

Supporting information

Critical Effects of Alkyl Chain Length on Fibril Structures in Benzene-*trans*(*RR*)- or (*SS*)-*N, N'*-Alkanoyl-1, 2-diaminocyclohexane Gels

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

2) Synthesis of C_6 : A THF solution containing trans (1*R*, 2*R*) -or (1*S*, 2*S*)-1,2-diaminocyclohexane (0.318 g, 2.78 mmol, Wako, Japan), *n*-hexanoylchloride (0.5 mL, 12.3 mmol, Kanto Kagaku, Japan) and triethylamine (1.3 mL, 9.35 mmol, Wako, Japan) 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 ^1H NMR and mass spectra. Other gelators ($\text{C}_7 \sim \text{C}_{10}$) were synthesized in the similar way by using the following reagents:

- C_7 : *n*-heptanoyl chloride (1.0 mL, 6.46 mmol, Aldrich)
- C_8 : *n*-octanoyl chloride (1.0 mL, 5.86 mmol, Tokyo Kasei, Ltd., Japan)
- C_9 : *n*-nonanoyl chloride (1.0 mL, 7.77 mmol, Kanto Kagaku, Ltd., Japan)
- C_{10} : *n*-decanoyl chloride (1.2 mL, 6.15 mmol, Wako, Ltd., Japan)
- C_{12} : *n*-Lauroyl chloride (1.3 mL, 5.62 mmol, Kanto Kagaku, Ltd., Japan)

^1H NMR data of synthesized C_n : The ^1H NMR spectra (JNM-AL400, JEOL, Japan, 400 MHz for ^1H) were measured on the CDCl_3 solutions at room temperature (25 °C).

The chemical shift data and an example of the spectra are given below:

***SS*- C_6 :**(yield 65%)

(400 MHz, CDCl_3) δ 0.88 (*t*, $J = 7.0$ Hz, 6H), 1.28 (*m*, 12H) 1.56 (*m*, 4H) 1.73 (*m*, 2H), 2.01 (*d*, $J = 12.7$ Hz, 2H) 2.13 (*m*, 4H), 3.64 (*m*, 2H), 5.90 (*br*, 2H).

Elemental analyses (Microcoda, JN10T; J-Science Lab. Co., Japan): calcd for $\text{C}_{18}\text{O}_2\text{N}_2\text{H}_{34}$: C (69.63%); H (11.04%); N (9.02%); O(10.31%); found: C (69.49%); H (11.05%); N (8.97%)

Mass spectrum: $m/z(1+) = \text{calc.}310.47$; found 311. (JMS-MS700V, JMOL, co. Japan)

***RR*- C_6 :** (yield 60%)

(400 MHz, CDCl_3) δ 0.88 (*t*, $J = 7.0$ Hz, 6H), 1.28 (*m*, 12H), 1.54 (*m*, 4H), 1.74 (*m*, 2H), 2.01 (*d*, $J = 12.9$ Hz, 2H), 2.12 (*m*, 4H), 3.64 (*m*, 2H), 5.90 (*br*, 2H).

Elemental analyses: calcd for $\text{C}_{18}\text{O}_2\text{N}_2\text{H}_{34}$: C (69.63%); H (11.04%); N (9.02%);

O(10.31%); found: C (69.45%); H (10.92%); N (8.94%)

Mass spectrum: $m/z(1+) = \text{calc.}310.47$; found 311.

SS-C₇:(yield 90%)

(400 MHz, CDCl₃) δ 0.85 (*t*, $J = 6.7$ Hz, 6H), 1.27 (*m*, 16H), 1.57 (*m*, 4H), 1.72 (*m*, 2H), 2.01 (*d*, $J = 12.5$ Hz, 2H), 2.10 (*m*, 4H), 3.65 (*m*, 2H), 5.91 (*br*, 2H).

Elemental analyses: calcd for C₂₀O₂N₂H₃₈: C (70.96%); H (11.31%); N (8.28%); O (9.45%); found: C (70.68%); H (11.4%); N (8.09%).

Mass spectrum: $m/z(1+) = \text{calc.}338.5$; found 339.

RR-C₇:(yield 60%)

(400 MHz, CDCl₃) δ 0.87 (*t*, $J = 6.8$ Hz, 6H), 1.27 (*m*, 16H), 1.57 (*m*, 4H), 1.74 (*m*, 2H), 2.01 (*d*, $J = 12.9$ Hz, 2H), 2.12 (*m*, 4H), 3.65 (*m*, 2H), 5.91 (*br*, 2H),

Elemental analyses: calcd for C₂₀O₂N₂H₃₈: C (70.96%); H (11.31%); N (8.28%); O (9.45%); found: C (71.02%); H (11.05%); N (8.36%).

