

Critical effects of alkyl chain length on fibril structures in benzene-*trans*(*RR*)- or (*SS*)-*N,N'*-alkanoyl-1,2-diaminocyclohexane gels†Hisako Sato,*^a Takahiro Nakae,^a Kazuya Morimoto^a and Kenji Tamura^b

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Vibrational circular dichroism (VCD) spectra were recorded on benzene-*d*⁶ gels formed by chiral low molecular mass gelators (LMGs), *trans*(*RR*)- or *trans*(*SS*)-*N,N'*-alkanoyl-1,2-diaminocyclohexane (denoted by *RR-C_n* or *SS-C_n*, respectively; *n* = the number of carbon atoms in an introduced alkanoyl group). Attention was focused on the effects of alkyl chain length on the structures of the gels. When *n* was changed from 6 to 12, the signs of the coupled peaks around 1550 cm⁻¹ in the VCD spectra, which were assigned to the symmetric and asymmetric C=O stretching vibrations from the higher to lower wavenumber, respectively, critically depended on the alkyl chain length. In the case of *RR-C_n*, for example, the signs of the couplet were plus and minus for *n* = 8, 9, 10 and 12, while the signs of the same couplet were reversed for *n* = 6 and 7. The conformations of LMGs in fibrils were determined by comparing the observed IR and VCD spectra with those calculated for a monomeric molecule. The observed reversal of signs in the C=O couplet was rationalized in terms of the different modes of hydrogen bonding. In the case of *C₈*, *C₉*, *C₁₀* and *C₁₂*, gelator molecules were stacked with their cyclohexyl rings in parallel, forming double anti-parallel chains of intermolecular hydrogen bonds using two pairs of >NH and >C=O groups. In case of *C₆* and *C₇*, gelator molecules were stacked through a single chain of intermolecular hydrogen bonds using a pair of >NH and >C=O groups. The remaining pair of >NH and >C=O groups formed an intramolecular hydrogen bond.

Introduction

Organogels form a continuous three-dimensional entangled network in organic solvents.¹ Knowledge of the molecular stacking structure in a fibril would be helpful to understand the origin of the driving force for gelation.^{1–4} For this purpose, a number of spectroscopic methods have been applied such as X-ray and neutron diffraction analyses. One difficulty, however, is that gels are often lacking in three-dimensional periodicity so that the molecular images of gels are often difficult to construct from the diffraction data alone.

Low molecular mass gelators based on *trans*-1,2-diaminocyclohexane were first reported by Hanabusa *et al.*⁵ Since then, these compounds have attracted extensive attention due to their high gelating capability towards a wide range of organic solvents. One of the outstanding properties of the gelators is that a fibril adopts a helical structure, where the helicity depended uniquely on the *RR/SS* molecular chirality. Based on these properties, there have been a number of attempts to use the gels as a template for asymmetric syntheses. In particular, chiral silica were prepared by the sol–gel reactions of silanols in the presence of the chiral gels.^{6,7} The main driving force for the formation of fibrils is thought to be the intermolecular hydrogen bonding between >NH and >C=O groups. It remains to be clarified, however, how the gelator molecules are stacked to achieve helical structures. Only recently gelators based on the diaminocyclohexane with various alkyl chains were reported, revealing the role of weak van der Waals interactions among the alkyl chains.⁸

Vibrational circular dichroism (VCD) is an extension into the infrared and near-infrared regions of the spectrum where vibrational transitions occur in the ground electronic state of a molecule.^{9–21} One of the advantages of VCD over electronic circular dichroism (ECD) is a large amount of information concerning $3N - 6$ vibrations (N = the number of atoms in a molecule). Accordingly the method has been proved to be a powerful tool

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†Electronic supplementary information (ESI) available: ¹H NMR, elemental analyses, mass spectra, DSC and ORD, yields for *C₆–C₁₂*; critical gel concentration; sol–gel transition temperatures in toluene; VCD of *C₇* and *C₁₀* in CDCl₃; VCD of powder samples of *C₁₀*, *C₈* and *C₇* in KBr; VCD of *RR-C₈* gel sample; The VCD spectra dependence on concentration of *RR-C₉* and *RR-, SS-C₇*; VCD calculation of dimer model of *RR-C₈* and *C₆*; VCD calculation of *RR-C₈* and *C₇* with benzene; optimized structure of *RR-C₈* and *C₇* with benzene; SEM image of *SS-, RR-C₇* and *SS-C₈*; XRD of powder in *C₁₂*, toluene-gel states of *C₈*, *C₇*, toluene solvent and glass. See DOI: 10.1039/c1ob06460f

