

Supplementary Information

A highly transparent and autonomic self-healing organogel from solvent regulation based on hydrazone derivatives

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Table S1. Gelation abilities ^{a, b} of BNB-*tn* (*n*=1, 2, 4 and 8) and BNBC-t4 in single organic solvents.

Solvents	BNB-t1	BNB-t2	BNB-t4	BNB-t8	BNBC-t4
DMSO	S	S	S	S	S
Methanol	S	S	S	S	P
DMF	S	S	S	S	S
Acetic acid	S	S	S	S	S
Acetone	S	S	S	S	S
Ethanol	S	S	S	S	S
THF	S	S	S	S	S
<i>n</i> -propanol	S	S	S	S	S
TCM	PS	PS	G	G	S
Dichloromethane	P	P	G	G	S
Anisole	I	P	G	G	S
Benzene	I	PS	G	G	S
Chlorobenzene	I	PS	G	G	S
Xylene	I	PS	G	G	S
Toluene	I	PS	G	G	S
CYH	I	I	I	G	I
Hexane	I	I	I	PS	I

^a G: stable gel formed at room temperature, concentration: 4 mg/mL; S: soluble; PS: partly soluble; I: insoluble; P: precipitate.

^b DMSO: dimethyl sulphoxide; DMF: dimethyl formamide; THF: tetrahydrofuran; TCM: chloroform; CYH: cyclohexane.

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Table S2 Gelation abilities ^a of BNB-t4 in TCM/CYH (V:V) mixtures.

TCM/CYH	State	CGC
100:0	G	2.2
90:10	G	1.1
80:20	G	0.8
70:30	G	0.7
60:40	G	0.7
50:50	G	0.6
40:60	G	2.5
30:70	G	3.2
20:80	Sus	-
10:90	Sus	-
0:100	I	-

^a G: stable gel formed at room temperature; Sus: suspension; I: insoluble; CGC: critical gelation concentration (mg/mL), the minimum concentration necessary for gelation of solvents.



Fig. S1 (a) Photographs of 4 mg/mL BNB-t8 gel in various ratios of TCM/CYH at room temperature. (b) Transmittance spectra of BNB-t8 gel (4 mg/mL) in various ratios of TCM/CYH.

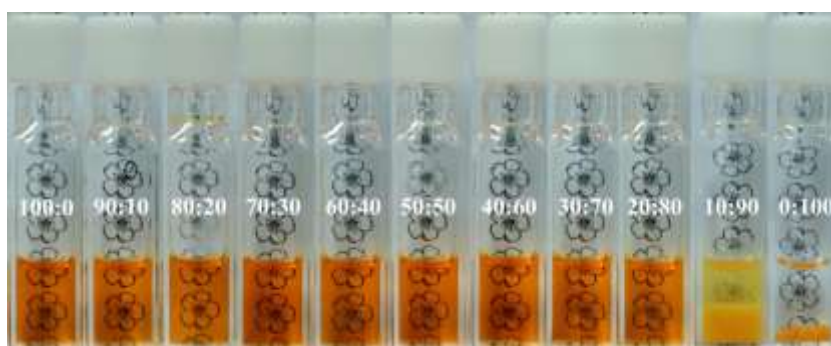


Fig. S2 Photographs of 4 mg/mL BNBC-t4 in various ratios of TCM/CYH at room temperature.

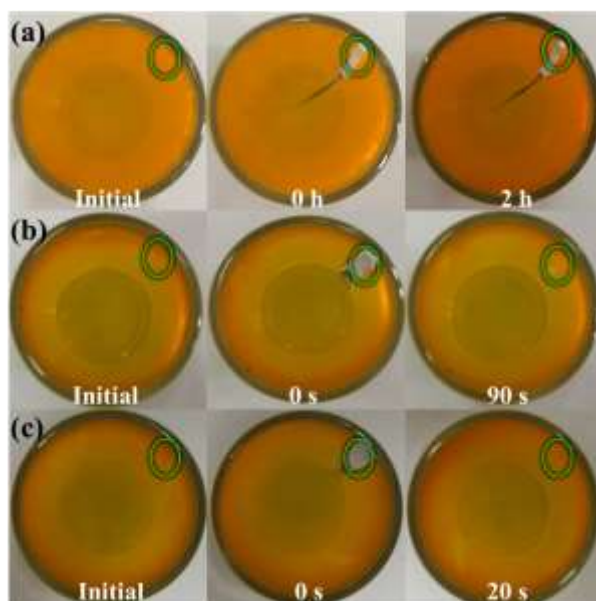


Fig. S3 Photographs of 16 mg/mL BNB-t4 gels (a) in TCM (b) 60:40 TCM/CYH and (c) 40:60 TCM/CYH upon mechanical damages after free standing.

