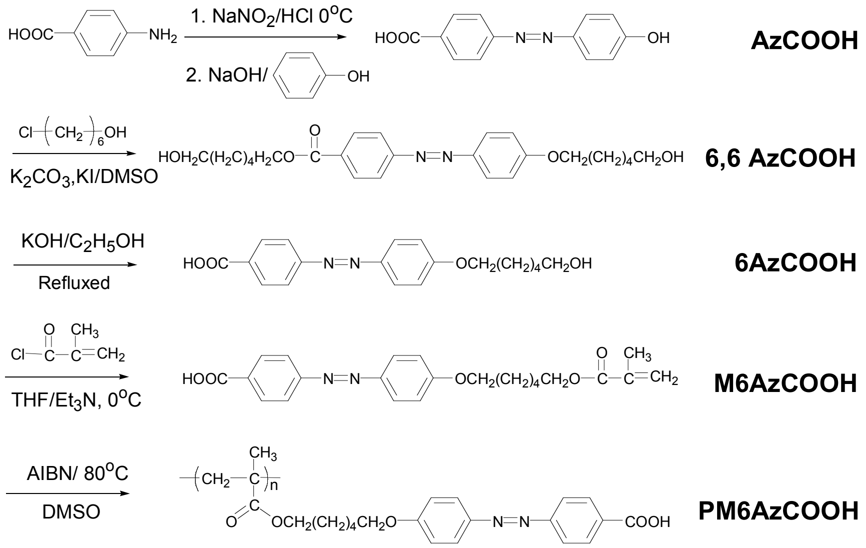
Synthesis of M6AzCOOH and PM6AzCOOH



Scheme S1. Synthetic route of the carboxylic azo monomer and polymer.

4-[(4'-Hydroxy)phenylazo]benzoic acid (AzCOOH)

A solution of $NaNO_2$ (4.14 g, 60 mmol) in 60 cm^3 H_2O was added to a solution of 4-aminobenzoic acid (8.23 g, 60 mmol) in 24 cm^3 HCl (37 %) at 0 °C. The solution was stirred for 30 min and diluted with 300 cm^3 ice water. Then phenol (5.92 g, 63 mmol) and NaOH (2.52 g, 63 mmol) in 30 cm^3 of H_2O was added dropwise at 0-5 °C. The mixture was stirred for 2 h and NaOH was added to precipitate the product. Orange product of 13.1 g was obtained with a yield of 90%. ^1H NMR ($CDCl_3$): $\delta = 6.95$ (d, 2H), 7.82 (d, 2H), 7.87 (d, 2H), 8.10 (d, 2H).

4-(6-Hydroxyhexyloxy)carboxy-4'-(6'-hydroxyhexyloxy) azobenzene

(6,6 AzCOOH)

A mixture of AzCOOH (3.63 g, 15 mmol), 6-chloro-1-hexanol (4.37 g, 32 mmol), K_2CO_3 (4.42 g, 32 mmol), KI (0.2 g), and dry dimethylsulfoxide (DMSO) (50 cm^3) was heated at 140 °C for 8 h. Then reaction mixture was cooled to room temperature and poured into water (50 cm^3). The obtained red-yellow precipitate was filtered off and dried under vacuum at 50 °C to yield 5.3 g red orange solids (80 %).

4-[4'-(6-Hydroxyhexyloxy)phenylazo]benzoic acid (6AzCOOH)

A mixture of 6,6 AzCOOH (4.42 g, 10 mmol), KOH (1.12 g, 20 mmol), C_2H_5OH 150 cm^3, and H_2O 40 cm^3 was refluxed for 12 h. Then the reaction mixture was cooled down to room temperature, and 1M HCl was added to the solution until pH<3, to precipitate the product. The yellow solid was filtered off, washed with C_2H_5OH, and dried under vacuum at 50 °C to yield 3.1 g red orange solids (90 %). ^1H NMR (CDCl3): $\delta = 1.3–1.7$ (m, 6H), 1.7–1.9 (m, 2H), 3.63 (t, 2H), 4.04 (t, 2H) 7.00 (d, 2H), 7.62 (d, 2H), 7.94 (d, 2H), 8.77 (d, 2H).

