Electronic Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information (ESI) for

Solvent Effects on Structure, Photoresponse and Speed of Gelation of a Dicholesterol-linked Azobenzene Organogel

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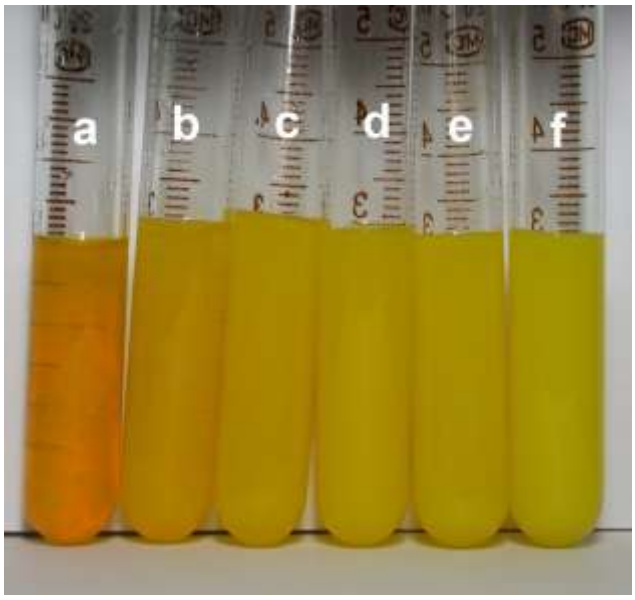

Fig. S1 Pictures of gels (1% w/v) at different methanol content: (a) 0%; (b) 5%; (c) 10%; (d) 15%; (e) 20%; (f) 30%.

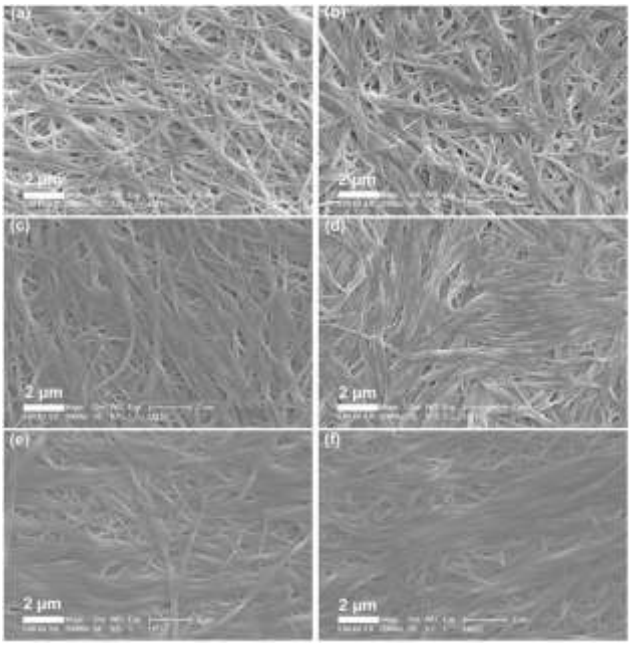

Fig. S2 SEM images of xerogels (1% w/v) prepared at different methanol content: (a) 0%; (b) 5%; (c) 10%; (d) 15%; (e) 20%; (f) 30%.