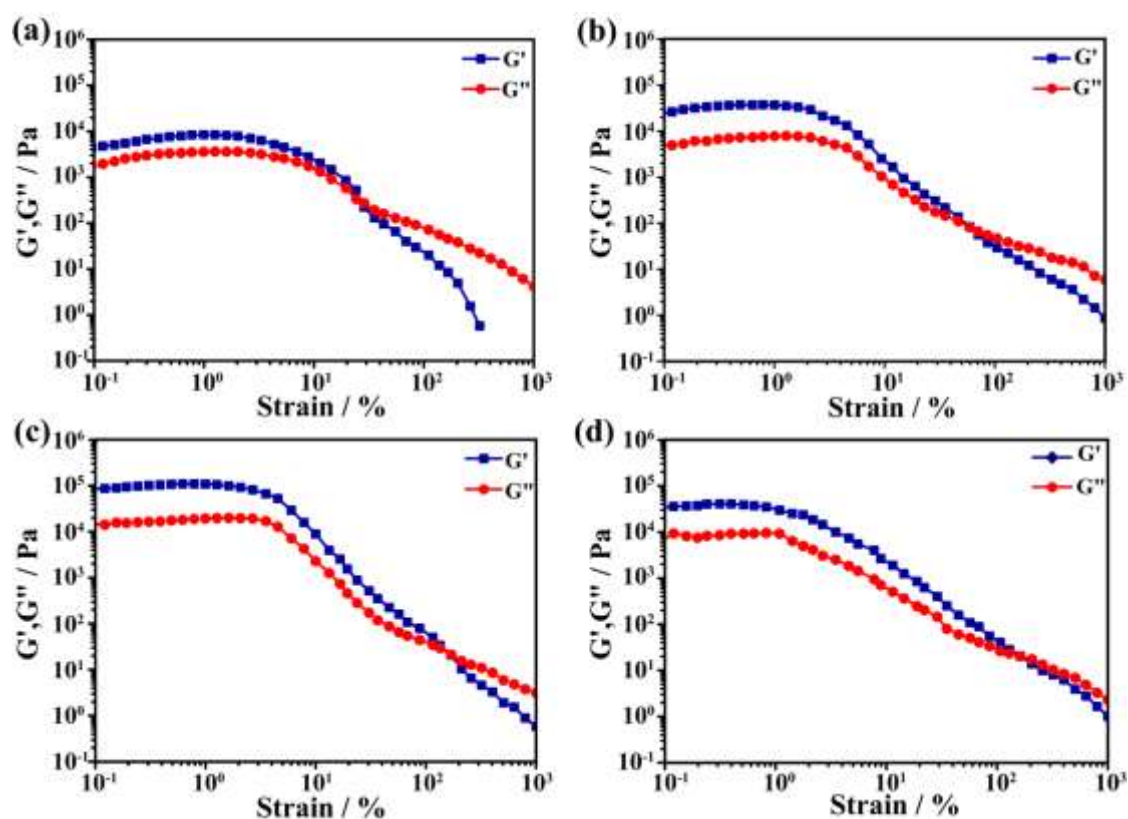


Fig. S4 Log-Log strain sweep with the frequency = 1.0 Hz of 16 mg/mL BNB-t4 gels in (a)100:0, (b)70:30, (c)50:50 and (d)30:70 TCM/CYH mixtures at 25 °C.

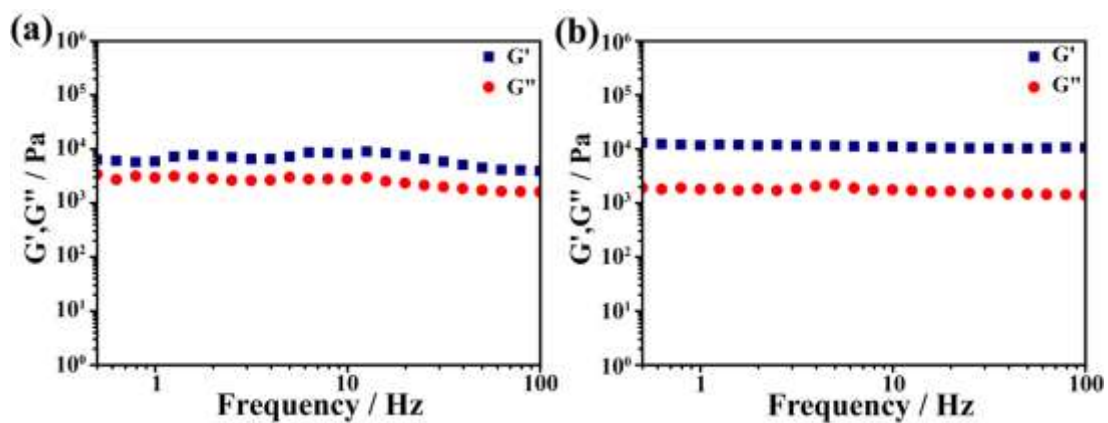


Fig. S5 Log-Log frequency sweep with the strain = 1.0 % of 16 mg/mL BNB-t4 gels in (a) 100:0 and (b) 70:30 TCM/CYH mixtures at 25 °C.

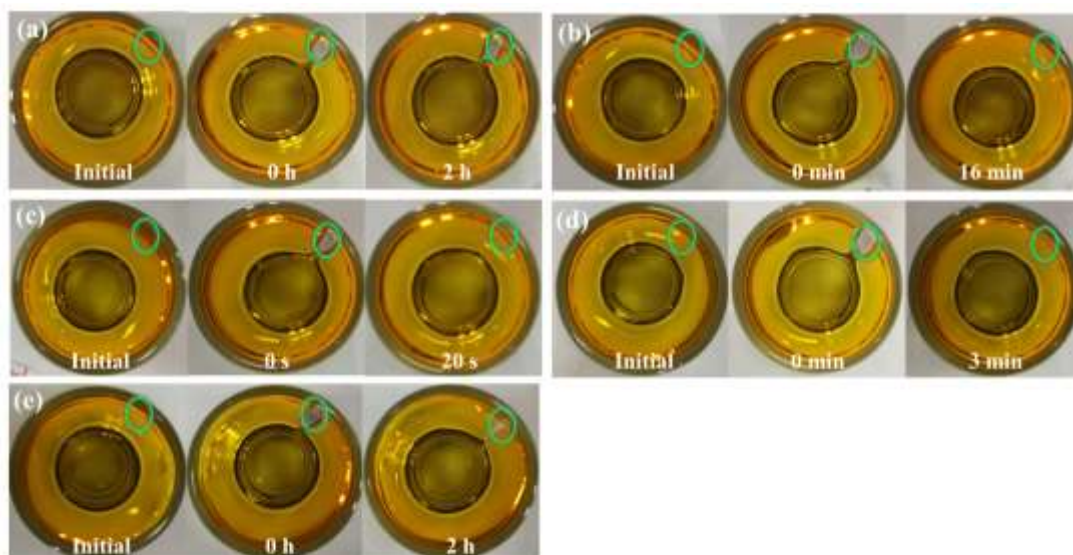


Fig. S6 Self-healing diagrams of 16 mg/mL BNB-t8 gels in (a) 100:0, (b) 70:30, (c) 50:50, (d) 30:70, (e) 0:100 TCM/CYH mixtures.

