

# Gelation Properties of Aprotic Low-Molecular-Mass Organic Gelators Based on a Gemini 4-[2-(Perfluoroalkyl)ethylsulfanyl]phenoxy Derivative Unit

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Received: May 7, 2015; Accepted: July 13, 2015; Web Released: October 15, 2015

Gelation properties of aprotic low-molecular-mass organic gelators (LMOGs) based on a gemini 4-[2-(perfluoroalkyl)ethylsulfanyl]phenoxy derivative unit are described. These LMOGs without hydrogen-bonding functional groups produced physical gels in several organic solvents such as ethanol, 1-octanol, acetonitrile, DMF, DMSO, propylene carbonate, and  $\gamma$ -butyrolactone at low concentration below 1 wt%. From the results of microscope observation and nuclear magnetic resonance spectroscopy, these aprotic LMOG molecules were aggregated into tape-shaped molecular nanofibers, and formed three-dimensional networks. In addition, the self-diffusion coefficient of the solvent molecules in these networks was similar to that of neat, although these solvent molecules have non-fluidity by gelation.

#### Introduction

In recent years, there has been a tremendously growing interest in low-molecular-mass organic gelators (LMOGs).<sup>1-6</sup> LMOGs aggregate into fiber-like structures via noncovalent intermolecular interaction such as hydrogen (H)-bonding, van der Waals forces,  $\pi$ - $\pi$  stacking, and electrostatic interactions, and then entangle to form three-dimensional (3D) networks in organic solvents. Generally, such LMOGs can be classified into two categories according to their driving forces for molecular aggregation: H-bond-based LMOGs and non H-bondbased ones, which are so-called "protic LMOGs" and "aprotic LMOGs", respectively. Typical examples of protic LMOGs are amino acid and sugar derivatives having some H-bonding functional groups (e.g. amide, carboxy, and hydroxy), in addition to long alkyl chains and chiral units. In particular, protic LMOGs including amino acids have been developed and energetically studied by Hanabusa, et al.<sup>5</sup>

On the other hand, typical examples of aprotic LMOGs, *n*-perfluoroalkylalkanes, 1,2- and 1,3-di(*n*-perfluoroalkylalkoxy)benzenes having long perfluoroalkyl chains form gels in hydrocarbon such as *n*-decane and cyclodecane, have been reported.<sup>7,8</sup> In this category, the major driving force for the gel formation is considered to be weak interactions. We have reported that 1-alkoxy-4-[2-(perfluorooctyl)ethoxy and ethylsulfanyl]benzenes formed gels in not only hydrocarbon but also alcoholic and polar solvents.<sup>9,10</sup> More recently, 1, $\omega$ -bis{4-[2-(perfluorobutyl)ethylsulfanyl]phenoxy}alkanes which have relatively short perfluoroalkyl chains formed gels in several alcoholic and polar solvents at low concentration.<sup>11</sup> However, detailed correlation between molecular structure and gelation ability, in addition, physicochemical properties of these organic

$$\begin{array}{c} F(CF_{2})_{n}C_{2}H_{4}X - \frown O(CH_{2})_{m}O - \frown YC_{2}H_{4}(CF_{2})_{n}F \\ \\ Compounds \ 1-m-n \ (X = Y = S) \\ 2-m-n \ (X = Y = SO) \\ 3-m-n \ (X = Y = SO_{2}) \\ 4-m-n \ (X = S, Y = SO_{2}) \end{array}$$

Figure 1. Chemical structures for 1–4.

gels are not clear. This understanding is necessary, when the LMOGs are utilized for industrial application.

In this study, aprotic low-molecular-mass organic compounds 1–4 (Figure 1 and Scheme S1) having different length of perfluoroalkyl and alkylene chains and oxidation state of sulfur atoms were prepared, and their gelation properties were examined by the minimum gel concentration (MGC), the solgel phase-transition temperature ( $T_{gel-sol}$ ), and the gel strength. In addition, the gelation process and the self-diffusion coefficient of solvent molecules in the gel were investigated with microscope observation and nuclear magnetic resonance (NMR) spectroscopy.

## **Results and Discussion**

Novel aprotic low-molecular-mass organic compounds 1–4 were prepared according to Scheme S1.

Tables 1 and 2 summarize the results of the gelation test for 1-*m*-*n* in several organic solvents. As can be seen from Table 1, most interestingly, 1-*m*-6 having a relatively long alkylene chain ( $m \ge 8$ ) formed gels in several alcoholic and polar solvents. Especially 1-12-6 formed gels at low concentration below 1 wt% (Figure S1), while 1-*m*-6 having a short alkylene chain ( $m \le 6$ ) were precipitated in examined organic solvents.

