Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Molecular Origin for Helical Winding of Fibrils Formed by Perfluorinated Gelators

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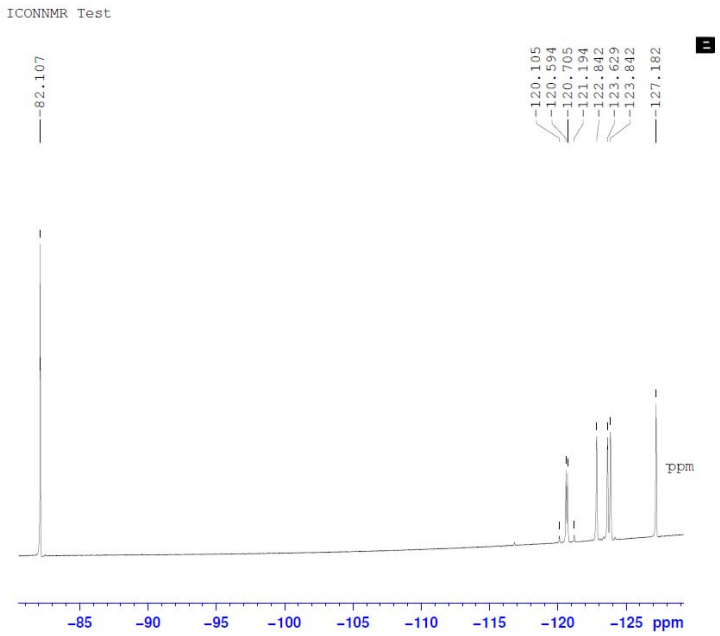


Figure S1. The ^{19}F NMR(564 MHz) spectrum of the CD_3CN solution of ***SS*-CF7**; δ = -82.11 (s, 6F, CF_3), -120.35 (d, 2F, J = 288 Hz, CF_2), -120.95 (d, 2F, J = 288 Hz, CF_2), -122.84 (s, 4F, CF_2), -123.63 (s, 4F, CF_2), -123.84 (s, 4F, CF_2), -127.18 (s,4F, CF_2).

Mass spectrum and elemental analyses of *SS*-CF7

Mass spectrum: m/z(1+) = calc. 806.28; found 806.

Elemental analyses: calcd for $C_{20}O_2N_2H_{12}F_{26}$: C (29.29%); H (1.50%); N (3.47%); found: C (29.71%); H (2.96%); N (3.66%).

Yield for ***SS*-CF7**: 14 %.

Table S1. The optical rotatory dispersion of the THF solutions of **CF7**.

[α]	mg	FW	Conc. $molL^{-1}$	$[\alpha]_D$ $deg/(molL^{-1}cm)$ 589 nm
***SS*-CF7**	14.3	806	0.0018	-4.7
***RR*-CF7**	22.4	806	0.0048	3.1