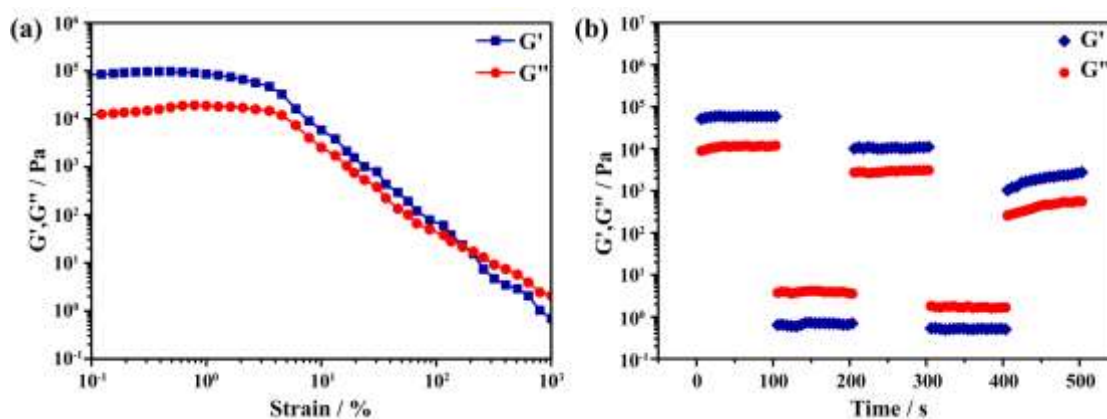


Fig. S7 (a) Log-Log strain sweep with the frequency = 1.0 Hz of 16 mg/mL BNB-t8 gels in 50:50 TCM/CYH mixtures at 25 °C. (b) Continuous-step measurements of 16 mg/mL BNB-t8 gels in 50:50 TCM/CYH mixtures with alternating the strain amplitudes between 1% and 1000% (frequency = 1.0 Hz).

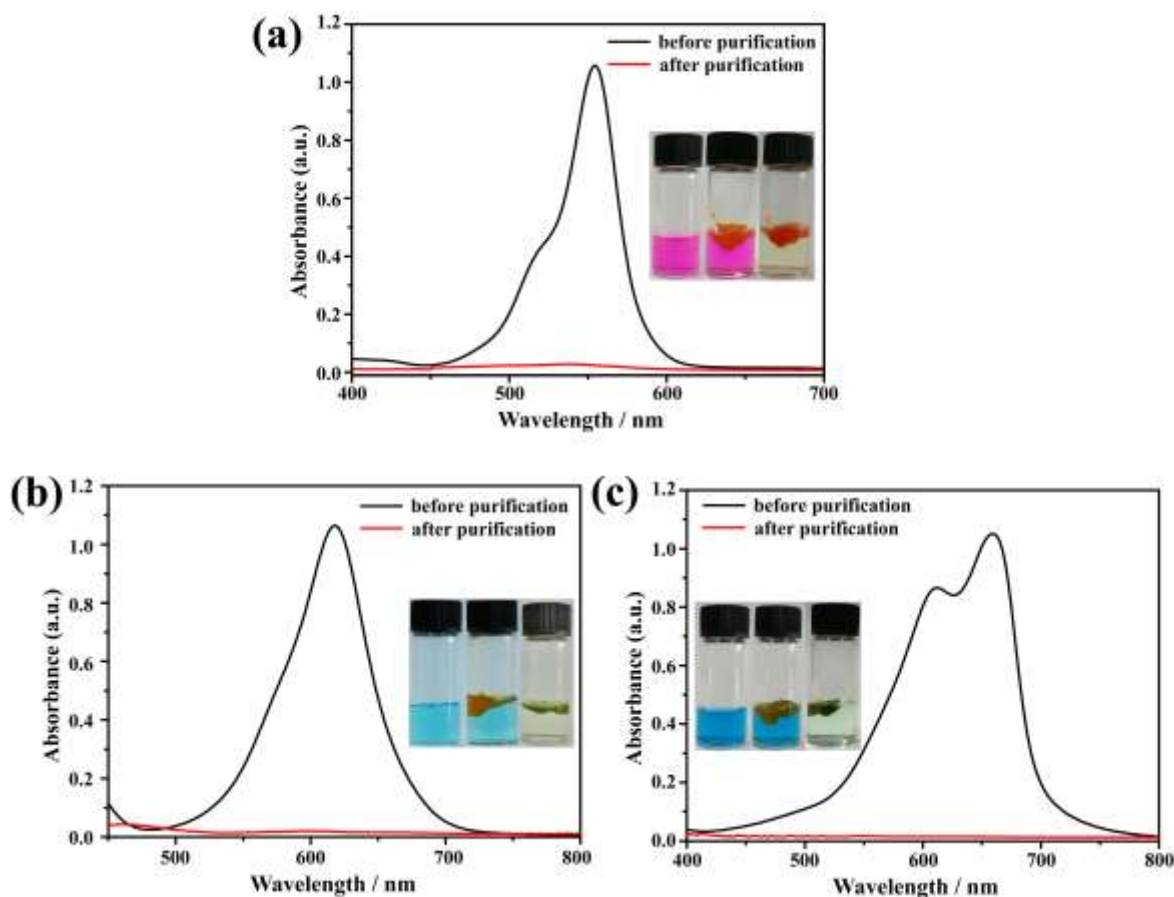


Fig. S8 Absorption spectra of water contaminated with (a) rhodamine B, (b) malachite green, (c) methylene blue dyes before (black) and after elimination (red). Insets: Photographs of removed dye molecules from aqueous solution by BNB-t4 organogel in 50:50 TCM/CYH mixtures.