Mass spectrum: $m/z(1+) = \text{calc.}338.5$; found 339.

SS-C₈:(yield 74%)

(400 MHz, CDCl₃) δ 0.87 (*t*, $J = 6.9$ Hz, 6H), 1.27 (*m*, 20H), 1.56 (*m*, 4H), 1.73 (*m*, 2H), 2.01 (*d*, $J = 12.7$ Hz, 2H), 2.15 (*m*, 4H), 3.65 (*m*, 2H), 5.97 (*br*, 2H).

Elemental analyses: calcd for C₂₂O₂N₂H₄₂: C (72.08%); H (11.55%); N (7.64%); O(8.73%); found: C (71.94%); H (11.47%); N (7.49%).

Mass spectrum: $m/z(1+) = \text{calc.} 366.58$; found 367.

RR-C₈:(yield 84%)

(400 MHz, CDCl₃) δ 0.87 (*t*, $J = 6.8$ Hz, 6H), 1.27 (*m*, 20H), 1.57 (*m*, 4H), 1.73 (*m*, 2H), 2.01 (*d*, $J = 12.9$ Hz, 2H), 2.12 (*m*, 4H), 3.65 (*m*, 2H), 5.93 (*br*, 2H).

Elemental analyses: calcd for C₂₂O₂N₂H₄₂: C (72.08%); H (11.55%); N (7.64%); O(8.73%); found: C (71.97%); H (11.57%); N (7.57%).

Mass spectrum: $m/z(1+) = \text{calc.} 366.58$; found 367.

SS-C₉:(yield 82%)

(400 MHz, CDCl₃) δ 0.87 (*t*, *J* = 6.8 Hz, 6H), 1.26 (*m*, 24H), 1.56 (*m*, 4H), 1.73 (*m*, 2H), 2.02 (*d*, *J* = 13.0 Hz, 2H), 2.11 (*m*, 4H), 3.65 (*m*, 2H), 5.96 (*br*, 2H).

Elemental analyses: calcd for C₂₄O₂N₂H₄₆: C (73.04%); H (11.75%); N (7.10%); O(8.11%) found: C (72.77%); H (11.46%); N (7.01%).

Mass spectrum: m/z(1+) = calc. 394.63; found 395.

RR-C₉:(yield 67%)

(400 MHz, CDCl₃) δ 0.87 (*t*, *J* = 6.8 Hz, 6H), 1.27 (*m*, 24H), 1.57 (*m*, 4H), 1.74 (*m*, 2H), 2.02 (*d*, *J* = 12.6 Hz, 2H), 2.12 (*m*, 4H), 3.65 (*m*, 2H), 5.92 (*br*, 2H).

Elemental analyses: calcd for C₂₄O₂N₂H₄₆: C (73.04%); H (11.75%); N (7.10%); O(8.11%) found: C (72.83%); H (11.64%); N (6.96%).

Mass spectrum: m/z(1+) = calc. 394.63; found 395.

SS-C₁₀:(yield 71%)

(400 MHz, CDCl₃) δ 0.87 (*t*, *J* = 6.8 Hz, 6H), 1.25 (*m*, 28H), 1.57 (*m*, 4H), 1.74 (*m*, 2H), 2.02 (*d*, *J* = 13.1 Hz, 2H), 2.11 (*m*, 4H), 3.64 (*m*, 2H), 5.94 (*br*, 2H).

Elemental analyses: calcd for C₂₆O₂N₂H₅₀: C (73.88%); H (11.92%); N (6.63%), O(7.57%); found: C (73.64%); H (11.62%); N (6.52%)

Mass spectrum: m/z(1+) = calc. 422.69; found 423.

RR-C₁₀:(yield 67%)

(400 MHz, CDCl₃) δ 0.87 (*t*, *J* = 6.8 Hz, 6H), 1.25 (*m*, 28H), 1.59 (*m*, 4H), 1.73 (*m*, 2H), 2.01 (*d*, *J* = 12.9 Hz, 2H), 2.12 (*m*, 4H), 3.65 (*m*, 2H), 5.91 (*br*, 2H).

Elemental analyses: calcd for C₂₆O₂N₂H₅₀: C (73.88%); H (11.92%); N (6.63%), O(7.57%); found: C (73.58%); H (11.94%); N (6.58%)

Mass spectrum: m/z(1+) = calc. 422.69; found 423.

