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Perfluorinated Gelators for Solidifying Fluorous Solvents : Effects of Chain Length and Molecular Chirality

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With a purpose of solidifying fluorous solvents, a novel series of perfluorinated gelators based on 1,2-diaminocyclohexane (denoted as CFn: n = the number of carbon chain in perfluoroalkanoyl moiety) were developed. The gelation ability for C_6F_6 was investigated. The length of a perfluoroalkyl chain (n = 4–9) was found to affect critically the gelation properties such as gel stability, chirality effects and aggregation modes in fibrils.

Introduction

Gelation of highly fluorinated solvents is a demand of various practical uses such as the delivery systems of oxygen or drugs and the treatment of industrial waste.[1–8] For the purposes, there have been several attempts using gelators with perfluorinated chains. Gelation is reported to be accelerated by the hydrophobic and lipophobic interactions of the fluorinated groups with solvent molecules.[9–12] However the reports on the gelation of fluorous solvents are limited. A few compounds that gelate one fluorocarbons are reported. [12–14] But the compounds that can gelate multiple perfluorinated liquids are very few.[11,15,16] Accordingly the development of gelators for fluorous solvents is highly anticipated.

We have studied the gelation behavior of a series of perfluorinated compounds. They were synthesized on the basis of chiral diaminocyclohexane moieties. The compounds are denoted as ***RR*-CFn** or ***SS*-CFn** (n = 4–10), indicating the stereochemistry and the number of carbon atoms (n) in a perfluoroalkanoyl chain (Chart 1). The *N*-alkalnoyl derivatives of diaminocyclohexane (denoted as ***RR*-Cn** or ***SS*-Cn**) were first reported by Hanabusa et al. as an efficient gelator.[17] The gelation of chiral **CF7** and **CF8** was studied using CH_3CN or 2-butanol as a solvent. For both gelators, helical fibrils were observed in gels.[18,19] The conformation of a gelator molecule was investigated by means of vibrational circular dichroism spectroscopy (VCD).[20–25] A model for molecular packing in a helical fibril was postulated.[26]

In the present study, the effect of chain length on gelation was investigated using C_6F_6 as a solvent. It was shown that the variation of perfluorinated chains by one -CF_2- unit resulted in the remarkable change of gelation properties such as the stability of a gel, the effects of molecular chirality and the aggregation modes in fibrils. Single crystal X-ray analyses were performed for racemic and enantiopure **CF4**.

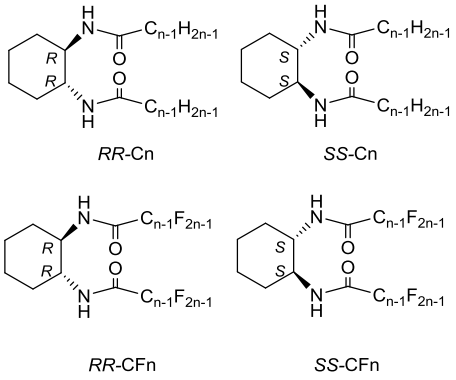

Chart 1 Molecular structures of ***RR*-Cn**, ***SS*-Cn**, ***RR*-CFn** or ***SS*-CFn** .

Results and discussion

Measurement of critical gel concentrations

Gelation by enantiopure and racemic **CFn**'s was studied for three fluorinated solvents, C_6F_6 (hexaflurorobezene), C_6F_{14} (perfluorohexane) and BTF (benzotrifluoride). No gelation of C_6F_{14} was observed on adding any of **CFn**'s. The critical gel concentration (CGC) of enantiopure and racemic **CFn**'s was measured for C_6F_6 and BTF. The results are summarized in Table 1. For both solvents, the gelation ability of a gelator was dependent remarkably on the length of perfluorinated chains. For example, in case of C_6F_6, chiral **CF4** gave a turbid gel, **CF5**–**CF6** crystal precipitated and **CF7**–**CF10** stable turbid or clear gel. Fig. 1 shows the effects of chain length and molecular chirality

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in case of **CF7**–**CF10**. As for the effect of chirality, the CGC values were smaller for the racemic mixtures than for the enantiomers. The CGC value showed a shallow minimum around **CF8** and **CF9** for racemic gelators, while the odd-even effect appeared with the minimum value at *RR*- (or *SS*)-**CF9** for enantiopure gelators. The fact that the racemic forms of CFn's showed considerable gelation ability was in marked contrast with what was observed for **Cn**'s. In case of the latter compounds with n = 8–12, only the enantiomeric form acted as a gelator. The racemic compounds were precipitated as a crystal. These facts demonstrated the important role of perfluorinated chains in forming fibrils. The formation of gels was confirmed by the inversion tests. The photograph of the example is given in the supporting information.