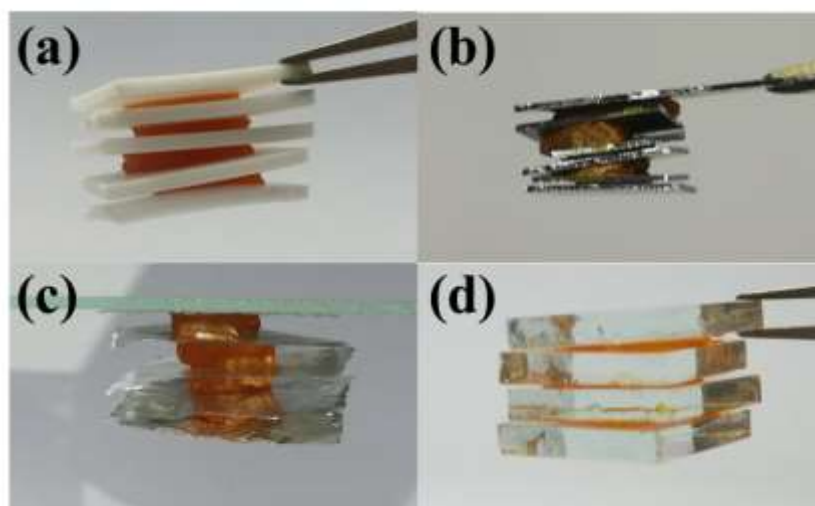


Fig. S9 Photographs of adhesion abilities in lifting up different adherends with BNB-t4 gels (50 mg/mL): (a) polyethylene foam, (b) silicon chip, (c) silver paper and (d) conductive glass.

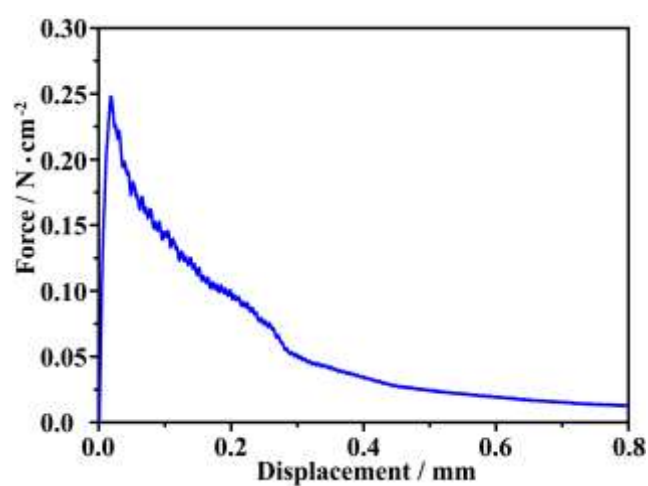


Fig. S10 Peeling strength of 16 mg/mL BNB-t4 gel in 50:50 TCM/CYH mixtures on stainless steel substrate.

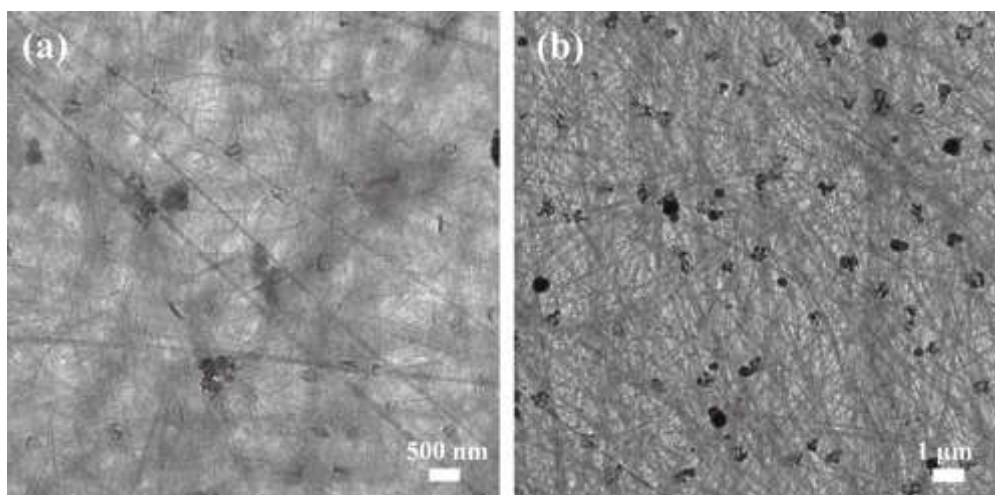


Fig. S11 TEM images of BNB-t4 suspension (2 mg/mL) in TCM/CYH mixtures: (a) 20:80 and (b) 10:90.

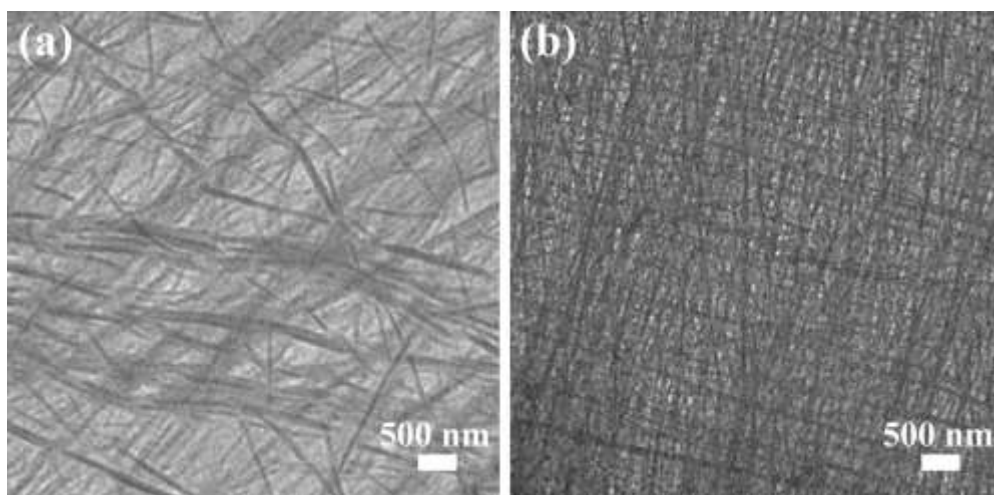


Fig. S12 TEM images of BNB-t4 gels from 30:70 TCM/CYH mixtures (4 mg/mL) at different temperatures: (a) 20 °C and (b) 70 °C.

