Supporting Information

Chemomechanical-Force-Induced Folding-Unfolding Directly Controls Distinct Fluorescence Dual-Color Switching

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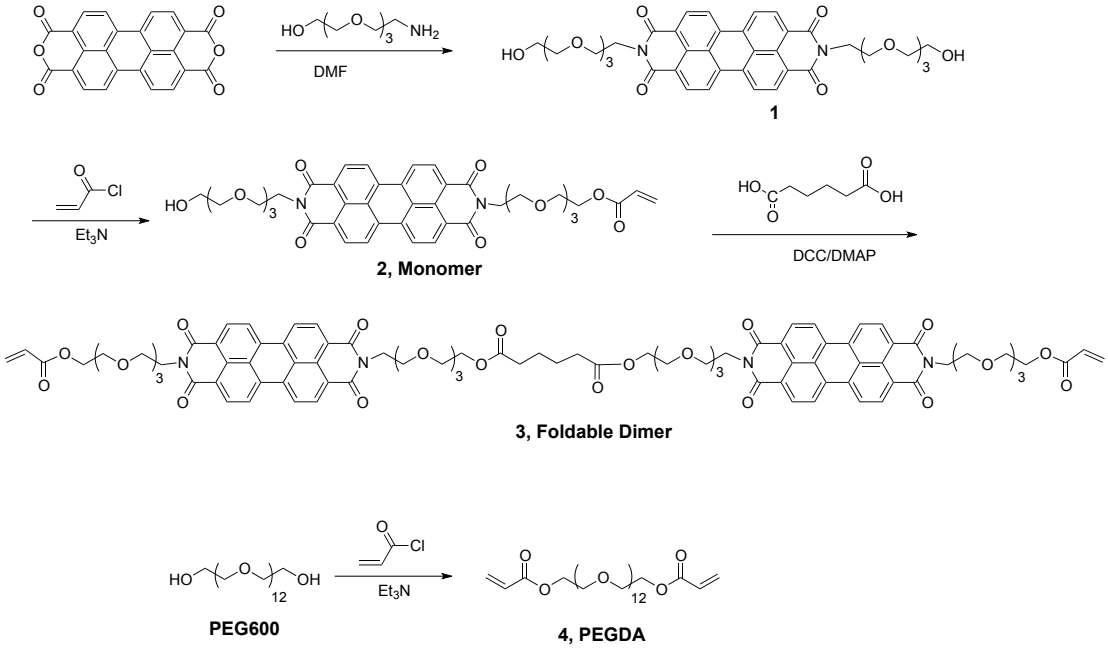
General Methods. Solvents and reagents were purified where necessary using literature methods. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker 400 MHz spectrometer in $CDCl_3$ (CD_3OD) solutions. TMS was used as a reference for ^{1}H-NMR; 77.23ppm was adopted as the central line of $CDCl_3$ for ^{13}C-NMR. UV-vis spectra were recorded with a Varian Cary 100 spectrophotometer. Fluorescence spectra were recorded with a SPEX Fluorolog-3-21 spectrofluorometer with excitation at 488 nm.



Scheme S1. Synthesis routes to foldable (**3**) and non-foldable (**4**) linkers used in the polymerization to construct lipogels.

Preparation of bis-N, N'-(2-(2-(2-(2-thioacetylethoxy)ethoxy)ethoxy)ethyl)-3, 4, 9, 10-perylene tetracarboxylic diimide (1)

The preparation of bis-N, N'-(2-(2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) ethyl)-3, 4, 9, 10-perylenetetracarboxylic diimide (1) was achieved according to the procedure in our early report[1].