Table 1. Gelation tests and MGCs for 1-m-6

Solvents	Compounds (concentration/wt%) <sup>a)</sup>					
	4	6	8	10	12	
Octane	Р	Р	Р	G (8.0)	G (6.0)	
Toluene	Р	Р	Р	S	S	
Ethanol	Р	Р	Р	G (1.0)	G (0.3)	
1-Octanol	Р	Р	Р	G (0.8)	G (0.5)	
Acetonitrile	Р	Р	Р	G (2.0)	G (0.8)	
DMF	Р	Р	G (8.0)	G (3.0)	G (0.8)	
DMSO	Р	Р	G (0.6)	G (0.3)	G (0.1)	
PC	Р	Р	G (2.0)	G (0.4)	G (0.5)	
GBL	Р	Р	G (2.0)	G (0.5)	G (0.7)	

a) G, S, and P are gel, sol, and precipitate states, respectively.

 Table 2. Gelation tests and MGCs for 1-12-n

Solvents	Compounds (concentration/wt%) <sup>a)</sup>					
	4	6	8	10		
Octane	S	G (6.0)	Р	Р		
Toluene	S	S	Р	Р		
Ethanol	G (0.9)	G (0.3)	Ι	Ι		
1-Octanol	G (0.6)	G (0.5)	Р	Р		
Acetonitrile	G (0.6)	G (0.8)	Ι	Ι		
DMF	G (0.8)	G (0.8)	Р	Р		
DMSO	G (0.1)	G (0.1)	G (0.3)	Р		
PC	G (0.2)	G (0.5)	G (0.6)	G (1.0)		
GBL	G (0.9)	G (0.7)	G (1.0)	G (1.0)		

a) G, S, P, and I are gel, sol, precipitate, and insoluble states, respectively.

The tendency is also observed in different perfluoroalkyl chain length. Thus, **1**-*m*-*n* needs to have a long alkylene chain to act as a LMOG in organic solvents, where the elongation of flexible alkylene chain leads to decrease in a crystallization, and stabilizes the gel states. As can be seen from Table 2, **1**-12-*n* having relatively short perfluoroalkyl groups (n = 4 and 6) formed gels in examined organic solvents except octane and toluene. These organic gels with 3 wt % **1**-12-6 or **1**-12-4 have been stable at 20 °C for >12 months and the syneresis was not observed in sealed tubes.

On the other hand, 1-12-*n* having relatively long perfluoroalkyl groups (n = 8 and 10) formed gels in propylene carbonate (PC) and  $\gamma$ -butyrolactone (GBL), but precipitated in alcoholic and nonpolar solvents. Thus, the balance of perfluoroalkyl and alkylene chain length was found to be important to act as a LMOG in organic solvents.

Correlation between gelation ability and oxidation state of sulfur were examined, as shown in Table 3. 1-12-6 having sulfanyl groups formed gels in examined organic solvents, and 2-12-6 having sulfinyl groups formed gels in only polar solvents, while 3-12-6 having sulfonyl groups did not form a gel in examined organic solvents. In addition, 4-12-6 having a sulfanyl and a sulfonyl groups formed gels in several alcoholic and polar solvents below 3 wt %. Thus, the oxidation state of sulfur is found to play an important role to act as a LMOG in organic solvents. These results suggest that not only the steric balance, but also the electrostatic balance are significantly

Table 3. Gelation tests for 1-4-12-6

Solvents	Compounds (concentration/wt%) <sup>a)</sup>					
	<b>1-</b> 12 <b>-</b> 6	<b>2-</b> 12-6	<b>3-</b> 12-6	<b>4</b> -12-6		
Octane	G (6.0)	G (1.0)	Ι	Р		
Toluene	S	Р	Ι	Р		
Ethanol	G (0.3)	Р	Ι	G (2.0)		
1-Octanol	G (0.5)	Р	Р	G (2.0)		
Acetonitrile	G (0.8)	G (5.0)	Ι	G (1.0)		
DMF	G (0.8)	Р	Р	G (3.0)		
DMSO	G (0.1)	G (0.3)	Р	G (2.0)		
PC	G (0.5)	G (2.0)	Р	G (1.0)		
GBL	G (0.7)	G (2.0)	Р	G (2.0)		

a) G, S, P, and I are gel, sol, precipitate, and insoluble states, respectively.