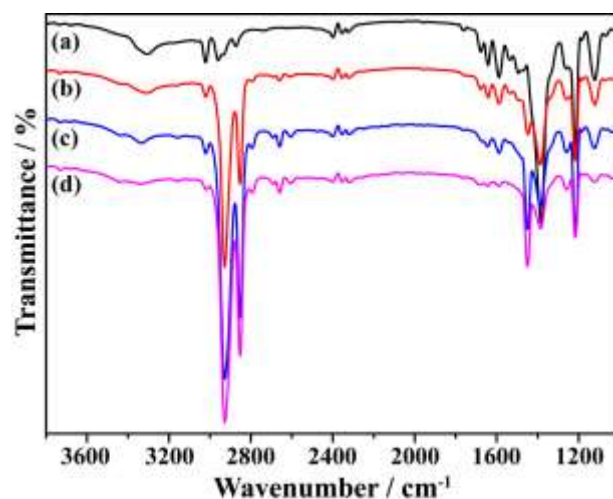


Fig. S13 FT-IR spectra of BNB-t4 gels in: (a) TCM, (b) 70:30 TCM/CYH, (c) 50:50 TCM/CYH and (d) 30:70 TCM/CYH mixtures.

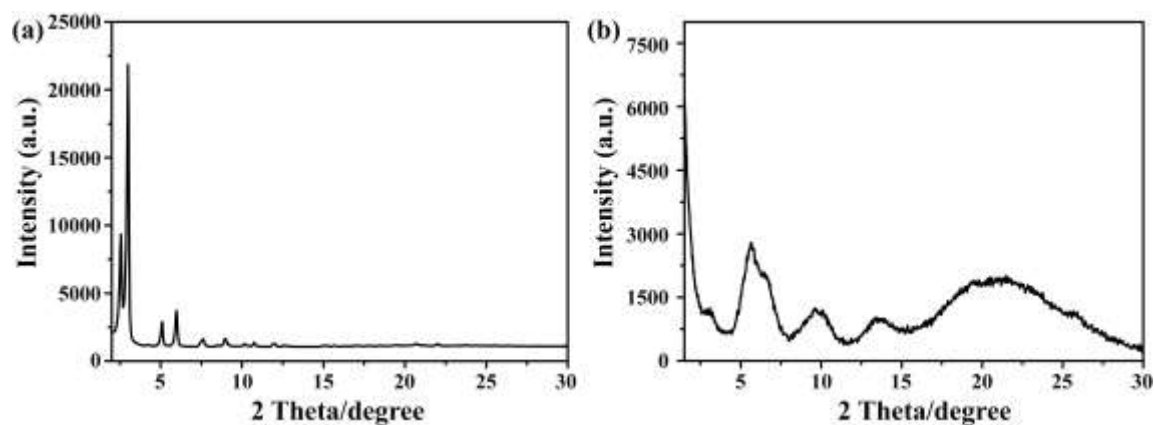


Fig. S14 XRD patterns of (a) BNB-t4 powder and (b) BNB-t4 xerogel from 50:50 TCM/CYH mixtures.

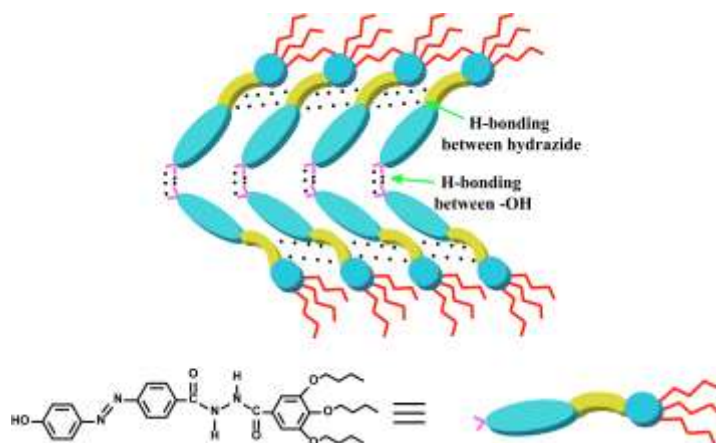


Fig. S15 A possible packing motif of BNB-t4 molecules in TCM/CYH mixtures.

Calculations of the solubility parameters of gelator BNB-t4

In this method, the basic equation to obtain the value of each property from molecular structure is:

$$f(x) = \sum_i N_i C_i + W \sum_j M_j D_j$$

where C_i is the contribution of the first-order group of type i that appears N_i times in the compound, and D_j is the contribution of the second-order group of type j that appears M_j times in the compound. $f(x)$ is the single equation of the property x , which is selected after a thorough study of the physicochemical and thermodynamic behaviors of property. The constant W is equal to 1 and 0 for compounds with and without second-order groups, respectively. The statistical values of the first-order and second-order approximations for Hansen solubility parameters can be found in “Int. J. Thermophys. 2008, 29, 568-585”.

By applying the group-contribution method for the estimation of Hansen solubility parameters, the equations can be written as:

$$\delta_d = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 17.3231 \right) \text{MPa}^{1/2}$$

$$\delta_p = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.3548 \right) \text{MPa}^{1/2}$$

$$\delta_h = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.9793 \right) \text{MPa}^{1/2}$$

where δ_d is the dispersion Hansen solubility parameter, δ_p is the polar Hansen solubility parameter, δ_h is the hydrogen-bonding Hansen solubility parameter. It should be mentioned that the equation of δ_p and δ_h are valid only for Hansen solubility parameter values greater than 3 MPa^{1/2}.