Table 1 The critical gel concentrations of CFn's.

Solvent	C_6F_6	C_6F_{14}	BTF
Chiral **CF4** (n = 3)	tg (36.0)	p	p
Chiral **CF5** (n = 4)	p	p	p
Chiral **CF6** (n = 5)	p	p	p
Chiral **CF7** (n = 6)	cg (20)	p	cg (5.8)
Chiral **CF8** (n = 7)	cg (37.5)	p	cg (17)
Chiral **CF9** (n = 8)	cg (7.5)	p	cg (16.4)
Chiral **CF10** (n = 9)	tg (24.5)	p	p
Racemic **CF4** (n = 3)	p	p	p
Racemic **CF5** (n = 4)	p	p	p
Racemic **CF6** (n = 5)	tvs	-	-
Racemic **CF7** (n = 6)	cg (13.0)	p	tg (30.0)
Racemic **CF8** (n = 7)	cg (6.8)	p	cg (4.1)
Racemic **CF9** (n = 8)	cg (6.9)	p	p
Racemic **CF10** (n = 9)	cg (8.6)	p	p

cg = clear gel; tg = turbid gel; p = crystal precipitated; tvs = turbid viscous solution. The values in parentheses denote the critical gel concentration at 298 K in terms of gL^{-1}. The values in Table 1 were the average obtained for the results for *RR*- and *SS*-gelators.

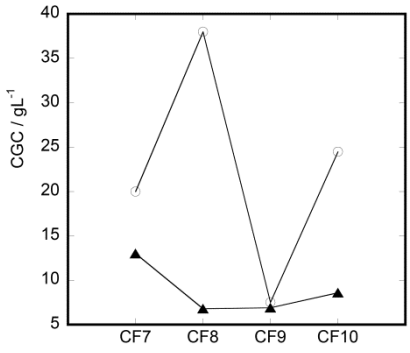

Fig. 1 The variation of the critical gel concentration of C_6F_6 for racemic or enantiopure **CF7**–**CF10**. Open circle; chiral and solid triangle; racemic.

SEM observation on the dried samples of gels or viscous solutions

SEM images were obtained for the xerogels or dried samples of viscous solutions containing the enantiopure or racemic gelators. The results for **CF8**, **CF9** and **CF10** are shown in Fig. 2(a)–(c), respectively. The results for **CF4**–**CF6** are shown in the supporting information. The SEM results for **CF7** were already reported previously.[18]

In all samples, the networks of thin string-like fibers of c.a. 0.1 nm in diameter were observed. In case of **CF4**–**CF6**, the fibers formed a plate-like aggregate with a size of 1−20 μm in width and >0.3 μm in thickness. The aggregates were as long as 100 μm with no winding or curving, indicating that they were rigid. In case of **CF7**–**CF9,** the thin string-like fibers aggregated to less extent so that some formed a network as a separate unit. The fibers were curved or entangled, suggesting that they were flexible. In case of **CF10**, the thin fibers formed a large plate-like aggregate. They were straight with no winding. In all samples, no helical structure was detected and little difference was observed between the enatiopure and racemic samples.

Measurement of IR and VCD spectra on enantiopure gels or viscous solvents

Vibrational circular dichroism (VCD) spectra[26–28] were measured on C_6F_6 gels or viscous solutions or solids containing enantiopure compounds. For obtaining the VCD spectra in case of **CF8** and **CF9**, an isotropic C_6F_6 solution containing a gelator a little over the critical gel concentration was prepared. It was mounted onto a sandwich-type cell at 70 °C. The spectrum was recorded during 0–15 minutes after the sample was cooled down to room temperature.