Synthesis of Monomer (2)

To a solution of **1** (742 mg, 1 mmol) in 500 mL dry CH_2Cl_2 (DCM, 4 Å activated molecular sieves, 3 days) at 0 ºC, were added acryloyl chloride (109 mg, 1.2 mmol) and dry triethylamine (NaOH, pellets 3 days) (0.5 ml, 3.6 mmol). The reaction mixture was then stirred for 2 h at 0 ºC, and left overnight at room temperature (RT) under an argon atmosphere. The solvent was evaporated and the residue was purified by chromatography on a silica gel column eluted with CH_2Cl_2/MeOH (25/1), and the title product (**2**), a red solid, was obtained in 36% yield (286 mg). ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, Figure S1) δ=8.60 (d, J =8.1 Hz, 4H, outside protons of perylene ring, Hα), 8.50 (d, J=8.1 Hz, 4H, inside protons of perylene ring, Hβ), 6.40 (dd, J=17.4 Hz, 1H, proton of propenyl), 6.13 (dd, J=17.4 Hz, 1H, proton of propenyl), 5.81 (dd, J=10.4 Hz, 1H, proton of propenyl), 4.47 (t, J=5.4 Hz, 4H, tetraethylene glycol), 4.27 (m, 2H, tetraethylene glycol), 3.87 (t, J=6.0 Hz, 4H, tetraethylene glycol), 3.75-3.62 (m, 20H, tetraethylene glycol), 3.56 (m, 2H, tetraethylene glycol). ^{13}C-NMR ($CDCl_3$, 77.00 MHz, Figure S2) δ 166.08, 162.93, 162.90, 133.76, 130.95, 130.82, 128.72, 128.22, 125.54, 122.84, 122.63, 72.46, 70.67, 70.62, 70.59, 70.55, 70.32, 70.07, 69.05, 67.91, 67.84, 63.64, 61.71, 39.28.

Synthesis of Dimer (3)

To a solution of **2** (318 mg, 0.4 mmol), adipic acid (29 mg, 0.2 mmol) and 4-(dimethylamino)pyridine (49 mg, 0.4mmol) in 80 mL dry CH_2Cl_2 (4 Å activated molecular sieves, 3 days) and 4 mL dry dimethylformamide (DMF) at 0 ºC, were added N,N′-dicyclohexylcarbodiimide (148 mg, 0.72 mmol) by dripping. The reaction mixture was then stirred for 2 h at 0 ºC, and left 48 h at room temperature (RT) under

an argon atmosphere. The solvent was evaporated and the residue was purified by chromatography on a silica gel column eluted with CH_2Cl_2/MeOH (25/1), and the title product (**3**), a dark red solid, was obtained in 62% yield (211 mg): ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm, Figure S3) δ=8.42-8.36 (d, J=8.1 Hz, 8H, outside protons of perylene ring, Hα), 8.16 (d, J=8.1 Hz, 8H, inside protons of perylene ring, Hβ), 6.42 (dd, J=17.4 Hz, 2H, proton of propenyl), 6.13 (dd, J=17.4 Hz, 2H, proton of propenyl), 5.80 (dd, J =10.4 Hz, 2H, proton of propenyl), 4.45 (t, J=5.4 Hz, 8H, tetraethylene glycol), 4.28-4.20 (m, 8H, tetraethylene glycol), 3.89 (t, J=6.0 Hz, 8H, tetraethylene glycol), 3.75-3.62 (m, 40H, tetraethylene glycol), 2.34 (m, 4H, methylene of adipic acid), 1.65 (m, 4H, methylene of adipic acid). ^{13}C-NMR ($CDCl_3$, 77.00 MHz, Figure S4) δ 173.20, 166.07, 162.70, 162.66, 133.40, 130.95, 130.56, 128.45, 128.22, 125.18, 122.70, 122.67, 122.42, 70.68, 70.55, 70.06, 69.09, 69.05, 67.84, 63.64, 63.46, 39.27, 33.73, 24.26.