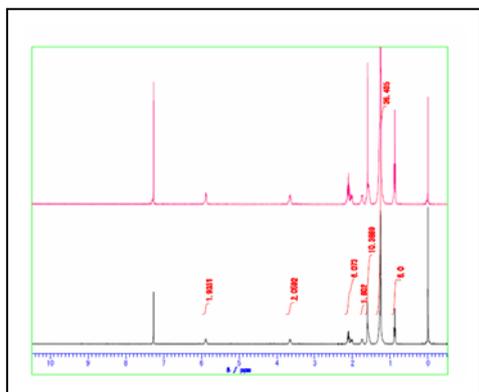


Fig. S1. ^1H NMR spectra of *RR*- (Under) and *SS*- C_{12} (Upper) in CDCl_3

***SS*- C_{12} :** (yield 76%)

Elemental analyses: calcd for $\text{C}_{30}\text{O}_2\text{N}_2\text{H}_{58}$: C (75.26%); H (12.21%); N (5.85%), O(6.68%);
found: C (75.18%); H (12.20%); N (5.85%)

Mass spectrum: $m/z(1+) = \text{calc. } 478.79$; found 480.

***RR*- C_{12} :** (yield 24%)

Elemental analyses: calcd for $\text{C}_{30}\text{O}_2\text{N}_2\text{H}_{58}$: C (75.26%); H (12.21%); N (5.85%), O(6.68%);
found: C (75.09%); H (12.33%); N (5.95%)

Mass spectrum: $m/z(1+) = \text{calc. } 478.79$; found 480.

3) **DSC analyses:** The purity of the synthesized compounds was checked by differential scanning calorimetry (DSC) measurements. All samples gave a single peak. The example is shown below for the case of **SS-C₈**.

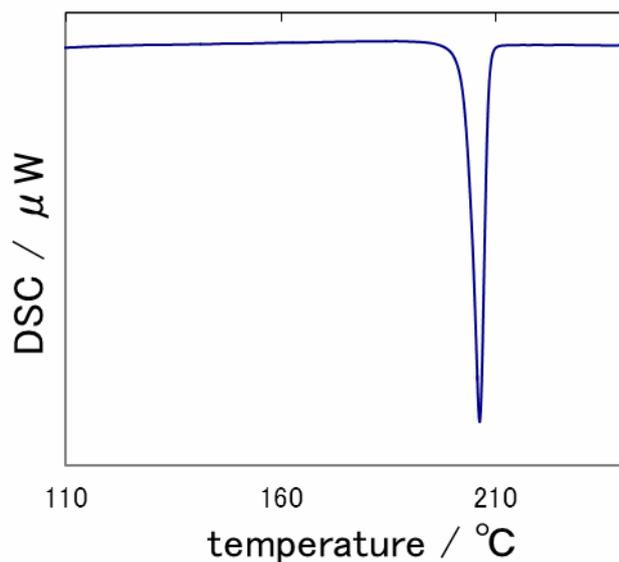


Fig. S2. The results of differential scanning calorimetry for **SS-C₈**.

- 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 from DSC measurements

Length of Alkyl chain	Temperature (°C)
C ₆	232
C ₇	220
C ₈	206
C ₉	196
C ₁₀	197
C ₁₂	194

5) ORD of gelators: The optical rotatory dispersion (ORD) of the synthesized compounds was obtained for their CH₃OH solutions. The results are given in the table below.

$[\alpha]$	Conc. molL ⁻¹	$[\alpha]_D$ deg/(molL ⁻¹ cm) 589 nm
<i>RR-C₆</i>	0.0051	17.5
<i>SS-C₆</i>	0.0051	-18.2
<i>RR-C₇</i>	0.0050	17.9
<i>SS-C₇</i>	0.0050	-17.8
<i>RR-C₈</i>	0.0051	18.3
<i>SS-C₈</i>	0.0051	-17.8
<i>RR-C₉</i>	0.0050	18.1
<i>SS-C₉</i>	0.0051	-17.8
<i>RR-C₁₀</i>	0.0050	17.8
<i>SS-C₁₀</i>	0.0051	-18.2
<i>RR-C₁₂</i>	0.0060	17.7
<i>SS-C₁₂</i>	0.0056	-22.0

6) Dependence of critical gelation concentration on alkyl chain length for gels of acetonitrile, acetone, hexane and methanol

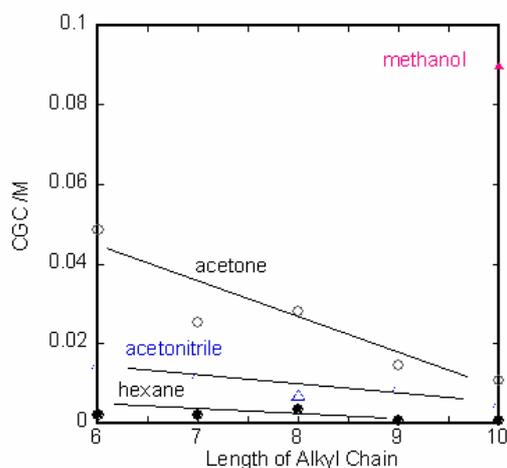


Fig. S3. The dependence of critical gelation concentration on the length of alkyl chains.