Fig. 3(a) and (b) show the results for **CF8** and **CF9**, respectively. The results for **CF8** were similar to those of **CF7**, which were reported previously.[18,29] The lower and upper curves in each figure represent IR and VCD spectra, respectively. Both **CF7** and **CF8** gave stable spectra during the measurements. In contrast, **CF9** showed the opposite sign of the peaks assigned to C=O stretching as shown in Fig. 3(b).

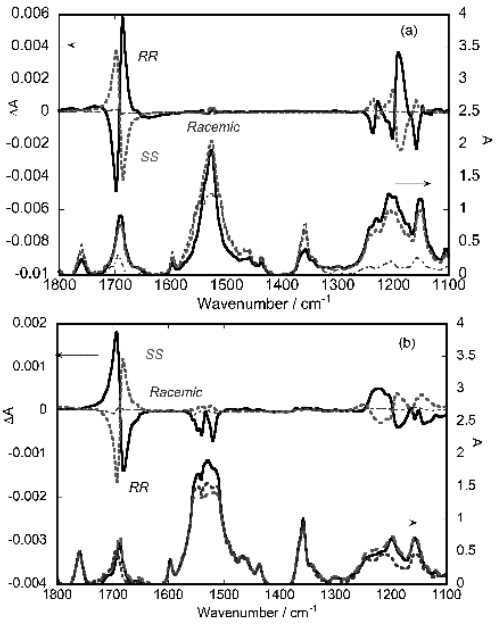

Fig. 3 The VCD (upper) and IR (lower) spectra of C_6F_6 gels containing enantiopure or racemic (a) **CF8** (37.5 gL^{-1}) and (b) **CF9** (7.5 gL^{-1}).

