Supporting Information

Terminal Effects on Gelation by Low Molecular Weight Chiral Gelators

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1) Reagents: Tetrahydrofuran (THF) was distilled in the presence of sodium salt of benzophenone ketyl radical anion and stored under nitrogen atmosphere. Triethylamine was distilled in the presence of CaH_2. Other reagents were used as received without further purification.

2) Synthesis of C*7*Br: 7-Bromoheptanoic acid (Tokyo Chemical Industry, Japan) and oxalyl chloride (Wako, Japan) reacted at 1:4 ratio in benzene at 60 ° C for 6 hrs. The solvent and excess oxalyl chloride were evaporated in vacuum and the residue (the corresponding acid chloride) was used as it was. THF solution containing trans(1*R*, 2*R*)- or trans(1*S*, 2*S*)-1,2-diaminocyclohexane (0.57 g, 5.0 mmol, Wako, Japan), triethylamine (2 mL, Wako, Japan) and 7-bromoheptanoyl chloride (2.0 g, 10 mmol) was refluxed for 6 hours under nitrogen atmosphere. After filtering out triethylammonium chloride from the reactant solution, the filtrate was evaporated to dryness. The residue was washed with an aqueous HCl solution (1 M) several times and thereafter dried in air. The compounds were identified by ^{1}H NMR and mass spectra. Other gelator molecules (CnBr's: n = 5 ~ 12) were synthesized in the similar way by using the following reagents:

C*5*Br: 5-brompentanoic acid (Aldrich):

C*6*Br: 6-bromhexanoic acid (Aldrich)

C*7*Br: 7-bromoheptanoic acid (Tokyo Chemical Industry, Japan)

C*8*Br: 8-bromooctanoic acid (Aldrich)

C*9*Br: 9-bromononanoic acid (Tokyo Chemical Industry Co, Ltd., Japan)

C*10*Br: 10-bromodecanoic acid (Aldrich)

C*11*Br:11-bromoundecanoic acid (Aldrich)

C*12*Br: 12-bromododecamoic acid (Aldrich)

3) ^{1}H NMR data of synthesized gelators: ^{1}H NMR spectra were recorded on a JEOL ESX-500 (500 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on the instruments operating at 125.8 MHz with $CDCl_3$ as the solvent and internal standard. Mass spectra (ESI) were obtained on a Thermo Exactive（Thermo Scientific）.

***RR*-C*5*Br** (yield 83%) and ***SS*-C*5*Br** (yield 81%): ^{1}H NMR δ 5.95 (m, 2H), 3.65 (m, 2H), 3.40 (t, J = 6.5 Hz, 4H), 2.17 (m, 4H), 2.03 (d, J = 13.0 Hz, 2H), 1.87 (m, 4H), 1.75 (m, 6H), 1.32 (m, 2H), 1.23 (m, 2H); ^{13}C NMR δ 172.9, 53.7, 35.7, 33.1, 32.4, 32.1, 24.6, 24.2; HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{28}O_2N_2Br_2Na$ [M+Na] 461.0410, found 461.0402.

***RR*-C*6*Br** (yield 81%) and ***SS*-C*6*Br** (yield 74%): ^{1}H NMR δ 5.99 (m, 2H), 3.65 (m, 2H), 3.40 (t, J = 6.5 Hz, 4H), 2.12 (m, 4H), 1.96 (m, 2H), 1.86 (m, 4H), 1.75 (m, 2H), 1.60 (m, 4H), 1.45 (m, 4H), 1.28 (m, 4H); ^{13}C NMR δ 173.8, 53.1, 36.4, 33.5, 32.3, 30.9, 27.6, 24.8, 24.7; HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{32}O_2N_2Br_2Na$ [M+Na] 489.0723, found 489.0724.

