Electronic Supplementary Information

Sol-gel Conversion Based on the Photo-switching between Noncovalently and Covalently Linked Netlike Supramolecular Polymers †

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1. Materials, general procedures and syntheses

1.1. Materials. Unless stated otherwise, all reagents were purchased from Sigma-Aldrich or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using $^1$H NMR, $^{13}$C NMR and high-resolution ESI mass spectroscopy.

1.2. General. $^1$H NMR spectra were measured on a Brüker AV-400 spectrometer. $^{13}$C and 2D ROESY NMR spectra were measured on a Brüker AV-500 spectrometer. The electronic spray ionization (ESI) high resolution mass spectra were tested on a HP 5958 mass spectrometer. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 25°C. AFM images were measured on Solver P47-PRO, NT-MDT. Elemental analysis were measured on a VARIO EL III. The sample was achieved by diluting the $2.5 \times 10^{-1}$ M solution to $1.0 \times 10^{-4}$ M in water, calculated from the monomer 4, and spin-coated on a mica plate. The photoirradiation was carried on a UV lamp of 6 W in a 1 mm × 1 cm quartz cell. The distance between the lamp and the sample cell was 1 cm. Photostationary states were ensured by taking UV spectra at distinct intervals until no changes in absorbance were observed.

1.3. Syntheses

\[ \text{7-(4-bromobutoxy)-2H-chromen-2-one (1)} \]

This compound was synthesized conveniently in one step from commercial materials 7-hydroxyl coumarin and 1,4-dibromobutane according to literature procedure. 1

\[ \text{1-(4-((2-oxo-2H-chromen-7-yl)oxy)butyl)-[4,4'-bipyridin]-1-ium bromide (2)} \]

Compound 1 (3 g, 10.1 mmol, 1 eq) and 4,4'-bipyridine 7.91g (50.7 mmol, 5eq) were dissolved in 80 mL DMF. The solution was stirred at 80 °C under argon for 12 h and cooled to room temperature. The reaction solution was then poured into 200 mL ethyl acetate. The precipitate was collected by filtration and washed with ethyl acetate and dried in vacuo to provide compound 2 as pale yellow powder (4.32 g, 94 % yield), m.p. 246.7-247.2 °C. $^1$H NMR (400 MHz, DMSO-\textit{d6}) δ 9.28 (d, J = 6.8 Hz, 2H), 8.94 – 8.84 (d, J = 6.1 Hz, 2H), 8.66 (d, J = 6.8 Hz, 2H), 8.04 (dd, J = 4.6, 1.5 Hz, 2H), 7.99 (d, J = 9.5 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 6.94 (dd, J = 8.6, 2.4 Hz, 1H), 6.29 (d, J = 9.5 Hz, 1H), 4.73 (t, J = 7.2 Hz, 2H), 4.14 (t, J = 6.2 Hz, 2H), 2.20 – 2.10 (m, 2H), 1.85 – 1.75 (m, 2H). $^{13}$C NMR (125 MHz, DMSO-\textit{d6})

1,3,5-tris(bromomethyl)benzene (3). This compound was synthesized conveniently in one step from commercial materials mesitylene and N-bromosuccinimide according to literature procedure.  

1',1''',1'''''-(benzene-1,3,5-triyltris(methylene))tris(1-(4-((2-oxo-2H-chromen-7-yl)oxy)butyl)-[4,4'-bipyridine]-1,1'-diium) (4). Compound 2 (2 g, 4.4 mmol, 3.3 eq) and Compound 3 (0.47 g, 1.3 mmol, 1 eq) were dissolved in 60 mL DMF. The solution was stirred at 80 °C under argon for 3 days and cooled to room temperature. The precipitate was collected by filtration and washed with a small amount of DMF and dried in vacuo to provide crude compound 2, which was then recrystallized with EtOH/H2O to get the pale yellow powder (1.17 g, 51% yield), m.p. 257.9-259.7 °C.

