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Electronic Supplementary Information (ESI) for

Estimation of organogel formation and influence of solvent viscosity and molecular size on gel properties and aggregate structures

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Ⅰ. Teas plots of eight gelators reported in literatures

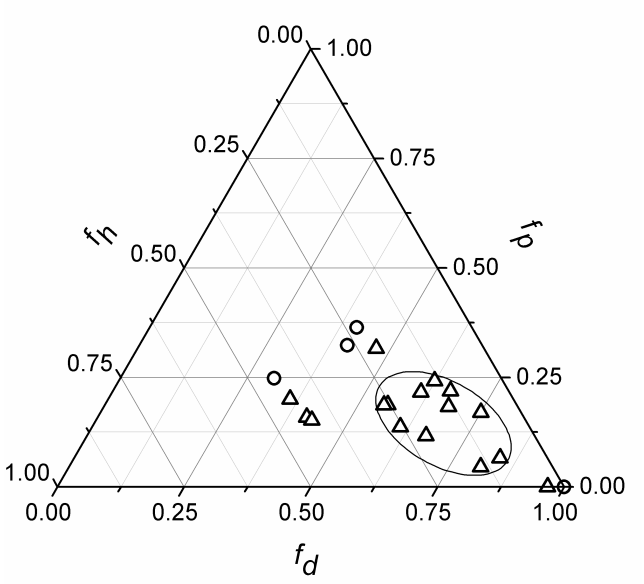

Figure S1. Teas plot of solubility parameters of the solvents in the gelation test for gelator 1 (< 40 mM, room temperature) (data taken from reference 1). Open circles: precipitate or insoluble; open triangles: gel; oval solid line: gelation domain.

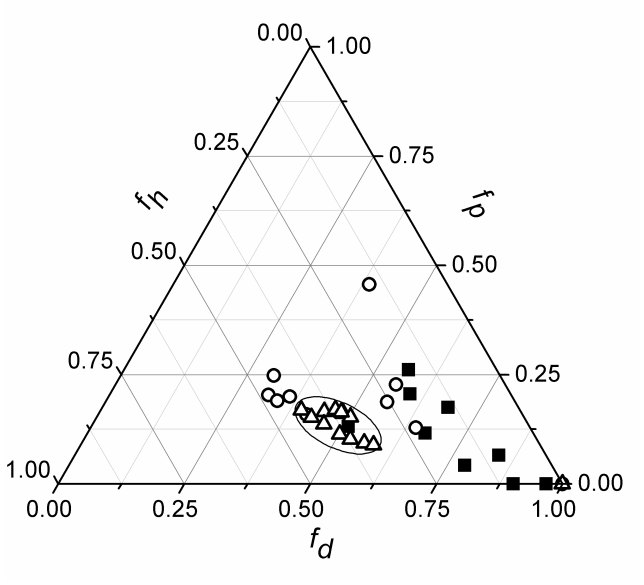

Figure S2. Teas plot of solubility parameters of the solvents in the gelation test for gelator 2 (20 g L^{-1}, room temperature) (data taken from reference 2). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; oval solid line: gelation domain.

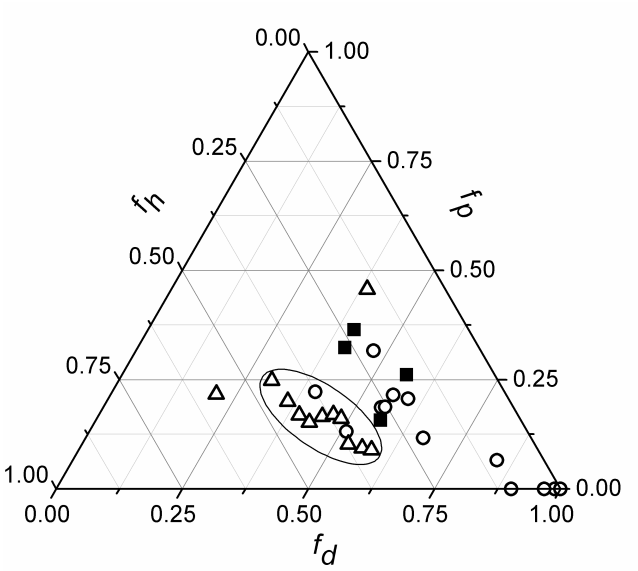

Figure S3. Teas plot of solubility parameters of the solvents in the gelation test for gelator 3 (25 g L^{-1}, room temperature) (data taken from reference 3). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; oval solid line: gelation domain.

