# Synthesis and Physicochemical Properties of Perfluorinated Organic Gelators

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This paper describes synthesis and physicochemical properties of low molecular-mass organic gelators; 4-(2-perfluorooctyl)ethoxy- and 4-(2-perfluorooctyl)ethylthio-1-alkoxybenzenes (compounds 1-n and 2-n). These compounds show remarkable gelation ability in various organic solvents, such as methanol, cyclohexane, acetonitrile, DMF, and so on. The critical gel concentration of 1-n is superior to that of 2-n, while the elongation of alkoxy chain length increase gelation ability in both compounds. Key words: low mass organic gelator, synthesis, semi-empirical molecular orbital calculation

## 1. INTRODUCTION

Partly fluorinated compounds have been studied in recent years in relation to their interesting characteristics such as excellent liquid crystalline properties, gelation ability in organic solvent and so on<sup>1-10</sup>.

In previous work<sup>11</sup>, we described synthesis and gel formations of 4-(2-perfluorooctyl)ethoxy-1-alkoxybenzenes (compounds 1-n, see Fig. 1) in which compounds 1-n play low molecular-mass gelators in wide variety organic solvents. However, details of the relationship between chemical structure and gelation properties could not be studied because the chemical yields of compounds 1-n were very poor.

This paper describe synthesis and gelation ability of 4-(2-perfluorooctyl)ethylthio-1-alkoxybenzenes (compounds 2-n, see Fig. 1), and the results are compared with the corresponding ether derivatives (compounds 1-n).

Fig 1. Chemical structures for compounds 1-n and 2-n.

## 2. EXPERIMENTAL

Method: Chemical structures for compounds 1-n, 2-n and synthetic intermediate were confirmed by FT-IR (Shimadzu, IR Prestage-21) and <sup>1</sup>H NMR spectra (JEOL EX-270), where TMS was used as an internal standard. Purity for each compound was 99% checked by HPLC and <sup>1</sup>H NMR spectra. A typical procedure of gelation test was as followed: a weighed sample was mixed with an organic solvent in a sample tube (8 mm $\phi$  X 35 mm) and the mixture was heated until the solid was dissolved. The resulting solution was cooled to room temperature and the gel or sol state was checked visually. When upon the sample tube was inversed there was no fluid running down the walls, it was judged to be gel state as shown in Fig. 2.

When the samples caused gel state, gelation ability was evaluated quantitatively by the critical gel concentration (cgc) that was the minimum concentration of the sample necessary for gelation at room temperature.



Fig. 2. Photographs of (a) sol and (b) get state.

*Materials*: Compounds 1-n were prepared according to ref. 11. Compounds 2-n were synthesized in moderate yields according to Scheme 1.



Scheme 1. Synthetic scheme for compounds 2-n. Reagents and conditions; a)  $C_8F_{17}C_2H_4I$ ,  $Et_3N$ , THF, reflux for 8h; b)  $C_nH_{2n+1}Br$ ,  $K_2CO_3$ , 3-pentanone, reflux

#### Synthesis of 4-(2-perfluorooctyl)ethylthiophenol:

To a solution of 4-mercaptophenol (2.0 g, 15.6 mmol) and Et<sub>3</sub>N (1.6 g, 18.7 mmol) in dry THF (100 ml) was added 2-perfluorooctylethyl iodide (9.0 g, 15.6 mmol) and refluxed for 8 h. After the reaction was completed, the reaction mixture was quenched with aqueous NaHCO<sub>3</sub>, extracted with ether. The organic layer was washed with H<sub>2</sub>O, brine and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the residue was purified by column chromatography on silica-gel using CHCl<sub>3</sub> as an eluent to give 4-(2-perfluorooctyl)ethylthiophenol as a colorless solid, 7.8 g (87%). mp=97°C; IR (KBr disc) v=1147, 1203, 1240, and 3400 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =2.23-2.44 (2H, m), 2.96-3.02 (2H, m), 5.20 (1H, s), 6.81 (2H, d, *J*=8.9Hz), and 7.31 (4H, d, *J*=8.9Hz) ppm.