7) Sol-gel transition temperature: The temperature of sol-gel transition was also determined for toluene gels. The results are given in the figure below, in which the transition temperature is plotted against the concentration of a gelator (mol L^{-1}) in a gel.

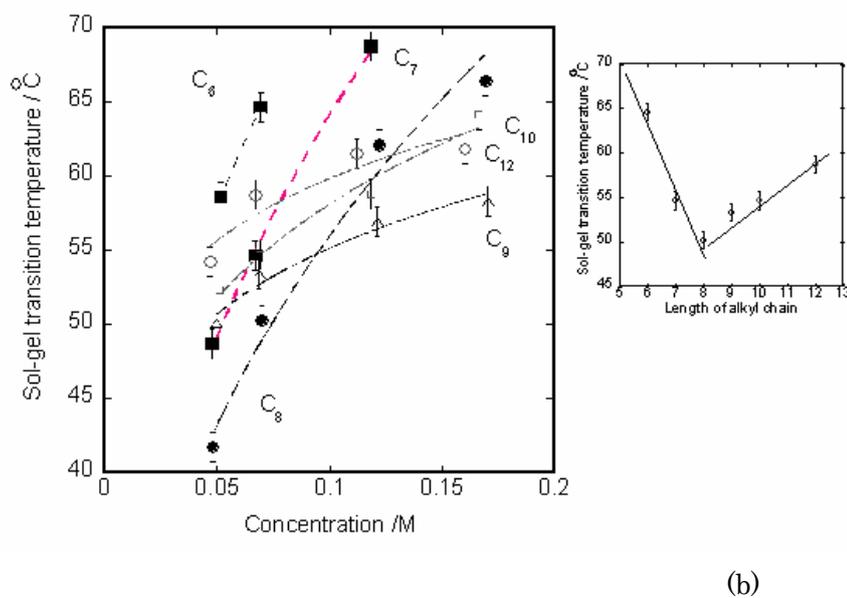


Fig. S4. (a) The dependence of sol-gel transition temperature on the concentration of a gelator for toluene. (b) The change of sol-gel transition temperature as a function of alkyl chain length at the concentration of 0.07 mol L^{-1} .

8) The IR and VCD spectra of a solution of a gelator: The IR and VCD spectra were measured on the CDCl_3 solutions of gelators.

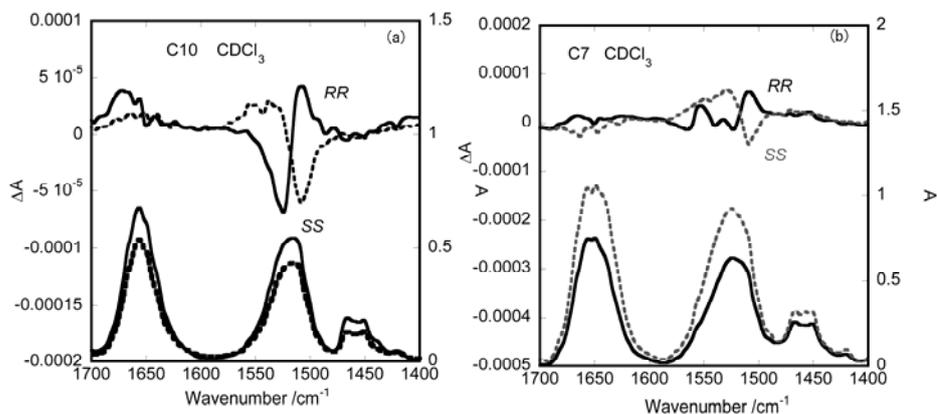


Fig. S5. The observed IR (lower) and VCD (upper) spectra of the CDCl_3 solution of C_{10} (left) and C_7 (right). Solid and dotted lines show *RR*- and *SS*-enantiomers, respectively. (Concentration : 0.08M ~ 0.3 M.)

9) The IR and VCD spectra of gelators in solid states: The IR and VCD spectra were measured on the KBr pellets of gelators.