Table S3 First-order group approximation ($W=0$) for the prediction of 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 BNB-t4.

first order group	Occurrences, N_i	Contributions, $C_i(\delta_d)$	$N_i C_i$ (δ_d)	Contributions, $C_i(\delta_p)$	$N_i C_i$ (δ_p)	Contributions, $C_i(\delta_h)$	$N_i C_i$ (δ_h)
-CH ₃	3	-0.9714	-2.9142	-1.6448	-4.9344	-0.7813	-2.3439
CH ₂ <	6	-0.0269	-0.1614	-0.3045	-1.827	-0.4119	-2.4714
ACH	10	0.1105	1.105	-0.5303	-5.303	-0.4305	-4.305
AC	7	0.8446	5.9122	0.6187	4.3309	0.0084	0.0588
ACOH	1	0.5288	0.5288	1.101	1.101	6.958	6.958
CH ₂ O-	3	0.031	0.093	0.8826	2.6478	-0.1528	-0.4584
NH	2	*	*	0.0103	0.0206	2.2086	4.4172
>CO	2	-0.4343	-0.8686	0.7905	1.581	1.8147	3.6294
N(except as above)	2	1.5438	3.0876	2.578	5.156	1.1189	2.2378
Constant,C			17.3231		7.3548		7.9793
$\sum N_i C_i + C$			24.1055		10.1277		15.7018

Table S4 Second-order group approximation ($W=1$) for the prediction of 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 BNB-t4.

Second order group	Occurrences, M_j	Contributions, $D_j(\delta_d)$	$M_j D_j$ (δ_d)	Contributions, $D_j(\delta_p)$	$M_j D_j$ (δ_p)	Contributions, $D_j(\delta_h)$	$M_j D_j$ (δ_h)
AC-O-C	3	0.2568	0.7704	0.8153	2.4459	0.6092	1.8276
W			1		1		1
$W \sum M_j D_j$			0.7704		2.4459		1.8276

With the first-order and second-order group approximations (Table S3 and S4), the Hansen parameters of BNB-t4 gelator were calculated to be:

$$\delta_d = (\sum N_i C_i + C) + W \sum M_j D_j = 24.1055 + 0.7704 = 24.8759 \text{ MPa}^{1/2}$$

$$\delta_p = (\sum N_i C_i + C) + W \sum M_j D_j = 10.1277 + 2.4459 = 12.5736 \text{ MPa}^{1/2}$$

$$\delta_h = (\sum N_i C_i + C) + W \sum M_j D_j = 15.7018 + 1.8276 = 17.5294 \text{ MPa}^{1/2}$$

The Teas parameter of BNB-t4 can be calculated according to the group contribution method as follow:

$$f_d = \delta_d / (\delta_d + \delta_p + \delta_h) = 24.8759 / (24.8759 + 12.5736 + 17.5294) = 0.452$$

$$f_p = \delta_p / (\delta_d + \delta_p + \delta_h) = 12.5736 / (24.8759 + 12.5736 + 17.5294) = 0.229$$

$$f_h = \delta_h / (\delta_d + \delta_p + \delta_h) = 17.5294 / (24.8759 + 12.5736 + 17.5294) = 0.319$$

Table S5 The Hansen parameters of different single organic solvents, and states ^{a, b} of BNB-t4 in various solvents.

Solvents	$\delta_d/\text{MPa}^{1/2}$	$\delta_p/\text{MPa}^{1/2}$	$\delta_h/\text{MPa}^{1/2}$	State
DMSO	18.4	16.4	10.2	S
Methanol	15.1	12.3	22.3	S
DMF	17.4	13.7	11.3	S
Acetic acid	14.5	8.0	13.5	S
Acetone	15.5	10.4	7.0	S
Ethanol	15.8	8.8	19.4	S
THF	16.8	5.7	8.0	S
<i>n</i> -propanol	16.0	6.8	17.4	S
TCM	17.8	3.1	5.7	G
Anisole	17.8	4.1	6.7	G
Dichloromethane	18.2	6.3	6.1	G
Benzene	18.4	0.0	2.0	G
Chlorobenzene	19.0	4.3	2.0	G
Xylene	17.6	1.0	3.1	G
Toluene	18.0	1.4	2.0	G
CYH	16.8	0.0	0.2	I
Hexane	14.9	0.0	0.0	I

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

^a S: soluble; G: stable gel formed at room temperature, concentration: 4 mg/mL; I: insoluble.

^b DMSO: Dimethyl sulphoxide; DMF: Dimethyl formamide; THF: Tetrahydrofuran; TCM: Chloroform; CYH: Cyclohexane.

Table S6 The Hansen parameters ($\text{MPa}^{1/2}$) of binary solvents and the states ^a of BNB-t4 in mixed solvents.

TCM/CYH (V:V)	δ_d	δ_p	δ_h	State
100:0	17.80	3.10	5.70	G
90:10	17.70	2.79	5.15	G
80:20	17.60	2.48	4.60	G
70:30	17.50	2.17	4.05	G
60:40	17.40	1.86	3.50	G
50:50	17.30	1.55	2.95	G
40:60	17.20	1.24	2.40	G
30:70	17.10	0.93	1.85	G
20:80	17.00	0.62	1.30	Sus
10:90	16.90	0.31	0.75	Sus
0:100	16.80	0.00	0.20	I

The Hansen parameters ($\text{MPa}^{1/2}$) of binary organic solvents calculated according to $\delta = \sum \phi_i \delta_i$, (Equ. 68 of Chemical Reviews, 1975, 75, 731-753.)

^a G: stable gel formed at room temperature, concentration: 4 mg/mL; Sus: suspension; I: insoluble.

Table S7 The Teas parameters of different single organic solvents ^a.