Synthesis of poly(ethylene glycol) diacrylate (PEGDA) crosslinker (4)

Poly(ethylene glycol) (PEG) diacrylate (PEGDA) was synthesized as described previously[2]. Briefly, PEG 600 (3 g, 5 mmol) and triethylamine (1.7 mL, 12.5 mmol) were dissolved in dry dichloromethane (40 mL) under Ar. Acryloyl chloride (1.624 mL, 20 mmol) was diluted in dichloromethane (10 mL) and added to the PEG suspension dropwise. The reaction proceeded under N_2 overnight. The solution was concentrated by rotary evaporation, and acetone was added to precipitate triethylamine salts. The salts were filtered, and the eluent was precipitated in 1 L of chilled diethyl ether. The precipitate was dried overnight by reduced pressure to yield a transparent viscous liquid (3.2 g, 90 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ=6.50 (d, J=6.4 Hz, 2H), 6.20 (m, 2H), 5.82 (d, J=5.8 Hz, 2H), 4.25 (t, J=4.3 Hz, 4H), 3.70−3.55 (m, 52H).

Synthesis of foldamer-crosslinked lipogel (5 and 6)

Foldamer-crosslinked lipogel was synthesized via a free radical polymerization. For preparation of typical sample Gel-D3 (Table S1), methyl acrylate (1.12 g, 13

mmol), PEGDA (24 mg, 0.03 mmol), dimer 3 (0.1 mg, 5.88×10^{-5} mmol) and azobisisobutyronitrile (2 mg, 0.01 mmol) were dissolved in dry dichloromethane (1 mL). After three times of freeze-pump-thaw cycle, the mixture was stirred at 60 °C for 10 min, then, it was transferred to NMR tubes and heated in 60 °C oven for 12 h to evaporate DCM and form final transparent red lipogel.

Such polymerization typically results in homogeneous distribution of dimer molecules in the gels. Therefore, the distance (D_d) between two "dimer" molecules in the lipogel was estimated via the following equation:

$$D_d = \sqrt[3]{\frac{V_{Gel}}{N_d}}$$

Where V_{Gel} is the total lipogel volume on contracted state, N_d is the number of "dimer" molecules in lipogel. The as-prepared lipogel was cut to fit for the further UV-Vis spectra and FL spectra measurements. Additional characterizations of the lipogels are shown in Figures 5-10 below.

Reference

[1] Wang, W.; Han, J. J.; Wang, L. Q.; Li, L. S.; Shaw, W. J.; Li, A. D. Q. *Nano Lett.* **2003,** *3*, 455.

[2] Käpylä, E.; Delgado, S. M.; Kasko, A. M. *ACS Appl. Mater. Interfaces* **2016,** *8*, 17885.