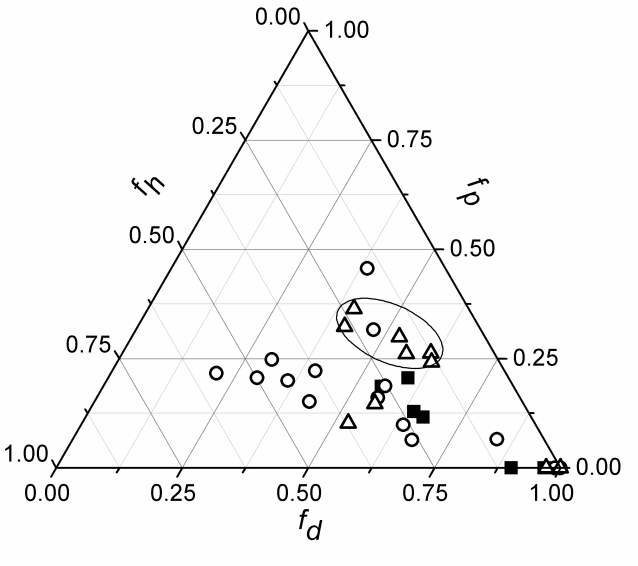

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Figure S4. Teas plot of solubility parameters of the solvents in the gelation test for gelator 4 (< 70 g L^{-1}, 2-20°C) (data taken from reference 4). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; oval solid line: gelation domain.

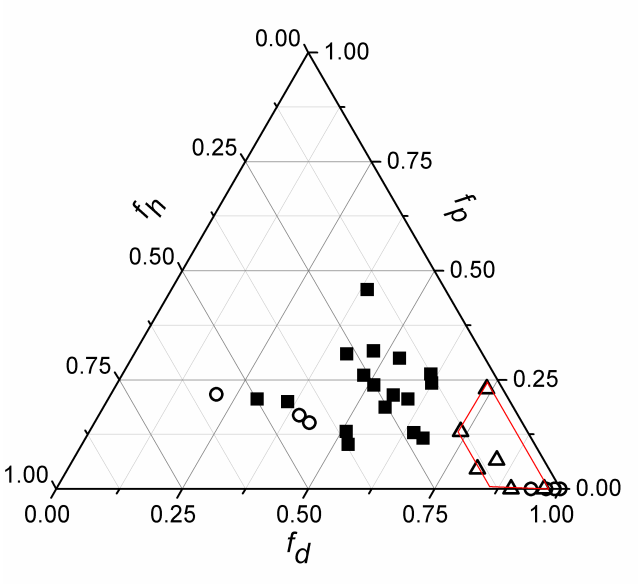

Figure S5. Teas plot of solubility parameters of the solvents in the gelation test for gelator 5 (30 g L^{-1}) (data taken from reference 5). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; red solid line: gelation domain.

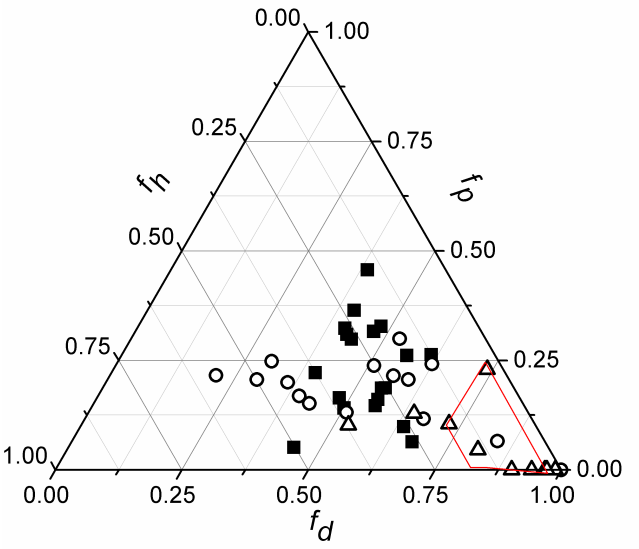

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Figure S6. Teas plot of solubility parameters of the solvents in the gelation test for gelator 6 (30 g L^{-1}, room temperature) (data taken from reference 6). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; red solid line: gelation domain.

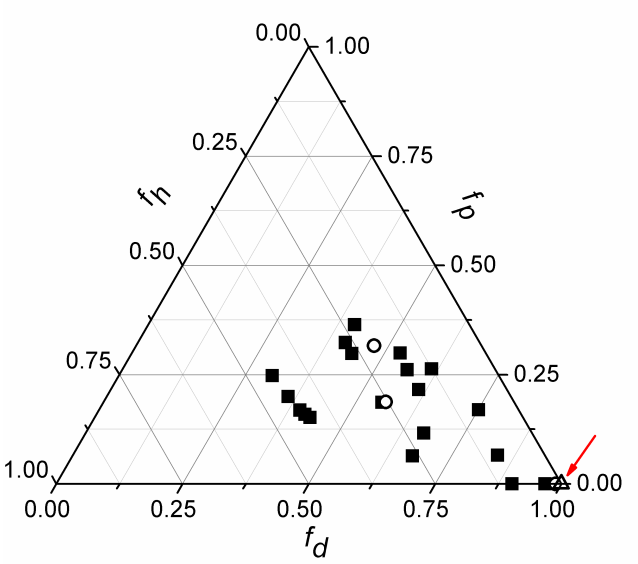

Figure S7. Teas plot of solubility parameters of the solvents in the gelation test for gelator 7 (< 16 g L^{-1}, 25°C) (data taken from reference 7). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution; red arrow: gelation domain (Overlapping to the point)