Table 1 Critical gelation concentration (CGC) in benzene for gelators C_n

	CGC/g L ⁻¹	CGC/mol L ⁻¹
C_6	11.5	0.037
C_7	8.0	0.024
C_8	13.8	0.038
C_9	11.4	0.029
C_{10}	7.4	0.018

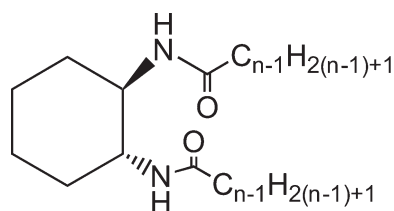
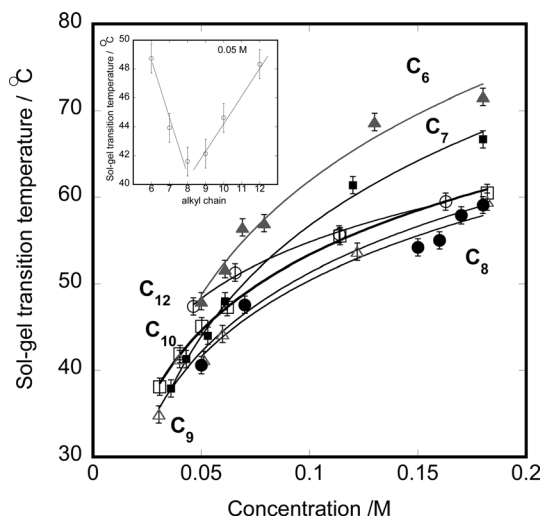
for determining the absolute configuration and molecular conformation of chiral molecules in solution.⁹

Over a number of years the VCD method has been applied to chiral molecular aggregates such as proteins, gels and films.^{10–21} We measured the VCD spectra of an organogel formed by perfluorinated gelators in order to analyze the conformation of a chiral gelator in a fibril.¹⁷ Notably such a gel was found to give more than one order stronger VCD signals than the same gelator in solution. By comparing the observed and calculated spectra, the conformation of a gelator, including the helical winding of perfluorinated chains, was determined to postulate a stacking model in a fibril.

In the present study, VCD investigation was performed on gels formed by *trans*-diaminocyclohexane derivatives with various alkyl chains. The experimental VCD spectra of the transparent gels of benzene-*d*⁶/*trans*(*RR*)- or (*SS*)-*N,N'*-alkanoyl-1,2-diaminocyclohexane (denoted by *RR-C_n* or *SS-C_n*, respectively; *n* = the carbon number of alkyl chains) were compared with the theoretical spectra calculated under various assumptions. It was found that there was a critical length of alkyl chain in determining the stacking modes in fibrils.

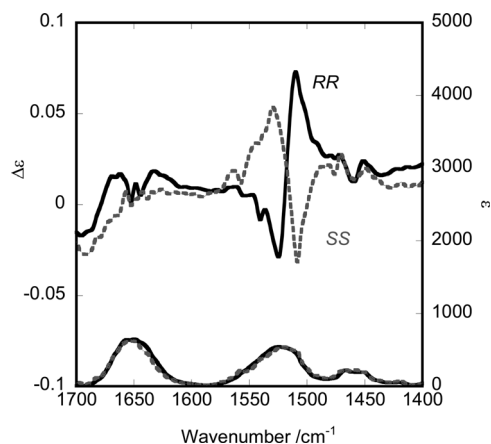
Results and discussion

RR- (or *SS*)-*N,N'*-dialkanoyl-1,2-diaminocyclohexane with alkyl chains of various length (denoted as *RR-C_n* or *SS-C_n*; *n* = the carbon number of alkyl chains. Chart 1) were synthesized according to the reported method.⁵ The purity of the materials was confirmed by mass spectra, elemental analyses, ORD (see ESI†) and HPLC measurements. The compounds (denoted by C_6 – C_{12}) gelled various solvents as shown in ESI†. Benzene and toluene gels were transparent, while the gels of other solvents (acetonitrile, acetone and hexane) were turbid. Methanol did not form a gel for C_n ($n < 9$). Table 1 summarizes the critical gel concentration (CGC) for benzene at 25 °C. It was noted that C_8 gave the highest CGC value or the gel capability was minimum at this length of an alkyl chain. Fig. 1 shows the sol–gel phase transition temperature (T_c) for benzene at constant concentration