***RR*-C*7*Br** (yield 89%) and ***SS*-C*7*Br** (yield 88%): ^{1}H NMR δ 6.56 (m, 2H), 3.61 (m, 2H), 3.41 (t, J = 6.5 Hz, 4H), 2.14 (m, 4H), 2.02 (d, J = 13.0 Hz, 2H), 1.85 (m, 4H), 1.75 (d, J = 8.0 Hz, 2H), 1.59 (m, 4H), 1.44 (m, 4H), 1.33 (m, 6H), 1.24 (m, 2H); ^{13}C NMR δ 173.6, 53.7, 36.7, 33.8, 32.5, 32.4, 28.3, 27.8, 25.5, 24.7; HRMS (ESI$^+$) *m/z* calcd for $C_{20}H_{36}O_2N_2Br_2Na$ [M+Na] 517.1036, found 517.1034.

***RR*-C*8*Br** (yield 88%) and ***SS*-C*8*Br** (yield 58%): ^{1}H NMR δ 5.90 (m, 2H), 3.65 (m, 2H), 3.40 (t, J = 6.5 Hz, 4H), 2.13 (m, 4H), 2.02 (d, J = 13.0 Hz, 2H), 1.84 (m, 4H), 1.75 (d, J = 8.0 Hz, 2H), 1.58 (m, 4H), 1.42 (m, 4H), 1.32 (m, 10H), 1.24 (m, 2H); ^{13}C NMR δ 173.7, 53.7, 36.8, 33.9, 32.7, 32.4, 29.1, 28.5, 28.0, 25.6, 24.7; HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{40}O_2N_2Br_2Na$ [M+Na] 545.1349, found 545.1351.

***RR*-C*9*Br** (yield 82%) and ***SS*-C*9*Br** (yield 84%): ^{1}H NMR δ 5.93 (m, 2H), 3.65 (m, 2H), 3.41 (t, J = 6.5 Hz, 4H), 2.11 (m, 4H), 2.02 (d, J = 13.0 Hz, 2H), 1.85 (m, 4H), 1.75 (d, J = 8.0 Hz, 2H), 1.57 (m, 4H), 1.42 (m, 4H), 1.30 (m, 14H), 1.24 (m, 2H); ^{13}C NMR δ 173.8, 53.6, 36.9, 34.0, 32.7, 32.4, 30.9, 29.1, 28.6, 28.1, 25.7, 24.7; HRMS (ESI$^+$) *m/z* calcd for $C_{24}H_{44}O_2N_2Br_2Na$ [M+Na] 573.1662, found 573.1657.

***RR*-C*10*Br** (yield 83%) and ***SS*-C*10*Br** (yield 84%): ^{1}H NMR δ 5.89 (m, 2H), 3.65 (m, 2H), 3.41 (t, J = 6.5 Hz, 4H), 2.12 (m, 4H), 2.02 (d, J = 13.0 Hz, 2H), 1.85 (m, 4H), 1.75 (d, J = 8.0 Hz, 2H), 1.57 (m, 4H), 1.41 (m, 4H), 1.28 (m, 18H), 1.22 (m, 2H); ^{13}C NMR δ 173.8, 53.6, 36.9, 34.0, 32.8, 32.4, 29.27, 29.25, 29.2, 28.7, 28.1, 25.7, 24.7; HRMS (ESI^{+}) *m/z* calcd for $C_{26}H_{48}O_2N_2Br_2Na$ [M+Na] 601.1975, found 601.1947.

***RR*-C*11*Br** (yield 84%) and ***SS*-C*11*Br** (yield 75%): ^{1}H NMR δ 6.08 (m, 2H), 3.65 (m, 2H), 3.41 (t, J = 6.5 Hz, 4H), 2.11 (m, 4H), 2.00 (d, J = 13.0 Hz, 2H), 1.85 (m, 4H), 1.75 (d, J = 8.0 Hz, 2H), 1.56 (m, 4H), 1.41 (m, 4H), 1.27 (m, 22H), 1.20 (m, 2H); ^{13}C NMR δ 174.0, 53.4, 36.9, 34.0, 32.8, 32.4, 29.4, 29.34, 29.28, 29.22, 28.7, 28.1, 25.8, 24.7; HRMS (ESI^{+}) *m/z* calcd for $C_{28}H_{52}O_2N_2Br_2Na$ [M+Na] 629.2289, found 629.2277.