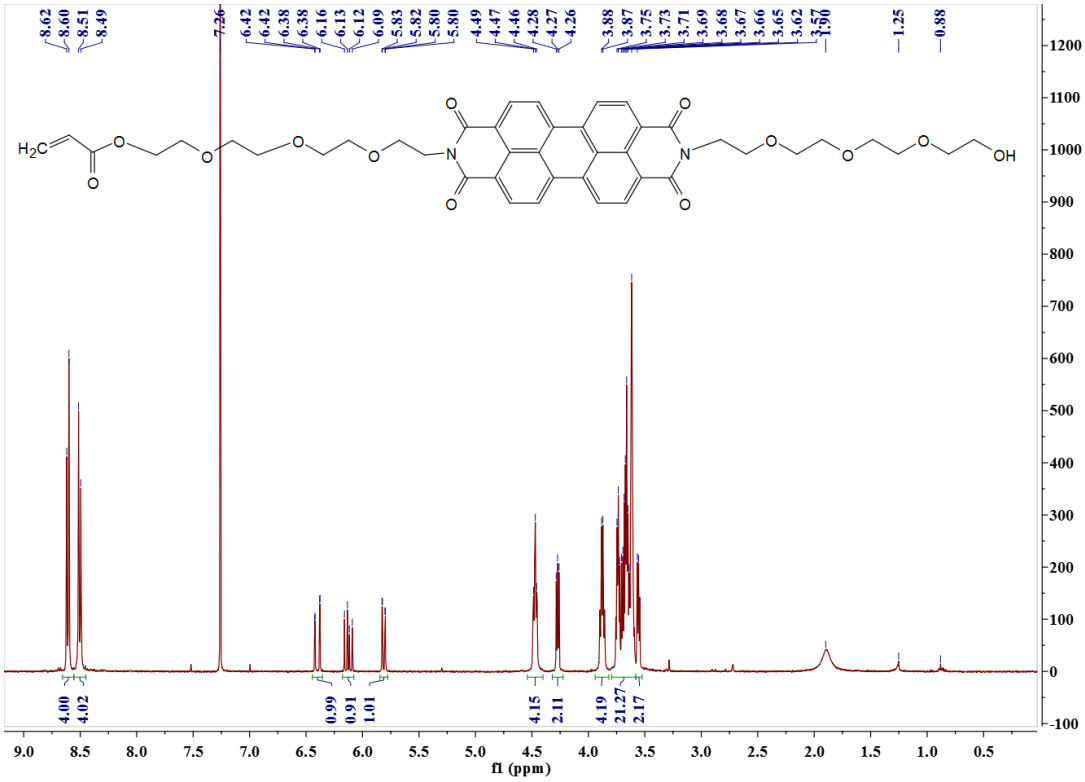


Figure S1. ^{1}H NMR spectral of single acrylate-linked monomer (2).

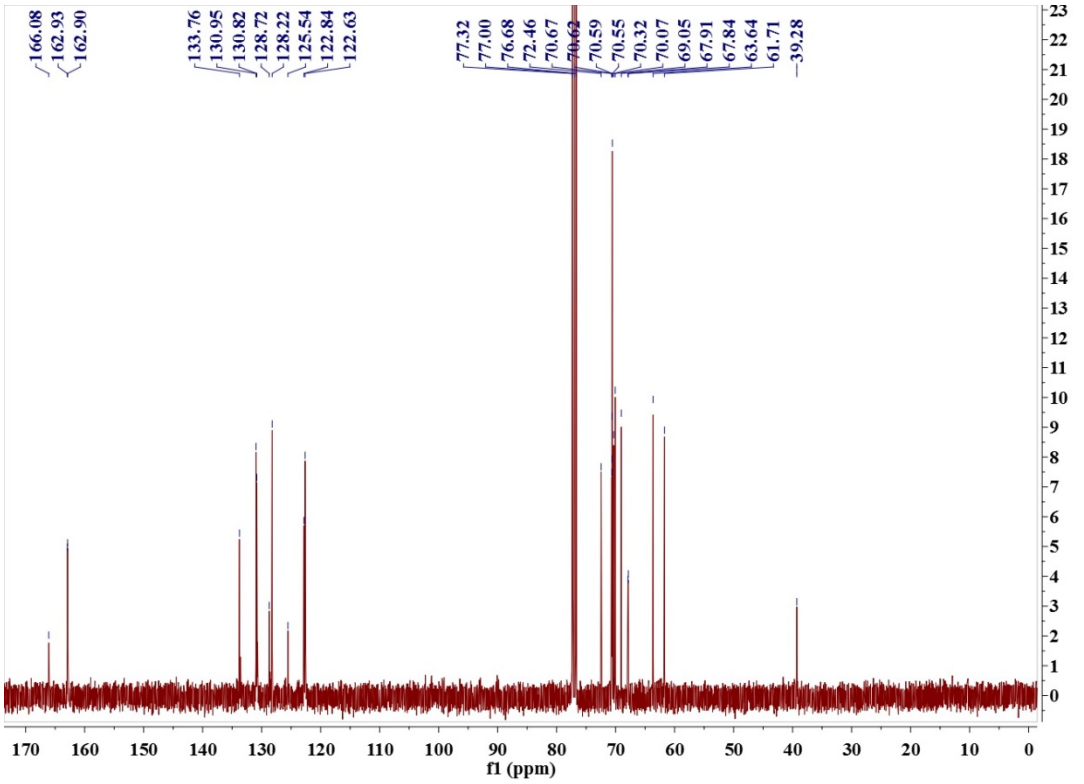


Figure S2. ^{13}C NMR spectral of single acrylate-linked monomer (2).