**Chart 1** The molecular structure of *RR-C_n*.**Fig. 1** Sol–gel transition temperature in benzene solvent. The inset figure shows the change of sol–gel transition temperature as a function of alkyl chain length at the concentration of 0.05 mol L⁻¹.

of a gelator. As shown in the figure, C_8 gave the lowest T_c , or it formed the least stable gel. This corresponded to the results in Table 1. Thus the present results suggested that a fibril underwent some structural change around the critical chain length of C_8 . Moreover, the gels formed by gelators with alkyl chains shorter than C_7 readily released the solvent to become white and turbid in about 2 h. The sol–gel transition temperature was also measured for toluene (see ESI†). According to the results, T_c exhibited a minimum at C_8 when plotted against C_n .

IR and vibrational circular dichorism (VCD) spectra of C_n were first recorded in $CDCl_3$ solution. As an example, the results for C_8 are shown in Fig. 2. The couplet peaks around 1524 cm⁻¹, which are assigned to symmetric and asymmetric N–H bending vibrations from the higher to lower wavenumber, respectively, showed opposite signs between *RR-C₈* and *SS-C₈*, confirming the reliability of the measurements. The observed frequencies suggested that no hydrogen bonds were formed in this solvent.⁵ No VCD peaks was observed around 1650 cm⁻¹,

**Fig. 2** The observed IR (lower) and VCD (upper) spectra of chiral C_8 in $CDCl_3$ solution.

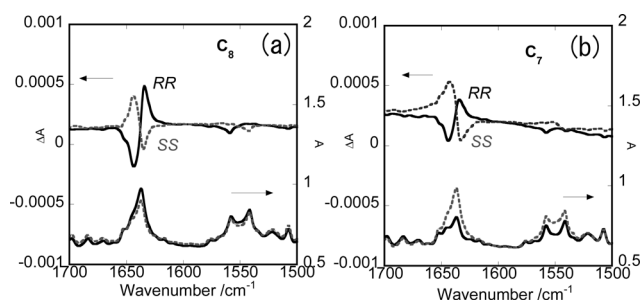


Fig. 3 Observed IR (lower) and VCD (upper) spectra of chiral C_8 and C_7 as solids in KBr pellets.

although the band assigned to the C=O stretching of a carboxyl group was observed at the same wavenumber region of IR spectra. The VCD spectra of C_7 and C_{10} in $CDCl_3$ solutions are shown in ESI†. According to these, the couplet assigned to NH bending had the same sign as for C_8 .

Next, the IR and VCD spectra of C_n in the solid state were measured as their transparent KBr pellets. Fig. 3a and b show the results for C_8 and C_7 , respectively. In contrast to the VCD spectra in solution, clear VCD peaks assigned to C=O stretches were observed around 1640 cm^{-1} (the IR and VCD spectra of C_{10} are shown in ESI†). The couplet signal around 1640 cm^{-1} gave the same signs for these compounds (plus and minus signs from the lower to higher wavenumber for RR - C_8 and C_7). In order to estimate dichroic effects on the VCD spectra in the solid state, the samples were rotated perpendicularly to the monitoring light. The spectra underwent no change, excluding any dichroic contribution. No signal was observed for solid samples of racemic compounds (see ESI†).

Finally, the IR and VCD spectra were measured for the C_6D_6 gels formed by chiral C_6 – C_{12} . The results are shown in Fig. 4a–f. The main peaks for the RR - and SS -gels were essentially mirror-images in the wavenumber range of 1700 – 1400 cm^{-1} . When the gel samples were rotated vertically to the monitoring light, no change of the spectra was observed (see ESI†). Comparing the peaks around 1550 cm^{-1} between the gels and the solutions, the VCD signals for the gel states were enhanced at least ten times in comparison to the solution spectra. Moreover, the peak assigned to N–H bending showed a blue shift by about 30 cm^{-1} , suggesting the occurrence of hydrogen bonding.