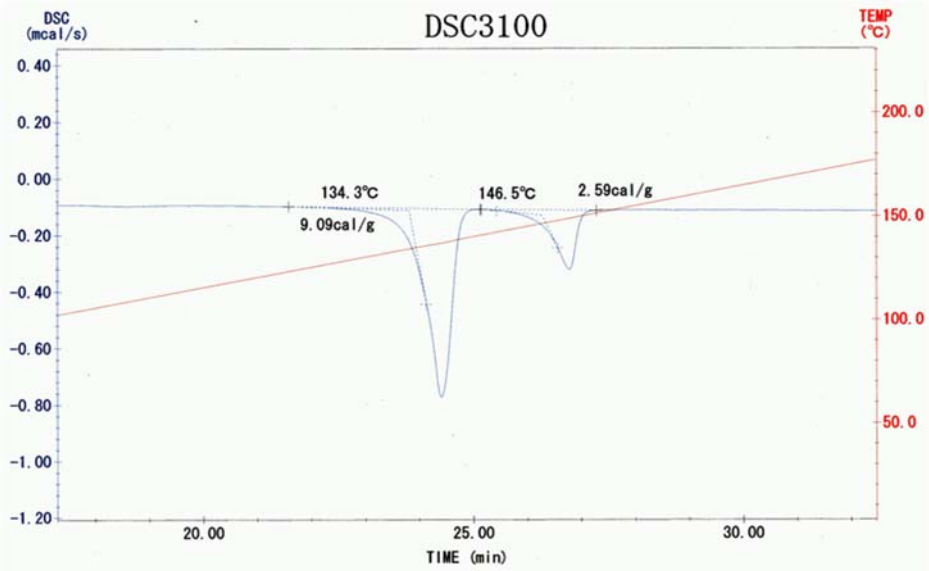
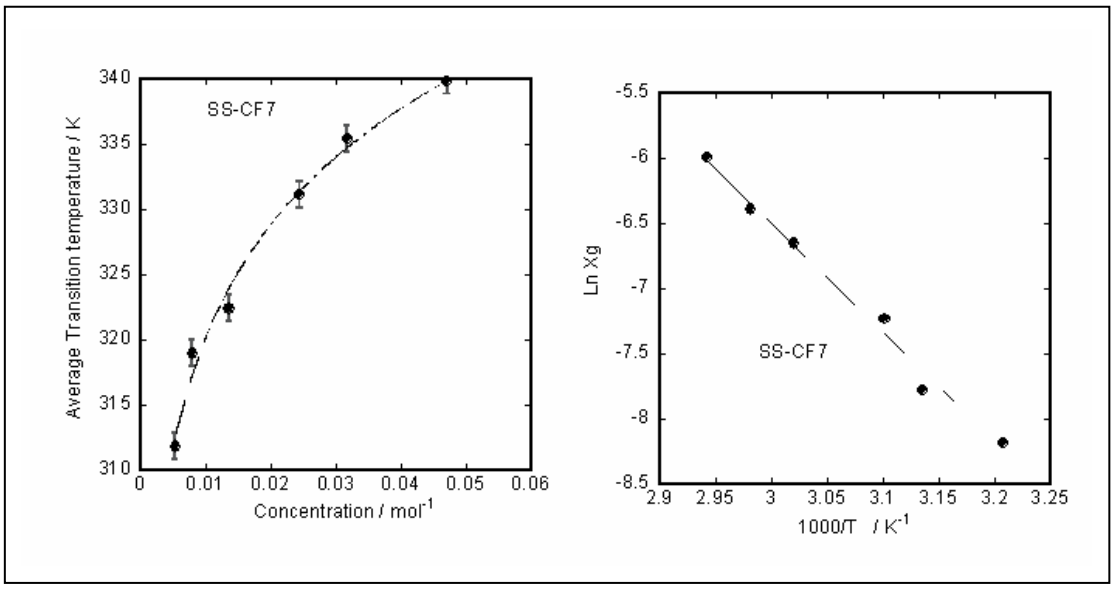


Figure S2. The results of differential scanning calorimetry for ***SS*-CF7**. Two endothermic peaks were observed at 134.3°C (9.09 cal g^{-1}) and 146.5°C (2.59 cal g^{-1}).



(a) (b)

Figure S3. (a) The dependence of the sol-gel temperature (T_g) on the concentration of a gelator (C_g) for ***SS*-CF7**: (a) T_g versus Cg; (lower); (b) $\ln X_g$ (X_g = the molar ratio of a gelator) versus $1/T_g$. The solvent was CH_3CN. The results are analyzed according to the following Schröder-van Laar equation:

$$\ln Xg = \frac{\Delta H_{fus}}{RT_g} + \frac{\Delta H_{fus}}{RT_{fus}}$$

in which ΔH_{fus} and T_{fus} are the enthalpy of sol-gel transition and the melting temperature of a gelator, respectively. The obtained thermodynamic parameters are listed in Table S2.

Table S2 Thermodynamic parameters of gelation by ***SS*-CF7**

	ΔH_{fus} /kJ mol^{-1}	T_{fus} (K)
***SS*-CF7**	69.3	450

(solvent: CH_3CN).

