Bulletin of the Chemical Society of Japan

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Advance Publication on the web November 1, 2018

doi:10.1246/bcsj.20180261

Synthesis of Perfluoroalkyl Gelators and Their Selective Gelation Ability for Fluorinated Solvents[1]

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Toshiaki Shimasaki received his B.Sc. degree in 1999 and his M.Sc. degree in 2001 from Okayama University of Science (Professor Shinji Toyota), and his Ph.D degree in 2006 from Kyushu University (Professor Teruo Shinmyozu). After working as a post-doctoral fellow at Osaka University (2007–2009) with Professors Naoto Chatani and Mamoru Tobisu, he joined the Faculty of Engineering, Chiba Institute of Technology as an assistant professor in 2010. He was promoted to associate professor in 2014. His research interest is physical organic chemistry.

Abstract

Novel perfluoroalkyl gelators without hydrogen bonds−bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) isophthalate (**1m**), bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) terephthalate (**1p**), and tris(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) benzene-1,3,5-tricarboxylate (**2**)−were synthesized. Their molecular structures were investigated by density functional theory calculations at the B3LYP/cc-pVDZ level. The gelation abilities of **1m**, **1p**, and **2** were examined and compared to their normal octyl homologues **1m'**, **1p'**, and **2'**. None of the gelators could be gelated in common organic solvents, but gelated well in fluorinated solvents.

Keywords: Perfluoroalkyl, Low-Molecular-Weight Organic Gelators, Rheology, FE-SEM, XRD

1. Introduction

In recent years, low-molecular-weight organic gelators (LMOGs) have received significant attention because of their applicability to a broad range of materials such as luminescent materials,[2,3] shape-memory materials,[4,5] liquid crystalline materials,[6] electro-conducting materials,[7] pH sensors,[8,9] and drug delivery[2,4,10] and other stimuli-responsive materials.[11] LMOGs self-assemble into fibers, strands, tapes, and other elongated objects to form fibrillar networks through intermolecular forces such as hydrogen bonds, π−π interactions, van der Waals forces, and dipole−dipole interactions. This type of organogel has thermal reversibility, i.e., it switches between sol and gel states when heated and cooled, respectively.[12] The predominant weak intermolecular force in LMOGs is the hydrogen bond, because the hydrogen bond is a relatively stronger attractive interaction than other forces. However, we examined and reported the influence of the number and position of cholesteryl groups on gelation behavior using three LMOGs lacking hydrogen-bonding moieties. In our previous report,[1] we clarified that the substitution by two cholesteryl groups at 1,3-positions of the benzene core of a gelator disrupted its gelation behavior, whereas the substitution at the 1,4- or 1, 3, 5-positions resulted in a good gelation ability in common solvents. This clearly showed that the gelation ability of a gelator without hydrogen bonds depends significantly on its molecular symmetry. Ajayaghosh et al. reported similar results using an oligo(*p*-phenylenevinylene) (OPV) derivative as the gelator.[13−17]

Many LMOGs contain van der Waals interaction moieties such as long alkyl chains or steroid groups.[18,19] On the other hand, recently, perfluoroalkyl and/or perfluoroaromatic substituents have attracted attention as the cohesive force is increased by the self-organization of perfluoro-substituents.[20−22] LMOGs having perfluoroalkyl / perfluoroaromatic groups instead of alkyl and steroid groups have also been reported.[23−35] For example, Okamoto et al. reported that perfluoroalkylbutoxybenzene derivatives without a hydrogen bonding group act as efficient phase-selective gelators of primary amines due to π−π stacking interactions and the weaker intermolecular interaction around the perfluoroalkyl chains, which can be used for the selective separation of organic pollutants from the aqueous mixtures.[35] Yajima, Sato and co-workers reported that *trans-N,N'*-perfluoroalkanoyl-1,2-diaminocyclohexanes gelate hexafluorobenzene and benzotrifluoride at a minimum critical concentration of 4%.[36] Perfluoroalkyl substances (PFASs) have been used as co-solvents for organic reactions, because the reusability, temperature-dependent miscibility with common organic solvents and easy to separation of the reaction product.[37−39] Meanwhile, PFASs, especially perfluorooctanoic acid (PFOA) and its analogs are recognized as the persistent organic pollutants (POPs)[40] and their biological accumulation have been concerned.[41,42] Thus, in the context of environmental sciences, the removal of POPs is one of quite an important issue, and several solution methods for the problem have been suggested. For instance, Baker et al. reported the perfluorinated host molecules based on calix[4]arene can quantitatively remove perfluorooctanoic acid (PFOA) from the water phase by forming host-guest complexes.[43]