In the measured VCD spectra of the gels, the strong couplet was observed around 1640 cm^{-1} , which was assigned to the stretching vibration of C=O bonds. The appearance of this band suggested the formation of intermolecular hydrogen bonds. In case of RR - C_n ($n = 8$ – 12), the signs of the couplet were plus at 1643 cm^{-1} and minus at 1632 cm^{-1} . In contrast, for C_6 and C_7 , the couplet assigned to the same C=O stretches showed reversed signs of minus to plus from the higher to lower wavenumber. When the concentration of a gelator was changed, no change was observed in the VCD spectra for all gelators, as shown in ESI†. In order to eliminate any linear dichroism effects, the cell was rotated along the direction of a monitoring light and also turned back-inside out; reproducible VCD signals were obtained for several samples independently prepared (see ESI†). At the near critical gel concentration, the sol–gel transition temperature indicates the presence of the minimum point

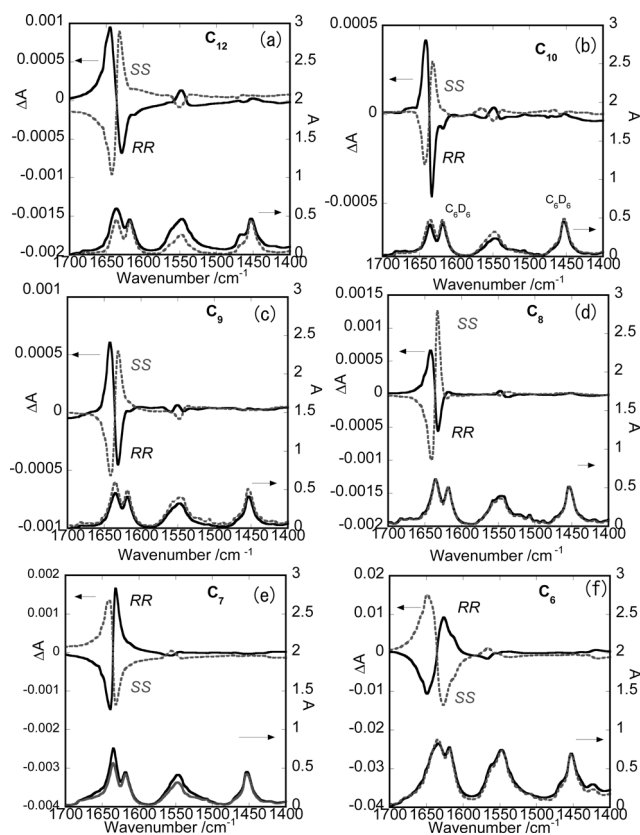


Fig. 4 Observed IR (lower) and VCD (upper) spectra of C_6D_6 gels of RR - C_n (black solid line) or SS - C_n (grey dotted line), respectively: (a) C_{12} , (b) C_{10} , (c) C_9 , (d) C_8 , (e) C_7 and (f) C_6 .

Table 2 Summary of observed VCD spectra (cm^{-1}) of RR - C_n

		C=O stretching	N–H bending
C_6 – C_{12}	Solution	1655^a	1524 (–), 1510 (+)
	Solid	1644 (–), 1634 (+)	1558 (–), 1538 (+)
C_8 – C_{12}	Gel	1643 (+), 1632 (–)	1547 (+), 1538 (–)
	C_6, C_7	1639 (–), 1632 (+)	1557 (–), 1544 (+)

^a IR spectrum; VCD showed no signal.

at C_8 as shown in the insert figure of Fig. 1; the same tendency is observed in the VCD spectra of gels.

Table 2 summarizes the observed VCD results of RR - C_n ($n = 6$ – 12). Comparing the peaks due to C=O stretches in the VCD spectra between the gels and the solids, it was concluded that the gelators with the alkyl chains shorter than C_7 adopted the same structures as in solids, while the gelators with alkyl chains longer than C_8 adopted different structures from those in solids. The difference was thought to lie in the mode of hydrogen bond as described below.