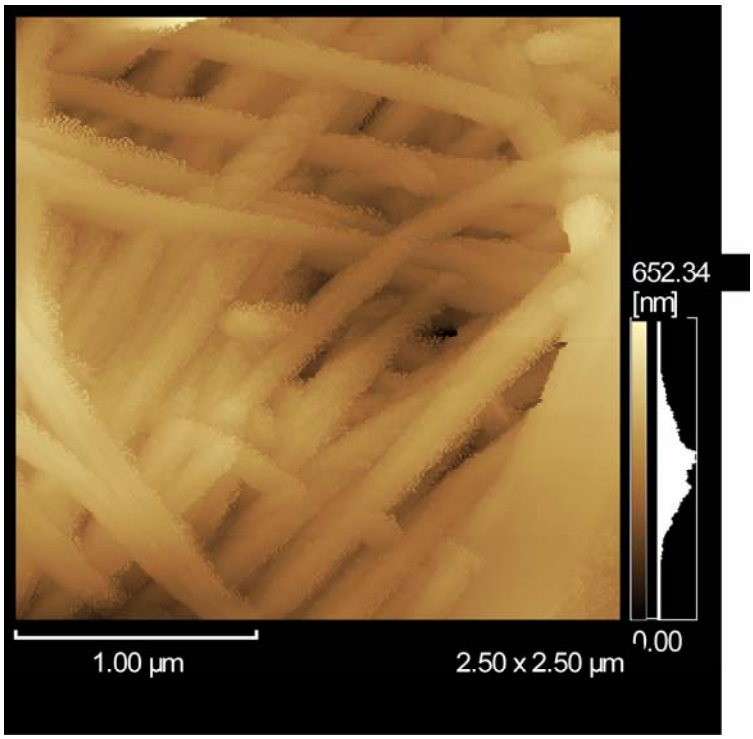


Figure S4. The AFM imgae of a CD_3CN gel of ***SS*-CF7** cast on a silicon wafer.

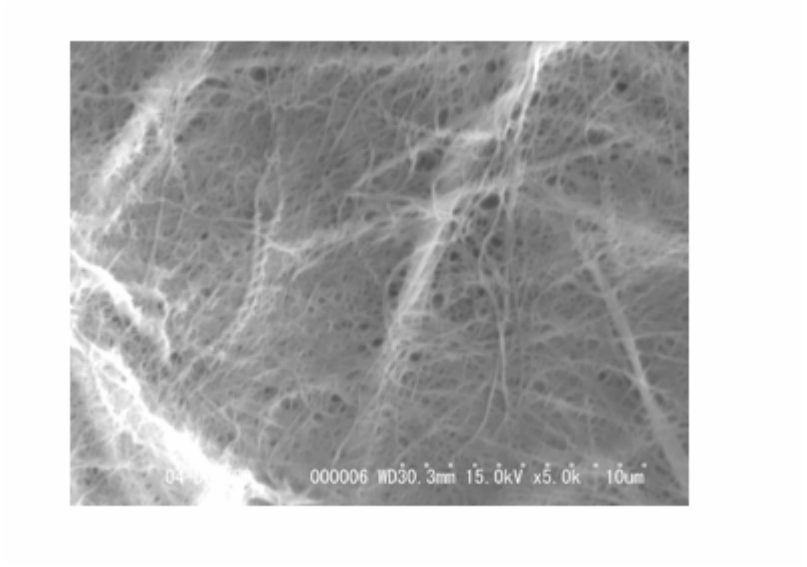


Figure S5. The SEM image of a CH_3CN gel of ***RR*-CF7**. The scale is indicated in the figure.