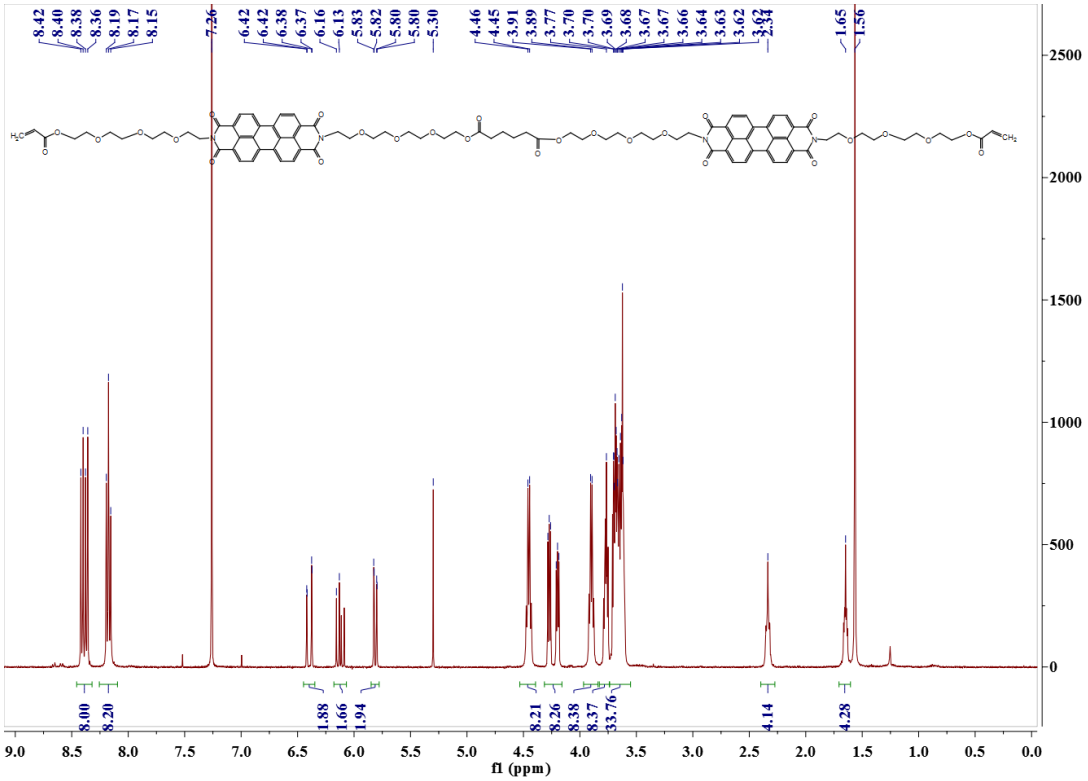


Figure S3. ^{1}H NMR spectral of double acrylate-linked dimer (3).