For assigning the observed peaks in Fig. 2, vibrational properties were theoretically studied for a single RR -molecule. The optimized structures of monomeric species are shown for RR - C_8 and RR - C_7 in Fig. 5a and b, respectively. According to the calculated results, the alkyl chains adopted an all *trans*-configuration for both cases. Fig. 6 shows the IR and VCD spectra calculated

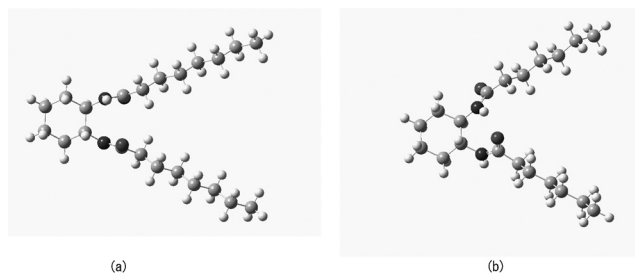


Fig. 5 Optimized structures of gelators: (a) *RR-C*₈ and (b) *RR-C*₇.

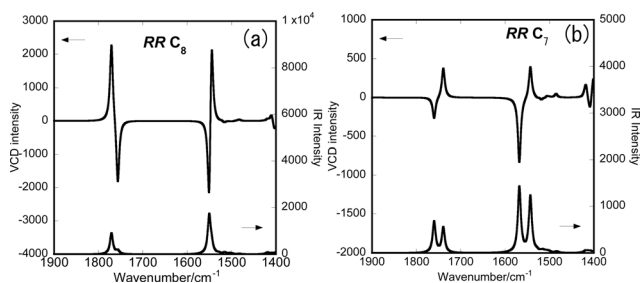


Fig. 6 Calculated IR (lower) and VCD (upper) of the monomer model of (a) *RR-C*₈ and (b) *RR-C*₇, respectively.

for this molecular conformation. For *RR-C*₈, the calculated spectra reproduced the observed one (Fig. 4d) to a satisfactory extent. For example, the signs of the couplet of N–H bending were calculated to be 1550 cm⁻¹ (–) and 1544 cm⁻¹ (+) for monomeric *RR-C*₈. When this was compared with the observed spectra of the solution samples, the calculated signs agreed with the experimental ones (1524 (–) and 1510 cm⁻¹ (+)). The couplet due to C=O stretching was predicted to be at 1770 (+) and 1756 cm⁻¹ (–). As described in the preceding section, no peak due to C=O stretching appeared in the observed spectra of the solution samples. When the calculated results were compared with the observed ones for gels, the predicted signs for N–H bending were opposite to the observed ones. This discrepancy might be caused by the effects of the aggregation of gelators in gel states. In fact, the calculation based on the dimer model succeeded in better predicting the observed spectra as described later. As for the peaks due to C=O stretching also, the predicted signs well reproduced the measured VCD spectra (1643 (+) and 1632 cm⁻¹ (–)).

In the optimized structure calculated for *RR-C*₈, two equatorial N–H and C=O groups are oriented anti-parallel to each other and perpendicular to the cyclohexyl ring. The molecules in fibrils are thought to aggregate under this conformation. Most probably they form intermolecular hydrogen bonds simultaneously at the positions of two pairs of >NH and >C=O groups. Accordingly two anti-parallel hydrogen-bonding chains were formed along the linear molecular aggregates. The enhancement of the VCD signals in the gels might be related to the infinite zigzag chains of hydrogen bonds. The formation of such molecular aggregates is expected to increase VCD intensity particularly when the vibration involves the chemical bonds participating in aggregate formation.

For *RR-C*₇ the optimized structure is shown in Fig. 5b. The couplet assigned to C=O stretching was predicted to appear at 1760 (–) and 1739 cm⁻¹ (+) as shown in Fig. 6b. The signs agreed with the measured spectra and the observed reversal of the signs was reproduced by the theoretical calculation based on the monomer model. The couplet assigned to NH bending was predicted to appear at 1567 (–) and 1543 cm⁻¹ (+). This prediction was the same as those for in solution. When the optimized structure was examined in detail, a pair of >NH and >C=O groups on different alkyl chains were positioned closely enough to form an intramolecular hydrogen bond. In this conformation, the molecules would find it difficult to form double infinite chains as found for *RR-C*₈. Instead, they probably form an aggregate through a single chain of hydrogen bonds by using a remaining pair of >NH and >C=O groups. In such an aggregate, the cyclohexyl rings were expected to be arranged on a plane in an alternatively opposite direction. Thus the aggregate would take a tape-like shape instead of a column-like aggregate expected for *RR-C*₈.

