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COMMUNICATION

Promotion effects of optical antipodes on the formation of helical fibrils: chiral perfluorinated gelators†‡

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A chiral gelator, *RR*- or *SS*-*N*,*N*′-diperfluorooctanoyl-1,2-diaminocyclohexane, gelated racemic 2-butanol. The gel was most stable at the racemic mixture, its stability lowered with the increase in the optical purity of the gelator. Notably, characteristic helically coiled fibrils were formed in the narrow region of enantiomer excess (ee = 0.2–0.4). Promotion effects of the antipodal enantiomers are proposed.

The self-assembly of low-molecular mass gelators is an attractive topic as an example for the supramolecular architecture through spontaneous aggregation.[1–7] Attention has been focused on the effects of the stereochemical properties of a gelator on gelation.[2] As a role of molecular chirality, for example, enantiopure forms are often more efficient in forming a gel than racemic ones. In some cases, however, racemic mixtures form gels as well as enantiopure forms.[2]

We recently studied the gelation of a chiral gelator, *N*,*N*′-diperfluoroheptanoyl-1,2-diaminocyclohexane (denoted as **CF_7**),[8] which is a perfluorinated analogue of well-known gelators based on 1,2-diaminocyclohexane, *N*,*N*′-dialkanoyl-1,2-diaminocyclohexanes (denoted as **CH_n**).[5,6] Enantiopure **CF_7** gelated several solvents, particularly fluorinated liquids, while its racemic mixture was highly crystalline and exhibited no gelating ability. In this respect, the stereochemical effects of **CF_7** on gelation were the same as those of **CH_n**.[9]

The present communication reports the gelating behavior of *N*,*N*′-diperfluorooctanoyl-(1*R*,2*R*)- or (1*S*,2*S*)-1,2-diaminocyclohexane (denoted as ***RR*-CF_8** or ***SS*-CF_8** or **racemic-CF_8**, for *RR*- or *SS*- or racemic diaminocyclohexane moieties, respectively (Chart 1)). It has been demonstrated that the elongation of perfluorinated chains by one CF_2 unit resulted in the drastic change in gelation behavior.

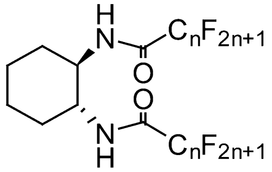

Chart 1 Molecular structures of gelator, n = 6: **CF_7**, n = 7: **CF_8**.

Gelators, ***RR*-CF_8**, ***SS*-CF_8** and **racemic-CF_8**, were synthesized by reacting *RR*-, *SS*-, and racemic diaminocyclohexane with perfluorooctanoyl chloride, respectively.[10,11] For preparation, diaminocyclohexane, perfluorooctanoyl chloride and triethylamine were dissolved in THF and stirred for 3 hours at 0 °C under a nitrogen atmosphere. Thereafter the mixture was continuously stirred overnight at room temperature. After filtering out triethylammonium chloride, the filtrate was evaporated to dryness. The residue was washed with water and dried in vacuum. The compounds were identified by ^{1}H NMR, mass spectra, ^{19}F NMR, differential scanning calorimetry and optical rotatory dispersion (see ESI†). The samples for PXRD measurements and SEM observation were prepared by freeze-drying gels under vacuum. For the PXRD measurements, solvent molecules remained in the samples. The VCD spectra were measured using a PRESTO-S-2007 spectrometer (JASCO, Japan). Experimental details are described in ESI.†

The gelating properties of ***RR*-CF_8**, ***SS*-CF_8** and **racemic-CF_8** were compared for a number of organic solvents (see ESI†). Sol–gel transition temperature and critical gel concentration were measured in case gelation occurred. One remarkable feature was that the enantiopure forms (***RR*-CF_8** and ***SS*-CF_8**) were unable to form a stable gel for any solvent investigated, while the racemic mixture (**racemic-CF_8**) gelated several polar and non-polar solvents. From the time-dependent observation with an optical microscope of a racemic 2-butanol solution containing a gelator, the enantiomer crystallized in minutes, while the racemic mixture still kept a gel for several hours (see ESI†).

For racemic 2-butanol as a solvent, gelation was investigated by changing the enantiomer excess (ee) of the gelator. From the dependence of the sol–gel transition temperature on ee (Fig. 1), the stability of gels was highest at the racemic mixture and

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† Electronic supplementary information (ESI) available: ^{1}H-NMR, ^{19}F-NMR, Mass spectra, IR spectra, material, yield, ORD, DSC, critical gel concentration, image of turbid viscous solution and racemic gel by optical microscopy, SEM of ***RR*/*SS*** = 6 : 4(4 : 6), 8 : 2(2 : 8), 9 : 1(1 : 9) and racemic, 1 : 1 in 2-butanol and ***RR*/*SS*** = 7 : 3(3 : 7) in 1-butanol, experimental and analyses details of PXRD, DSC and VCD, PXRD in powder of *SS* and racemic, the geometry of the gelator and the model of gel. See DOI: 10.1039/c2cc18164a

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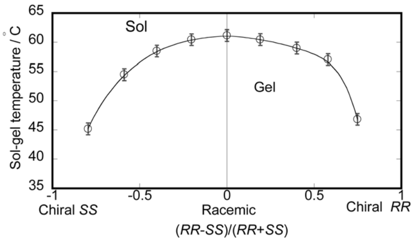

Fig. 1 The dependence of sol–gel transition temperature on the enantiomeric excess of $\mathbf{CF_8}$. The total concentration of the gelator was 0.015 M.