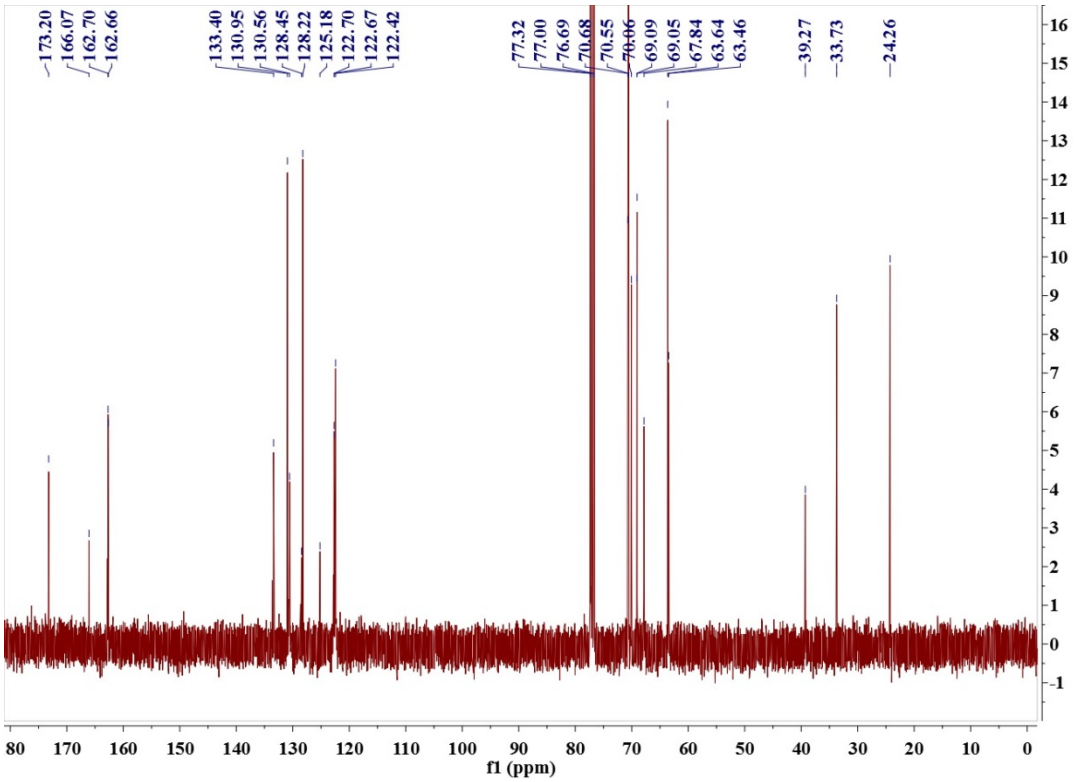


Figure S4. ^{13}C NMR spectral of double acrylate-linked dimer (3).

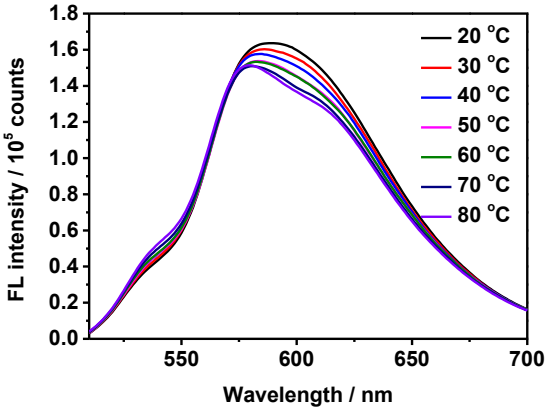


Figure S5. Fluorescence spectra of Gel-D3 (Gel-D3) in the dense state (before solvent swelling) were measured at various temperatures.

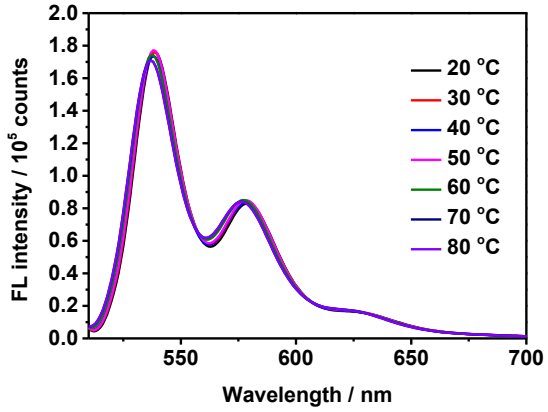


Figure S6. Fluorescence spectra of the gel (Gel-D3) after swollen in 1,1,2,2-tetrachloroethane were measured at various temperatures.