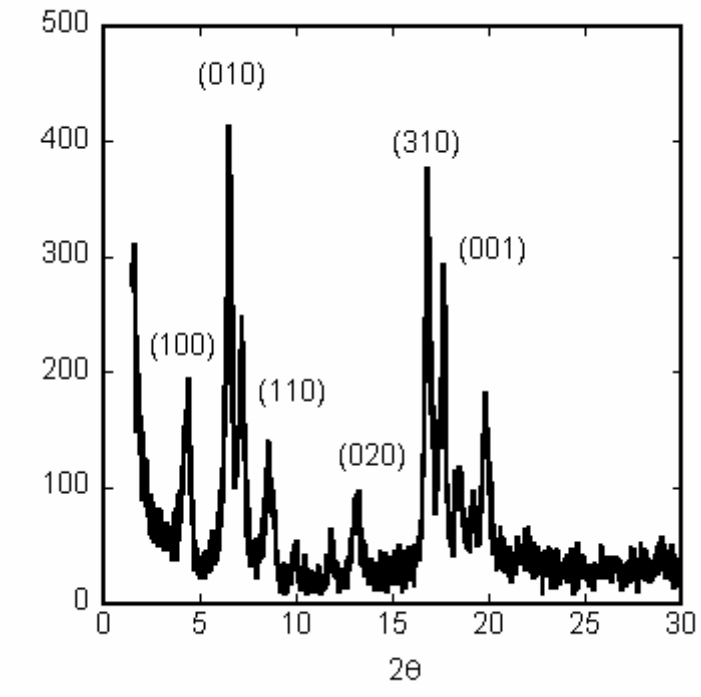


Figure S6. The X-ray diffraction pattern recorded on a powder sample of ***SS*-CF7** (wavelength: 1.54 nm from CuKα) The measurements were performed with an X-ray diffractometer (Ultima IV, Rigaku. Japan). Peaks were indexed by assuming the unit cell of a = 2.00 nm, b = 1.34 nm and c = 0.50 (α = β = γ = 90.0 degree). Here the analyses were made by use of the SFC and EDA program for the optimized unit cell size (Kogure, T. *Journal of the crystallographic Society of Japan,* (2003) **45**, 391-395; http:/www.gbs.eps.s.u-tokyo.ac.jp/kogure/edana).

	2θ	d /nm
crystal	4.42	2.00
	6.58	1.34
	7.18	1.23
	16.84	0.53
	17.66	0.50

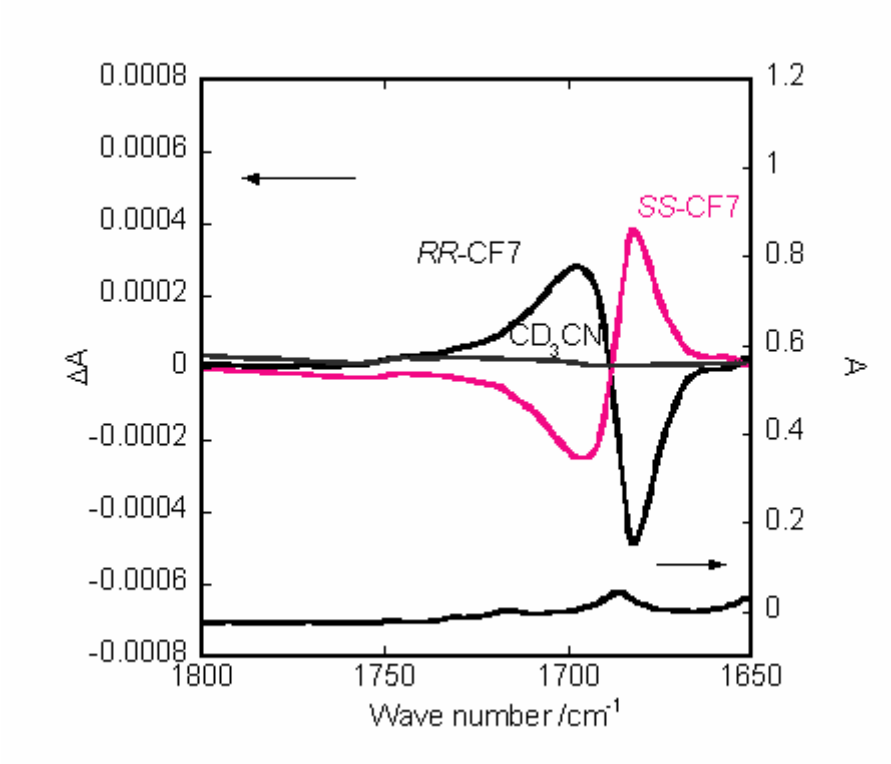


Figure S7. The VCD spectra of the CD_3CN solutions (5 gL^{-1}); ***RR*-CF7** (black) and ***SS*-CF7** (red) and a CD_3CN solvent (base line).