Solvents	f_d	f_p	f_h
DMSO	0.41	0.36	0.23
THF	0.55	0.19	0.26
DMF	0.41	0.32	0.27
Acetone	0.47	0.32	0.21
Ethanol	0.36	0.20	0.44
Methanol	0.30	0.25	0.45
<i>n</i> -propanol	0.40	0.17	0.43
Acetic acid	0.40	0.22	0.38
Benzene	0.90	0.00	0.10
Toluene	0.84	0.07	0.09
Chlorobenzene	0.75	0.17	0.08
TCM	0.67	0.12	0.21
Xylene	0.81	0.05	0.14
Dichloromethane	0.60	0.21	0.19
Anisole	0.62	0.14	0.24
CYH	0.98	0.00	0.012
Hexane	1	0.00	0.00

^a DMSO: Dimethyl sulphoxide; THF: Tetrahydrofuran; DMF: Dimethyl formamide; TCM: Chloroform; CYH: Cyclohexane.

Table S8 The Teas parameters of binary organic solvents.

TCM/CYH (V/V)	f_d	f_p	f_h
100 : 0	0.67	0.12	0.21
90 : 10	0.69	0.11	0.20
80 : 20	0.71	0.10	0.19
70 : 30	0.74	0.09	0.17
60 : 40	0.76	0.08	0.15
50 : 50	0.79	0.07	0.14
40 : 60	0.83	0.06	0.11
30 : 70	0.86	0.05	0.09
20 : 80	0.90	0.03	0.07
10 : 90	0.94	0.02	0.04
0 : 100	0.99	0.00	0.01

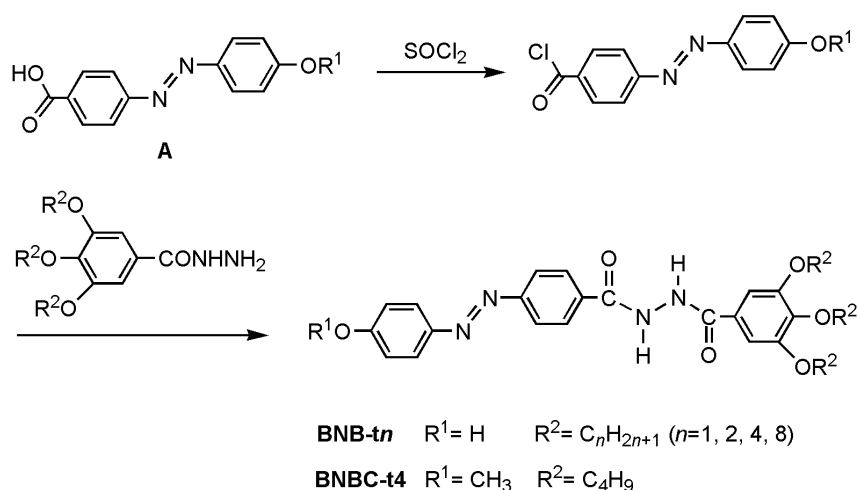
The Teas parameters were calculated according to the following equations:

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

Chemical reagent:

All chemicals were commercial and used without further purification. Ethanol (Tianjin Fuyu Fine Chemical Co., Ltd., AR, $\geq 99.7\%$), methanol (Tianjin Fuyu Fine Chemical Co., Ltd., AR, $\geq 99.5\%$), tetrahydrofuran (Tianjin Kemiou Chemical Reagent Co., Ltd, AR, $\geq 99.0\%$), thionyl chloride (Shanghai Aladdin Bio-chem. Technology Co., Ltd, AR, 99.0%), dimethyl sulphoxide (Tianjin Fuyu Fine Chemical Reagent Co., Ltd, AR, $\geq 99.0\%$), dimethyl formamide (Shanghai Aladdin Bio-chem. Technology Co., Ltd, AR, $\geq 99.9\%$), acetic acid (Shanghai Aladdin Bio-chem. Technology Co., Ltd, AR, $\geq 99.7\%$), acetone (Sinopharm Chemical Reagent Co., Ltd, AR, $\geq 99.0\%$), *n*-propanol (Tianjin Kemiou Chemical Reagent Co., Ltd, AR, $\geq 99.5\%$), chloroform (Sinopharm Chemical Reagent Co., Ltd, AR, $\geq 99.0\%$), dichloromethane (Tianjin Fuyu Fine Chemical Co., Ltd., AR, $\geq 99.5\%$), anisole (Sinopharm Chemical Reagent Co., Ltd, CP, $\geq 98.0\%$), benzene (Shanghai Aladdin Bio-chem. Technology Co., Ltd, AR, $\geq 99.5\%$), chlorobenzene (Tianjin Kemiou Chemical Reagent Co., Ltd, AR, $\geq 99.0\%$), *p*-xylene (Shanghai Aladdin Bio-chem. Technology Co., Ltd, 98%), toluene (Tianjin Fuyu Fine Chemical Co., Ltd, AR, $\geq 99.0\%$), cyclohexane (Tianjin Fuyu Fine Chemical Co., Ltd., AR, $\geq 99.5\%$), *n*-hexane (Tianjin Fuyu Fine Chemical Co., Ltd., AR, $\geq 98.0\%$).

Synthesis



Scheme S1. Synthetic routes for BNB-*tn* ($n=1, 2, 4, 8$) and BNBC-t4.

The compounds, N-(3,4,5-trialkoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl]benzohydrazide (BNB-*tn*) and N-(3,4,5-tributoxyphenyl)-N'-4-[(4-methoxyphenyl)azophenyl]benzohydrazide (BNBC-t4), were synthesized through the routes in Scheme S1. The synthetic details of BNB-t4 and BNB-t8 were reported in our previous papers [1, 2], and the synthetic

routes for BNB-t1, BNB-t2 and BNBC-t4 were similar to that of BNB-t8.