1H NMR (500 MHz, D2O) δ 9.11 (d, J = 6.8 Hz, 6H), 9.00 (d, J = 6.8 Hz, 6H), 8.36 (d, J = 6.7 Hz, 6H), 8.31 (d, J = 6.6 Hz, 6H), 7.78 (s, 3H), 7.53 (d, J = 9.4 Hz, 3H), 7.25 (d, J = 8.7 Hz, 3H), 6.67 (dd, J = 8.7, 2.3 Hz, 3H), 6.37 (d, J = 2.1 Hz, 3H), 5.88 (s, 6H), 5.55 (d, J = 9.4 Hz, 3H), 4.65 (m, 6H), 3.90 (t, J = 5.8 Hz, 6H), 2.21 – 2.13 (m, 6H), 1.82 – 1.69 (m, 6H). 13C NMR (125 MHz, D2O) δ 163.74, 161.22, 154.48, 149.79, 149.11, 145.62, 145.59, 143.86, 134.38, 134.01, 129.93, 129.59, 127.04, 126.72, 113.25, 112.59, 111.25, 101.24, 67.39, 62.81, 61.91, 26.84, 24.60. HRMS (ESI) (m/z): [M-6Br]6+/6 calcd for [C78H72O9N6Br6]6+/6, 206.0888; found, 206.0883. Elem Anal. calcd for C78H72O9N6Br6: C 54.74, H 4.24, N 4.91. Found: C 54.63, H 4.16, N 4.76.

2. Spectra on the self-assembled polymer NNP.

Fig. S1 1H NMR spectra of a) 4 and b) 4@γ-CD complex (NNP) (1:1.5 molar ratio, 8 mM), D2O, 25 °C.
Fig. S2 2D ROESY NMR spectrum of 4@γ-CD complex (NNP) ([4]_{mol}:[γ-CD]_{mol} =1:1.5, 8 mM), D$_2$O, 25 °C.

Fig. S3 The FT-IR absorbance spectra of γ-CD, 4, their mixture (gained by simply mixing 4 and γ-CD in solid state and grinding), and the inclusion complex NNP (obtained by removing the solvent of NNP solution under reduced pressure), 25 °C.
Fig. S4 DLS result of NNP aqueous solution (0.1 mM, calculated from the repeat units), 25 °C.

Fig. S5 DOSY NMR spectra of (a) γ-CD, (b) monomer 4 and (c) NNP, ([4]_mol:[γ-CD]_mol=1:1.5, 10 mM), D₂O, 25 °C.
3. Spectra on the photochemistry of NNP.

Fig. S6 Partial $^1$H NMR spectra (400 MHz, D$_2$O, 25 °C) of NNP solution irradiated with 365 nm UV light, (a) 0 h, (b) 6 h, (c) 12 h, (d) 365 nm for 12 h, and then 254 nm for 18 h. The peaks marked with asterisk correspond to H$_2$O.

Fig. S7 Partial $^1$H NMR spectra (400 MHz, D$_2$O, 25 °C) of 4 solution (8 mM, 0.5 mL) (a) before and (b) after irradiation with 365 nm UV light for 12 h.
Fig. S8 FT-IR spectra of the complex 4@γ-CD before (NNP) and after (CNP) irradiation at 365nm UV light.

Fig. S9 DLS result of CNP aqueous solution (obtained from 2 mL NNP solution, 5 mM, calculated from the repeat units and irradiated by 365 nm UV light for 12 h and diluted to 0.1 mM), 25 °C.
Fig. S10 Photographic representation of the sample obtained from irradiation with 365 nm UV light for solution 4 (2.5×10^{-1} M, 300 μL, 15 °C). (Though high concentration might, to some extent, facilitate the intermolecular photo-dimerization of 4, the conversion is still inefficient under this experimental condition to form a large enough network without γ-CD. Additionally, because of the decrease of the solubility, the compound 4 aqueous solution separated to two layers after photo-irradiation. So we confirmed that γ-CDs are essential to form the dual-responsive hydrogel in our experimental condition.)

4. Dynamic oscillatory measurement for NNP-sol.

![Graph](image)

Fig. S11 Dynamic oscillatory data for CNP-gel irradiated by 254 nm UV light for five days, on strain sweep at a frequency of 1 rad s^{-1} (15 °C).
5. References


6. Additional spectra.

\[ ^1H \text{NMR of compound 2, DMSO-}d_6, 25^\circ\text{C} \]
**13C NMR of compound 2, DMSO-\textit{d}_6, 25 \, ^\circ\text{C}**

**ESI-MS of compound 2**
\(^1\)H NMR of compound 4, D\(_2\)O, 25 °C

\(^{13}\)C NMR of compound 4, D\(_2\)O, 25 °C