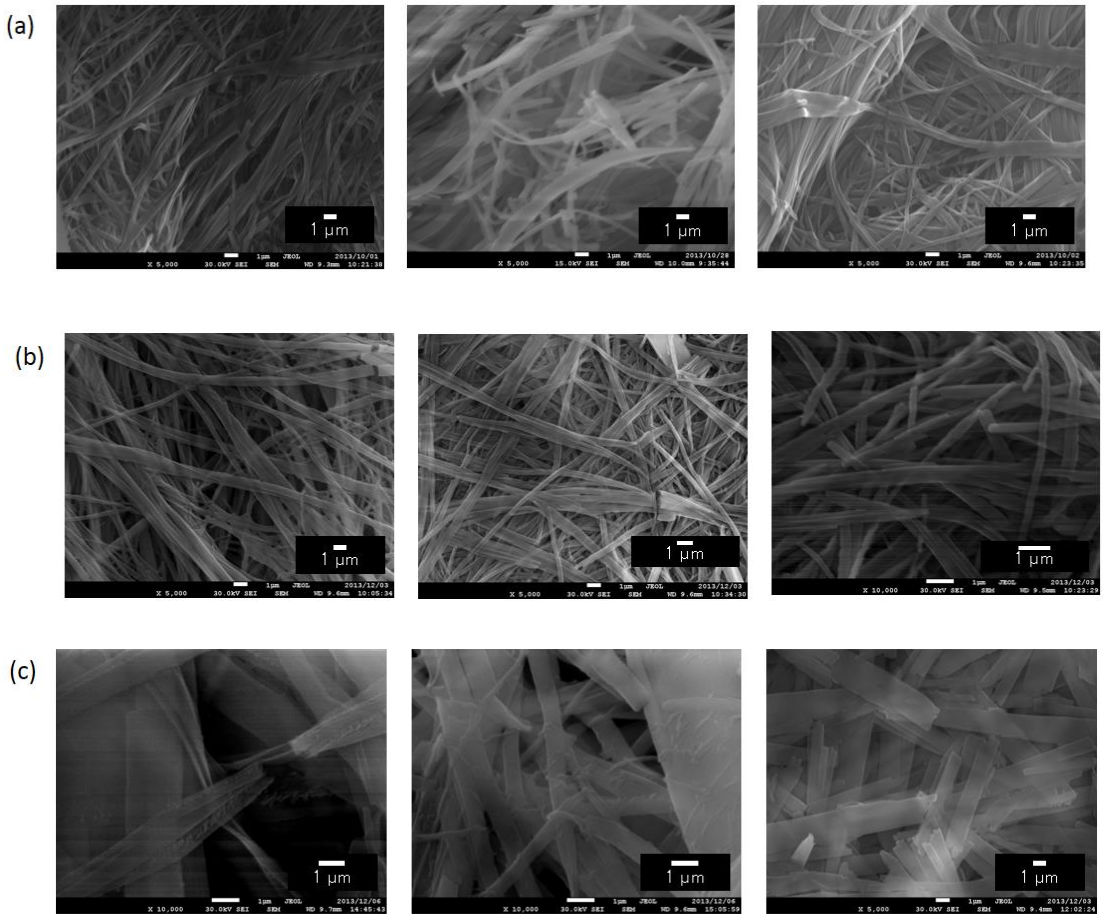

Fig. 2 The SEM images of the dried samples of C_6F_6 gels. Left; *RR*-**CFn**, middle; *SS*-**CFn**, right; racemic-**CFn**. (a) **CF8** (b) **CF9** (c) **CF10**.

All of the measured spectra exhibited a mirror-image relation between the samples containing *RR*- or *SS*-enantiomers in the whole wavenumber range. The rotation of a cell around an incident light gave no change in the spectra, confirming the reliability of the measurements. In the VCD spectra, the strong couplet around 1688 cm^{-1} was assigned to the stretching vibration of C=O bonds. The multiple peaks in the region of 1238–1170 cm^{-1} were assigned to the stretching vibrations of C-F bonds. The peaks due to the stretching vibration of N-H around 1550 cm^{-1} were small in spite of the strong absorption in the IR spectra.

An attention was focused on the signs of a couplet assigned to C=O vibrations. According to the theoretical calculation, its signs are dependent on the conformation of the >CH(NH)CO- moiety. The previous results on the CD_3CN and CD_3CN/C_6F_6 gels formed by *RR*-**CF7** indicated that the gelator molecule took a conformation with two anti-parallel intermolecular hydrogen bonds, if the couplet showed the positive to negative (+/-) signs from high to low wavenumber.[26] Instead, if the same couplet showed the negative to positive (-/+) signs, it took a conformation with one intermolecular and one intramolecular hydrogen bonds. On the basis of this diagnosis, **CF9** took a conformation with two anti-parallel hydrogen bonds, while **CF7** and **CF8** took a conformation with one intermolecular and one intramolecular hydrogen bonds. In other words, the elongation of a single -CF2- unit resulted in the drastic change of the stacking modes of gelators in fibrils. The effect might be caused by the steric constraint arising from the stacking structures of perfluoroalkyl chains. Comparing the VCD results with the tendency for gelation (Table 1), the high stability of a gel formed by enantiopure **CF9** was correlated with the formation of stable two-antiparallel hydrogen bonds in fibrils.

Another attention was paid to the multiplet regions due to the stretching vibration of C-F bonds. The VCD activity of the region reflected the helical conformation of perfluorinated groups. According to the previous theoretical calculation, it was deduced that the positive or negative sign of the strongest peak in the multiplet band around 1200 cm^{-1} represented the right- or left-handed helicity of the perfluorinated chain.[31,32] On the basis, *RR*-**CF7,** *RR*-**CF8** and *RR*-**CF9** had their perfluorinated chains left-, left- and right-handed in C_6F_6 solvent, respectively. Most probably the helicity was determined by the interaction of the hydrogen atom in the –NH-C=O moiety with the fluorine atom in the perfluorinated chain.