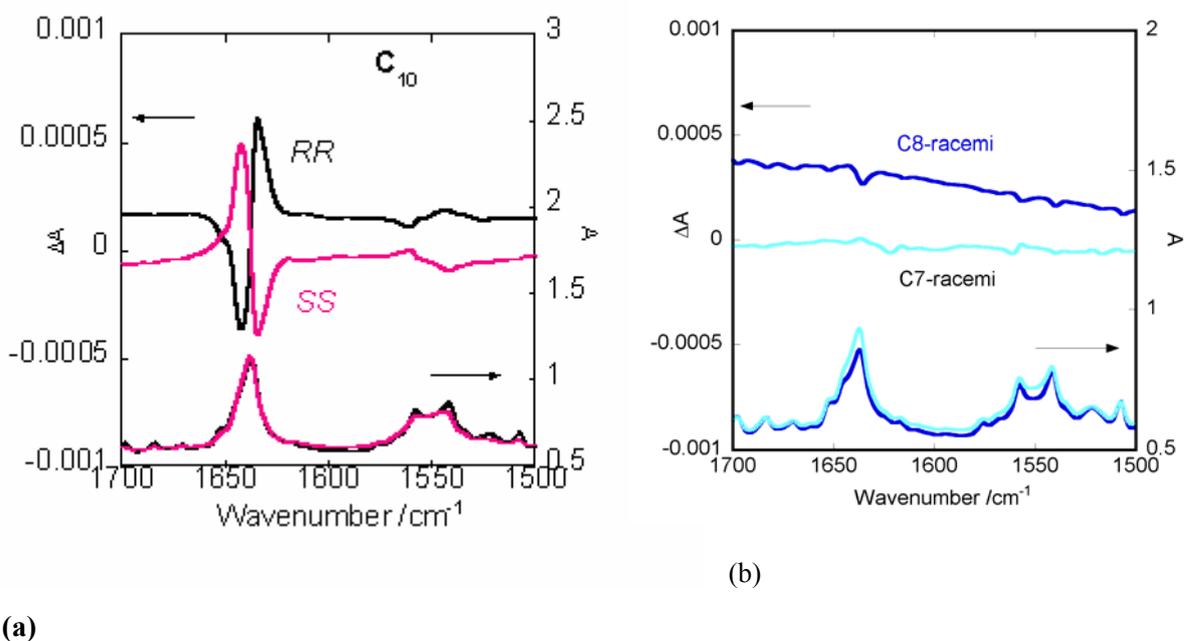


Fig. S6. (a) The observed IR (lower) and VCD (upper) spectra of the powders of C_{10} in KBr pellet method. Black, red lines show RR , SS , respectively. (b) The observed IR (lower) and VCD (upper) spectra of the powders of racemic C_7 and C_8 in KBr pellet method. Blue and sky blue lines show C_8 and C_7 , respectively.

10) The contribution of linear dichroism to VCD spectra: The samples were rotated perpendicularly to the monitoring light in order to see the linear dichoric contribution.

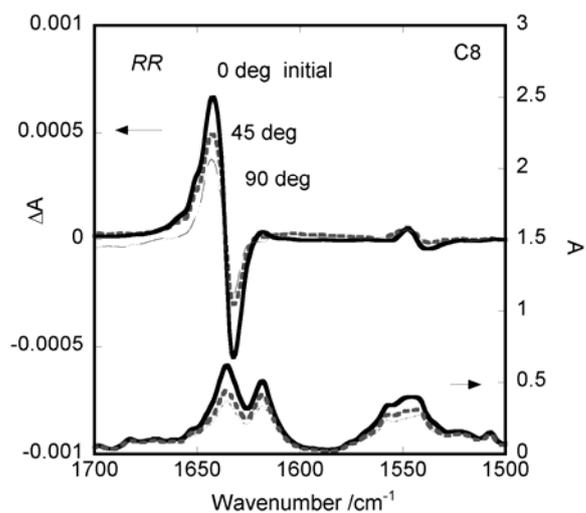


Fig. S7. The observed IR (lower) and VCD (upper) spectra of the C_6D_6 gels of **RR-C₈**. The sample is rotated by 0, 45 and 90 deg.

11) **The concentration dependence of VCD spectra:** The VCD spectra were measured by changing the concentration of a gelator. No effect of the concentration was observed. The examples are shown below:

