Electronic Supplementary Information

Gel Thermoresponsiveness driven by Switch of Charge-Transfer Interaction

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Experimental section

Materials

All reagents and solvents were purchased from commercial suppliers and were used without further purification. All experiments were carried out under nitrogen atmosphere. The effector **2** and **3** was synthesized via the reported procedure.[1]

Measurements

^{1}H NMR spectra were measured on a Bruker AV300 and a JEOL JNM-AL300 apparatus, using 0.05% tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra were observed with a JASCO FTIR-4100 SK spectrometer with a ZnSe prism kit PKS-ZNSE for ATR technique. For all gel samples the images were taken using KEYENCE VW-5000 Optical Microscope. For the heating cycle all gel samples in a sealed glass tube were heated using a NISSIN-Thermo block ND-MO1 temperature controller.

Synthesis of monomer 1[1]

For preparation of **1**, 1858 mg(8 mmol) of 1-pyrenemethanol, 796 mg(8.8 mmol) of acryloyl chloride, 890 mg (8.8 mmol) of tetraethyl amine in 80 mL of dry dichloromethane was mixed, cooled with ice bath and reacted at room temperature under nitrogen gas for 3 hours. The organic layer was washed with water and extracted with dichloromethane. The organic layer was then dried using magnesium sulfate, filtered and the solvent was evaporated. The crude product was separated using silica gel column chromatography (dichloromethane/hexane 1:1) to obtain **1** as a white solid (2.00 g, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.28-7.99 (m, 9H, Pyrene *H*) 6.47 (dd, J=17.2, 1.5 Hz, 1H, alkenyl H), 6.18 (dd, J = 17.2, 10.3 Hz, 1H, alkenyl *H*), 5.92 (s, 2H, Ar-CH_2 -), 5.84 (dd, J = 1.5, 10.3 Hz, 1H, alkenyl *H*).

Preparation of PPMAgel

PMMAgel was prepared by free radical polymerization. A typical protocol is as follows; 3.4 mg (0.015 mmol) of 1,6-bis(acryloyloxy)hexane, 2.5 mg (0.015 mmol) of azobisisobutyronitrile (AIBN) and 0.3 mL of dehydrated *N*,*N*-dimethylacetamide was mixed and degassed for 30 minutes by passing dry nitrogen gas. The mixture was then added into 430 mg (1.5 mmol) of monomer **1**, degassed again and allowed to polymerize in a sealed capillary tube under 65 °C for 48 hours. After cooling, the formed gel was then removed from capillary tube and repeatedly washed with chloroform and air-dried at room temperature followed by vacuo for 24 hours. The yield was found to be 266 mg (61%).