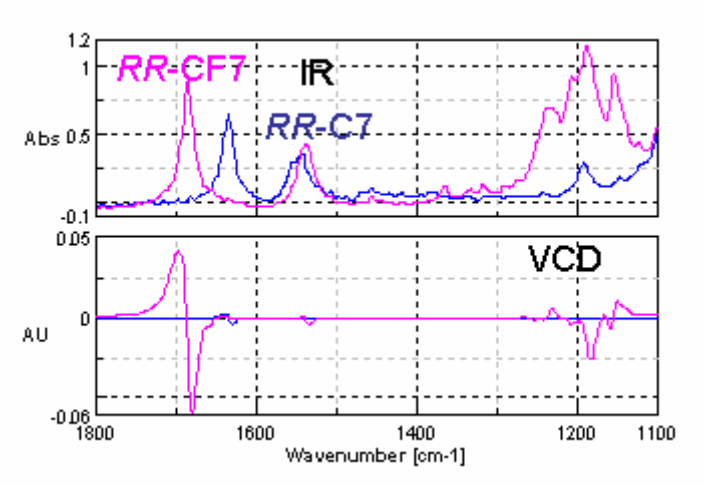


Figure S8. The VCD spectra of the CD_3CN gel; ***RR*-CF7** (pink) and ***RR*-C7** (blue) (***RR*-C7** = *N,N'*-diheptanoyl-1,2(*R*,*R*)-diaminocyclohexane). The compound, ***RR*-C7**, was synthesized in the similar way as ***RR*-CF7** by using heptanoyl chloride instead of perfluoroheptanoyl chloride.* The figure shows that ***RR*-CF7** exhibited a red shift in comparison to ***RR*-C7**, which was ascribed to the interchain interaction of C=O groups with the C_6F_{13} moiety. ***RR*-CF7** formed a clear gel, while ***RR*-C7** formed a turbid gel.

*) K. Hanabusa, M. Yamada, M. Kimura and H. Shirai, *Angew. Chem. Int. Ed.,* 1996, **35**, 1949

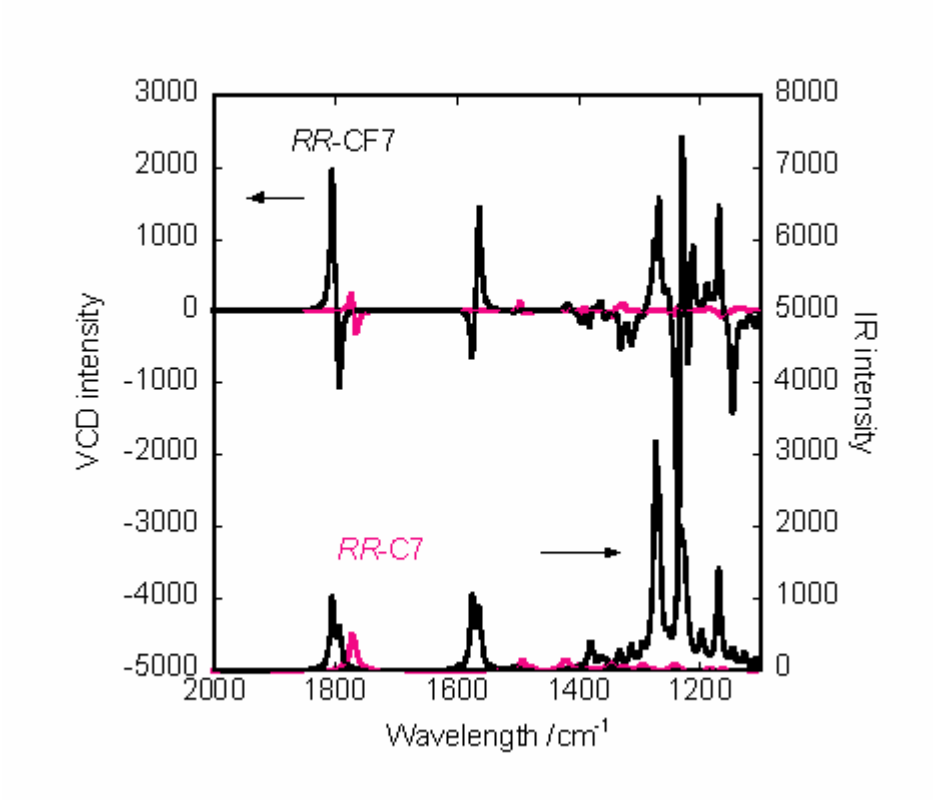


Figure S9. The calculated IR and VCD spectra ; ***RR*-CF7** (black) and ***RR*-C7** (red).

The figure shows that the observed red shift for ***RR*-CF7** is also predicted theoretically.

