

Supporting Information

Dual-responsive two-component supramolecular gels for self-healing materials and oil spill recovery

Liwei Yan, Guangzhe Li, Zhongbin Ye, Feng Tian and Shihong Zhang*

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General remarks

¹H NMR spectra were obtained with a Bruker AV-400 (400 MHz). The ¹H NMR chemical shifts were measured relative to CDCl₃ as the internal references. Transmission electron microscopy (TEM) studies were carried out on a HITACHI H-600, operating at 100 kV. Tapping mode AFM imaging was performed under ambient conditions on a SEIKO SPA400 instrument by using BS-Tap 300Al levers (Budget Sensors, silicone cantilevers). FT-IR spectroscopy was performed using WQF-510A/520A FT-IR Spectrometer produced by Beijing Beifen-Ruili Analytical Instruments. X-ray diffraction experiments were carried out by using an X'Pert Pro MPD diffractometer produced by PANalytical B.V. Rheological characterisation was performed on a HAAKE MARS III produced by Thermo Scientific Instruments. A parallel plates viscometer (diameter: r = 35 mm) was used with a cap to prevent the evaporation of the solvent and the gap between the plates is 1 mm. Data was collected and analysed using the HAAKE RheoWin 3 software produced by Thermo Scientific Instruments. Data presented here is for gel **1** at 4 % by weight. Frequency sweep measurement was performed at 25 °C and the stress amplitude was maintained at 5 Pa and 17 data points were taken between 0.0215 and 10 Hz. Stress amplitude oscillations were taken after the frequency oscillations experiments. The temperature was held at 25 °C. A frequency of 1 Hz was used and 40 data points were taken over the entire stress amplitude range.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise indicated, all syntheses and manipulations were carried out under dry N₂ atmosphere. Anhydrous solvents were dried by standard procedures. Ligands **1-4** were synthesized according to our previously reported methods.^{S1}

Preparation of samples for AFM. Samples of the solution of gel **1** (0.2 wt %) in dioxane were cast onto a freshly cleaved mica under ambient conditions, and then dried at room temperature for 0.5 h before making AFM images.

Preparation of samples for TEM. TEM specimens were prepared by gently placing a carbon-coated copper grid on a surface of the gel sample. The TEM grid was removed, dried for 0.5 h at room temperature, and then subjected to observation.

Gelation tests. A capped vial was charged with a solution of the mixture of ligand **1-3** and alkylamine, the resulting mixture was heating at 50-60 °C and then cooled to room temperature

for several minutes. The sample was simply confirmed by the “stable to inversion of a test tube” method, was formed.

Table S1 Gelation test of ligands **1-3** with n-octadecylamine (OA) (1:1) in different solvents

Entry	Solvent	1	2	3
1	toluene	G (28.3)	G (11.0)	G (22.6)
2	xylene	G (14.1)	G (16.6)	G (15.1)
3	benzonitrile	G (7.1)	G (4.7)	G (9.9)
4	dioxane	G (2.8)	G (5.5)	G (22.6)
5	ethyl ester	G (4.0)	G (3.3)	G (30.0)
6	dichloromethane	P	G (4.1)	G (45.2)
7	1,2- dichloroethane	G (4.0)	G (4.7)	G (12.9)
8	chloroform	P	S	G (45.2)
9	petroleum ether	G (10.3)	I	G (30.0)
10	THF	G (4.7)	S	G (45.2)
11	hexane	G (14.1)	G (17.8)	G (18.1)
12	cyclohexane	G (14.1)	G (06.0)	G (7.5)
13	DMF	G (14.1)	G (35.7)	G (45.2)
14	pyridine	G (5.7)	S	G (30.0)
15	ether	I	G (35.7)	S
16	acetonitrile	I	I	S
17	diethylamine	G (14.1)	S	P
18	triethylamine	S	S	P
19	methanol	P	S	S
20	ethanol	P	S	S
21	n-propanol	S	S	S
22	n- butanol	P	S	S
23	acetone	S	S	S
24	acetic acid	PG	P	P
25	water	G (5.5)	PG	P

G: steady gel with critical gelation concentrations (CGCs); Gels were formed by cooling the corresponding hot solution. PG: partial gel; P: precipitate; I: insoluble; S: solution.