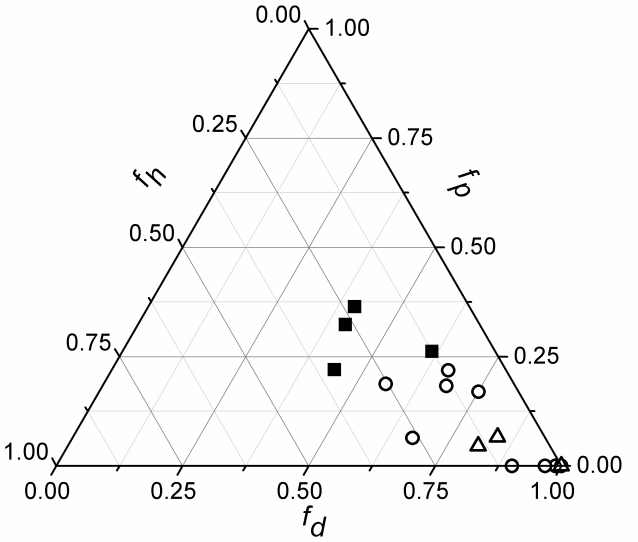

Figure S8. Teas plot of solubility parameters of the solvents in the gelation test for gelator 8 (< 50 g L^{-1}, room temperature) (data taken from reference 8). Open circles: precipitate or insoluble; open triangles: gel; filled squares: solution.

Ⅱ. Plots of correlation T_{gel} vs. δ, δ_d, δ_p and δ_h

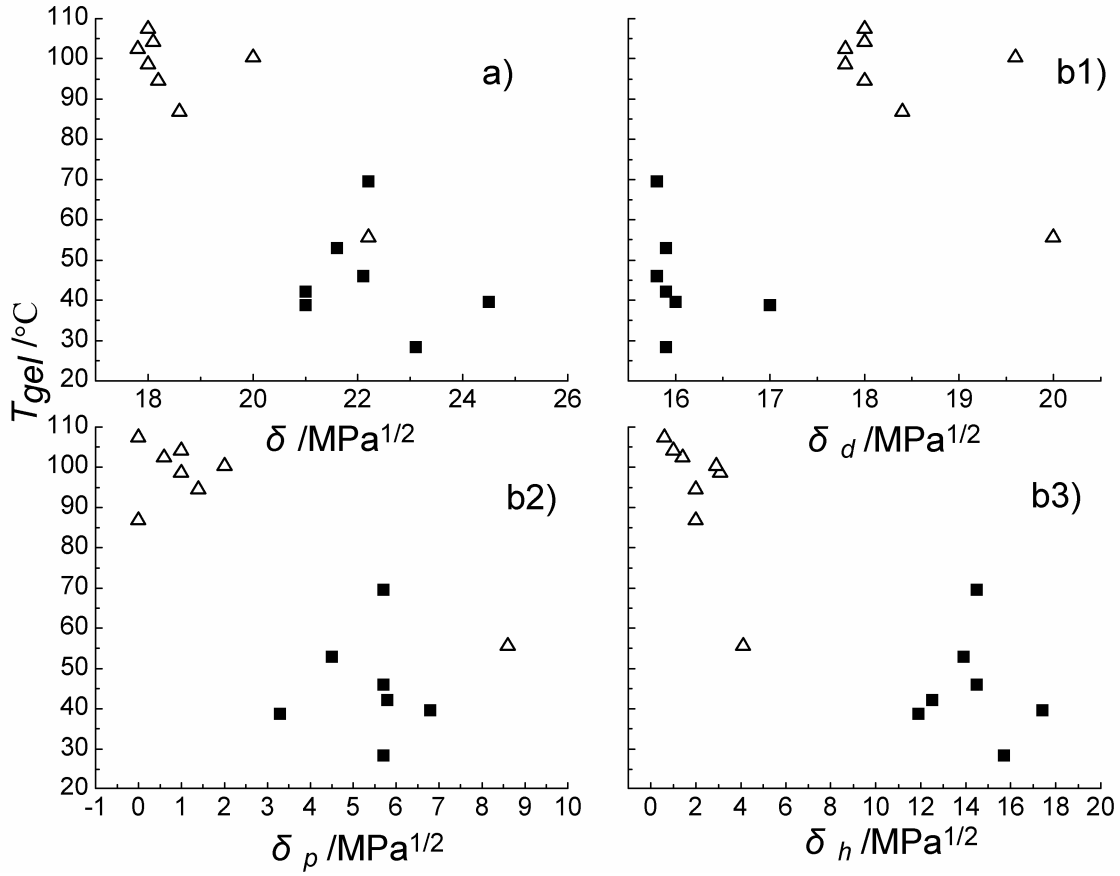

Figure S9. Effect of solvent Hildebrand solubility parameter, (a) δ, and individual Hansen solubility parameters, (b1) δ_d, (b2) δ_p, (b3) δ_h, on the thermally reversible gel-sol transition temperature, T_{gel}. Open triangles: non-polar aromatic hydrocarbons; filled squares: polar monohydric alcohols. [MPBG]= 40 g L^{-1}.