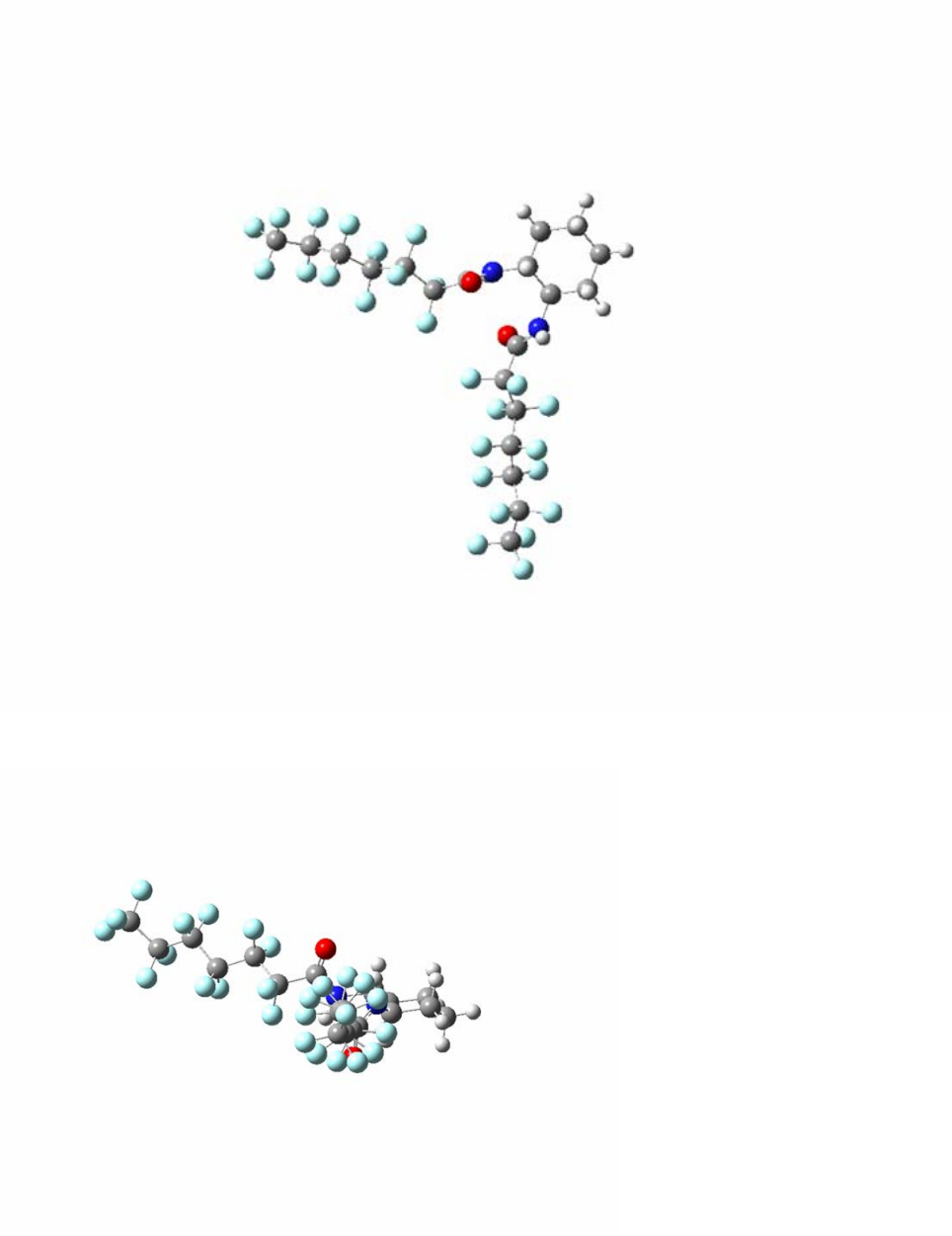


Figure S10. The optimized conformation of a single molecule of ***RR*-CF7**; .(upper) the overviewed of the cyclohexyl ring and (lower) the sideviewof the cyclohexyl ring, in which one of the perfluorinated rings orients in the vertical direction from the paper.