***RR*-C*12*Br** (yield 90%) and ***SS*-C*12*Br** (yield 88%): ^{1}H NMR δ 6.16 (br, 2H), 3.64 (m, 2H), 3.41 (t, J = 6.5 Hz, 4H), 2.11 (m, 4H), 1.99 (d, J = 13.0 Hz, 2H), 1.85 (m, 4H), 1.74 (d, J = 8.0 Hz, 2H), 1.56 (m, 4H), 1.42 (m, 4H), 1.26 (m, 26H), 1.21 (m, 2H); ^{13}C NMR δ 174.0, 53.4, 36.9, 34.0, 32.8, 32.4, 29.5, 49.40, 29.38, 29.3, 29.2, 28.7, 28.1, 25.8, 24.7; HRMS (ESI^{+}) *m/z* calcd for $C_{30}H_{56}O_2N_2Br_2Na$ [M+Na] 657.2601, found 657.2615.

4) **Melting temperature of gelators:** The melting point of the synthesized compounds was obtained from DSC measurements. The results are given in the table below.

Table S1. Melting temperature of enantiomeric gelators

Gelators (*RR*-CnBr)	Temperature (°C)
C*5*Br	210
C*6*Br	188
C*7*Br	180
C*8*Br	169
C*9*Br	166
C*10*Br	168
C*11*Br	166
C*12*Br	168

5) ORD of gelators: The optical rotatory dispersion (ORD) of the synthesized gelators was measured for their CH_3OH solutions. The results are given in the table below.

Table S2. Specific ORD values of ***RR***- or ***SS***-C***n***Br

Gelator	Conc. $molL^{-1}$	$[\alpha]_D$ $deg/(molL^{-1}cm)$ 589 nm	Gelator	$[\alpha]_D$ $deg/(molL^{-1}cm)$ 589 nm
***RR*-C*6*Br**	0.0020	43.4	***SS*-C*6*Br**	-33.4
***RR*-C*7*Br**	0.0020	36.3	***SS*-C*7*Br**	-37.5
***RR*-C*8*Br**	0.0020	33.4	***SS*-C*8*Br**	-36.8
***RR*-C*9*Br**	0.0020	35.5	***SS*-C*9*Br**	-29.0
***RR*-C*10*Br**	0.0020	40.4	***SS*-C*10*Br**	-35.7
***RR*-C*11*Br**	0.0020	28.9	***SS*-C*11*Br**	-28.4
***RR*-C*12*Br**	0.0020	37.1	***SS*-C*12*Br**	-32.8

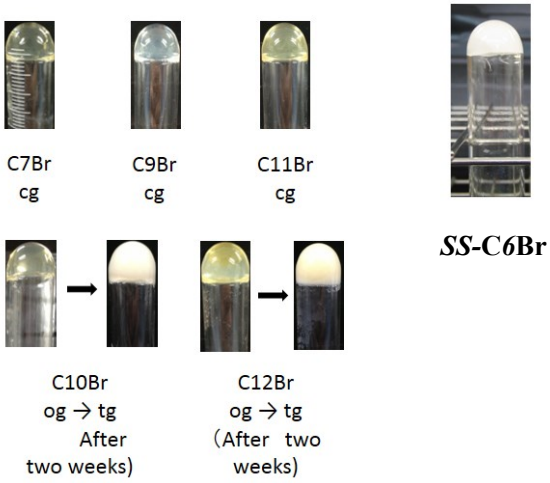
6) **The critical gelation concentrations of gelators:** The critical gelation concentration was determined for the gels of various solvents formed by enantiomeric *RR*- and *SS*-**C*n*Br** at room temperature.