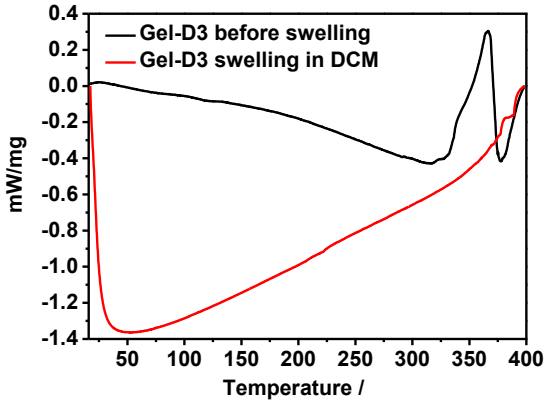


Figure S7. The shrunk Gel-D3 and the DCM-swollen Gel-D3 were characterized using DSC with the following parameters: rate of scanning: 5°C/min; Temperature，17 °C~400 °C；Environment，N_2.

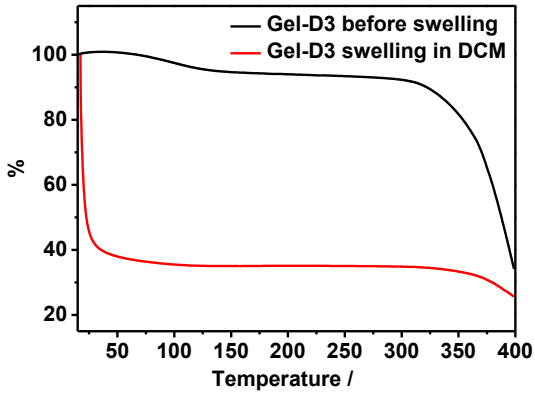


Figure S8. TG diagrams contrast the shrunk Gel-D3 to the DCM-swollen Gel-D3, revealing the huge difference due removal of the solvent (parameters: rate of scanning: 5°C/min; Temperature，17 °C~400 °C；Environment，N_2).

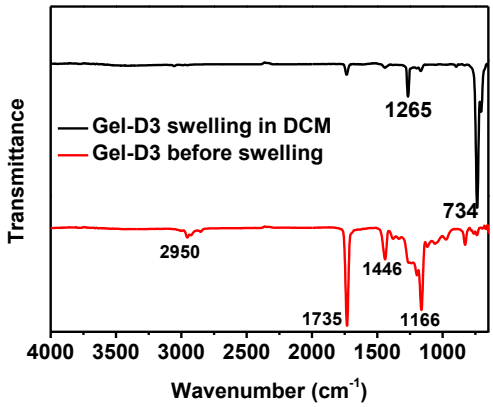


Figure S9. FTIR spectra of the "dry" Gel-D3 (before solvent swelling) and the DCM-swollen Gel-D3 reveal the huge difference caused by DCM solvent. The dry gel shows the characteristics of the polymer frameworks and their structural units at 2950 cm^{-1}: C-H; 1735 cm^{-1}: C=O; 1446 cm^{-1}: C-O-C; 1166 cm^{-1}: C-O-C. The DCM-swollen gel predominantly show the peak corresponding to DCM at 1265 cm^{-1}: C-H; 734 cm^{-1}: C-Cl.

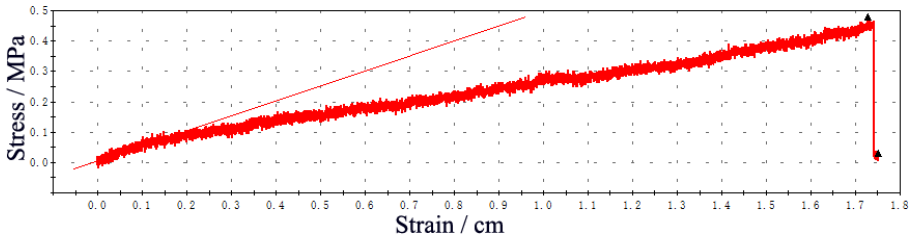


Figure S10. Stress-strain curves of Gel-D3 under tensile loading reveal that the gels have remarkable ductility, yielding 561% elongation from 38 mm to 175 mm and maximum tensile stress of 0.478 MPa

Table S1: List of data for various samples with difference dye feed amount.