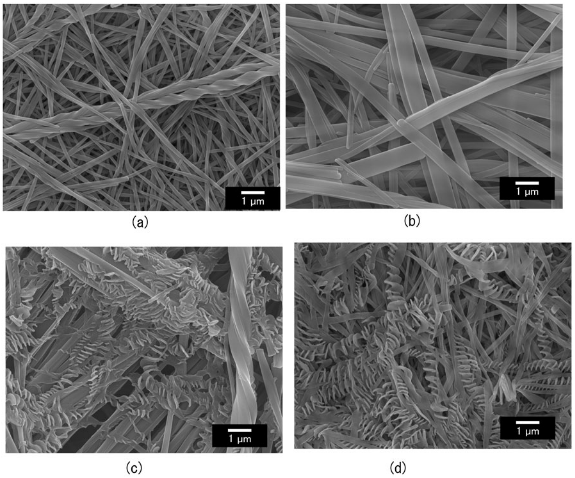

Fig. 2 SEM images of xerogels: (a) racemic (0.015 M), (b) *SS* (0.02 M), (c) *RR*/*SS* = 7 : 3 (ee = 0.4) (0.015 M) and (d) *RR*/*SS* = 3 : 7 (0.015 M).

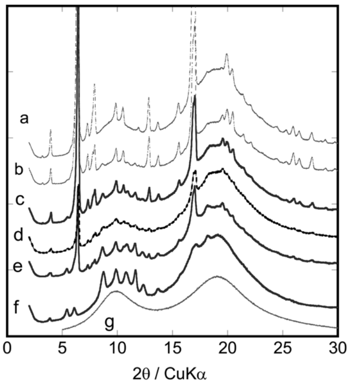

Fig. 3 PXRD peaks of xerogels: (a) *SS*, (b) *RR*/*SS* = 1 : 9 (ee = 0.8), (c) *RR*/*SS* = 2 : 8 (ee = 0.6), (d) *RR*/*SS* = 3 : 7 (ee = 0.4), (e) *RR*/*SS* = 4 : 6 (ee = 0.2), (f) racemic and (g) racemic-2-butanol solvent. The concentrations were *ca.* 0.10 M.

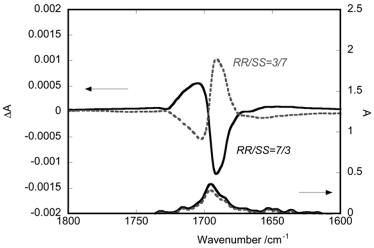

Fig. 4 The IR and VCD spectra of racemic 2-butanol gels at *RR*/*SS* = 7 : 3 (solid line) or 3 : 7(dotted line).

lowered with the increase in optical purity. The photographic images of the gel and turbid viscous solutions are given in ESI.†

Fig. 2 shows the SEM images of the racemic 2-butanol xerogels formed at ee = 0 (racemic), 0.4, and 1.0. For $\mathbf{racemic\text{-}CF_8}$, tape-shaped fibrils were observed with *ca.* 0.1 μm width. Helical fibrils were also observed, winding in either the left-handed or right-handed direction. In a certain fibril, helicity switched from one direction to the other on the halfway (see ESI†). At ee = 0.4, helically coiled fibrils were observed predominantly with the same handedness over the pitch length range of 50–300 nm. Helicity was right- or left-handed, when *RR*- or *SS*-enantiomer was used as a major component, respectively. Some of the tape-shaped fibrils wound helically with the pitch length larger than 1 μm. In the case of these fibrils, no unique relation existed between helicity and molecular chirality. A similar SEM image was obtained at ee = 0.2 (see ESI†). At ee = 0.8, fibrils took a tape-like shape with no winding in resemblance to the turbid viscous solution formed from pure enantiomers (see ESI†).