Single crystal X-ray analyses

A single crystal was obtained successfully in case of *RR*-**CF4** and racemic-**CF4** alone among the present series of gelator molecules. Fig. 4 shows the results of the X-ray crystal analyses of *RR*-**CF4**. Molecules were stacked forming a molecular array along the a-axis, in which their cyclohexyl rings were in parallel. In the array, molecules are connected by two anti-parallel intermolecular hydrogen bonds at >C=O and >NH groups (204.0 pm). This mode of aggregation was in accord with the prediction from the VCD spectra of the solid on the basis of the sign of couplet assigned to C=O stretching. Since the VCD spectra of the gels gave the same signals, the same connection was thought to exist in fibrils. In the crystal, the distance of fluorine in the neighboring arrays was shorter than sum of the van der Waals radii of the two fluorine (272.3 pm). It was uncertain, however, whether such an interaction existed in gel fibrils. The sequence of fluorine atoms represented slightly left-handed helical winding along a perfluorinated butyl chain.

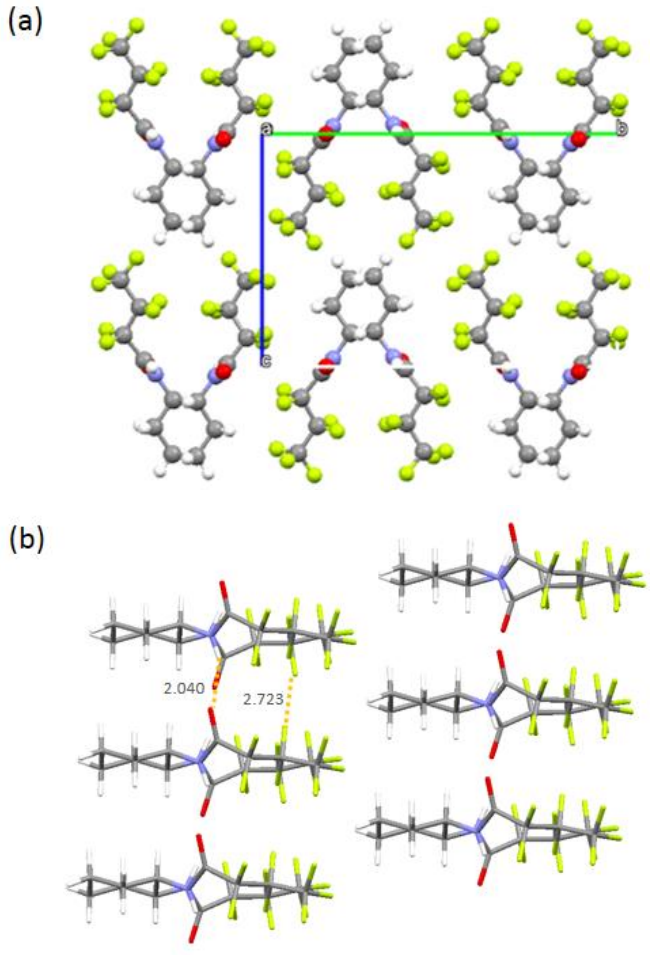

Fig. 4 The molecular structure and packing in a single crystal of *RR*- **CF4**.

By contrast, in the case of racemic-**CF4**, cyclohexyl ring and perfluoroalkyl moiety were stacked alternately (Fig. 5). The main factor of this array is two anti-parallel intermolecular hydrogen bonds among *RR*- or *SS*-enantiomers at >C=O and >NH groups (201.0 pm). One of the perfluoroalkyl groups is bent. The bent conformation of side chain was also observed in our previous terminally-brominated gel.[33] The fluorine in the neighboring molecules do not interact with each other, but fluorine atoms of cater-corner molecules are slightly contacted (290.3 pm) .