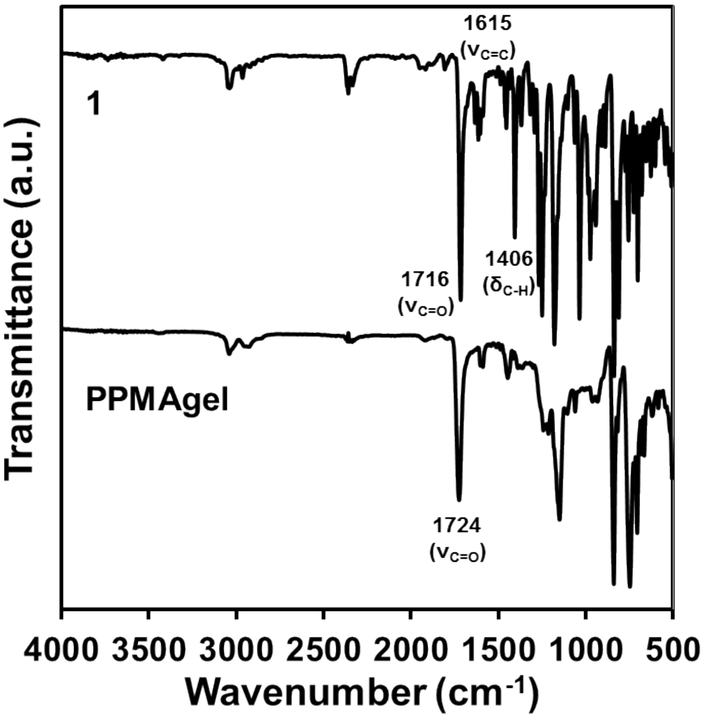

Fig. S1 FTIR spectra of monomer **1** and **PPMAgel.**

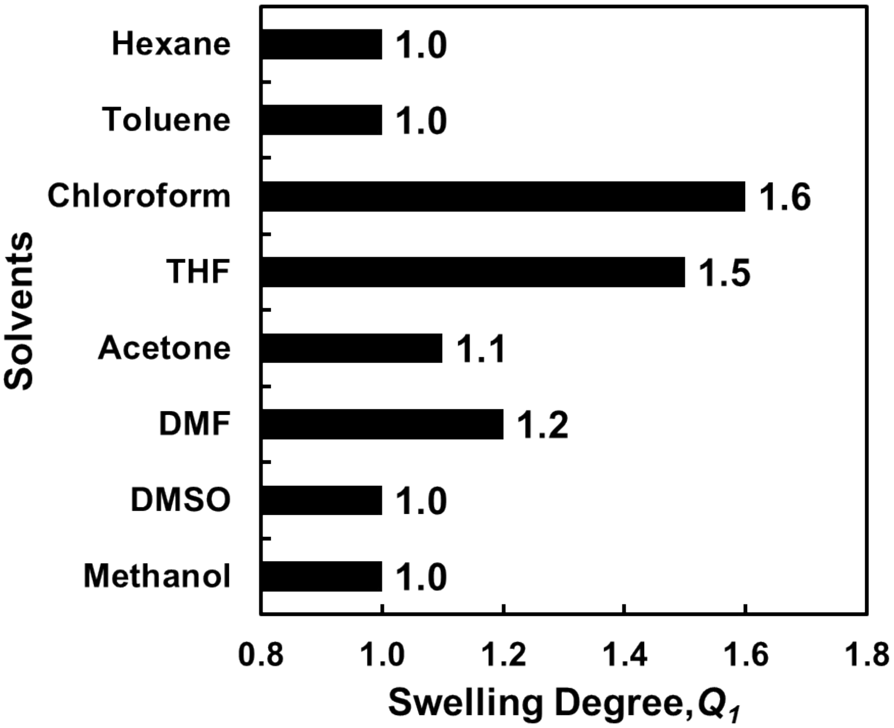

Fig.S2 Swelling degree ($Q_1 = L_{wet}/L_{dry}$) of the **PPMAgel** in various organic solvents.

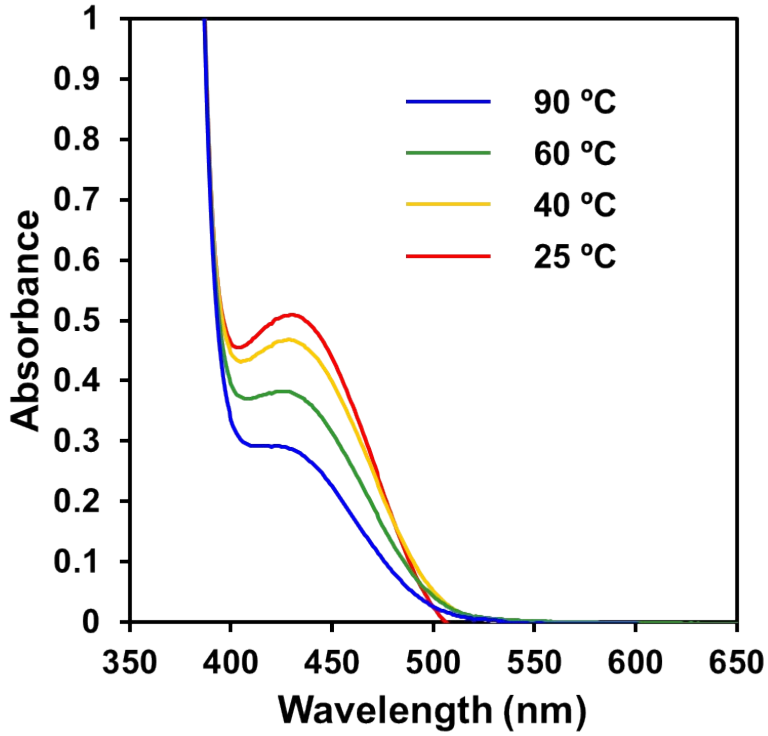

Fig.S3 UV-Vis absorption spectra of monomer **1** (4 mM) with effector **2** (200 mM) in toluene from 25 °C to 100 °C.

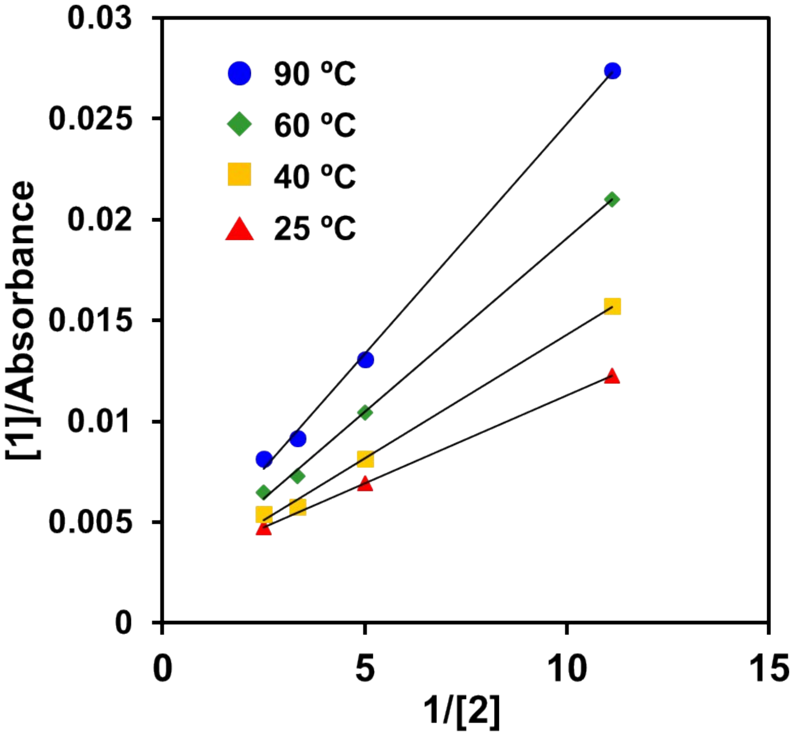

Fig. S4 Benesi-Hildebrand plot of [**1**]/ absorbance vs. 1/[**2**] from 25 °C to 90 °C.

Table S1. Association constants between **1** and **2**.[a]

Temperature (°C)	K_a[b] (M^{-1})
25	2.77
40	1.67
60	1.11
90	0.83

[a] Measured in toluene. [b] Determined by Benesi-Hildebrand plot.

Reference

1. S. Amemori, K. Kokado and K. Sada, *Angew. Chem. Int. Ed.* 2013, **52**, 4174-4178