Ⅲ. X-ray diffraction patterns of the gels

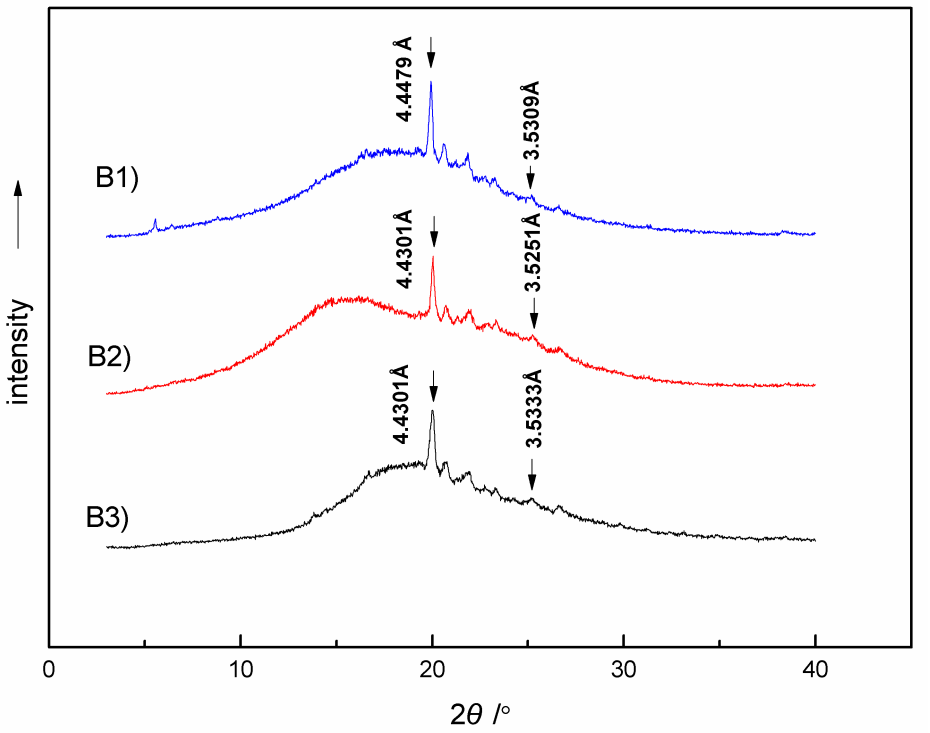

Figure S10. X-ray diffraction patterns of the gels from MPBG in (B1) ethylbenzene, (B2) 1,2,4-trimethylbenzene and (B3) toluene. The concentration of MPBG is 40 g L^{-1}