Table S2 Gelation test of ligand **1-3** with various alkylamine, imidazole and pyridine derivatives (1:1) in solvents

Entry	Building block	1^a	2^b	3^c
1	octylamine	G (18.4)	S	G (37.9)
2	decylamine	G (14.2)	S	G (34.5)
3	dodecylamine	G (9.4)	S	G (30.1)
4	tetradecylamine	G (4.7)	G (16.6)	G (18.1)
5	cetylamine	G (3.5)	G (8.3)	G (15.1)
6	octadecylamine	G (2.8)	G (3.3)	G (7.5)
7	ethanediamine	P	S	P

8	1,3-propanediamine	P	S	P
9	methenamine	S	P	P
10	imidazole	S	S	P
11	benzimidazole	S	S	P
12	pyridine	S	S	S
13	3-cyanopyridine	S	P	P
14	4-cyanopyridine	S	P	P
15	4-hydroxypyridine	P	P	P
16	2-picolinic acid	P	P	P

^a in dioxane; ^b in ethyl ester; ^c in hexane.

Table S3 Gelation test of ligand **1-3** with OA at different molar ratios (CGC)

Entry	ratio	1 ^a	2 ^b	3 ^c
1	3:1	3.5	4.7	11.3
2	2:1	3.1	4.2	9.0
3	1:1	2.8	3.3	7.5
4	1:2	3.5	4.2	9.9
5	1:3	3.1	6.7	11.3

^a in dioxane; ^b in ethyl ester; ^c in hexane.

Table S4 T_{gel} (°C) of Gel **1-OA**^a, gel **2-OA**^b and gel **3-OA**^c at their CGC

T_{gel} (°C)		
Gelator 1-OA	Gelator 2-OA	Gelator 3-OA
45 (dioxane)	44 (ethyl ester)	105 (cyclohexane)
54 (Crude oil)	58 (Crude oil)	81 (Crude oil)
55 (water)		

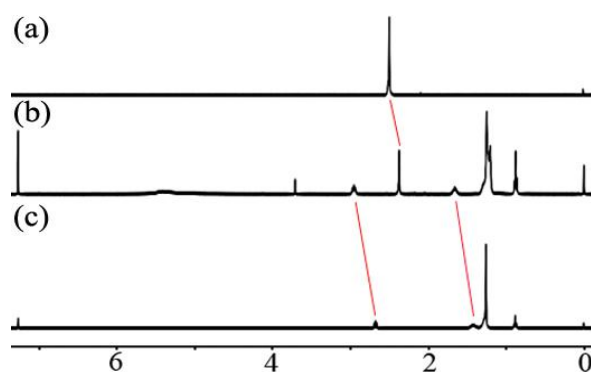


Figure S1 ¹H NMR spectra for OA with ligand **1** in CDCl₃ at 293 K: (a) the ligand **1**, (b) **1**/OA = 1:1, (c) OA.

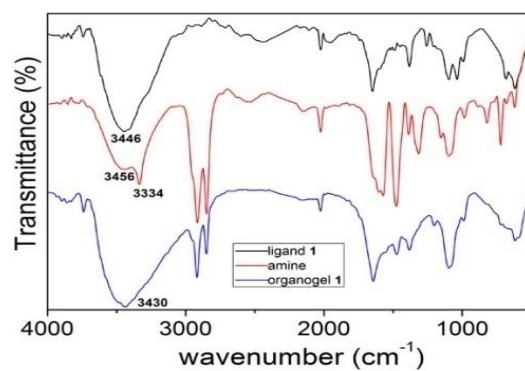


Figure S2 Comparison of FT-IR spectra: ligand **1** (black), OA (red) and the xerogel **1-OA** (blue) obtained from dioxane.