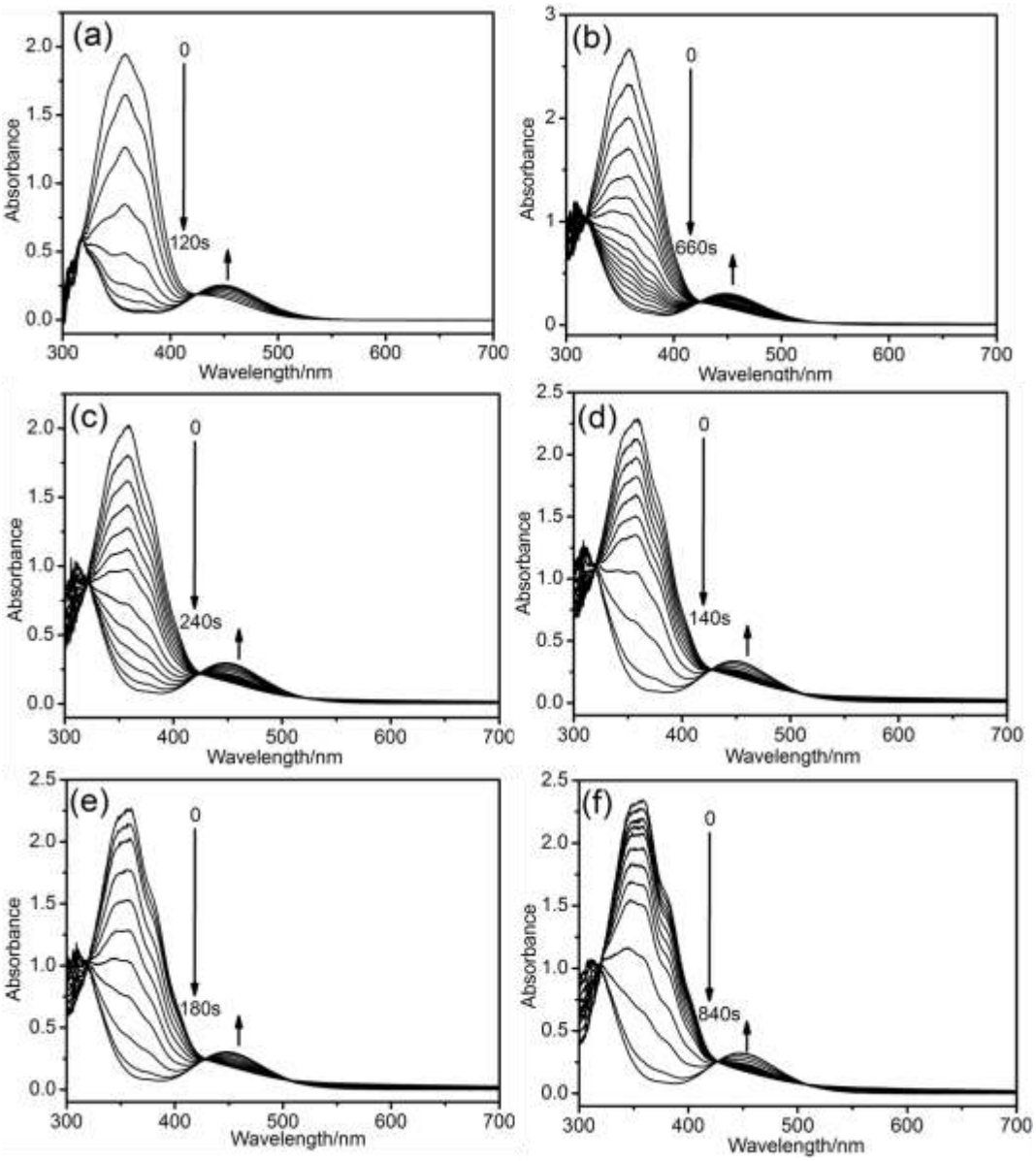

Fig. S3 UV-vis spectral changes of the gels (1% w/v, 0.13 mm path length) irradiated with 365 nm light at different methanol content: (a) 0%; (b) 5%; (c) 10%; (d) 15%; (e) 20%; (f) 30%.