Figure 2. (a)  $T_{\text{gel-sol}}$  for several gels with 1-12-6, and (b) that for PC gels with 1-12-n (n = 4, 6, 8, and 10).

important factors in consideration of molecular design for these LMOGs.  $^{\rm 12}$ 

Sol-gel phase-transition temperature ( $T_{gel-sol}$ ) was plotted against concentrations of a LMOG. As can be seen in Figure 2a,  $T_{gel-sol}$  for DMSO and PC gels with 1-12-6 were increased with increasing the concentration of 1-12-6 and became constant above ca. 3 wt %, and exhibited 60–70 °C at 5 wt %, while that for 1-octanol gel was gradually increased and reached 70 °C at 5 wt %. The other gels also exhibited similar  $T_{gel-sol}$  (Figure S2). As can be seen in Figure 2b,  $T_{gel-sol}$ for PC gels with 10 wt % 1-12-*n* (*n* = 10, 8, 6, and 4) were 105, 88, 68, and 35 °C, respectively. The elongation of perfluoroalkyl chains led to increase in  $T_{gel-sol}$ . Thus,  $T_{gel-sol}$  significantly depended more on the chemical structure of gelator than the physicochemical properties of solvents.

In addition, relevant thermodynamic information can be extracted from the  $T_{\text{gel-sol}}$  data. The slope and intercept of the best linear fit to the data for PC gel with 1-12-6 in Figure 3 have been interpreted according to the Schröder–van Laar equation (eq 1),<sup>13</sup>

$$n(\chi_{\rm g}) = \frac{\Delta H_{\rm fus}}{RT_{\rm gcl-sol}} + \frac{\Delta H_{\rm fus}}{RT_{\rm fus}} \tag{1}$$

where  $\chi_g$  is the molar fraction of 1-12-6,  $\Delta H_{\text{fus}}$  is the enthalpy change of melting of the gel assemblies, and  $T_{\text{fus}}$  is the melting temperature of the neat gelator. Herein, Weiss et al. hypothesized that the nearer the values of  $\Delta H$  from DSC thermogram

1



**Figure 3.** Semilog plot of the mole fraction of 1-12-6 in PC  $(\chi_{gel})$  vs. the inverse of  $T_{gel-sol}$ .



Figure 4. Gel strengths of organic gels; (●) PC gel with 1-12-6, (○) PC gel with 1-12-4, (■) 1-octanol gel with 1-12-6, and (□) 1-octanol gel with 1-12-4.

of the neat solids and  $\Delta H_{\rm fus}$ , the smaller the influence of the liquid component on the dissolution of the gel network at  $T_{\rm gel-sol}$ , and the packing arrangements of the gel networks are isomorphous to the neat solids.<sup>1</sup> In the case of 1-12-6, the values of  $\Delta H (84 \text{ kJ mol}^{-1})$  are somewhat higher than the  $\Delta H_{\rm fus}$  values calculated from Figure 4 (66 kJ mol<sup>-1</sup> from the slope and 53 kJ mol<sup>-1</sup> from the intercept). The data of other organic gels are summarized in Table S4, and their  $\Delta H_{\rm fus}$  from slope were 41–85 kJ mol<sup>-1</sup> and the  $\Delta H_{\rm fus}$  from intercept were 24–76 kJ mol<sup>-1</sup>.

Gelation process was observed with <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR spectra of acetonitrile- $d_3$  (CD<sub>3</sub>CN) gel with 3 wt % 1-12-6 at different temperatures are summarized in Figure S3. On heating, their <sup>1</sup>H NMR signals were not observed at 20 °C, and



Figure 5. (a) SPM height trace image and 3D mix image and (b) SEM image of PC xerogel with 3 wt % 1-12-6.

broadened from 50 °C. Sharpening of all the resonance lines above 80 °C, that is, the gel phase has changed to sol phase by a disruption of the self-assembly of 1-12-6 was observed. On cooling, their <sup>1</sup>H NMR signals were broadening again by gelation. This phenomenon also shows that the gel is a physical gel with a thermally reversible sol–gel phase transition.<sup>14</sup> In addition, the temperature where CD<sub>3</sub>CN gel starts to melt is similar to  $T_{gel-sol}$  of acetonitrile (CH<sub>3</sub>CN) gel, as shown in Figure S4.