Synthesis of 4-(2-perfluorooctyl))ethylthio-1-methoxy benzene (compounds 2-1):

The mixture of 4-(2-perfluorooctyl)ethylthiophenol 1.5 g (2.6 mmol), bromomethane 0.37 g (2.6 mmol), and  $K_2CO_3$  0.39 g (3.9 mmol) in 3-pentanone (30 ml) was refluxed for 8h. After the reaction was completed, the reaction mixture was quenched with H<sub>2</sub>O and then extracted with ether. The organic layer was washed with H<sub>2</sub>O, brine and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the residue was purified by column chromatography on silica-gel using CHCl<sub>3</sub> as an eluent to give 2-1 as a colorless solid, 0.91 g (59%).

Physical data for compound 2-1

mp=47°C; IR (KBr disc) v=1147, 1201, 1238, and 2931 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =2.23-2.44 (2H, m), 2.96-3.02 (2H, m), 3.82 (3H, s), 6.88 (2H, d, J=8.9Hz), and 7.37 (2H, d, J=8.9Hz) ppm.

The other homologous series were also synthesized in a similar method.

Physical data for compound 2-2

mp=52°C; IR (KBr disc) v=1147, 1201, 1241, and 2923 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =1.42 (3H, t, *J*=7.0Hz), 2.23-2.42 (2H, m), 2.96-3.02 (2H, m), 4.02 (2H, q, *J*=7.0Hz), 6.86 (2H,d, *J*=8.9Hz), and 7.35 (2H, d, *J*=8.9Hz) ppm.

Physical data for compound 2-3

mp=50°C; IR (KBr disc) v=1145, 1201, 1251, and 2931 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =1.04 (3H, t, *J*=7.4Hz), 1.81 (2H, six., *J*=7.1Hz), 2.23-2.43 (2H, m), 2.96-3.01 (2H, m), 3.92 (2H, t, *J*=6.6Hz), 6.86 (2H,d, *J*=8.9Hz), and 7.35 (2H, d, *J*=8.9Hz) ppm. Physical data for compound 2-4

mp=50°C; IR (KBr disc) v=1147, 1201, 1247, and 2962 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.98 (3H, t, *J*=7.4Hz), 1.30-1.36 (2H, m), 1.75-1.82 (2H, m), 2.23-2.39 (2H, m), 2.96-3.02 (2H, m), 3.92 (2H, t, *J*=6.5Hz), 6.89 (2H, d, *J*=8.9Hz), and 7.36 (2H, d, *J*=8.7Hz) ppm.

Physical data for compound 2-5

mp= 51°C; IR (KBr disc) v=1114, 1203, 1238, and 2937 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.93 (3H, t, *J*=7.1Hz), 1.37-1.44 (4H, m), 1.75-1.82 (2H, m), 2.23-2.39 (2H, m), 2.96-3.02 (2H, m), 3.95 (2H, t, *J*=6.6Hz), 6.89 (2H, d, *J*=8.9Hz), and 7.36 (2H, d, *J*=8.7Hz) ppm.

Physical data for compound 2-6

mp=51°C; IR (KBr disc) v=1147, 1201, 1238, and 2930 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.91 (3H, t, *J*=7.0Hz), 1.25-1.38 (6H, m), 1.73-1.83 (2H, m), 2.29-2.36 (2H, m), 2.96-3.01 (2H, m), 3.95 (2H, t, *J*=6.4Hz), 6.87 (2H,d, *J*=8.9Hz), and 7.36 (2H, d, *J*=8.7Hz) ppm.

Physical data for compound 2-7

mp=53°C; IR (KBr disc) v=1147, 1201, 1238, and 2921 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.87 (3H, t, *J*=7.0Hz) 1.25-1.40 (8H, m), 1.78 (2H, quin., *J*=6.7Hz), 2.29-2.36 (2H, m), 2.29-3.02 (2H, m), 3.94 (2H, t, *J*=6.6Hz), 6.87 (2H, d, *J*=8.9Hz), 7.36 (2H, d, *J*=8.7Hz) ppm.

Physical data for compound 2-8

mp=54°C; IR (KBr disc) v=1147, 1201, 1247, and 2935 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.89 (3H, t, *J*=6.6Hz), 1.28-1.42 (10H, m), 1.78 (2H, quin., *J*=6.7Hz), 2.23-2.44 (2H, m), 2.95-3.01 (2H, m), 3.94 (2H, t, *J*=6.6Hz), 6.86 (2H, d, *J*=8.6Hz), and 7.36 (2H, d, *J*=8.9Hz) ppm.