Table S3 CGC of *RR*- and *SS*-CnBr

solvent	C5Br	C6Br	C7Br	C8Br	C9Br	C10Br	C11Br	C12Br	C11H
benzene	tg(0.016)	tg(0.028)	cg(0.058)	p	cg(0.15)	og(0.10)	cg(0.14)	og(0.14)	cg(0.0108)
toluene	tg(0.016)	tg(0.028)	cg(0.035)	p	cg(0.11)	og(0.085)	cg(0.10)	og(0.14)	cg(0.0086)
o-xylene	tg(0.021)	tg(0.028)	cg(0.026)	p	cg(0.051)	og(0.065)	cg(0.051)	og(0.049)	cg(0.0067)
m-xylene	tg(0.022)	tg(0.021)	cg(0.025)	p	cg(0.051)	og(0.068)	cg(0.050)	og(0.040)	cg(0.0059)
p-xylene	tg(0.014)	tg(0.020)	cg(0.021)	p	cg(0.050)	og(0.068)	cg(0.051)	og(0.046)	cg(0.0057)
mesitylene	tg(0.008)	tg(0.016)	cg(0.019)	p	cg(0.042)	og(0.068)	cg(0.035)	og(0.046)	cg(0.0067)

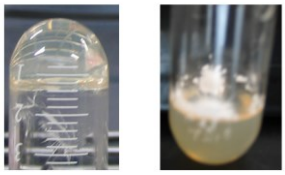
※（mol/L）	
cg	clear gel
og	opaque gel
tg	turbid gel
p	precipitate

7) The photographic images of gels



***SS*-C*6*Br**

(a) The photographs of gels taken two weeks after preparation (solvent: benzene) ((left (upper)) ***RR*-CnBr,** n=7,9,11, (left (lower)) n=10 and 12**,** (right) ***SS*-C*6*Br**)



(b) The photographs of the gels of ***RR*-C*7*Br** taken ten months after the preparation (solvent: benzene): the concentration was (left) 0.15 M and 0.30 M (right). In the right sample, a white solid appeared around the edge region.

8) The dependence of sol-gel transition temperature on the concentration of *RR*-C*7*Br for various solvents: The temperature of sol-gel transition was determined for various gels formed by ***RR*-C*7*Br** as a function of the gelator concentration.

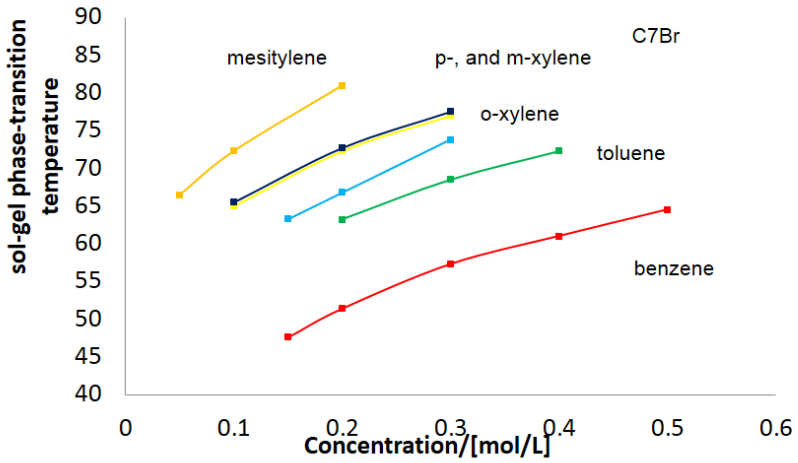


Fig. S1. The dependence of sol-gel transition temperature on the concentration of ***RR*-C*7*Br**.

9) The SEM images of dried benzene gels: The SEM measurements were performed on the freeze-dried samples of benzene gels.