We evaluated gel strength as the power necessary to sink a cylindrical bar into the gels (see the experimental section). As can be seen in Figure 4, the gel strength for 1-octanol with 1-12-6 and 1-12-4, PC with 1-12-6 and 1-12-4 were 164, 213, 66, and 391 g cm<sup>-2</sup>, respectively. These gel strengths sharply increased with increasing concentration of gelator expect PC gel with 1-12-6, while that of PC gel with 1-12-6 became constant on ca.  $70 \text{ g cm}^{-2}$  at 3 wt % and more concentration. Thus, the increasing concentration of a LMOG led to increase in the gel strength. Unfortunately it is not clear what factor affects the gel strength, although the gel strength is an important factor in the application of gels.

Gel network structure was observed with scanning probe microscopy (SPM) and scanning electron microscopy (SEM) after solvent removal. **1**-12-6 aggregates into tape shaped molecular nanofibers of ca. 20 nm width, and <5 nm height as shown in Figure 5a. The nanofibers form bundles of 100–300 nm width as shown in Figure 5b. They entangle to form the 3D networks in PC. The nanofibers probably confine the liquid component by surface tension and capillary forces, since the gelator concentration is usually very low. These results indicate that there need not be specific gelator–solvent interactions on the molecular scale. On the other hand, from SEM observation of PC xerogel with **1**-8-6 having short alkylene chain, gel fibers and crystals were observed (Figure S5). As alkylene chain length is short, crystals domain increased, and finally recrystallized in a solvent.

Furthermore,  $\Delta H$  of PC xerogel with 3 wt % 1-12-6 was detected with DSC. The value of  $\Delta H$  of xerogel was 84 kJ mol<sup>-1</sup>, and the value was similar to that of powder (86



**Figure 6.** (a)  $\Delta$ -dependence of *D* in neat PC and its gel at 30 °C and (b) *T*-dependence of *D* in neat PC and its gel with 3 wt % 1-12-6.

kJ mol<sup>-1</sup>). These melting temperatures of xerogel and powder were both 94 °C. These results indicate that the stability of xerogel and powder were similar. In fact, PC gel with 1-12-6 has been stable at 20 °C for >12 months.

To the best of our knowledge, there are few reports pertaining to the self-diffusion coefficient (*D*) of solvent molecules in gels. The values were determined with pulsed field gradient (PFG)-NMR spectroscopy.<sup>15</sup> Figure 6a shows diffusion time ( $\Delta$ )-dependence of *D* of PC in neat PC and its gel with 3 wt % 1-12-6 at 30 °C. The *D* values were independent between 50 and 100 ms, in addition these *D* values of its gel were similar to those of the neat, and these *D* values of neat PC and its gel were determined to be  $5.8 \times 10^{-10}$  and  $5.4 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, respectively. The 3D diffusion distance of particular based on Brownian motion follows as the equation below:

$$R = \sqrt{6D \times \Delta} \tag{2}$$

where *R* is the diffusion distance (square displacement). The Brownian motion of PC molecules in the gel was not affected at least radius  $18 \,\mu\text{m}$  by gel networks. Thus, the mesh size of the nanofiber in the gel (Figure 5) is probably micron scale, thereby it is natural and predictable that solvents molecules in the gel behaved as the neat-like solvent.

Figure 6b shows temperature (*T*)-dependence of *D* in neat PC and its gel between 0 and 80 °C. Herein, above room temperature, a convection of neat PC molecules in an NMR tube resulted from the deviation of *D* values,<sup>16</sup> therefore such *D* values corrected with Arrhenius plot at low temperature, as shown in Figure S10. In contrast, the *D* values in gels (including sol phase) were not affected by convection. It is thought that gel networks inhibit the convection of PC molecules with increasing temperature. Same phenomenon has been reported by Takekawa et al.<sup>17</sup> As can be seen in Figure 6b, the *D* values of its gel were similar to those of the neat between 0 and 80 °C. In addition, the relationship of *T*-dependence and activation energy is shown in Figure 6b, with the Arrhenius equation below:<sup>18</sup>

$$D = D_0 \exp(-E_{\rm A}/RT) \tag{3}$$

where  $D_0$  is the constant (frequency factor),  $E_A$  is the activation energy, R is universal gas constant, and T is the temperature. The  $E_A$  for self-diffusion of PC molecules in neat PC was determined to be  $13.3 \text{ kJ mol}^{-1}$ , while that of the gel was determined to be  $15.3 \text{ kJ mol}^{-1}$ . On the other hand, the relationship of diffusibility and viscosity of solvent molecules in gel follows as the Stokes–Einstein equation below:<sup>19</sup>