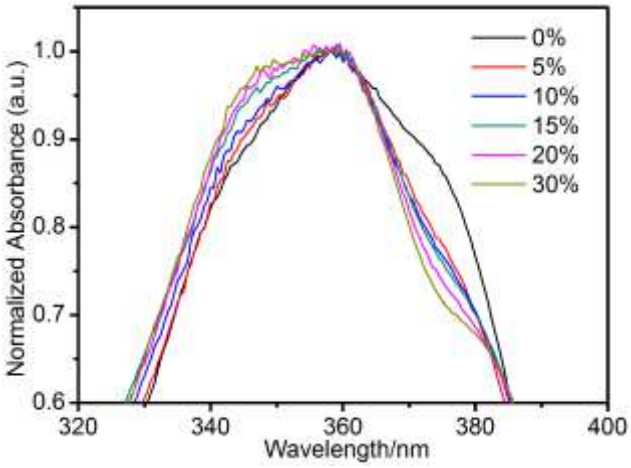

Fig. S4 Normalized UV-vis spectra of the gels (1% w/v, 0.13 mm path length) at different methanol content.

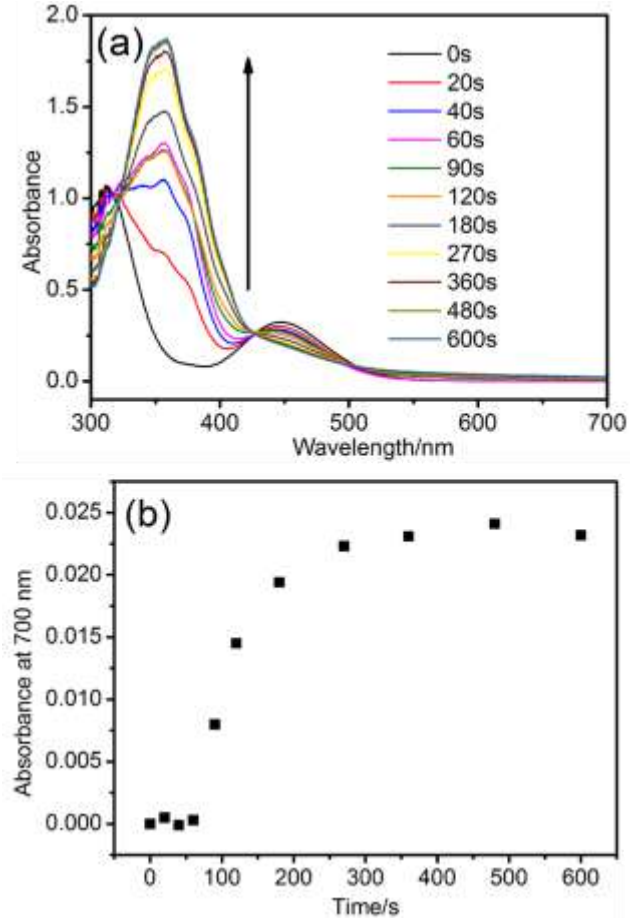

Fig. S5 (a) UV-vis spectral changes of the gel with 30% methanol (1% w/v, 0.13 mm path length) irradiated with 435 nm light after irradiation with 365 nm light for 840 s. (b) Intensities of UV-vis absorbance at 700 nm as a function of time during the visible light (435 nm) irradiation of the gel with 30% methanol (1% w/v, 0.13 mm path length).

As shown in Fig. S5a, compared to the spectrum of irradiated for 60 s, a shoulder

peak shown at the left part of the π-π* absorption band of the spectrum for 90 s, and this shoulder peak became obvious afterwards. For Fig. S5b, absorbance at 700 nm is ascribed to scattering caused by the fiber network of the gel, which became obvious gradually since irradiated for 90 s. These results both indicate that the gel began to reform when the sol was irradiated with visible light for 90 s (before the entire *cis-trans* isomerization (visible light irradiation) was accomplished, corresponding to the "0 min" in Table 2).