In order to investigate the effects of molecular aggregation in more detail, the dimer model was constructed by connecting two *RR-C*₈ molecules through the hydrogen bond between the >C=O (upper) and >NH (lower) groups. This was regarded as a part of a column-like aggregate. The optimized structure as well as the calculated IR and VCD spectra are shown in ESI†. The predicted couplets assigned to N–H bending and C=O stretching were both in accord with the experimental observation.

As a possible model for the stacking of *C*_n with shorter alkyl chains, the optimum structure of a *RR-C*₆ dimer was calculated theoretically. This was regarded as a part of tape-like aggregate and calculated IR and VCD spectra are shown in ESI†. The signs of the main C=O stretching peaks and N–H bending agreed with the observed ones.

As mentioned previously, the gel formed by *C*₇ maintained solvent molecules so weakly to release them in hours from gel networks. Based on the present models, such low ability of gelation might be related to the weak binding in the molecular aggregation of *C*₇ through a single chain of hydrogen bonding. In order to study the interaction of solvent molecules with a gelator, calculation was made for the systems containing a gelator and a single benzene molecule. The results are shown in ESI† for the cases of *RR-C*₈ and *RR-C*₇. Comparing these two structures, it was deduced that the angle between two alkyl chains in *RR-C*₇ was larger than that in *RR-C*₈ in order to include a benzene molecule. This was thought to be a main cause for the situation that one of the >N–H and >C=O pairs was close enough to form an intramolecular hydrogen bond.

The morphology of the gel samples of *SS-*, *RR-C*₇ and *SS-C*₈ was studied by SEM measurements and results are shown in ESI†. In the case of *SS-C*₇ and *RR-C*₇, fibrils adopted a planar form with no helical winding. In contrast, in case of *SS-C*₈, fibrils adopted a string form with helical winding as already reported for *C*₁₂ gels.⁵ Thus the structural change on a molecular stacking level was reflected on the fibril properties on a micrometre scale. No helical sense was determined for the fibrils of *SS-C*₈ gels by the SEM images. Thus the helicity could not be related to the chirality of a gelator at the present stage.²²

The XRD patterns of *RR-C*₇ and *RR-C*₈ gel states in toluene showed a broad diffraction peak around $2\theta \sim 18.5^\circ$ (*ca.*

0.48 nm) in contrast to the sharp peaks observed for the crystalline states of the **RR-C₁₂** compounds. This indicates that the gels of **RR-C₇** and **RR-C₈** were composed of less ordered domains with no crystalline phase (see ESI†).

No odd–even effect was observed for benzene gels. It was concluded that intermolecular hydrogen bonding was dominant for the alkyl chain length longer than **C₈**, while the intramolecular hydrogen bonding was dominant for the alkyl chain length shorter than **C₇**. In the latter cases, the gel structures were thought to be similar to those in the solid states.

Experimental

Syntheses of **RR-** and **SS-C_n** (*n* = 6–12)

N,N'-dialkanoyl-*trans*-1,2-diaminocyclohexanes (denoted as **RR-** or **SS-C_n**) were synthesized according to the reported method by Hanabusa *et al.*⁵ One equivalent of (1*R*,2*R*)- or (1*S*,2*S*)-1,2-diaminocyclohexane was coupled with 2 equiv. of an alkyl acid chloride using excess triethylamine in THF. The product was purified by washing with an aqueous 1 M HCl solution (yields 60–90%). The molecules were identified by ¹H NMR, optical rotation and mass spectra. The results of ¹H NMR, elemental analyses, mass spectra and optical rotation are shown in ESI†. The purification was confirmed compared in the previous paper.⁸

Measurements of sol–gel transition temperature

CGC values and melting temperatures were determined by the method using a magnetic stirrer according to the previous reports.^{5,8} As a pre-treatment, the gel was heated to dissolve and subsequently cooled to room temperature. A stirrer was placed onto a cooled gel and the gel was heated slowly. At the melting temperature, the stirrer went down from a surface into the inside of the gel. The test was repeated at least three times. Melting temperatures were obtained reproducibly within ±1 °C. These melting tests were performed for benzene and toluene gels. The stability of a toluene-**C₇** gel was found to change with time. After three days, the gel became turbid with release of solvent. The sol–gel temperature increased during this change. Finally the material became solid and was not dissolved in toluene after 10 days.