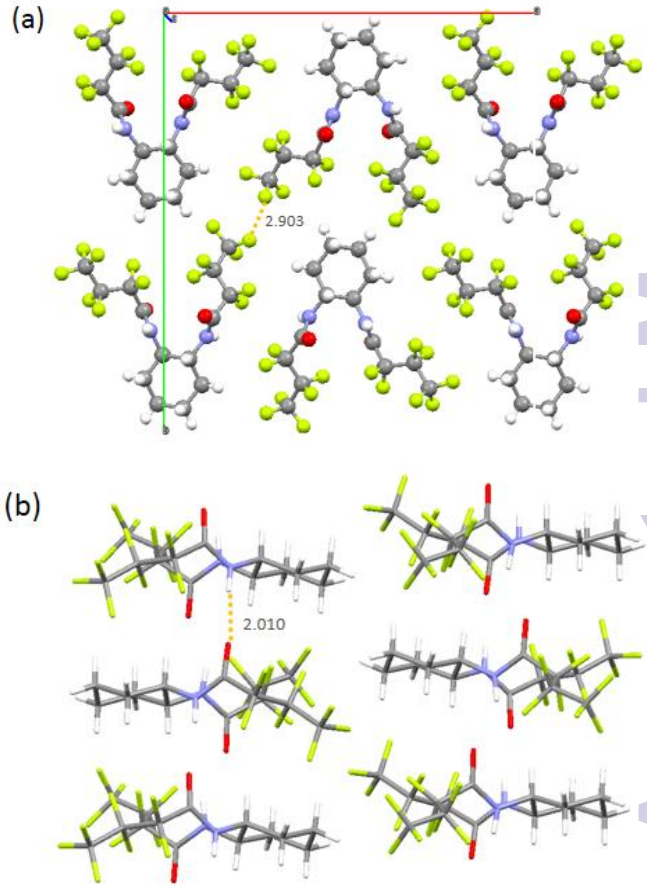

Fig. 5 The molecular structure and packing in a single crystal of racemic- **CF4**.

Molecular stacking models for enantiopure or racemic gelators

As summarized in Fig. 1, gelation ability was affected by the length of perfluorinated chains in the different fashion between the racemic and enantiomeric gelators. For racemic **CF7**–**CF10**, gelation ability was little dependent on the chain length, while it changed drastically for enantiomeric ones. The features were in contrast with what was reported for non-fluorinated analogous gelators (denoted as **Cn**). Using benzene as a solvent, for example, only enantiopure **Cn**'s formed a gel, while racemic ones much less stable gels than pure enantiomers.[17,34] As for the effect of the chain length, the CGC values decreased monotonously from **C8** to **C12**. It should be emphasized that no gelation occurred for a series of **Cn** (n = 7–12) for C_6F_6 due to low solubility.

The above features suggested that the stacking interaction among perfluorinated chains has a main factor to bring about chirality effects on gelation. According to the VCD analyses, the stable aggregation mode for enantiopure **CF9** was achieved by

the formation of two anti-parallel intermolecular hydrogen bonds (Fig. 6(a)). The same connection was confirmed to exist in the single crystal of **CF4**. Since a single array was estimated to have a radius of >2 nm, the thin fibrils with a radius of >2 μm, which were observed in the SEM images contained more than ten such arrays. For enantiopure **CF7** and **CF8**, the molecules formed a single intermolecular hydrogen bond. Thus they might form a weaker array. In both cases, however, the outer surface of the array possessed the region of perfluorinated chains. It is speculated therefore that the odd-even effect observed for the gelation ability of enantiopure **CFn**'s (Fig. 1) appeared when the array was bundle to a thin fibril.

In contrast, *RR*- or *SS*-enantiomers formed a homochiral pair and oriented in a head-and-tail way in crystal structure and each array consisted of the opposite enantiomers arranged in an alternative way through the two-antiparallel intermolecular hydrogen bonds. It is proposed that the aggregation of the array to form a thinner fibril is achieved by the interdigitation of perfluorinated chains. Under such an aggregation mode, no contact of the end groups of perfluorinated chains would appear, leading to the absence of odd-even effect.

It should be emphasized that the aim of the above stacking model was to rationalize the difference of gelation behavior between racemic and enantiomeric gelators. It is intended to present no speculative details of fibril structures but simply demonstrates the possible connectivity of the gelator molecules. Presently an experimental support is now under progress by finding any periodic structure that depends on molecular chirality such as neutron diffraction or small angle X-ray diffraction measurements.

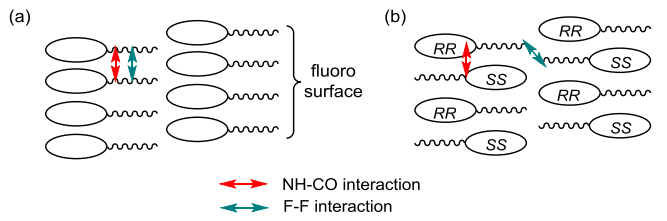

Fig. 6 The molecular models (a) enantiopure-**CFs**, (b) racemic-**CFs**.