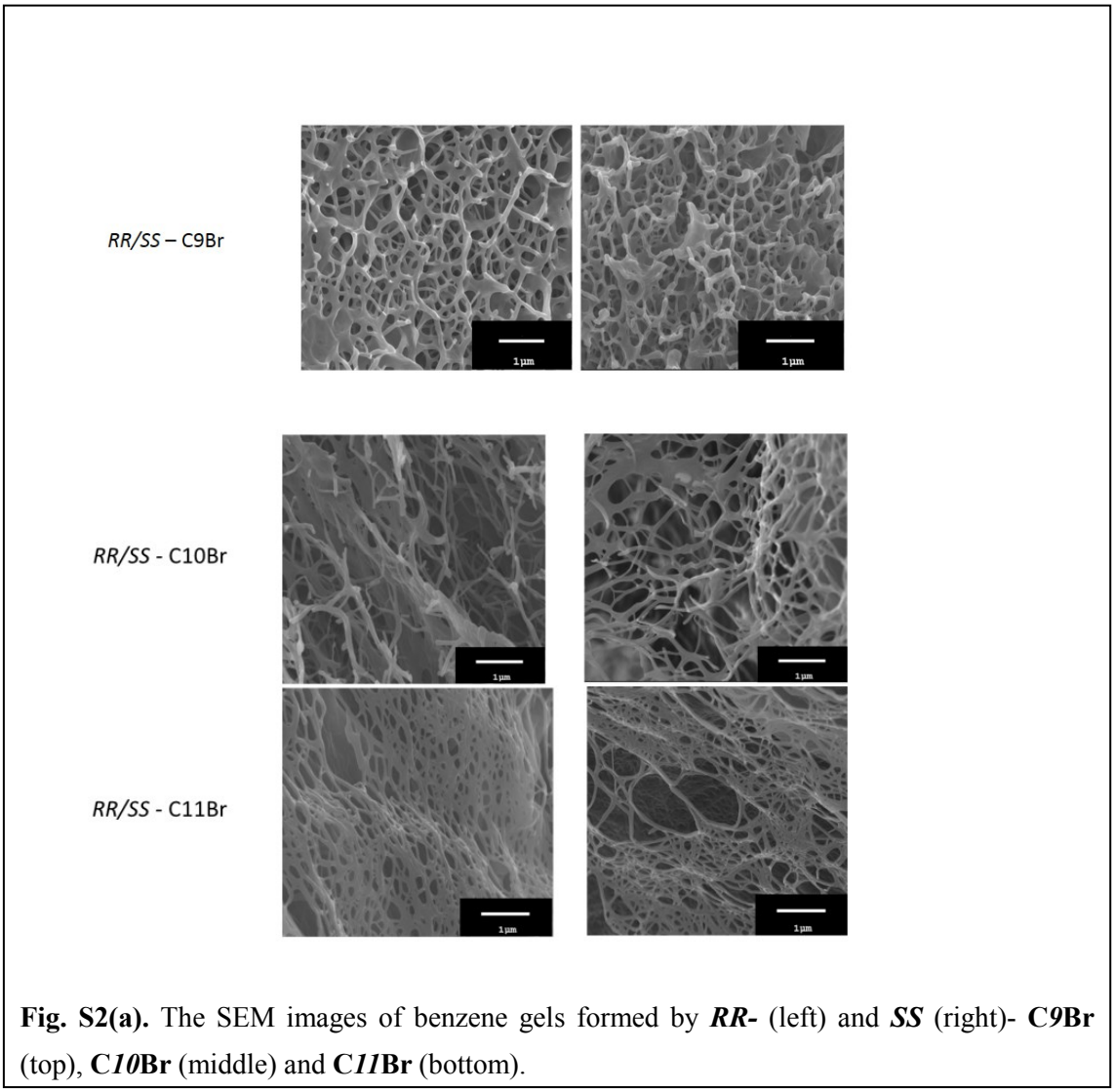


Fig. S2(a). The SEM images of benzene gels formed by ***RR-*** (left) and ***SS*** (right)- **C*9*Br** (top), **C*10*Br** (middle) and **C*11*Br** (bottom).