Physical data for compound 2-9

mp= 55°C; IR (KBr disc) v=1147, 1201, 1245, and 2921 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.87 (3H, t, J=6.6 Hz), 1.28-1.36 (12H, m), 1.78(2H, quin., J=7.0Hz), 2.30-2.44 (2H, m), 2.96-3.02 (2H, m), 3.94 (2H, t, J=6.6Hz), 6.87 (2H, d, J=8.9Hz), and 7.36 (2H, d, J=8.6Hz) ppm.

Physical data for compound 2-10

mp=57°C; IR (KBr disc) v=1147, 1201, 1249, and 2921 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.88 (3H, t, J=6.6 Hz), 1.27-1.38 (14H, m) ,1.78 (2H, quin., J=7.0Hz), 2.26-2.43 (2H, m), 2.96-3.02 (2H, m), 3.94 (2H, t, J=6.6Hz), 6.87 (2H, d, J=8.9Hz), and 7.36 (2H, d, J=8.6Hz) ppm.

Physical data for compound 2-11

mp=59°C; IR (KBr disc) v=1147, 1201, 1247, and 2919 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.88 (3H, t, J=6.6 Hz), 1.26-1.37 (16H, m), 1.80 (2H, quin., J=6.8Hz), 2.29-2.36 (2H, m), 2.96-3.02 (2H, m), 3.94 (2H, t, J=6.6Hz), 6.87 (2H, d, J=8.9Hz), and 7.36 (2H, d, J=8.6Hz) ppm.

Physical data for compound 2-12

mp=60°C; IR (KBr disc) v=1147, 1201, 1247, and 2917 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.88 (3H, t, J=6.6Hz), 1.27-1.37 (18H, m), 1.80 (2H, quin., J=7.0Hz), 2.29-2.42 (2H, m), 2.96-3.02 (2H, m), 3.94 (2H, t, J=6.6Hz), 6.86 (2H, d, J=8.6Hz), 7.36 (2H, d, J=8.6Hz) ppm.

Physical data for compound 2-13

mp=63°C; IR (KBr disc) v=1147, 1201, 1238, and 2918 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.88 (3H, t, J=6.6 Hz), 1.26-1.38 (20H, m), 1.80 (2H, quin., J=6.8Hz), 2.23-2.43(2H, m), 2.96-3.02 (2H, m), 3.94 (2H, t, J=6.6Hz), 6.86 (2H, d, J=8.9Hz), 7.36 (2H, d, J=8.6Hz) ppm.

Physical data for compound 2-14

mp=65°C; IR (KBr disc) v=1147, 1201, 1243, and 2917 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ =0.88 (3H, t, *J*=6.8Hz), 1.26-1.45 (22H, m), 1.78 (2H, quin., *J*=6.6Hz), 2.23-2.44 (2H, m), 2.95-3.01 (2H, m), 3.94 (2H, t, *J*=6.8Hz), 6.86 (2H, d, *J*=8.9Hz), 7.36 (2H, d, *J*=8.9Hz) ppm.

#### 3. RESULTS AND DISCUSSION

Synthesis of compounds 2-n: Details of synthetic procedure and spectra data are mentioned above. For compounds 1-n, chemical yields of the perfluoroalkylation of the phenols are extremely low (ca. 10%, see ref. 11). These results suggest that an elimination reaction occurs extensively to give perfluoroalkylethylene (Scheme 2, path A).

For compounds 2-n, on the other hand, the substitution reaction is preferred to give 4-(2-perfluorooctyl)ethylthiophenol in a moderate yield (Scheme 2, path B).

These results indicate the nucleophilicity of thiolate anion (ArS<sup>-</sup>) is higher than that of phenoxide anion (ArO<sup>-</sup>).



Scheme 2. Mechanisms for (a) elimination and (b) substitution reactions.

Gelation ability: The gel samples in 1-octanol are shown in Fig. 3, where the concentrations of compounds 2-n are ca. 9.0wt%.



Fig. 3. Photographs of gel samples in 1-octanol, 9.0wt% of compounds (a) 2-3, (b) 2-5, (c) 2-8, (d) 2-10, (e) 2-12, and (f) 2-14.

For earlier members of compounds 2-n, the formed gel shows transparent state, while the latter ones show opaque and/or semi-transparent states.

Values of the critical gel concentrations (cgc) and optical properties of the gels for compounds 1-n and 2-n are summarized in Table I and II.