Differential scanning calorimetry (DSC)

DSC measurements were carried out with a DSC6200 (SEIKO, Japan). Heating and cooling were performed at a scan rate of 10 °C min⁻¹. The results are shown in ESI†.

Optical rotatory dispersion (ORD) measurements

ORD measurements were carried out a DIP-1000 (JASCO, Japan). The gelator was dissolved in methanol at about 0.16–0.20 mol L⁻¹. The ORD of a methanol solution of a gelator was measured at 589 nm by using a 10 cm cell and results are given in ESI†. The molar optical rotation ($[\alpha]_{589}$) was obtained to be +18.0 and –18.0 deg/(mol L⁻¹cm) for **RR-C_n** and **SS-C_n**, respectively.

Powder XRD measurements

X-Ray diffraction measurements were performed with a XRD (Ultima IV, Rigaku) using Cu-K α radiation ($\lambda = 0.15406$ nm) at the conditions of 40 kV, 30 mA, and 2θ ° min⁻¹ scanning; results are shown in ESI†.

SEM observation

The morphology of the gel samples was investigated with a SEM (JSM-6700FT, JEOL) at 7 kV.

VCD measurements

The VCD spectra were measured using a PRESTO-S-2007 spectrometer (JASCO, Japan).^{14,17–18} The absorption signals were detected using a liquid-nitrogen cooled MCT infrared detector equipped with ZnSe windows. Spectra were recorded at 4 cm⁻¹ resolution. Signals were accumulated for 3000–10000 scans in about 0.5–2 h. The FT-IR absorbance was adjusted below 1.0 in order to attain the optimal signal-to-noise ratio in VCD measurements. The gel concentration was varied from *ca.* 0.02 to *ca.* 0.1 M. A gel sample for VCD measurements was prepared in the following manner: first a weighed amount (*ca.* 10 mg) of the enantiomeric sample was dissolved in C₆D₆ (*ca.* 200–500 μ L) at 40 °C. Thereafter about 50 μ L of the solution was sandwiched between two CaF₂ plates with a 50 μ m spacer and a transparent film was formed between the two CaF₂ plates. After cooling to room temperature, the stock solution was transformed into a transparent gel. A solution sample was prepared by dissolving a weighed amount of the compound in CDCl₃ and injected in a assembled cell with BaF₂ windows of 50 μ m optical path. The viscosity of the sample solutions was so high that a solution cell was not used. The powder sample was ground in an agate mortar with KBr. The VCD was measured on the compressed pellets. In order to eliminate linear dichroism effects, the cell was rotated along the direction of a monitoring light and also turned back–inside out in gel and KBr samples. Reproducible VCD signals were obtained for several samples prepared independently.

Computational details

Monomeric species under *C₂* or *C₁* symmetry of **RR-C₈** and **C₇** were optimized by the Gaussian 09 program at the DFT level (B3LYP functional) with 6-31G(d,p).²³ A monomer with one benzene molecule was also optimized to study the capture of the benzene molecule. The dimer models of **RR-C₈** and **RR-C₆** were optimized for aggregation states. The IR and VCD spectra were calculated on the basis of magnetic field perturbation (MFP) theory. Description of calculated modes was made from animations of the modes and spectra with Gaussview 5.08 (Gaussian Inc.).

Conclusions

The present paper studied the effects of alkyl chain length on the structures of gels of benzene/*trans*-1,2-diaminocyclohexane derivatives with various alkyl chain lengths. When the carbon

number of an attached alkyl chain (n) was changed from 6 to 12, the coupled VCD peaks around 1550 cm^{-1} assigned to the symmetric and asymmetric C=O stretching vibrations changed signs at $n = 8$. From the analyses of VCD results, it was concluded that, in the gels by **C**₈, **C**₉, **C**₁₀ and **C**₁₂, the gelators formed a column-like aggregate by double anti-parallel chains of intermolecular hydrogen bonds. On the other hand, for the gels by **C**₆ and **C**₇, the gelators formed a tape-like aggregate through a single chain of intermolecular hydrogen bonds.

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