Fig. 3 shows the PXRD patterns of the xerogel samples at ee = 1 (pure enantiomer), 0.8, 0.6, 0.4, 0.2, 0.0 (racemic mixture) and 2-butanol. The broad peaks at around $2\theta = 10°$(0.90 nm) and 19°(0.45 nm), respectively, were due to the diffraction of trapped solvent molecules. For the racemic gel, several small peaks were observed at $2\theta = 5.4°$(1.63 nm), 8.8°(1.01 nm), 10.8°(0.82 nm), 11.7°(0.76 nm) and 12.4°(0.71 nm). These peaks were ascribed to the tape-shaped fibrils as shown in Fig. 2(a). Each peak was indexed under the assumption that racemates formed a hexagonal lattice of **a** = 2.7 nm, **b** = 2.7 nm and **c** = 1.6 nm. The PXRD pattern of the racemic gel was different from that of the racemic crystal (see ESI†). At ee = 0.2, in addition to the peaks due to the racemate, new sharp peaks appeared at $2\theta = 6.4°$(1.38 nm) and 17.0°(0.52 nm) together with small peaks at $2\theta = 4.0°$(2.23 nm), 7.3°(1.21 nm), 8.0°(1.11 nm), 9.9°(0.89 nm), 10.5°(0.84 nm), 12.9°(0.69 nm), 13.7°(0.65 nm), 15.6°(0.57 nm), 19.9°(0.45 nm) and 20.5°(0.43 nm). The latter peaks continued to be seen until the sample was formed at the pure enantiomer (ee = 1.0). The diffraction peaks were indexed on the basis of a monoclinic lattice of **a** = 2.2 nm, **b** = 1.4 nm and **c** = 0.5 nm, $\alpha = 90.0$, $\beta = 90.0$, $\gamma = 95.0°$ (see ESI†).

Fig. 4 shows the IR and VCD spectra of the racemic 2-butanol gels at ee = 0.4. In the VCD spectra, a strong couplet was observed around 1688 cm^{-1}, satisfying the mirror-image relation between the samples of *RR*/*SS* = 3 : 7 and 7 : 3. Thus the observed VCD peaks were due to the major enantiomeric components in helically coiled fibrils. The couplet was assigned to the stretching vibration of C═O bonds. The signs of the observed couplets for C═O stretching vibrations were the same as those reported for the acetonitrile gels by $\mathbf{CF_7}$.[8] In the latter cases, it was deduced that the molecules formed a helical aggregate by the sequential formation of hydrogen bonding between >NH and >C═O. In the aggregates, the cyclohexyl rings are stacked in a rotating way whose direction depends on the molecular chirality.

Comparing the gelation behavior between $\mathbf{CF_7}$ and $\mathbf{CF_8}$, the elongation of perfluorinated chains by one –CF$_2$– unit resulted in the complete change of chirality effects on gelation. That is, enantiopure $\mathbf{CF_7}$ and racemic $\mathbf{CF_8}$ are good gelators, while racemic $\mathbf{CF_7}$ and enantiopure $\mathbf{CF_8}$ are too crystalline. According to the model derived from the VCD results, the cyclohexyl rings of gelators were stacked as a central core with all *trans*-perfluorinated chains ejecting outwards. Thus the observed reversal of chirality effects might be rationalized in terms of the terminal effects of perfluorinated chains on the inter-aggregate interactions. The main influence of the elongation of one $–CF_2–$ unit was the decrease in cohesion energy among the racemic aggregates, leading to the increase in gelation ability of racemic $\mathbf{CF_8}$. Similar effects of the end group of an alkyl chain on cohesion energy were reported previously.[12]

Another notable feature in $\mathbf{CF_8}$ was the formation of helically coiled fibrils at ee = 0.2 (see ESI†)–0.4 (Fig. 2(c) and (d)). Helicity with a pitch less than 300 nm was related to the absolute configuration of the major enantiomeric components. Therefore the results are considered to be an example of the *Majority Rule* of chirality amplification.[13] According to the PXRD results, the characteristic peaks due to racemic aggregates disappeared rapidly with the increase in ee, while the peaks due to homochiral aggregates maintained their intensity throughout the range of ee = 0.2–0.8. We noticed that the coiled fibrils existed predominantly at ee = 0.4, at which the racemic peak nearly disappeared. In other words, the generation of helically coiled fibrils was realized by the disappearance of racemic aggregates in the presence of a surplus amount of homochiral aggregates. In the present case, it is noted that no helical fibril was formed at ee larger than 0.8.

There are two possible roles of optical antipodes in the formation of helically coiled fibrils; (i) to retard the transformation rate of the homochiral aggregates into tape-like fibrils and (ii) to participate as a minor component in the homochiral aggregates to induce the helical winding in the range of 50–300 nm. If the effects of antipodes were limited to possibility (i), it is difficult to rationalize the fact that helical fibrils existed predominantly in the narrow ee region (ee = 0.2–0.4). We suspect that, under the assumption of possibility, (ii) homochiral *RR*- and *SS*-aggregates were associated at an unequal ratio to form hybridized helically coiled fibrils. One example is schematically shown in ESI†, in which *RR*- and *SS*-aggregates combine at a 12 : 7 ratio to form a hexagonal lattice in fibrils. Similar hybridization with unequal amounts of optical isomers is reported for the formation of stereo-complexes in stereoregular polymers or the columnar liquid crystal phases consisting of chiral tris(chelated) metal complexes.[14] The validity of the above assumption would be verified if the molecular stacking structures in the helical fibrils are revealed by means of atomic force microscopy, for example.[15]

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