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Molecular origin for helical winding of fibrils formed by perfluorinated gelators[†]

Hisako Sato,*^a Tomoko Yajima^b and Akihiko Yamagishi^c

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A chiral low-molecular weight gelator, N,N'-diperfluoroheptanoyl-1,2(R,R)- or -1,2(S,S)-diaminocyclohexane, was prepared to form a gel of acetonitrile. The conformation of the gelator in fibrils was determined by vibrational circular dichroism spectra, providing a molecular model for self-assembly in a helical fibril.

Self-assembly with low-molecular mass gelators is an attracting topic as an example for achieving supramolecular architectures through the spontaneous aggregation of small molecules.¹ A chiral gelator is of particular interest because gelation often leads to the helical winding of fibrils. Attention has been focused on how the molecular chirality of a gelator is amplified to the helicity of fibrils.¹

A vibrational circular dichroism (VCD) spectrum is an extension to the infrared and near-infrared regions of the circular dichroism spectrum.^{2–7} We recently applied the VCD spectroscopy to the transparent C_6D_6 , gels of 12-hydroxyocta-decanoic acid.⁶ As a result, the long-range chiral transfer was evidenced by the fact that the carboxyl group, which was distant from the asymmetric carbon at the 12 position, gave strong VCD signals in a gel. It was rationalized that the dimerized carboxyl groups took a chiral conformation in fibrils. The VCD spectroscopy has been extended to the Langmuir–Blodgett (LB) films of the same compounds, revealing the difference in hydrogen bonding formation between the gels and LB films.⁶

The present work reports the VCD application to the gels formed by chiral perfluorinated gelators. The chains are known to wind helically due to the steric hindrance among fluorine atoms.^{8,9} The role of perfluorinated carbon chains on gelation was examined. A novel gelator, N,N'-diperfluoroheptanoyl-1,2(R,R)- or -1,2(S,S)-diaminocyclohexane (denoted by **RR-CF7**



Chart 1 The molecular structure of RR-CF7.

or *SS*-CF7, respectively) (Chart 1), was synthesized.^{10,11} For preparation, a THF solution of *trans*-(1*R*,2*R*)- or (1*S*,2*S*)-1,2-diaminocyclohexane and perfluoroheptanoyl chloride was stirred overnight at room temperature under a nitrogen atmosphere in the presence of triethylamine. After filtering out triethylammonium chloride, the filtrate was evaporated to dryness. The residue was dried after being washed with water. The compounds were identified by ¹H NMR, mass spectra, ¹⁹F NMR and differential scanning calorimetry (ESI[†]).

The VCD spectra were measured using a spectrometer PRESTO-S-2007 (JASCO, Japan). Signals were accumulated for 10⁴ scans in about 2 hours at 4 cm⁻¹ resolution, using a liquid nitrogen cooled MCT infrared detector equipped with ZnSe windows. For the preparation of a gel sample, a weighed amount (ca. 5 mg) of the enantiomeric sample was dissolved in CD₃CN (ca. 200 µL) at 40 °C. Thereafter about 50 µL of the solution was sandwiched between two CaF2 plates with a 50 µm spacer. The solution was transformed into a transparent gel at room temperature. For measuring a solution sample, a CD₃CN solution whose concentration was lower than the critical concentration of sol-gel transition was injected into a cell with CaF₂ windows of 50 µm optical path length. Vibrational frequencies and VCD intensities were simulated by the use of Gaussian 09 program at the DFT level (B3LYP functional) with 6-31G(d,p), respectively.¹² The IR and VCD spectra were calculated on the basis of the magnetic field perturbation (MFP) theory. Description of calculated modes was made from the animations of the modes and spectra with Gauss view 5.08 (Gaussian Inc.).

The gelating ability of chiral **CF7** was studied for a number of solvents in order to see the effect of perfluoroalkyl chains on gelation (ESI†). As a result, **CF7** was found to form a gel of fluorinated solvents such as perfluorobenzene and perfluorotoluene. A similar effect of fluorinated chains was reported recently for achiral perfluoroalkaneamides.^{13–15} The

^a Graduated School of Science and Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan. E-mail: h-sato@ehime-u.ac.jp; Fax: +81 89-927-9599; Tel: +81 89-927-9599

^b Graduate School of Humanities and Sciences,

Ochanomizu University, Tokyo 112-8610, Japan

^c Department of Chemistry, Toho University, Funabashi, Chiba 274-8510 Japan

[†] Electronic supplementary information (ESI) available: ¹⁹F-NMR, mass spectra, elementary analysis, ORD measurement, DSC measurement, transition temperature, ΔH and T by Schröder-van-Laar equation, AFM and SEM of **RR-CF7**, XRD in powder of **SS-CF7**, VCD solution sample, comparison of IR and VCD between **RR-CF7** and non-fluorinated gel in the experimental and DFT calculations, model of helix formation, gelation of solvent, complete ref. 12. See DOI: 10.1039/c0cc05802e



Fig. 1 The SEM image of a CH₃CN gel of SS-CF7.

dependence of the sol-gel transition temperature on the concentration of a gelator was studied for acetonitrile gels. By applying Schröder-van-Laar equation to the observed results,¹⁶ the main cause for the stabilization by **CF7** was concluded to lie in the larger heat of fusion (ESI[†]).