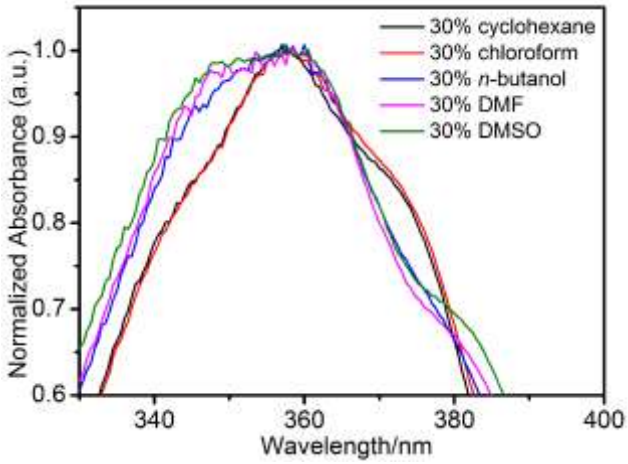

Fig. S6 Normalized UV-vis spectra of the solutions ((a) 30% cyclohexane and (b) 30% chloroform) and the gels ((c) 30% *n*-butanol, (d) 30% DMF and (e) 30% DMSO). The concentration of **DCAZO2** is 1% w/v in all the samples.

Calculations of the solubility parameters of the solvents

Table S1. Hansen parameters of cyclopentanone, methanol, cyclohexane, *n*-butanol, chloroform, DMF and DMSO

Solvent	δ_d/MPa$^{1/2}$	δ_p/MPa$^{1/2}$	δ_h/MPa$^{1/2}$
cyclopentanone	17.9	11.9	5.2
methanol	15.1	12.3	22.3
cyclohexane	16.8	0.0	0.2
n-butanol	16.0	5.7	15.8
chloroform	17.8	3.1	5.7
DMF	17.4	13.7	11.3
DMSO	18.4	16.4	10.2

These data are taken from C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC Press, Boca Raton, 2007.

Table S2. The Hansen parameters of the mixed solvents calculated according to $\delta_{average} = \Sigma\phi_i\delta_i$ (Equ. 68 of *Chemical Reviews*, 1975, 75, 731-753.)

Mixed solvents	δ_d/MPa$^{1/2}$	δ_p/MPa$^{1/2}$	δ_h/MPa$^{1/2}$
0% methanol	17.9	11.9	5.2
5% methanol	17.8	11.9	6.1
10% methanol	17.6	11.9	6.9
15% methanol	17.5	12.0	7.8
20% methanol	17.3	12.0	8.6
30% methanol	17.1	12.0	10.3
30% cyclohexane	17.6	8.3	3.7
30% *n*-butanol	17.3	10.0	8.4
30% chloroform	17.9	9.3	5.4
30% DMF	17.8	12.4	7.0
30% DMSO	18.1	13.3	6.7
50% methanol	16.5	12.1	13.8

Table S3. The Teas parameters of the solvents

Mixed solvents	f_d	f_p	f_h
0% methanol	0.511	0.340	0.149
5% methanol	0.497	0.332	0.170
10% methanol	0.484	0.327	0.190
15% methanol	0.469	0.322	0.209
20% methanol	0.456	0.317	0.227
30% methanol	0.434	0.305	0.261
methanol	0.304	0.247	0.449

30% cyclohexane	0.595	0.280	0.125
30% *n*-butanol	0.485	0.280	0.235
30% chloroform	0.549	0.285	0.166
30% DMF	0.478	0.333	0.188
30% DMSO	0.475	0.349	0.176
50% methanol	0.389	0.285	0.326

These parameters are calculated according to the following equations.

$$f_d = \delta_d / \left(\delta_d + \delta_p + \delta_h\right)$$
$$f_p = \delta_p / \left(\delta_d + \delta_p + \delta_h\right)$$
$$f_h = \delta_h / \left(\delta_d + \delta_p + \delta_h\right)$$

Calculations of the solubility parameters of the gelator DCAZO2

The Hansen parameters of **DCAZO2** are calculated according to a group-contribution method reported in "Int. J. Thermophys. 2008, 29, 568–585".