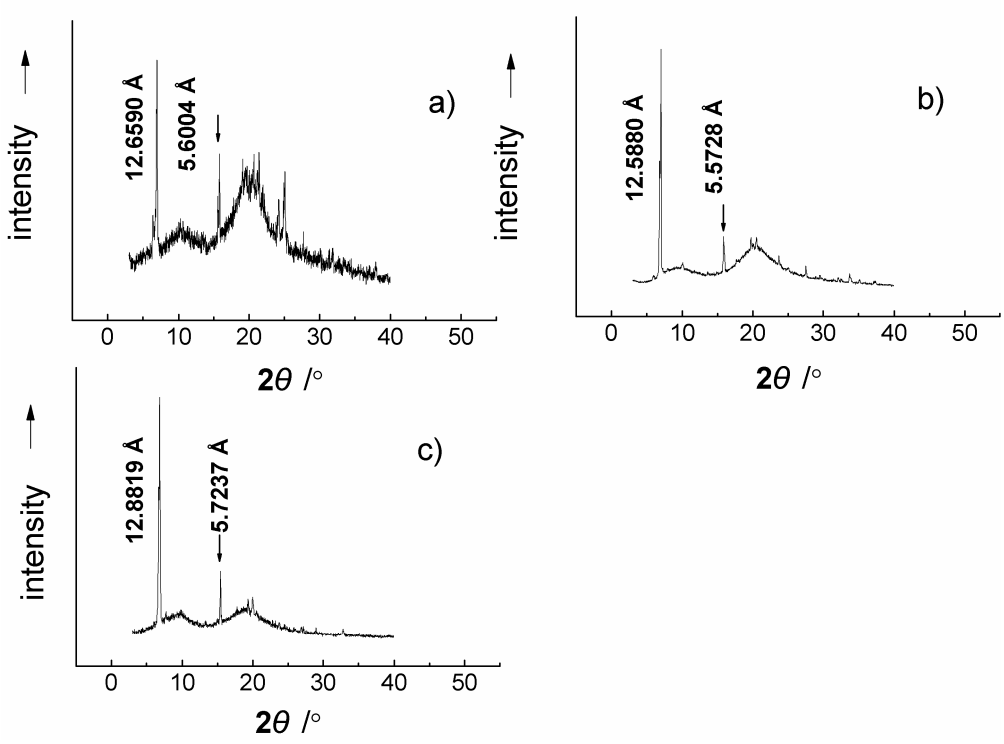

Figure S11. X-ray diffraction patterns of the gels from MPBG in (a) 2-propanol, (b) 1-propanol and (c) 2-butanol. The concentration of MPBG is 40 g L^{-1}

Ⅴ. Data of gelation test and Hansen solubility parameters

Table s1. Gelation test of MPBG in different solvents [a] and Hansen solubility parameters of solvents

solvent	State [b]	δ_d /MPa$^{1/2}$	δ_p /MPa$^{1/2}$	δ_h /MPa$^{1/2}$
1-propanol	G	16.0	6.8	17.4
1-pentanol	S[c]	15.9	4.5	13.9
1-heptanol	S[c]	-	-	-
1-octanol	S[c]	17.0	3.3	11.9
isobutanol	G	-	-	-
1-butanol	S[c]	15.9	5.7	15.7
glycol	S[c]	17.0	11.0	26.0
Isopropyl alcohol	G	15.8	5.7	14.5
2-butanol	G	15.8	5.7	14.5
1-hexanol	S[c]	15.9	5.8	12.5
cyclohexanol	G	17.4	4.1	13.5
anisole	G	17.8	4.1	6.7
ethylene glycol monomethyl ether	S	16.2	9.2	16.4
ethylene glycol monobutyl ether	S	16.0	5.1	12.3
methanol	S	15.1	12.3	22.3
ethanol	S	15.8	8.8	19.4
benzyl alcohol	S	18.4	6.3	13.7
water	I	15.5	16.0	42.3
benzene	G	18.4	0.0	2.0
toluene	G	18.0	1.4	2.0
ethylbenzene	G	17.8	0.6	1.4
mesitylene	G	18.0	0.0	0.6
nitrobenzene	G	20.0	8.6	4.1
xylene	G	-	-	-
p-xylene	G	-	-	-
o-xylene	G	17.8	1.0	3.1
2-propylbenzene	G	18.1	1.2	1.2
1,2,4-trimethylbenzene	G	18.0	1.0	1.0
diphenyl	G	19.7	1.0	2.0
1,2,3,4-tetrahydronaphthalene	G	19.6	2.0	2.9
chlorobenzene	G	19.0	4.3	2.0
bromobenzene	G	20.5	5.5	4.1
o-dichlorobenzene	G	19.1	6.3	3.3
chloroform	G	17.8	3.1	5.7
dichloromethane	G	18.2	6.3	6.1
dibromoethane	G	-	-	-
1,2-dibromoethane	G	19.6	6.8	12.1
1,2-dichloroethane	G	19.0	7.4	4.1
1-bromobutane	G	-	-	-
carbon tetrachloride	G	17.8	0.0	0.6
1,1,2,2-tetrachloroethane	S	18.8	5.1	9.4
Cyclohexane	I	16.8	0.0	0.2
1-hexane	I	14.9	0.0	0.0
Methylcyclohexane	I	16.0	0.0	0.5
1-dodecane	I	16.0	0.0	0.0
1-octane	I	15.5	0.0	0.0

[a] the gelation was tested in different pure solvents by MPBG (30 g L^{-1}) at 16℃. [b] G: gel; S: solution; I: precipitate or insoluble at solvent boiling temperature. [c] MPBG was soluble after cooling (12hr), but the gels were formed after 48hr.

Ⅵ. Data of gelation time

Table s2. Gelation behavior of MPBG in various monohydric alcohols at room temperature [a]

	t /hr		
	12	24	48
1-propanol	G	G	G
Isopropyl alcohol	G	G	G
2-butanol	G	G	G
1-butanol	S	CG	CG
1-pentanol	S	PG	G
1-hexanol	S	S	CG
1-heptanol	S	S	CG
1-octanol	S	S	CG

[a] Concentration: 30 g L^{-1}. Time: t. G: gel; PG: partial gel; CG: clear gel; S: solution.