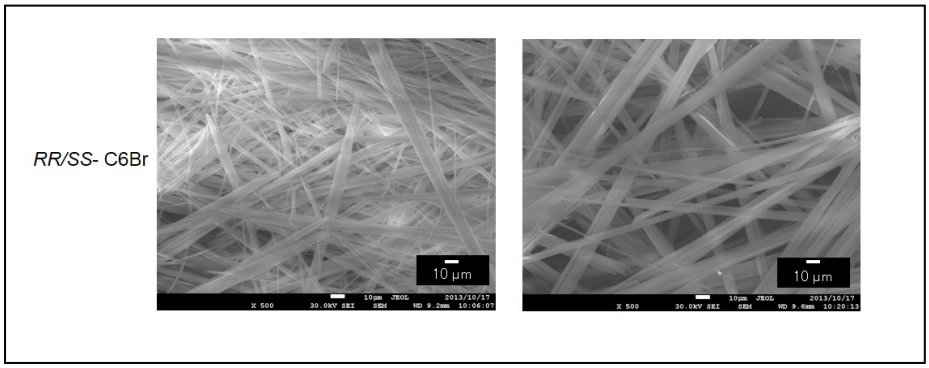


Fig. S2(b). The SEM images of benzene gels formed by ***RR-*** (left) and ***SS*** (right)- **C*6*Br**

10) The XRD measurements of toluene gels: The XRD measurements were performed on the samples of toluene gels.

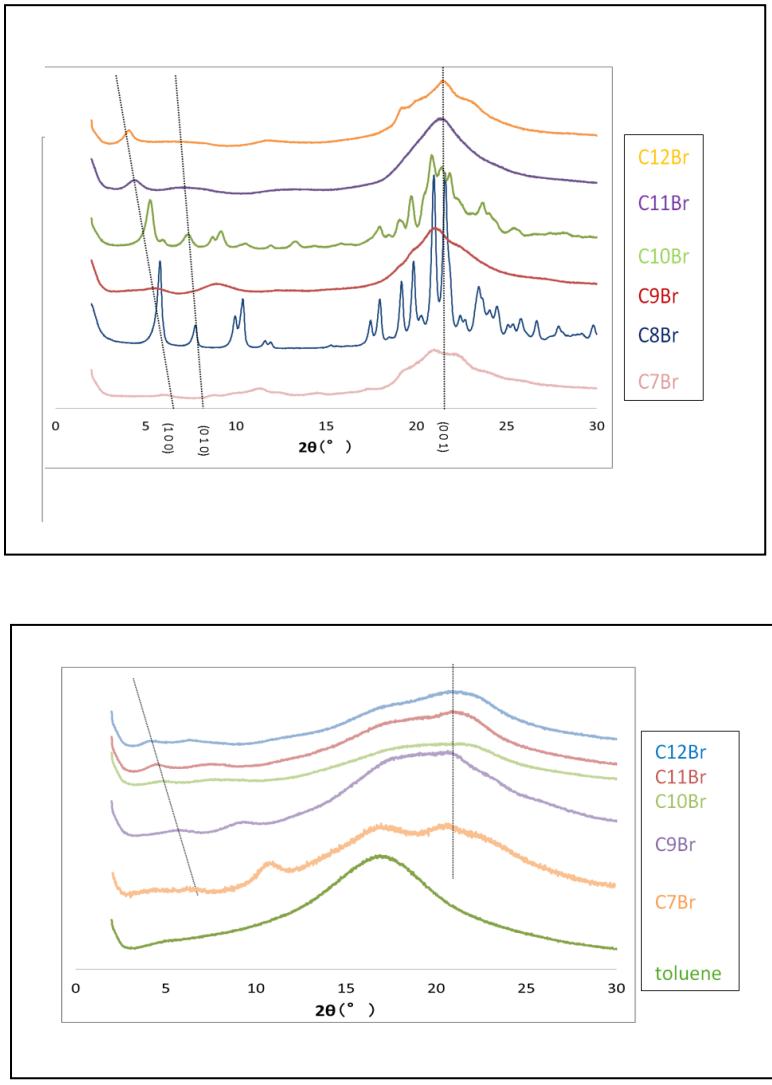
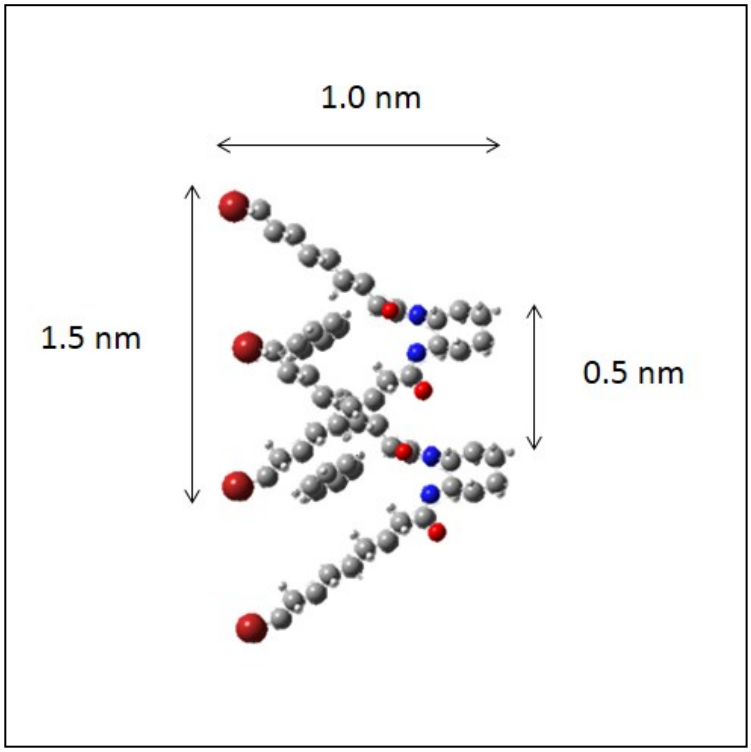