Our previous work and the reports on gelation abilities of perfluoroalkyl LMOGs led us to design star-shaped perfluoroalkyl LMOGs **1m**, **1p** and **2** which are effective for

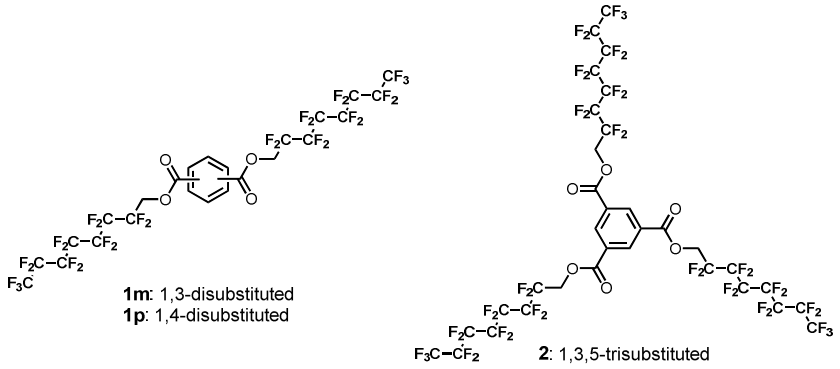
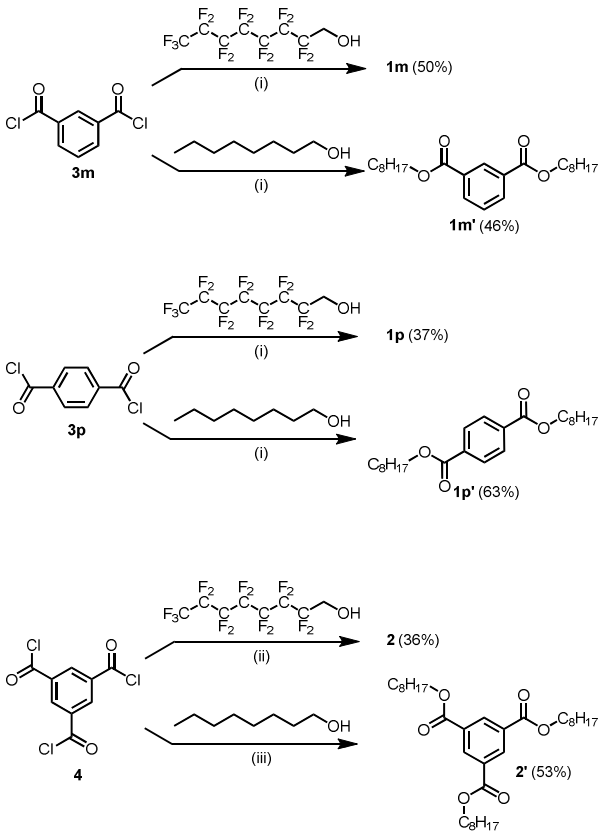


Chart 1. Molecular structures of compounds **1m**, **1p** and **2** having pentadecafluorooctyl groups.

fluorinated solvents (Chart 1). We predicted that compound **2** also possesses the highest gelation ability among them because the cholesteric gelator having C_3-symmetrical structure in our previous study displayed the best result for common organic solvents. Since there is no report of LMOGs having such structural feature, it is an interesting subject to elucidate their aggregation property.

In this study, molecular structures, gelation behavior, and morphology of the aggregated gelator **2** as well as **1m** and **1p** were investigated by ^{1}H NMR, FT-IR spectroscopy, XRD, and FE-SEM analyses and by density functional theory (DFT) calculations. Additionally, their properties were compared to those of their normal alkyl homologs **1m'**, **1p'**, and **2'**, and we examined the influence of the number and position of perfluoroalkyl groups on the gelation ability. Moreover, we examined the exclusive gelation for the fluorinated solvents by using **1m**, **1p** and **2**.