Ⅵ. Data of T_{gel}, N_{gel}, molar volume and viscosity of solvents

Table s3. Molar volume (V) and viscosity (η) values for different solvents and the corresponding T_{gel} and N_{gel} values [a]

Solvent	T_{gel} /℃	N_{gel}	V /cc $mole^{-1}$	η [b] /mN s m^{-2}
1-propanol	39.6	275.4	-	1.4
1-pentanol	53.0	91.4	-	1.7
1-heptanol	-	80.0	-	-
1-octanol	38.7	64.6	-	4.6
isobutanol	-	218.0	-	-
1-butanol	28.4	60.7	-	2.4
Isopropyl alcohol	69.5	554.8	-	0.6
2-butanol	46.0	238.6	-	1.6
1-hexanol	42.1	79.3	-	2.8
anisole	-	78.1	-	-
benzene	86.8	337.3	89.4	-
toluene	94.5	421.6	106.8	-
ethylbenzene	102.5	795.3	-	-
mesitylene	107.5	469.2	-	-
nitrobenzene	55.6	138.6	-	-
p-xylene	-	686.8	-	-
o-xylene	98.7	475.0	121.2	-
2-propylbenzene	-	1028.3	-	-
1,2,4-trimethylbenzene	104.2	641.9	-	-
1,2,3,4-tetrahydronaphthalene	100.4	552.8	136.0	-

[a] T_{gel} values using different solvents, determined using a ball-drop method; [MPBG]= 40 g L^{-1}. N_{gel}: gelation number (determined by measuring critical gelator concentration). [b] η: viscosity at T_{gel}.

Ⅶ Characteristic XRD data of the crystals and the xerogels

Table s4. The characteristic X-ray diffraction data of the crystals and the xerogels obtained from different solvents

Crystals and solvents	d /Å			
MPBG crystals	12.01	6.02	3.90	3.48
toluene	12.10	6.03	3.91	3.49
1,2,4-trimethylbenzene	12.04	6.02	3.90	3.48
2-propanol	13.53	6.96	4.59	3.59
2-butanol	13.70	7.01	4.61	3.60
1-propanol	13.66	7.01	4.60	3.60

Ⅶ. Analytical data of MPBG

This compound was synthesized by the method reported in literature.[9] White solid (yield 20.1%). M.p. 166.5-168.2 □. ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): 7.83 (2H, d, J= 8.5 Hz, Ar), 7.43 (2H, d, J= 8.5 Hz, Ar), 5.49 (1H, s, ArCH[OR]$_2$), 4.79 (1H, d, J= 3.9 Hz, H-1), 4.28 (1H, dd, J= 9.8, 4.4 Hz, H-6), 3.91 (1H, t, J= 9.3 Hz, H-3), 3.85–3.69 (2H, m, H-5, H-6), 3.61 (1H, dd, J= 6.7, 3.3 Hz, H-2), 3.56–3.36 (4H, m, H-4, OCH_3), 2.36 (2H, br s, OH × 2). ^{13}C NMR (125 MHz, DMSO-d_6, δ ppm): 137.42, 134.09, 128.96, 128.80, 101.23, 100.61, 82.00, 73.10, 70.54, 68.86, 62.99, 55.46. Anal. Calcd. for $C_{14}H_{17}O_6Cl$: C, 53.1; H, 5.4; Found: C, 51.7; H, 5.6; $C_{14}H_{17}O_6Cl{\cdot}0.4H_2O$ requires: C, 51.9; H, 5.5%.