Fig. S3. The XRD patterns of powder (upper) and xerogel (lower) samples prepared from toluene gels

11) Molecular models of gels: The molecular model for the aggregation of gelators was constructed on the basis of the VCD results as shown below: (keys: Br (large dark red), O (small red), N (blue), H (small white) and C (grey)).



12) Vibrational circular dichroism of a turbid gel in case of C*6*Br

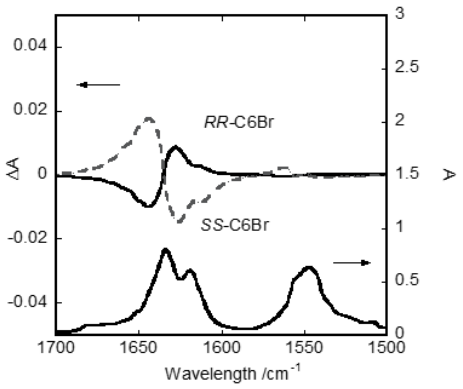


Fig. S4. The observed IR (lower) and VCD (upper) spectra of the turbid C_6D_6 gels of ***RR*-C*6*Br** (black solid line) and ***SS*- -C*6*Br** (grey dotted line), respectively.

13) Crystallographic data from single crystal X-ray analyses

Table S4. Crystallographic data

Compound reference	*SS*-C6Br	*SS*-C8Br
Chemical formula	C18H32Br2N2O2	C22H40Br2N2O2
Formula Mass	468.27	524.38
Crystal system	Orthorhombic	Orthorhombic
a/Å	4.8656(8)	4.8466(7)
b/Å	16.426(3)	17.841(3)
c/Å	25.783(4)	28.081(4)
α/°	90.00	90.00
ß/°	90.00	90.00
γ/°	90.00	90.00
Unit cell volume/Å^3	2060.6(6)	2428.1(6)
Temperature/K	296(2)	296(2)
Space group	*P*21 21 21	*P*21 21 21
No. of formula units per unit cell, Z		4 4
Radiation type	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	3.946	3.358
No. of reflections measured	10964	15510
No. of independent reflections	3639	5612
R_{int}	0.0368	0.0417
Final R_1 values ($I > 2\sigma(I)$)	0.0264	0.0404
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.0499	0.0787
Final R_1 values (all data)	0.0322	0.0552
Final w$R(F^2)$ values (all data)	0.0513	0.0824
Goodness of fit on F^2	1.066	1.085
Flack parameter		
Rogers parameter		
CCDC number	946263	946264