Synthesis of N-(3,4,5-trialkoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl] benzohydrazide (BNB-t1 and BNB-t2)

4-(4'-hydroxyphenyl)azobenzoic acid (A, 1.46 g, 0.006 mol) [3] and thionyl chloride (50 mL) were refluxed for 10 h. 4-(4'-hydroxyphenyl)azobenzoic acid chloride was collected after removing unreacted thionyl chloride. 4-(4'-hydroxyphenyl)azobenzoic acid chloride was dissolved in tetrahydrofuran, 3,4,5-trialkoxy-benzoyl hydrazine [4] was added slowly, and the resulting mixture was stirred for 8 h. The resulted reaction mixture was poured into an excess of ice water, and the precipitate was recrystallized from methanol and ethanol.

N-(3,4,5-trimethoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl] benzohydrazide (BNB-t1)

¹H NMR (400MHz, DMSO-*d*₆), (ppm, from TMS): 10.64 (s, 1H), 10.50 (s, 1H), 10.43(s, 1H), 8.15-8.07 (d, 2H, *J*=8.4 Hz), 7.97-7.89 (d, 2H, *J*=8.4 Hz), 7.89-7.81 (d, 2H, *J*=8.8 Hz), 7.28 (s, 2H), 7.02-6.93 (d, 2H, *J*=9.2 Hz), 3.86 (s, 6H), 3.74(s, 3H).

FT-IR (KBr, pellet, cm⁻¹): 3369, 3257, 2944, 2840, 1681, 1650, 1595, 1502, 1465, 1425, 1441, 1330, 1276, 1237, 1173, 1130, 995, 852, 745, 675.

Elemental analysis: calculated for C₂₃H₂₂N₄O₆ (%): C, 61.33; H, 4.92; N, 12.44. Found: C, 61.17; H, 5.15; N, 12.20.

Melting point of BNB-t1 powder: 233 °C.

N-(3,4,5-triethoxyphenyl)-N'-4-[(4-hydroxyphenyl)azophenyl] benzohydrazide (BNB-t2)

¹H NMR (400MHz, DMSO-*d*₆), (ppm, from TMS): 10.62 (s, 1H), 10.46 (s, 1H), 10.43 (s, 1H) 8.14-8.05 (d, 2H, *J*=8.4 Hz), 7.96-7.89 (d, 2H, *J*=8.4 Hz), 7.89-7.81 (d, 2H, *J*=8.8 Hz), 7.25 (s, 2H), 7.02-7.93 (d, 2H, *J*=8.8 Hz), 4.18-3.95 (m, 6H), 1.44-1.17 (m, 9H).

FT-IR (KBr, pellet, cm⁻¹): 3330, 3262, 2981, 2935, 2894, 1682, 1642, 1585, 1500, 1466, 1436, 1391, 1330, 1271, 1230, 1130, 1026, 897, 852, 756, 689.

Elemental analysis: calculated for C₂₆H₂₈N₄O₆ (%): C, 63.40; H, 5.73; N, 11.38. Found: C, 63.52; H, 5.61; N, 11.54.

Melting point of BNB-t2 powder: 223 °C.

Synthesis of N-(3,4,5-tributoxyphenyl)-N'-4-[(4-methoxyphenyl)azophenyl] benzohydrazide (BNBC-t4)

4-(4'-methoxyphenyl)azobenzoic acid (1.92 g, 0.0075 mol) [3] and thionyl chloride (50 mL) were refluxed for 10 h. 4-(4'-methoxyphenyl)azobenzoic acid chloride was collected after

removing unreacted thionyl chloride. 4-(4'-methoxyphenyl)azobenzoic acid chloride was dissolved in tetrahydrofuran, 3,4,5-tributoxy-benzoyl hydrazine [4] was added slowly, and the resulting mixture was stirred for 8 h. The resulted reaction mixture was poured into an excess of ice water, and the precipitate was recrystallized from methanol.

N-(3,4,5-tributoxyphenyl)-*N'*-4-[(4-methoxyphenyl)azophenyl] benzohydrazide (BNBC-t4)

¹H NMR (400MHz, DMSO-*d*₆), (ppm, from TMS): 10.64 (s, 1H), 10.46 (s, 1H), 8.17-8.08 (d, 2H, *J*=8.4 Hz), 8.00-7.91 (d, 4H, *J*=8.8 Hz), 7.25 (s, 2H), 7.20-7.15 (d, 2H, *J*=9.2 Hz), 4.10-3.85 (m, 9H), 1.80-1.58 (m, 6H), 1.55-1.40 (m, 6H), 1.00-0.84 (m, 9H).

FT-IR (KBr, pellet, cm⁻¹): 3201, 2955, 2870, 1632, 1595, 1576, 1502, 1458, 1387, 1334, 1298, 1248, 1120, 1031, 895, 850, 751, 677.

Elemental analysis: calculated for C₃₃H₄₂N₄O₆ (%): C, 67.10; H, 7.17; N, 9.48. Found: C, 67.28; H, 7.02; N, 9.54.

Melting point of BNBC-t4 powder: 174 °C.

References

1. L. Shi, X. Ran, Y. Li, Q. Li, W. Qiu, L. Guo, RSC Adv., 2015, **5**, 38283.
2. X. Ran, H. Wang, P. Zhang, B. Bai, C. Zhao, Z. Yu and M. Li, Soft Matter, 2011, **7**, 8561.
3. Liu, J.; Chiu, Y. J. Polym. Sci. Part A Polym. Chem. 2010, 48, 1142–1148.
4. Y. D. Zhang, K. G. Jespersen, M. Kempe, J. A. Kornfield, S. Barlow, B. Kippelen, S. R. Marder, Langmuir, 2003, **19**, 6534.

Supporting Video:

Video S1: BNB-t4 gel instantly repaired itself after destructed by vigorous stirring. 1 mL of BNB-t4 gel (16 mg/mL) in 50:50 TCM/CYH was prepared in a vial via the heating-cooling method. Then a stirring bar was added into the vial and the gel was stirred vigorously with a rate of 1000 rpm on a magnetic stirring apparatus. After stirring, the gel repaired itself instantly (within 1s).