Ⅷ. ^{1}H and ^{13}C NMR Spectras of MPBG

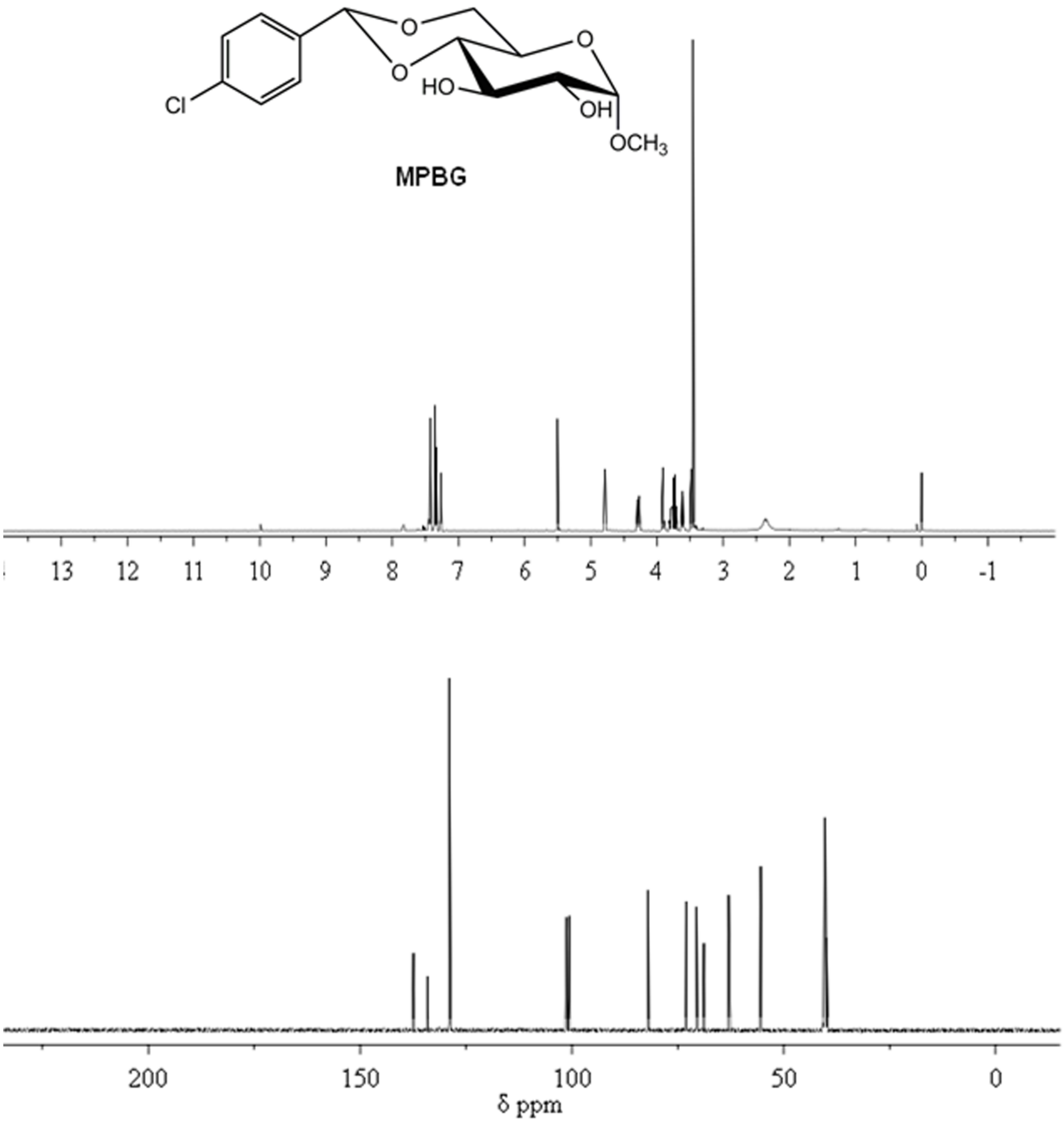

Figure S12. ^{1}H and ^{13}C NMR spectra of MPBG. ^{1}H NMR: 500MHz, $CDCl_3$; ^{13}C NMR: 125 MHz, DMSO-d_6

Ⅸ. Calculation of the Teas plot of the gelator MPBG

Table s5. Teas parameters of solvents in gelation test of MPBG

solvent	$f_d \times 10^2$	$f_p \times 10^2$	$f_h \times 10^2$
1-propanol	39.80099502	16.91542289	43.28358209
1-pentanol	46.35568513	13.11953353	40.52478134
1-heptanol	–	–	–
1-octanol	52.79503106	10.2484472	36.95652174
isobutanol	–	–	–
1-butanol	42.62734584	15.28150134	42.09115282
glycol	31.48148148	20.37037037	48.14814815
Isopropyl alcohol	43.88888889	15.83333333	40.27777778
2-butanol	43.88888889	15.83333333	40.27777778
1-hexanol	46.49122807	16.95906433	36.5497076
cyclohexanol	49.71428571	11.71428571	38.57142857
anisole	62.23776224	14.33566434	23.42657343
ethylene glycol monomethyl ether	38.75598086	22.00956938	39.23444976
ethylene glycol monobutyl ether	47.90419162	15.26946108	36.82634731
methanol	30.38229376	24.74849095	44.86921529
ethanol	35.90909091	20	44.09090909
benzyl alcohol	47.91666667	16.40625	35.67708333
water	21.00271003	21.6802168	57.31707317
benzene	90.19607843	0	9.803921569
toluene	84.11214953	6.542056075	9.345794393
ethylbenzene	89.8989899	3.03030303	7.070707071
mesitylene	96.77419355	0	3.225806452
nitrobenzene	61.16207951	26.29969419	12.5382263
xylene	–	–	–
p-xylene	–	–	–
o-xylene	81.27853881	4.566210046	14.15525114
2-propylbenzene	88.29268293	5.853658537	5.853658537
1,2,4-trimethylbenzene	90	5	5
diphenyl	86.78414097	4.405286344	8.810572687
1,2,3,4-tetrahydronaphthalene	80	8.163265306	11.83673469
chlorobenzene	75.09881423	16.99604743	7.90513834
bromobenzene	68.10631229	18.27242525	13.62126246
o-dichlorobenzene	66.55052265	21.95121951	11.49825784
chloroform	66.91729323	11.65413534	21.42857143
dichloromethane	59.47712418	20.58823529	19.93464052
dibromoethane	–	–	–
1,2-dibromoethane	50.90909091	17.66233766	31.42857143
1,2-dichloroethane	62.29508197	24.26229508	13.44262295
1-bromobutane	–	–	–
carbon tetrachloride	96.73913043	0	3.260869565
1,1,2,2-tetrachloroethane	56.45645646	15.31531532	28.22822823
Cyclohexane	98.82352941	0	1.176470588
1-hexane	100	0	0
Methylcyclohexane	96.96969697	0	3.03030303
1-dodecane	100	0	0
1-octane	100	0	0