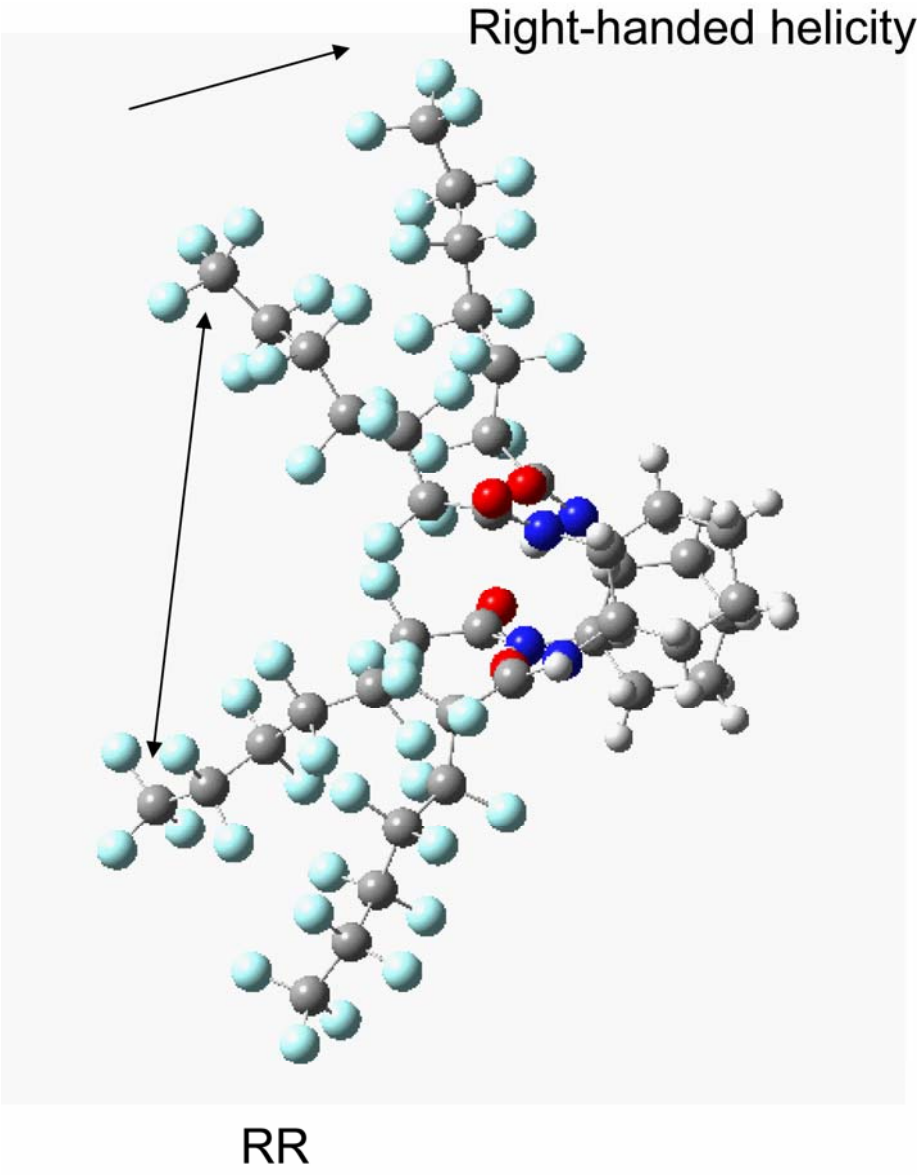


Figure S11. The optimized structure of a pair of two ***RR*-CF7** molecules when they are stacked in a parallel way. The upper molecule rotates with respect to the lower one in the right-hand direction. Two molecules are associated through the intermolecular hydrogen bondings between C=O and NH groups.

Table S3. Gelation by ***SS*-CF7** for various solvents at 25 °C. The concentraion of a gelator was 50 mg per 1mL of solvent.

	SS-CF7
acetonitrile	○ (CG)
Benzene	X***
Toluene	X
trifluoromethylbenzene	○ (CG)
dimethylsulfoxide	○ (TG)
2,2,2-trifuloroethanol	x
silicon oil	x
perfluorotoulene	○ (TG)
perfluorobenzene	○ (TG)

* CG = clear gel, **TG = turbid gel, ***X = crystal precipitated.

Full Names of reference 12.

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