Supplementary material (ESI) for Chemical Communications

Enzymatic Formation of A Photoresponsive Supramolecular Hydrogel

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Materials

All the chemicals used in this work were purchased from Aldrich or Fluka, and used without futher purifcation. Nanopure water was used for all the tests of hydrogelation.

Instrumentation

NMR experiments were performed on a 400 MHz Varian Unity Inova 400 using DMSO-d⁶ as the solvent. Circular dichroism (CD) spectra were recorded in the ultraviolet region (185–300 nm) using a JASCO 810 spectrometer and a 1.0 mm quartz cuvette, the UV-visible spectra on a Varian Cary 50 Spectrophotometer, and the TEM images on Morgagni 268 transmission electron microscope. Rheological studies were measured on TA ARES G2 rheometer.

Rheology

Rheology test was done on TA ARES G2 rheometer (with TA Orchestrator Software). 25 mm cone plate was used during the experiment. 0.5 ml of hydrogel sample was placed on the parallel plate.

i) Dynamic Strain Sweep Test

Test range (0.1 to 1.0% strain, frequency = 10 rads⁻¹), 10 points per decade. Sweep mode is "log" and temperature was carried out at 25° C.

ii) Dynamic Frequency Sweep Test

Initial frequency = 0.1 rads^{-1} and final frequency = 100.0 rads^{-1} , strain = 1.0 %, 10 points per decade. Sweep mode is "log" and temperature was carried out at 25 °C.



Scheme S1 Synthetic scheme of the photo-responsive hydrogelator precursor (1) and a gelator (7) as the analogue of the hydrogelator 2.



Fig. S1 (A) strain (B) and frequency dependence of the dynamic storage moduli (G') and the loss moduli (G") of the recovered gel of *trans*-2 in Fig. 1d.



Fig. S2 Optical images of (A) the solution of **7** (7.0 mg of **7** dissolved in 400 μ L DMSO and 300 μ L water); (B) the gel of *trans*-**7**, (C) the system after irradiation of 365 nm UV light for 30 min, and (D) the gel recovered after the irradiation of visible light.



Fig. S3 Optical image of the less stable gel prepared at the concentration of 0.7%.



Fig. S4 HPLC trace of (left) sample **1** in Fig 1a and (right) sample **2** in Fig 1b. From the HPLC trace, we can find that the hydrogel is formed from compound **2**, not by the mixture of compound **2** and compound **1**.



Fig. S5 Pure compound of **2** has poor solubility in aqueous solution at pH=9 and fail to form hydrogel directly from **2**.