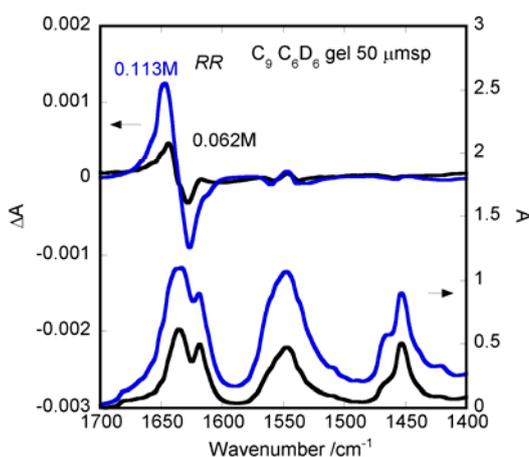
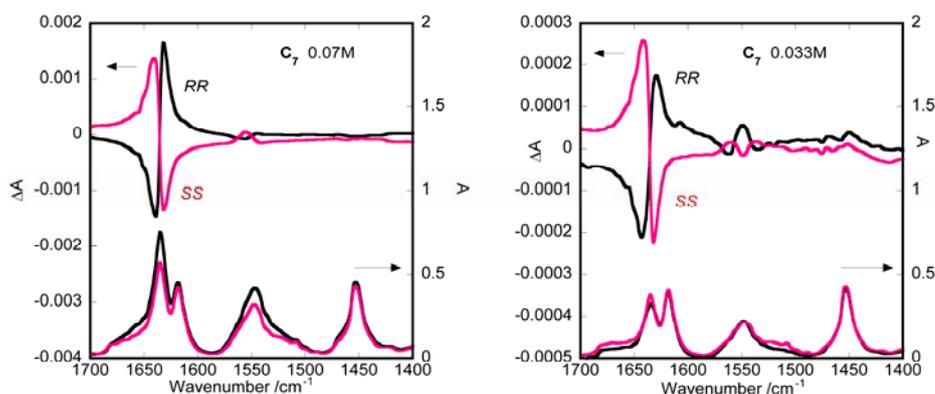


Fig. S8. The concentration dependence on the observed IR (lower) and VCD (upper) spectra of the C_6D_6 gels of $RR-C_9$. Black and Blue lines correspond to the concentration of 0.062M and 0.113 M of $RR-C_9$, respectively.



(a)

(b)

Fig. S9. The dependence of concentration on the observed IR (lower) and VCD (upper) spectra of the C_6D_6 gels of C_7 : (a) 0.07 M (b) 0.03 M. Black and red lines show RR - or SS - C_7 , respectively.

12) Two-types of dimer model: Type I: parallel and double chains of hydrogen bonding between two pairs of >NH and >C=O groups

parallel and double chains of hydrogen bonding between two pairs of >NH and >C=O groups

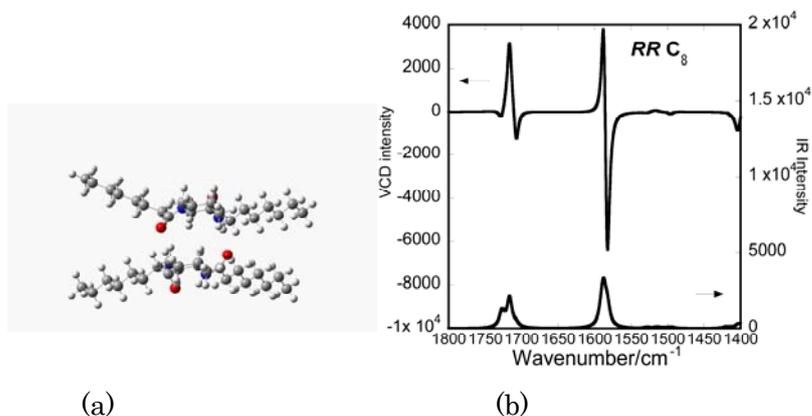


Fig. S10. (a) Optimized structures of dimer model (b) Calculated IR and VCD of *RR-C*₈ dimer

Type II: anti-parallel and single chain of hydrogen bonding between a pair of >NH and >C=O groups. The remaining pair of >NH and >C=O groups formed an intramolecular hydrogen bond