6-[4-(4-Carboxylphenylazo)phenoxyl]hexyl methacrylate (M6AzCOOH)

M6AzCOOH was prepared by the Schotten-Baumann reaction between methacryloyl chloride and 6AzCOOH. 6AzCOOH (5.13 g, 15 mmol) and triethylamine (5.06 g, 50 mmol) were dissolved in dry tetrahydrofuran (THF) (50 cm^3), and cooled in an ice-water bath. A solution of methacryloyl chloride (5.23 g, 50 mmol) in dry THF (15 cm^3) was added over 2 hours, and the mixture was stirred for 48 hours. After filtration, the mixture was concentrated and then poured into methanol; yellow precipitate was recrystallized from acetate acid and 3.1 g yellow solid was obtained (50 %).

PM6AzCOOH

The carboxylic azo polymer PM6AzCOOH was obtained with free radical polymerization of M6AzCOOH in DMSO by using AIBN as initiator. Fig. S1 gives the ^1H NMR spectrum of PM6AzCOOH and M6AzCOOH in DMSO-d6. The peaks at 5.7 ppm and 6.1 ppm corresponding to the protons in double bonds of M6AzCOOH disappeared completely after polymerization, indicating that PM6AzCOOH was obtained. Protons in $-CH_2-$ and -CHCOO- appeared in 1.15–2.0 ppm, and $-CH_2O-$ protons appeared at 4.1 ppm in NMR spectrum of PM6AzCOOH.

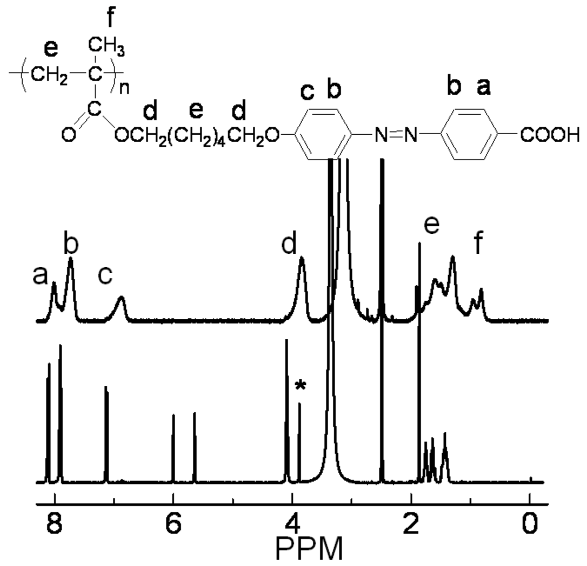


Fig. S1. ^{1}H NMR spectra of PM6AzCOOH (at 70 °C) and M6AzCOOH (at room temperature) in DMSO-d_6. * Attributes to the residual THF.

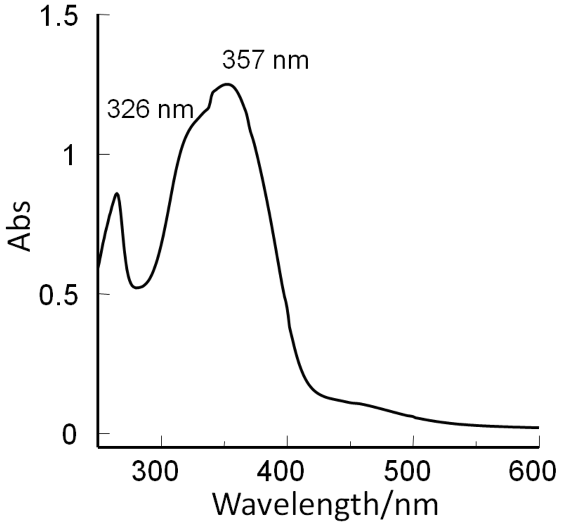


Fig. S2. UV–vis absorption spectrum of PM6AzCOOH in DMF, an extra absorption peak at 326 nm appeared beside the peak centered around 357 nm.