Fig. 1 shows the SEM image of a CH₃CN gel by *SS*-CF7. Fibrils wound helically over a wide range of pitch lengths (0.1–10 μ m). Helicity was always left-handed irrespective of the scale of helices. The fibrils of *RR*-CF7 gels of the same solvent were right-handed, indicating that helicity was determined uniquely by the chirality of a gelator. The AFM images indicated that the fibrils were the aggregates of thinner fibers of *ca*. 20 nm in radius (ESI[†]).

The VCD spectra were measured on the CD₃CN gels of CF7 in the wavenumber range of 1000–1800 cm⁻¹ (Fig. 2(a)). The measurements were also performed for the CD₃CN solutions of CF7 at the lower concentration. In both cases, main peaks showed mirror-imaged relation between *RR*-CF7 and *SS*-CF7. When the intensity of the VCD peak around 1680 cm⁻¹ was compared, the gel samples gave a *g*-value ($\Delta A/A$) 18 times higher than the solution samples. Thus the formation of a gel resulted in the enhancement of the VCD intensity.

In the measured VCD spectra of the gels, a strong couplet was observed around 1688 cm⁻¹, which was assigned to the stretching vibration of C=O bonds (indicated by 1 in the figure). There was a small couplet around 1539 cm⁻¹ in VCD spectra, which was assigned to the bending vibration of N-H bonds (indicated by 2). The multiple peaks in the region of 1238–1170 cm⁻¹ were assigned to the stretching vibrations of C-F bonds (indicated by 3, 4 and 5).

For assigning the observed peaks in Fig. 2(a), vibrational properties were studied theoretically for a trans-(1R,2R)molecule. The molecular structure of a monomeric form was optimized under C_1 symmetry (ESI[†]). It was noted that two C=O or N-H groups orient in an opposite direction with respect to the molecular plane of a cyclohexyl ring. All transperfluorinated chains ejected outwards with the C-F bonds wounded helically in a right handed direction. The FT-IR and VCD spectra were calculated under this molecular conformation. According to the calculated spectrum (Fig. 2(b)), the negative and positive VCD peaks at the lower and higher wavenumbers around 1811 cm⁻¹ correspond to the couplet around 1688 cm^{-1} in the observed spectra. These peaks were assigned to the symmetric and asymmetric stretches of C=O groups, respectively. The calculated peaks corresponding to the N-H bending vibration have much higher intensity than the observed peaks. Thus the VCD behavior of N-H bonds is thought to be delicately dependent on the molecular



Fig. 2 (a) The observed IR (lower) and VCD (upper) spectra of the CD₃CN gels of RR-CF7 (black) and SS-CF7 (gray), respectively. (b) The calculated IR and VCD spectra of a single molecular state of RR-CF7.

conformation in the aggregated states. The multiple VCD peaks assigned to the C–F stretches are well predicted by the present model. Thus the perfluorinated carbon chains in *RR*-CF7 are concluded to take a right-handed helix along the C–C skeletons.

In a fibril, CF7 molecules might be aggregated through the intermolecular hydrogen bonding between C=O and N-H groups.⁷ When one molecule is placed over the other in a parallel fashion, they stack closely, forming two intermolecular hydrogen bonds between C=O and N-H groups (ESI[†]). In the case of a pair of **RR-CF7** molecules, the upper molecule should rotate in the right-handed way with respect to the lower molecule in order to attain the simultaneous formation of two hydrogen bonds. If the gelator molecules are stacked sequentially under this rotation, the resultant tape-like aggregate would wind helically in a right-handed fashion. The above intermolecular interaction is regarded as an origin for hierarchical development attaining the helical fibril on a micrometre scale. The outer region of the aggregate would be the layer of perfluorinated groups. This might explain the tendency of CF7 for gelating fluorinated solvents. As an additional aspect, the frequency of C=O stretching showed a red-shift ($\sim 40 \text{ cm}^{-1}$) in comparison to the non-fluorinated gel (ESI[†]). This might reflect the presence of the interchain interaction between carbonyl groups and fluorinated chains. Such weak non-covalent interactions are previously postulated for hierarchical structures in the case of fluorinated polysilane gelators.¹⁴

The X-ray diffraction measurements on the powder sample of *SS*-CF7 showed the sharp peaks at 1.87 nm and 0.47 nm, which were assigned to the molecular length of CF7 and the intermolecular distance of stacked molecules, respectively (ESI†). The X-ray diffraction measurements on the gel samples are now under progress. In summary, the application of the VCD method gave an insight into the molecular arrangement in a fiber by determining the precise conformation of a gelator.

VCD spectroscopy has revealed the molecular conformation of a chiral perfluorinated gelator in fibrils. A molecular mode was constructed to explain the molecular origin for the helical winding of fibrils.

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