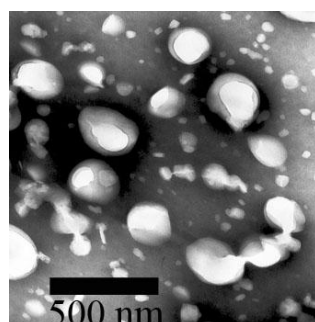


Figure S3 TEM image of organogel **1-OA** in dioxane (0.2 wt %) on a carboncoated copper grid stained with phosphotungstic acid aqueous solution (10 g dm^{-3}).

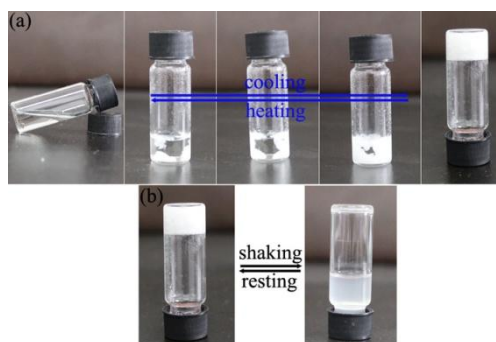


Figure S4 The dual responsiveness of organogel **1-OA**.

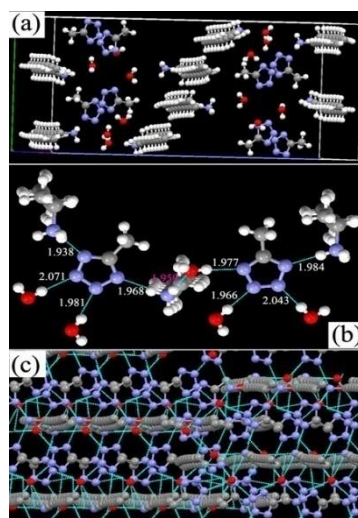


Figure S5 The X-ray crystal structure of the complex formed by ligand **1** and n-hexadecylamine in H₂O. **The crystal was obtained by resting the corresponding hydrogel for *ca.* 2-3 weeks.**^{S2} (a) Ligand **1** (8), n-hexadecylamine (8) and H₂O (12) in one crystal cell. (b) The ligand **1** had two coordination modes. One coordinated with two H₂O molecules and two n-hexadecylamine molecules; another one coordinated with three H₂O molecules and one n-hexadecylamine molecule. The length of the three N-H bonds of the n-hexadecylamine were equal, which indicated that the *NH* group of ligand **1** was deprotonated by the n-hexadecylamine via hydrogen-bond interaction, and the *NH*₂ group of the n-hexadecylamine turned into *NH*₃⁺ group accordingly. (c) The stacking mode of H₂O-mediated hydrogen-bond network.

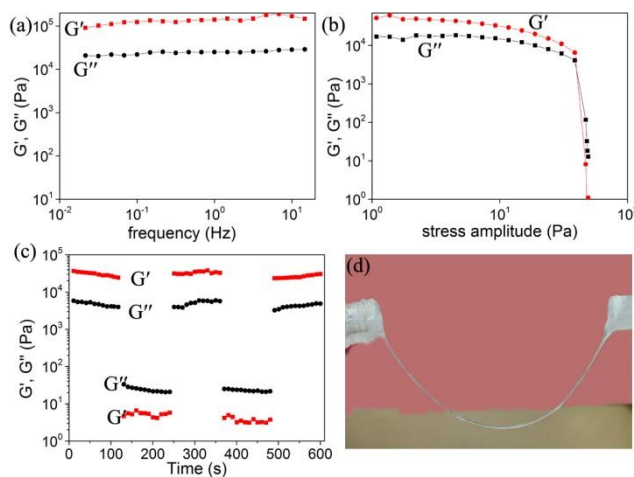


Figure S6 (a) Frequency sweep rheometry of hydrogel **1-OA** (5.5 %). The angular frequency (Hz), storage modulus G' (Pa) and loss modulus G'' (Pa) are shown as log scale. The frequency sweep data showing no crossover point throughout the experimental region, (b) Stress sweep rheometry of organogel **1-OA** (2.8 %, dioxane) showing G' and G'' as functions of stress amplitudes at constant frequency 1Hz. A sharp decrease in G' and G'' occurs at a value of *ca.* 40 Pa. (c) A loop test of organogel **1-OA** via continuous step-stress measurements at 1 Hz. The organogel **1-OA** was subject to 50 Pa stress for 2 mins, then back to 5 Pa in the linear regime for 2 mins, and this process was repeated three times. (d) A semicircular string was made by hydrogel **1-OA**.