2. Results and Discussions.



Scheme 1. Synthesis of perfluoroalkyl gelators **1m**, **1p** and **2**, and normal alkyl homologues **1m'**, **1p'**and **2'**. (i): toluene/Et_3N (1:1 v/v), alcohol (4.0 mol eq.), DMAP (0.25 mol eq.), 100°C, 48 h. (ii): acetonitrile/Et_3N (1:2 v/v), hexafluorobenzene 1.0 mL, alcohol (6.0 mol eq.), DMAP (0.33 mol eq.), 80°C, 120 h. (iii) toluene/Et_3N (1:1 v/v), alcohol (6.0 mol eq.), DMAP (0.33 mol eq.), 100°C, 78 h. DMAP = 4-dimethylaminopyridine.

2.1. Synthesis and Characterizations. The synthetic routes for the perfluoroalkyl gelators **1m**, **1p**, and **2**, as well as their normal alkyl homologs **1m'**, **1p'**, and **2'** are described in Scheme 1. All compounds were derived from the corresponding acid chlorides **3m**, **3p** and **4** and 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol. The gelators and reference compounds **1m**, **1p**, **1m'**, **1p'**and **2'** were afforded under typical esterification conditions (i) and (iii), with modest yields (**1m**: 50%, **1p**: 37%, **1m'**: 46%, **1p'**: 63%, **2'**: 53%). The synthesis of compound **2** required a 5/1 (v/v) mixture of acetonitrile and hexafluorobenzene instead of toluene as the reaction solvent (condition (ii), 35%). For compound **1m**, the ^{1}H signals at 4.85 (4H, t), 7.64 (1H, t), 8.32 (2H, d), and 8.73 ppm (1H, s) were ascribed to methylene and aromatic protons (see Figure *S*1). The ^{1}H signals for **1p** and **2** were simpler than those of **1m**. Thus, only methylene and aromatic ^{1}H signals were observed at 4.86 ppm (4H, t) and protons at 8.17 ppm (4H, s) for 1p, and at 4.98 ppm (6H, t) and 9.01 ppm (3H, s) for **2**, respectively (see Figures *S*2 and *S*3). The ^{1}H signals for compound **2** were appeared at lower magnetic fields than those for **1m** and **1p**.

2.2. Molecular Structures. As shown in Figure 1, the molecular structural features of perfluoroalkyl-substituted gelators **1m**, **1p**, and **2** were investigated by the DFT method at the B3LYP/cc-pVDZ level. The distances between the terminal perfluoroalkyl groups and the central benzene rings of **1m**, **1p**, and **2** were 15.6−15.9 Å. Interestingly, DFT calculations revealed that the perfluoroalkyl groups were significantly deviated from the benzene-carbonyl plane in comparison with the alkyl groups of the normal benzoates. The degree of deviation of 1,4-substituted **1p** (74.4°) was larger than those of **1m** (4.6° and 10.7°) and **2** (3.6°, 4.2°, and 8.2°). These predictions almost coincide with experimental results reported by Hori, Okamoto and co-workers.[44] On the other hand, calculations showed that gelator **2** had a nearly planar structure, which probably favored the formation of self-assembled fibrillar networks.

2.3. Gelation Behaviors. We examined the gelation abilities of perfluoroalkyl gelators **1m**, **1p**, and **2** as well as the normal alkyl homologs **1m'**, **1p'**, and **2'**, and the results are summarized in Table 1. The gelation tests were carried out using the standard heating-and-cooling method with a gelator concentration of 10.0% (w/v). All gels described in Table 1 were opaque, because light-scattering large aggregates were formed upon cooling. Among the perfluoroalkyl solvents in this