$$D = kT/c\pi\eta r_{\rm S} \tag{4}$$

where k is the Boltzmann constant, T is the temperature, c is the constant (6 or 4),  $\pi$  is the circular constant,  $\eta$  is the viscosity, and  $r_{\rm S}$  is the Stokes radius. As can be seen in Figure 6b, the D values in neat PC and its gel were determined to be  $4.34 \times 10^{-10}$  and  $4.30 \times 10^{-10} \,{\rm m}^2 \,{\rm s}^{-1}$  at 20 °C, respectively. Herein, assuming that the  $r_{\rm S}$  is equal to the van der Waals radius ( $r_v = 0.276 \,{\rm nm}$ )<sup>20</sup> and c = 4, the  $\eta$  of PC in neat and gel were determined to be both 2.7 mPas at 20 °C. Their values were similar to the literature data which is 2.8 mPas at 20 °C.<sup>21</sup> These results indicate that the micro-viscosity is similar to neat PC, although this gel has non-fluidity, that is, the macroviscosity is very high by gelation.

## Conclusion

Aprotic low-molecular-mass organic compounds 1-4 based on a gemini 4-[2-(perfluoroalkyl)ethylsulfanyl]phenoxy derivative unit formed physical gels in several alcoholic and polar solvents at low concentration. It was found MGC depends on alkylene chain length (m) and oxidation state of sulfur through screening for the molecular structures. In particular, the organic gels with 3 wt % 1-12-*n* have been stable at 20 °Cfor >12 months and syneresis is not observed in sealed tubes, thus far.  $T_{\text{gel-sol}}$  depends on perfluoroalkyl chain length (n). Probably, MGC and  $T_{gel-sol}$  significantly depends on steric and electrostatic balance. From the results of microscope observation and NMR spectroscopy, 1-12-6 aggregates into the tape shaped molecular nanofibers, and entangle to form the 3D networks in PC. On the other hand, D values of PC molecules in gel are similar to those in neat PC, although PC molecules have no fluidity by gelation.

#### Experimental

**Materials.** 2-(Perfluoroalkyl)ethyl iodide were purchased from Daikin Industries, Ltd. reagent chemicals; 4-hydroxybenzenethiol was purchased from Sankyo Kasei Co., Ltd. reagent chemicals;  $1,\omega$ -dibromoalkane were purchased from Tokyo Chemical Industry Co., Ltd. reagent chemicals. All reagents and solvents were obtained from generally commercial sources.

**Instrumentation.** Melting point (mp) was obtained with a Yanaco MP-J3 micro melting point apparatus. High-performance liquid chromatograms were recorded on a Shimadzu Prominence HPLC System. Infrared (IR) spectra were recorded on a Shimadzu IR Prestige-21 spectrometer using KBr disc or KRS-5 film. <sup>1</sup>H NMR spectra were recorded with a JEOL JMN-LA500 and JNM-ECA500 spectrometer (500 MHz), where tetramethylsilane (TMS) was used as an internal standard. High-resolution mass spectra (HRMS) were recorded with a Waters LCT Premier<sup>TM</sup> XE. Phase transition latent heats were recorded on a Seiko Instruments SSC/5200, where  $\alpha$ -alumina was used as a caloric standard material. Gel strength was measured with Rheometer CR-500X (Sun Scientific Co., Ltd.). Scanning probe microscopy (SPM) and scanning electron

microscopy (SEM) images were observed with a Shimadzu SPM-9600 and a JEOL JSM-6510LA, respectively.

**Synthesis.** 1–4 were prepared as shown in Scheme S1. Their detailed synthetic procedures and analytical data are given in the SI. The chemical structures for 1–4 including synthetic intermediates were identified with IR, <sup>1</sup>H NMR, and HRMS spectra. Purity were checked with <sup>1</sup>H NMR and HPLC spectra.

**Differential Scanning Calorimetry (DSC).** Samples of 5 mg were loaded into aluminium-sealed containers (Seiko Instruments P/N 50-023) with an ultra science balance (Mettler Toledo UM3). The heating and cooling rates for DSC measurements were both  $5 \,^{\circ}\text{C}\,\text{min}^{-1}$ .