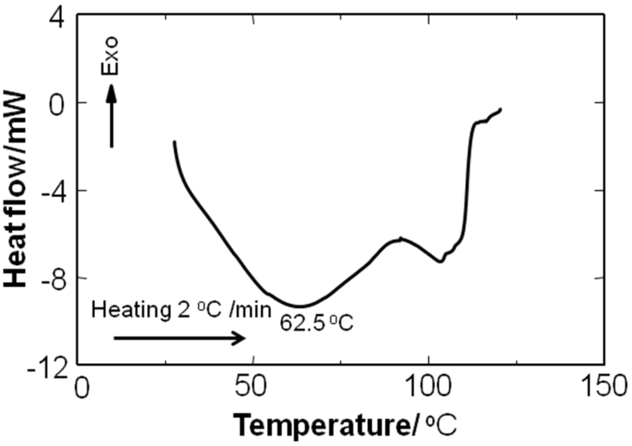


Fig. S3. DSC curve of PM6AzCOOH gel in DMSO with a concentration of 10 g dm^{-3}.

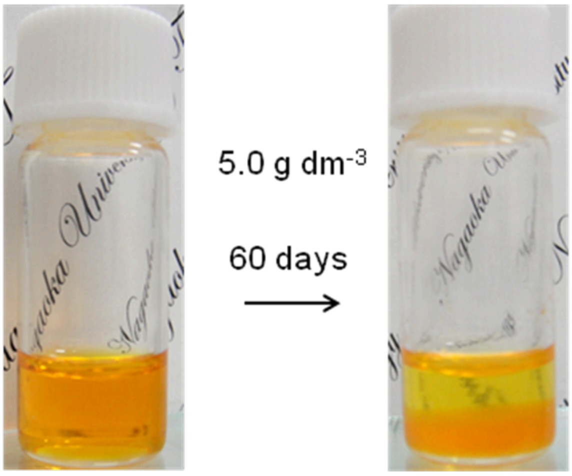


Fig. S4. Photographs of PM6AzCOOH in DMSO with higher concentration before and after being stored for 60 days.

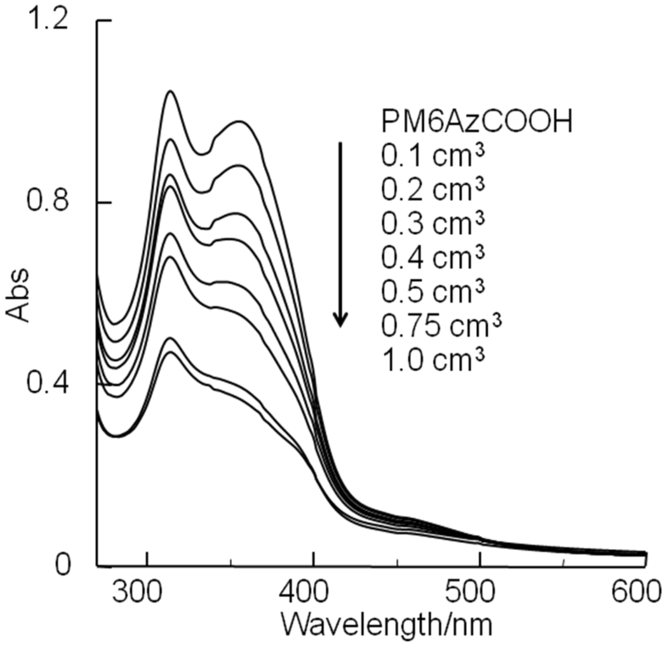


Fig. S5. UV-vis absorption spectra of PM6AzCOOH in DMSO with adding different amount of H_2O. Here, 2 cm^3 PM6AzCOOH solution in DMSO (0.041 g dm^{-3}) was used.

Fig. S6. Photographs of organogels prepared with PM6AzCOOH in DMSO (10 g dm^{-3}) before and after UV irradiation, then being kept in dark for 2 days and 10 days.