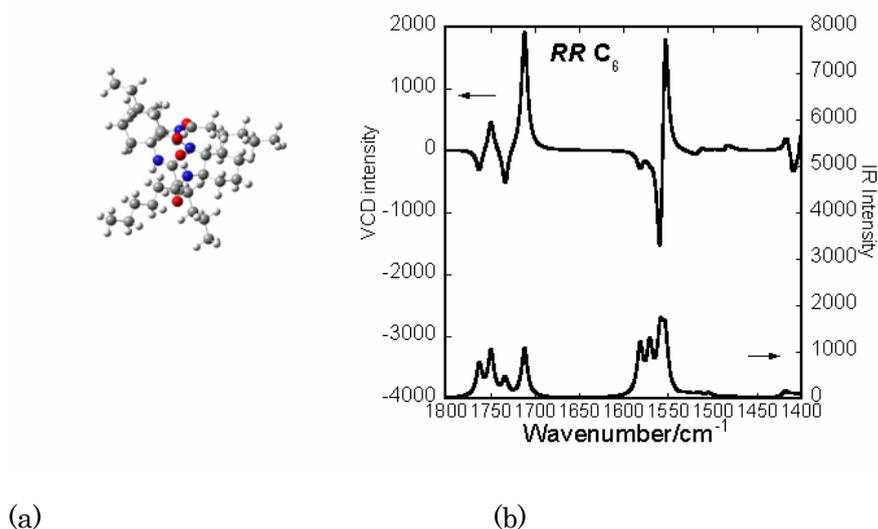


Fig. S11. Optimized structures of dimer model

(a) *RR-C*₆ dimer model

(b) Calculated IR and VCD of *RR-C*₆ dimer

13) VCD calculation for a monomeric C₈ with a benzene molecule

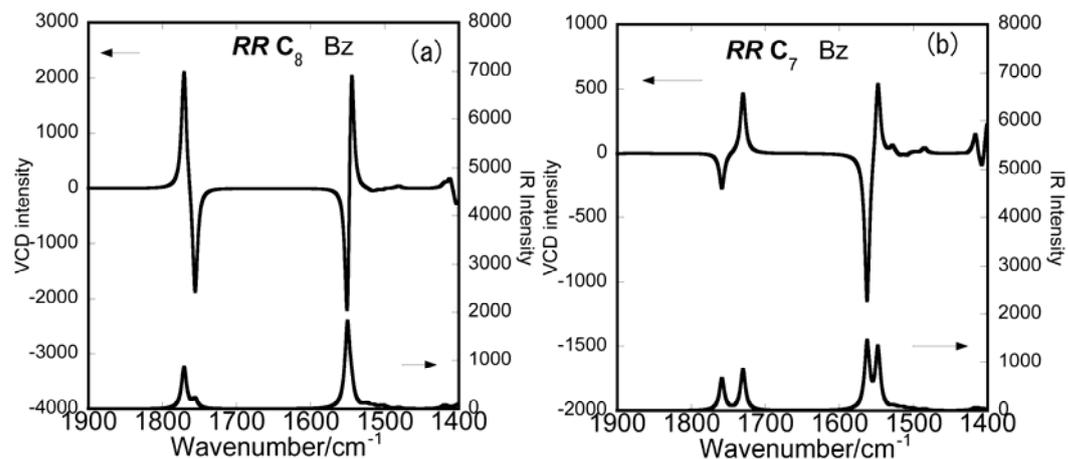


Fig. S12. VCD calculation of (a) *RR*-C₈ and (b) C₇ with a single benzene molecule

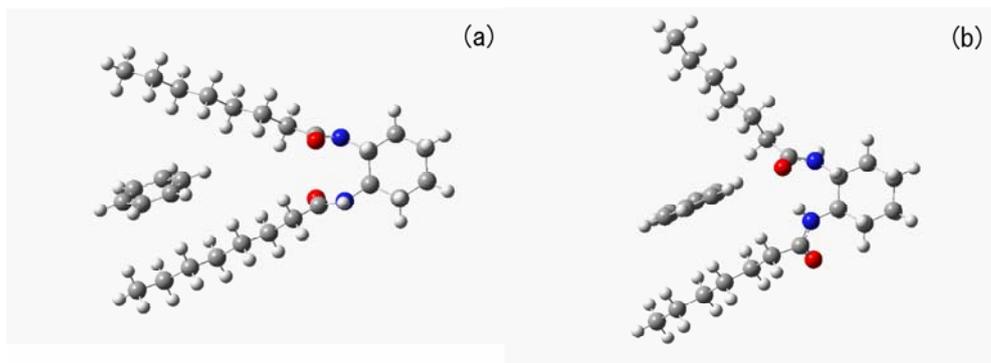
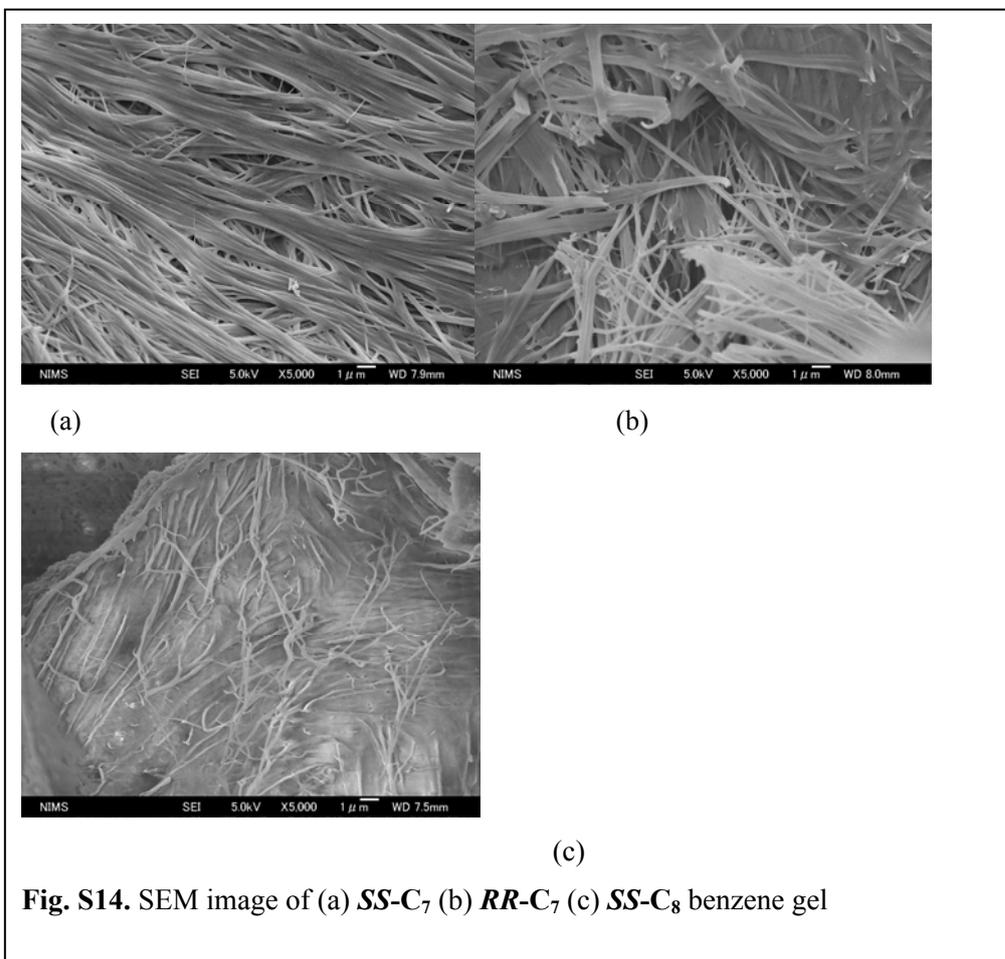
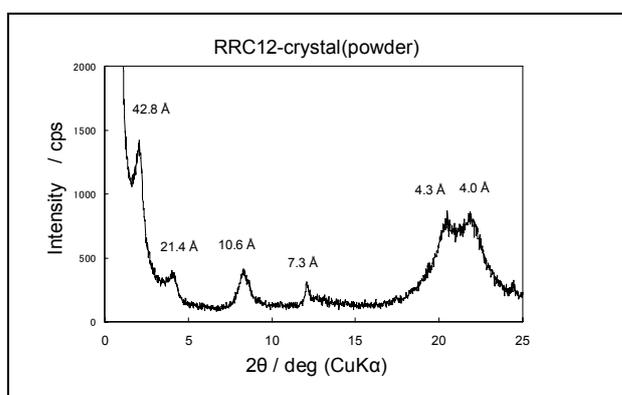