Teas parameters are calculated according to the equation 1(see the paper). Hansen solubility parameters of the solvents (see table s1)are taken from the references.[10,11]

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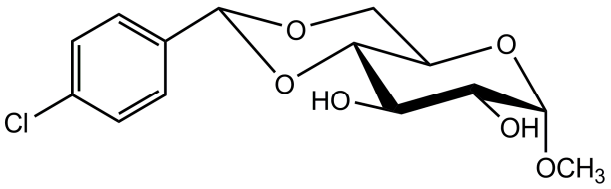
Calculations of the solubility parameters of the gelator MPBG

The Hansen parameters of MPBG are calculated according to the group-contribution method reported in refs.[12]



Scheme s1. Chemical structure of the gelator MPBG

Table S6. 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, of MPBG

First-order groups	Occurrences, N_i	Contributions, $C_i(\delta_d)$	N_iC_i (δ_d)	Contributions, $C_i(\delta_p)$	$N_iC_i(\delta_p)$	Contributions, $C_i(\delta_h)$	$N_iC_i(\delta_h)$
CH_3O	1	-0.5828	-0.5828	0.1764	0.1764	0.146	0.146
−CH<	6	0.645	3.87	0.6491	3.8946	-0.2018	-1.2108
OH	2	-0.3462	-0.6924	1.1404	2.2808	7.1908	14.3816
$-CH_2$	1	-0.0269	-0.0269	-0.3045	-0.3045	-0.4119	-0.4119
CH_2O (cyclic)	1	0.2753	0.2753	0.1994	0.1994	-0.1610	-0.1610
CHO (ethers)	2	0.8833	1.7666	1.6853	3.3706	0.447	0.894
AC	1	0.8446	0.8446	0.6187	0.6187	0.0084	0.0084
ACH	4	0.1105	0.442	-0.5303	-2.1212	-0.4305	-1.722
ACCl	1	0.8475	0.8475	-0.0339	-0.0339	-0.7840	-0.7840
Constant, C			17.3231		7.3548		7.9793
$\Sigma N_iC_i + C$			24.067		15.4357		19.1196

Table S7. 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, of MPBG

Second-order groups	Occurrences, M_j	Contributions, D_j (δ_d)	M_jD_j (δ_d)	Contributions, D_j (δ_p)	$M_jD_j(\delta_p)$	Contributions, $D_j(\delta_h)$	M_jD_j (δ_h)
>C{H or C}–C=	1	-0.2798	-0.2798	…	…	-1.1164	-1.1164
C_{cyclic}–OH	2	-0.0876	-0.1752	-3.5220	-7.044	0.5914	1.1828
W			1		1		1
W ΣM_jD_j			-0.455		-7.044		0.0664

δ_d= 24.067-0.455=23.612 $MPa^{1/2}$
δ_p= 15.4357-7.044=8.3917 $MPa^{1/2}$
δ_h= 19.1196+0.0664=19.186 $MPa^{1/2}$

The Teas parameters of MPBG can be calculated as follows:

f_d=23.612/51.1897=0.4613

f_p=8.3917/51.1897=0.1639

f_h=19.186/51.1897=0.3748

References

1 J. W. Liu, J. T. Ma and C. F. Chen, *Tetrahedron*, 2011, 67, 85-91.
2 R. Mukkamala and R. G. Weiss, *Langmuir*, 1996, 12, 1474-1482.
3 N. Yan, G. He, H. Zhang, L. Ding and Y. Fang, *Langmuir*, 2010, 26, 5909-5917.
4 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, 116, 6664-6676.
5 O. Gronwald and S. Shinkai, *Chem. Eur. J.*, 2001, 7, 4329-4334.
6 N. Amanokura, K. Yoza, H. Shinmori, S. Shinkai and D. Reinhoudt, *J. Chem. Soc., Perkin Trans.* 2, 1998, 2585-2591.
7 K. Hanabusa, H. Kobayashi, M. Suzuki, M. Kimura and H. Shirai, *Colloid Polym. Sci.*, 1998, 276, 252-259.
8 D. R. Trivedi, A. Ballabh, P. Dastidar and B. Ganguly, *Chem. Eur. J.*, 2004, 10, 5311-5322.
9 R. L. Colbran, R. D. Guthrie and Margaret A. Parsons, *J. Chem. Soc.*, 1960, 3532-3539.
10 A. F. M. Barton, *Chemical Reviews*, 1975, 75, 731-753.
11 C. M. Hansen, *Hansen Solubility Parameters A User's Handbook*, ed. C. Hansen, Taylor & Francis Group-CRC, Boca Raton, 2nd edn., 2007.
12 Emmanuel Stefanis · Costas Panayiotou, *Int J Thermophys*, 2008, 29, 568-585.