Sample[a]	Linked dye[b]	Dye feed [mg]	A_1/A_2 before swelling	A_1/A_2 after swelling in DCM	A_1/A_2 after swelling in TCE
Gel-M1	**2**	0.02	1.36	NA	1.44
Gel-M2	**2**	0.05	1.35	1.42	1.45
Gel-M3	**2**	0.10	1.32	1.44	1.46
Gel-D1	**3**	0.02	0.72	1.10	1.26
Gel-D2	**3**	0.05	0.70	1.13	1.32
Gel-D3	**3**	0.10	0.72	1.12	1.32

a: The MA/PEGDA/AIBN feed is 1.12/0.024/0.002 g, respectively; **b**: the linked dye is the single acrylate-linked monomer (2) or the double acrylate-linked dimer (3).

Table S2: The data of volume before and after swelling in DCM.

Content	Dimeter (mm)	Length (mm)	Volume (mm^3)
Before swelling	2.97	16.30	112.94
After swelling in DCM	6.19	34.10	1026.32
Swelling ratio	2.08	2.09	9.09

Gel Measurements and further characterizations

1) Absorption measurements of lipogels in expanded and contracted states

UV-vis spectra at room temperature were recorded with a Varian Cary 100 spectrophotometer. The prepared lipogel (contracted state) with ca. 1.2 cm length was fixed in the center of 2 ml glass vial for absorption spectra test. Then the vial was filled with DCM and sealed for 2 h. The lipogel was expanded to maximum, and the absorption spectra were measured.

2) Fluorescence measurements of lipogels in expanded and contracted states

Fluorescence spectra at room temperature were recorded with a SPEX Fluorolog-3-21 spectrofluorometer with excitation at 488 nm. The prepared lipogel (contracted state) with ca. 1.2 cm length was fixed in the center of 2 ml glass vial for fluorescence spectra test. Then the vial was filled with DCM and sealed for 2 h. The lipogel was

expanded to maximum, and the fluorescence spectra were measured. The slit of excitation and emission is 1.0 nm.

3) Volume growth rate measurements

The prepared columned lipogel (contracted state) with ca. 1.2 cm length was weighed (W_0), its diameter and length was also measured to get the volume in contracted state (V_0). Then it was fixed in the 2 ml glass vial for absorbance ratio (A_1/A_2) test. Then the vial was filled with TCE, after several minutes, the lipogel was weighed (W_n) and its absorbance ratio (A_1/A_2) was tested at the same time. Finally, the expanded lipogel was weighed (W_1), its absorbance ratio (A_1/A_2) was tested, and its diameter and length was also measured to get the volume in expanded state (V_1). The volume growth rate (V/V_0) can be estimated by the follow formula:

$$V/V_0=(W_n-W_0)/(d*V_0)$$

$$d=(V_1-V_0)/(W_1-W_0)$$

4) Temperature dependence measurements.

The prepared lipogel (contracted state) with ca. 1.2 cm length was fixed in the center of 2 ml glass vial for absorbance ratio (A_1/A_2) spectra test at different temperature (293K-353K). The corresponding expanded lipogel or dimer in TCE at different temperature (293K-353K) was also tested.

5) Switching cycles measurements for both absorbance and fluorescence

For the switching cycles (both absorbance and fluorescence) test, the prepared lipogel (contracted state) with ca. 1.2 cm length was fixed in the center of 2 ml glass vial for absorption and fluorescence spectra test. Then the vial was filled with DCM and sealed for 2 h. The lipogel was expanded to maximum, and the absorption fluorescence spectra were measured. Then, the solvent in the vial was removed and the inside expanded lipogel was slightly blew by air for 2h to return to totally contracted lipogel again. The repeated expanding and contracting were performed for the switching cycles test.