Fig. S13. Optimized structures of (a) *RR*-C₈ and (b) C₇ with a single benzene molecule

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



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



(a) *RR-C*₁₂ powder sample

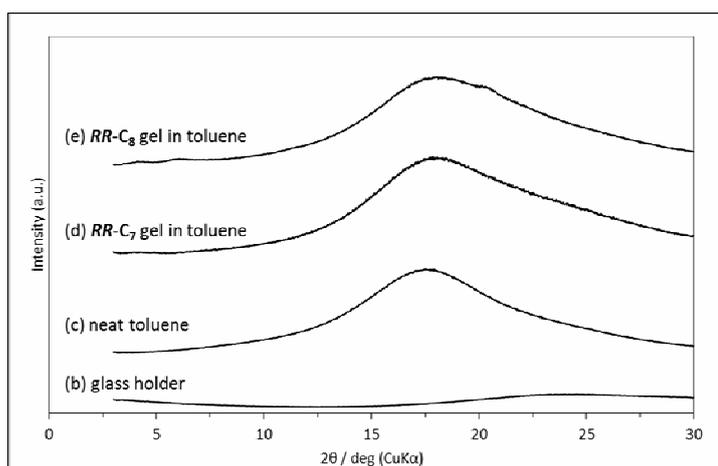


Fig. S15. XRD patterns of (a) powder of *RR-C*₁₂, (b) glass holder (c) neat toluene, (d) gel states of *RR-C*₇, and (e) *RR-C*₈ in toluene (ca. 0.1 M).

The XRD pattern of a *RR-C*₁₂ powder sample (Fig. S15 (a)) showed a set of specific peaks associated with a crystalline phase. In contrast, the XRD patterns of *RR-C*₇ and *RR-C*₈ gel samples in toluene (Fig. S15 (d) and (e)) represented a broad diffraction peak at around 2θ~18.5° (approximately 0.48 nm), and also the XRD profile of neat toluene showed a similar pattern (Fig. S15 (c)). There was no other sharp peak in the gel state samples with toluene. It indicates that the gels of *RR-C*₇ and *RR-C*₈ were composed of little ordered domains without crystalline phase.