Table S5 Gelation test of ligand **1-3** with OA (1:1) in different oils (CGC)

Entry	Solvent	1	2	3
1	crude oil	4.7	6.7	12.1
2	diesel	9.4	6.7	15.1
3	petrol	7.1	33.3	15.1
4	kerosene	4.7	16.6	15.1
5	paraffin oil	4.7	4.7	12.1

Table S6 Physical properties and element contents of the crude oil ^a

density (g.mL ⁻³)	viscosity (mPas)	acid number (mg of KOH/g)	element analysis (%)				
			C	H	S	N	O
0.902 ^b	2381 ^c	3.12	84.15	12.02	1.68	0.65	1.5

^a Crude oil sample was collected from the Tuha oilfield in China; ^b at 20 °C; ^c at 70 °C.

Table S7 Simulated seawater formula

Metal Salts	Contents (g/L)
MgCl ₂ ·6H ₂ O	8.7
CaCl ₂	1.1
NaCl	27.2
KCl	0.1
NaHCO ₃	0.2
Na ₂ SO ₄	0.6

Table S8 Comparison of CGC and BCGC of gelator **1** in various oils and their biphasic mixtures in water and seawater

Entry	Solvent	CGC	BCGC	
			Pure water	Simulated seawater
1	Crude oil	4.7	4.8	4.8
2	diesel	9.4	10.2	10.2
3	petrol	7.1	7.4	7.4
4	kerosene	4.7	4.9	4.9
5	paraffin oil	4.7	4.9	4.9

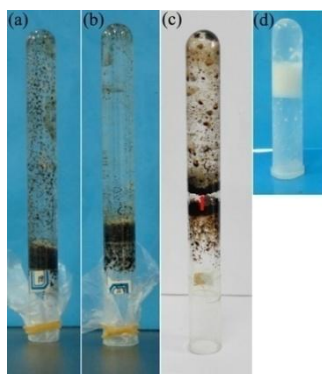


Figure S7 (a, b) Gels formed by gelator **2-OA** or **3-OA** in crude oil were stable to inversion when support up to *ca.* 10-fold its own weight. (c) A crude oil gel formed could be stable for several months at room temperature with slight evaporation of water, and the oil layer was shifted as the arrow showed accordingly. (d) A gel formed by gelator **1-OA** in kerosene and water.

Reference:

[S1] L. Yan, S. Gou, Z. Ye, S. Zhang, L. Ma, *Chem. Commun.* **2014**, 50, 12847-12850.

[S2] W. Fang, Z. Sun, T. Tu, *J. Phys. Chem. C.*, **2013**, 117, 25185-25194.

Table S9 X-ray data collection parameters for complex of ligand **1** and n-hexadecylamine

	complex
formula	2(C ₁₆ H ₃₆ N ¹⁺),2(C ₂ H ₃ N ₄ ¹⁻),3(H ₂ O)
Fw	705.13
color	colorless
space group	P 21/n
a/Å	7.2825(1)
b/Å	14.9699(2)
c/Å	42.2469(8)
<i>a</i> /deg	90°
<i>β</i> /deg	93.473(2)
<i>γ</i> /deg	90°
V/Å ³	4597.23(12)
Z	4
D _c /g cm ⁻³	1.019
F(000)	1576.0
T/K	293
R ₁ ^a (<i>I</i> > 2σ)	0.0757
wR ₂ ^b (all data)	0.2185
abs coeff/mm ⁻¹	0.516

^[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(F_o^2)^2]^{1/2}$.