Compounds 1-n can gelatinize various organic solvents, such as alcohols, hydrocarbons, polar, and non-polar solvents, except chloroform. This tendency was also observed in compounds 2-n, while aromatic and hydrocarbon solvents are not good for gelation due to a low solubility of compounds 2-n.

As can be seen from Table I and II, optical properties are not directly connected with gelation ability, so that the relationship between optical and gelation properties is not clear.

Table I. Value of the cgc (wt%) for compounds 1-n.

Solvent	1-1	1-5	1-14
MeOH	5.3*	1.3 (op)	0.6 (op)
1-Octanol	8.0 (op)	1.3 (tr)	0.5 (tr)
n-Octane	14 (tr)	4.8 (tr)	4.1 (op)
Cyclohexane	11 (tr)	4.0 (tr)	4.1 (se)
Toluene	33 (se)	11 (se)	8.9 (se)
Acetonitrile	10 (op)	1.7 (se)	0.2 (se)
DMF	16 (tr)	1.6 (tr)	0.6 (tr)
Chloroform	23*	15*	11*

\*Mixture of gel and crystal. Abbreviation: on, onaque: tr.

Abbreviation: op, opaque; tr, transparent gel; se, semi-transparent gel.

1 able II. Value of cgc (wt%) for compour	nds 2-n.
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Solvent	2-1	2-5	2-14
MeOH	7.0 (op)	3.3 (op)	0.7 (op)
1-Octanol	8.6 (tr)	5.8 (tr)	3.0 (se)
n-Octane	4.5*	7.1*	5.2 (op)
Cyclohexane	. 7.7*	5.4*	2.4 (op)
Toluene	3.3*	10*	10*
Acetonitrile	7.5 (tr)	4.5 (op)	10 (op)
DMF	11 (tr)	4.0 (tr)	0.7 (tr)
Chloroform	4.5*	12*	8.5*

\*Mixture of gel and crystal.

Abbreviation: op, opaque; tr, transparent gel; se, semi-transparent gel.

The cgc is plotted against the carbon number (n) for compounds 1-n and 2-n in order to clarify the effect for the gelation properties shown in Fig. 4.



Fig. 4. The cgc of gel samples in 1-octanol for compounds 1-n  $(\Box)$  and 2-n  $(\bigcirc)$  against the carbon number (n).

As can be seen from Fig. 4, the gelation ability for compounds 1-n increases unexpectedly with increasing the carbon number (n), and the cgc is about 1 wt% for pentyloxy or longer homologues. For compounds 2-n, the elongation of the carbon number (n) causes a monotonous increase of the gelation ability, where the cgc is always larger than that for compounds 1-n.

Theses results indicate that the gelation ability for 2-n is lower than that for 1-n.

In order to clarify the relationship between the gelation ability and molecular structure, the core structures of compounds 1-n and 2-n are estimated by a semi-empirical molecular orbital calculation (MOPAC, AM1 method<sup>12</sup>) and the results are shown in Fig. 5.

For compounds 1-n, bond angle for C-O-C is calculated to be 115.5°, and bond lengths for C (aliphatic, sp<sup>3</sup>)-O and O-C (aromatic, sp<sup>2</sup>) are 1.43 Å and 1.39 Å, respectively as shown in Fig. 5 (a). For compounds 2-n, on the other hands, bond angle for C-S-C is calculated to be 105.5°, and bond lengths for C (aliphatic, sp<sup>3</sup>) -S and S-C (aromatic,  $sp^2$ ) are calculated to be 1.77 Å and 1.70 Å, respectively, as shown in Fig. 5 (b). These results suggest that the molecular breadth of compounds 2-n is wider a little than that of 1-n.

Furthermore, Mulliken charges<sup>13</sup> for S (sulfur) atom and the corresponding O (oxygen) one are calculated to be 0.2317 and -0.2140, respectively.

These slight differences between molecular geometry and the electrostatic properties should affect the gelation abilities of compounds 1-n and 2-n.



Fig. 5. Core structures estimated by MOPAC (AM1) for compounds (a) 1-n and (b) 2-n.

In our previous work<sup>14</sup>, slight differences of the molecular geometry between ester and thioester groups affect liquid crystalline properties, such as transition temperatures, mesomorphism, and so on. If both the gels and liquid crystals is considered to be a self-assembly phenomena, the slight differences of the molecular geometry should affect the physicochemical properties of gels.

The details of the relationship between molecular structure and gelation ability is now underway.

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