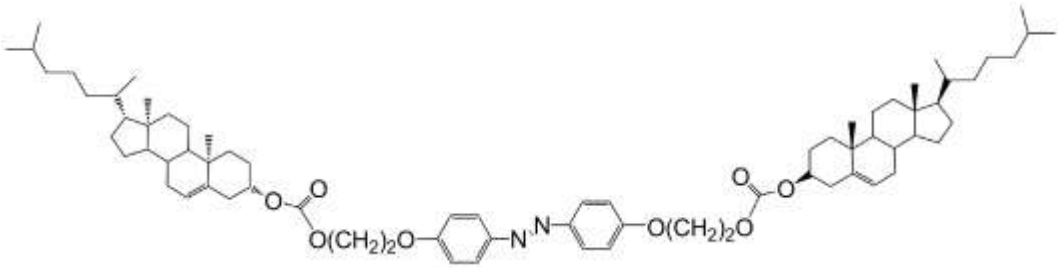

Fig. S8 Molecular structure of **DCAZO2**.

Table S4. First-order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, the polar partial solubility parameter, δ_p, and the hydrogen bonding partial solubility parameter, δ_h, for the repeat unit of **DCAZO2**

First order group	Occurrences, N_i	Contributions, C_i (δ_d)	N_iC_i (δ_d)	Contributions, C_i (δ_p)	N_iC_i (δ_p)	Contributions, C_i (δ_h)	N_iC_i (δ_h)
N(except as above)	2	1.5438	3.0876	2.5780	5.1560	***	***
AC	4	0.8446	3.3784	0.6187	2.4748	-0.17405	-0.6962
ACH	8	0.1105	0.884	-0.5303	-4.2424	0.13532	1.08256
CH_2O	4	0.0310	0.124	0.8826	3.5304	***	***
COO	2	0.2039	0.4078	3.4637	6.9274	0.37204	0.74408
-CH=C<	2	0.5372	1.0744	-0.9024	-1.8048	-0.03066	-0.06132
-CH<	14	0.6450	9.03	0.6491	9.0874	0.1386	1.9404
>C<	4	1.2686	5.0744	2.0838	8.3352	***	***

$-CH_2-$	22	-0.0269	-0.5918	-0.3045	-6.699	-0.11610	-2.5542
$-CH_3$	10	-0.9714	-9.714	-1.6448	-16.448	0.29901	2.9901
Constant, C			17.3231		7.3548		1.3720
$\Sigma N_i C_i$ +C			30.0779		13.6718		4.81742

Table S5. Second-order group approximation for the prediction of the dispersion partial solubility parameter, δ_d, the polar partial solubility parameter, δ_p, and the hydrogen bonding partial solubility parameter, δ_h, for the repeat unit of **DCAZO2**

Second order group	Occurrences, M_j	Contributions, D_j (δ_d)	M_jD_j (δ_d)	Contributions, D_j (δ_p)	M_jD_j (δ_p)	Contributions, D_j (δ_h)	M_jD_j (δ_h)
$(CH_3)_2$-CH-	2	0.0460	0.092	0.0019	0.0038	10^{-8}	$2*10^{-8}$
AC-O-C	2	0.2568	0.5136	0.8153	1.6306	***	***
String in cyclic	2	−0.1945	-0.389	***	***	−0.280859	-0.561718
ΣM_jD_j			0.2166		1.6344		-0.561718

δ_d=30.0779+0.2166=30.2945
δ_p=13.6718+1.6344=15.3062
δ_h=4.81742-0.561718=4.255702

The Teas parameter of **DCAZO2** can be calculated as follows:
$f_d=\delta_d/(\delta_d+\delta_p+\delta_h)$=30.2945/49.856402=0.608
$f_p=\delta_p/(\delta_d+\delta_p+\delta_h)$=15.3062/49.856402=0.307
$f_h=\delta_h/(\delta_d+\delta_p+\delta_h)$=4.255702/49.856402=0.085