**Gelation Test.** A typical procedure for gelation test is as follows: a weighed compound was mixed with an organic solvents in a micro tube (11 mm $\phi$ ), and the mixture was heated until the solid was dissolved. The resulting solution was cooled to 20 °C and then the gelation was checked visually. When upon inversion of the glass tube no fluid ran down the walls of the tube, we judged it a successful gel. When the gel was formed, we evaluated quantitatively the gelation ability by determining the MGC, which is the minimum concentration of gelator necessary for gelation at 20 °C. The  $T_{gel-sol}$  were determined by the inverse flow method.<sup>22</sup>

**Gel Strength.** Gel strength  $(g \text{ cm}^{-2})$  was determined as the power necessary to sink a cylindrical bar  $(10 \text{ mm}\phi) 4 \text{ mm}$  deep  $(60 \text{ mm} \text{min}^{-1})$  into the gel, which was stood 12 h at 20 °C after gelation in a sample tube  $(14.8 \text{ mm}\phi)$ .

**Scanning Probe Microscope (SPM).** The organic solvent was completely removed from samples, that is, xerogels then samples were prepared on cover glass in vacuo and observed by means of dynamic phase mode.

**Scanning Electron Microscope (SEM).** The xerogels were coated with a platinum vapor with autofinecoater (JEOL JFC-1600). All samples were observed by means of secondary electron image (SEI) method operated at acceleration voltage of 3 to 15 kV.

**Variable Temperature <sup>1</sup>H NMR.** The samples were prepared in a general NMR tube, and heated for 1 h at target temperature in a JNM-ECA500 spectrometer. <sup>1</sup>H NMR spectra of these samples were recorded at every 5 °C between 20 and 80 °C.

**Pulsed Field Gradient (PFG)-NMR.** We prepared dried PC as a solvent. The samples were placed into a 5 mm $\phi$  magnetic susceptibility compensated symmetrical micro NMR tube (BMS-005J, Shigemi Inc.) to a height of 5 mm and were sealed with an epoxide resin. The PFG-NMR spectra were recorded with a JEOL JNM-ECA500 spectrometer and a JEOL 50TH5GR probe controlled by a JEOL Delta console. The *D* values were measured with PFG BPP LED which combined PFG bipolar pulse pairs stimulated echo (BPP STE) with PFG longitudinal eddy current delay (LED) methods. This detailed pulse sequence is shown in Figure S11. The echo signal attenuation (*E*) was analyzed using the Stejskal–Tanner equation:<sup>23</sup>

$$E(\delta, g, \Delta) = I(g)/I(0) = \exp[-\gamma^2 g^2 \delta^2 D(4\Delta - \delta)/\pi^2] \quad (5)$$

where I(g) and I(0) are the echo signal intensities,  $\gamma$  is the gyromagnetic ratio, g is the strength of the gradient pulse of

duration (set 0.1–0.8 T m<sup>-1</sup>),  $\delta$  is the width of gradient pulse, and  $\Delta$  is the interval of gradient pulse (i.e. diffusion time).

The authors thank Prof. S. Sakurai (JEOL Resonance Inc.) for their technical help and advice about PFG NMR measurement. This work is partly supported by Industrial Technology Research Grant Program in 2006 from New Energy and Industrial Technology Development Organization (NEDO) of Japan and Grant-in-Aids for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

# **Supporting Information**

Synthetic procedures, melting point, IR data, <sup>1</sup>H NMR assignments, and HRMS data of 1–4 including synthetic intermediates. The results of the gelation test for 1-*m*-8. SEM images of PC xerogel with 3 wt % 1-8-6 and acetonitrile xerogel with 3 wt % 1-12-6. IR spectra of 1-12-6 powder, CD<sub>3</sub>CN, and CD<sub>3</sub>CN gel in 3 wt % 1-12-6. XRD pattern of acetonitrile xerogel with 3 wt % 1-12-6. Diffusion plots of signal attenuation (ln(*I*/*I*<sub>0</sub>)) vs.  $\gamma^2 g^2 \delta^2$  (4 $\Delta - \delta$ ) $\pi^{-2}$  for <sup>1</sup>H PFG BPP LED echo signal for PC and its gel with 3 wt % 1-12-6 at  $\Delta = 50$  ms. Original data of *T*-dependence of *D* in neat PC and its gel with 3 wt % 1-12-6 and Arrhenius plot with corrected data. This material is available electronically on J-STAGE.

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12 In the case of using m = 6 instead of m = 12, only 2-6-6 having sulfinyl groups formed gels in DMSO, PC, and GBL below 3 wt % as shown in Table S2. On the other hand, in the case of

using n = 4 instead of n = 6, **3**-*m*-4 (m = 6 and 12) formed gels in alcoholic and polar solvents below 4 wt % as shown in Table S3. Probably, **3** having an alkylene chain is longer than a perfluoro-alkyl one tends to act as a LMOG.

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