Experimental

Synthesis and characterization of gelators

Materials: All commercially available solvents and reagents for synthesis and analysis were used as received without further purification. Benzotrifluoride (>98%) was obtained from Kanto Chemical Co. Inc. Perfluorobenzen (>99%) was obtained from Aldrich. (1*R*,2*R*)-, (1*S*,2*S*)- and racemic-1,2-diaminocyclohexane (>98%) and tetradecafluorohexane (>96%) were obtained from Tokyo Kasei, Ltd. Perfluoroalkanoys chlorides were synthesized according to previous report.[35]

Characterization methods: ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were measured on a JEOL GSX-400 spectrometer (400 MHz for ^{1}H, 100.5 MHz for ^{13}C, and 376.2 MHz for ^{19}F). All chemical shifts (δ) are reported on parts per million downfield of acetonitrile for ^{1}H NMR (δ = 1.96) and ^{13}C NMR (δ = 118.26) and trichlorofluoromethane for ^{19}F NMR (δ = 0.0) were used as internal standard for CD_3CN solutions. ESI mass spectra were measured on a Thermo Scientific Exactive mass spectrometer. Optical rotations were measured on a JASCO P-2200 polarimeter at room temperature, using the sodium D line.

General procedure: To a solution of 1,2-diaminocyclohexane (0.31 mmol) in dry THF (3 ml) were added Et_3N (0.93 mmol, 3.0 eq.) and perfluoroalkanoyl chloride (0.93 mmol, 3.0 eq.) at 0 °C, and the mixture was stirred for 1 hour. The resulting mixture was filtrated and the residue was washed with water. Chemical data of **CF7** and **CF8** were previously reported.[13,14]

***trans*-*N*,*N*'-perfluorobutanoyl-1,2-diaminocyclohexane (CF4):** (1*R*,2*R*)-**CF4** $[\alpha]^{27}_D$ 35.63 (*c* 0.19, THF), (1*S*,2*S*)-**CF4** $[\alpha]^{28}_D$ -37.49 (*c* 0.19, THF); ^{1}H NMR (400 MHz, CD_3CN) δ 7.64 (2H, m, N*H*CO), 3.87 (2H, m, CH_2CHNH), 1.78 (4H, m, cyclohexyl), 1.47 (2H, m, cyclohexyl), 1.34 (2H, m, cyclohexyl); ^{13}C NMR (126 MHz, CD_3CN) δ 52.3 (2C), 30.0 (2C), 23.3 (2C); ^{19}F NMR (376 MHz, CD_3CN) δ -80.3 (6F), -119.9 (4F),-126.5 (4F); HRMS (ESI$^-$) $C_{14}H_{11}O_2N_2F_{14}$ [M-H] (calcd 505.0597, found 505.0578.

***trans*-*N*,*N*'-perfluoropentanoyl-1,2-diaminocyclohexane (CF5):** (1*R*,2*R*)-**CF5** $[\alpha]^{27}_D$ 35.91 (*c* 0.20, THF), (1*S*,2*S*)-**CF5** $[\alpha]^{27}_D$ -34.64 (*c* 0.19, THF); ^{1}H NMR (400 MHz, CD_3CN) δ 7.63 (2H, m, N*H*CO), 3.86 (2H, m, CH_2CHNH), 1.77 (4H, m, cyclohexyl), 1.45 (2H, m, cyclohexyl), 1.32 (2H, m, cyclohexyl); ^{13}C NMR (126 MHz, CD_3CN) δ 52.8 (2C), 30.8 (2C), 23.7 (2C); ^{19}F NMR (376 MHz, CD_3CN) δ -81.8 (6F), -120.4 (4F), -124.1 (4F), -126.5 (4F); HRMS (ESI$^-$) $C_{16}H_{11}O_2N_2F_{18}$ [M-H] (calcd 605.0533, found 605.0524).

***trans*-*N*,*N*'-perfluorohexanoyl-1,2-diaminocyclohexane (CF6):** 1*R*,2*R*)-**CF6** $[\alpha]^{28}_D$ 20.17 (*c* 0.19, THF), (1*S*,2*S*)-**CF6** $[\alpha]^{28}_D$ -22.40 (*c* 0.19, THF); ^{1}H NMR (400 MHz, CD_3CN) δ 7.65 (2H, m, N*H*CO), 3.86 (2H, m, CH_2CHNH), 1.75 (4H, m, cyclohexyl), 1.45 (2H, m, cyclohexyl), 1.33 (2H, m, cyclohexyl); ^{13}C NMR (126 MHz, CD_3CN) δ 52.8 (2C), 30.8 (2C), 23.8 (2C); ^{19}F NMR (376 MHz, CD_3CN) δ -81.5 (6F), -120.2 (4F), -123.1 (4F), -123.3 (4F), -126.7 (4F); HRMS (ESI$^-$) $C_{18}H_{11}O_2N_2F_{22}$ [M-H] (calcd 705.0469, found 705.0461).

***trans*-*N*,*N*'-perfluorononanoyl-1,2-diaminocyclohexane (CF9):** (1*R*,2*R*)-**CF9** $[\alpha]^{27}_D$ 19.492 (*c* 0.19, THF), (1*S*,2*S*)-**CF9** $[\alpha]^{27}_D$ -23.841 (*c* 0.19, THF); ^{1}H NMR (400 MHz, CD_3CN) δ 7.64 (2H, m, N*H*CO), 3.86 (2H, m, CH_2CHNH), 1.76 (4H, m, cyclohexyl), 1.47 (2H, m, cyclohexyl), 1.33 (2H, m, cyclohexyl); ^{13}C NMR (126 MHz, CD_3CN) δ 52.5 (2C), 30.9 (2C), 23.6 (2C); ^{19}F NMR (376 MHz, CD_3CN) δ -81.6 (6F), -119.7 (4F),-122.1 (4F), -122.5 (8F), -123.1 (4F), -123.7 (4F), -126.6 (4F); HRMS (ESI$^-$) $C_{24}H_{11}O_2N_2F_{34}$ [M-H] (calcd 1005.0278, found 1105.0273.

***trans*-*N*,*N*'-perfluorodecanoyl-1,2-diaminocyclohexane (CF10):** (1*R*,2*R*)-**CF10**$[\alpha]^{28}_D$ 13.69 (*c* 0.19, THF), (1*S*,2*S*)-**CF10** $[\alpha]^{28}_D$ -16.53 (*c* 0.25, THF); ^{1}H NMR (400 MHz, CD_3CN) δ 7.64 (2H, m, N*H*CO), 3.86 (2H, m, CH_2CHNH), 1.76 (4H, m, cyclohexyl), 1.47 (2H, m, cyclohexyl), 1.33 (2H, m, cyclohexyl); ^{13}C NMR (126 MHz, CD_3CN) δ 52.4 (2C), 30.7 (2C), 23.5 (2C); ^{19}F NMR (376 MHz, CD_3CN) δ -81.6 (6F), -119.8 (4F),-122.2 (4F), -122.5 (12F), -123.2 (4F), -123.7 (4F), -126.7 (4F); HRMS (ESI$^-$) $C_{26}H_{11}O_2N_2F_{38}$ [M-H] (calcd 1105.0214, found 1105.0211).

Measurements

SEM observation was performed with a S-3100H (Hitachi, Japan). A gel was prepared at the concentration little above cgc A gel sample was deposited onto a silicon wafer. It was freeze-dried after being dried under air. The samples were coated with platinum for the measurements.

VCD spectra were measured using a spectrometer PRESTO-S-2007 (JASCO, Japan). The detector was a liquid nitrogen cooled MCT infrared detector equipped with ZnSe windows. About a gel was sandwiched between two CaF_2 plates with a 50 μm spacer at the critical concentration. No dichroic effect was observed when the samples were rotated with respect to an incident light.

Conclusions

The gelation of C_6F_6 was compared for a series of low-molecular gelators with the perfluorinated chains of various length. Notably gelation was achieved by the racemic form of the perfluorinated molecules. The stacking models for racemic and enantiopure gelators are proposed to explain the difference of their gelation ability.

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