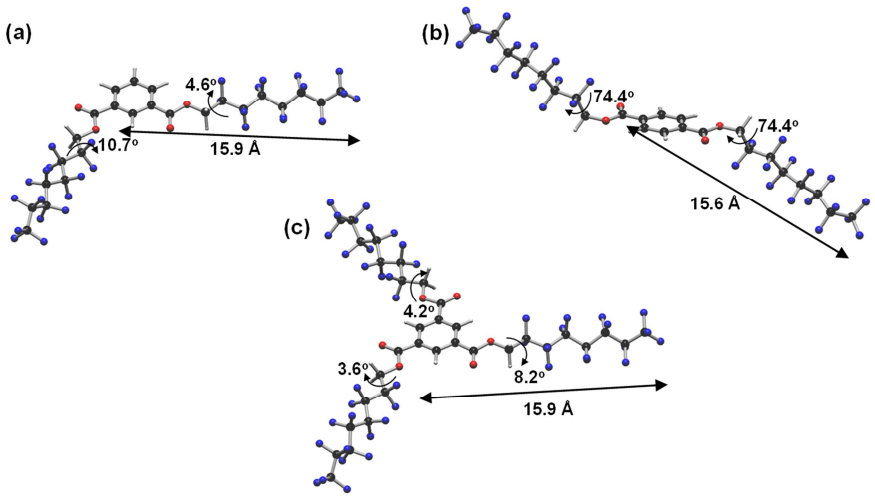


Figure 1. Energy minimized structures of gelators (a) **1m**, (b) **1p**, and (c) **2** derived at the B3LYP/cc-pVDZ level. Black, red, white, and blue balls indicate carbon, oxygen, hydrogen, and fluorine atoms, respectively.

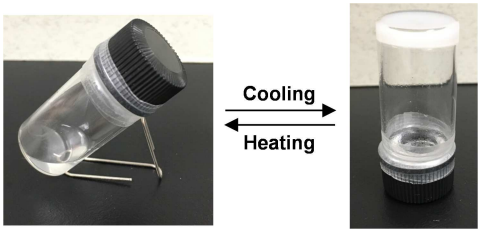


Figure 2. Thermo-reversible gelation of **2** in heptacosafluorotributylamine (1.0% (w/v) at 25°C).

Table1. Gelation properties of **1m**, **1p**, and **2**, as well as **1m'**, **1p'**, and **2'**.[a]

Solvent	**1m**	**1m'**	**1p**	**1p'**	**2**	**2'**
Dichloromethane	P	S	I	S	I	S
Chloroform	S	S	S	S	I	S
1,2-Dichloroethane	I	S	P	S	I	S
Hexane	P	S	I	S	I	S
Cyclohexane	P	S	I	S	I	S
Ethanol	PG	S	I	**G**	I	S
Methanol	I	S	I	P	I	S
Diethylether	P	S	P	I	I	S
Tetrahydrofuran (THF)	PG	S	S	S	PG	S
Benzene	P	S	I	S	I	S
Bromobenzene	P	S	P	S	I	S
Toluene	P	S	P	S	I	S
Dimethylformamide (DMF)	P	S	P	**G**	P	S
Dimethylsulfoxide (DMSO)	P	S	I	PG	I	S
Hexafluorobenzene	S	S	S	I	S	S
1,2-Difluorobenzene	PG	S	**G**	P	**G** (6.0)[b]	S
1,3-Difluorobenzene	P	S	PG	P	**G**	S
1,4-Difluorobenzene	P	S	P	P	**G** (4.0)[b]	S
Tetradecafluorohexane	PG	S	I	I	I	I

Hexadecafluoroheptane	**G**	S	**G**	I	I	I
Nonafluorobutyl iodide	P	P	**G**	I	**G**	S
3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexene	P	I	**G**	I	P	I
1*H*,1*H*-Nonafluoro-1-pentanol	**G**	I	**G**	I	**G**	I
Methyl 2,2,3,3,4,4,5,5,5-nonafluoropentanoate	S	I	S	I	**G** (1.0) [b]	I
Heptacosafluorotributylamine	PG	S	**G** (3.0)[b]	I	**G** (1.0)[b]	I

[a]Concentration of gelator: 10.0% (w/v) at 5°C; [b]Temperature: 25°C; G: gel; PG: partial gel; P: precipitate; I: insoluble; S: solution. The values in parentheses denote the critical gel concentration (w/v).

study, 2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanoic acid, nonafluorobutyl iodide, 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene, 1*H*,1*H*-nonafluoro-1-pentanol and methyl 2,2,3,3,4,4,5,5,5-nonafluoropentanoate were used as the model compounds of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9, 9,10,10,10-heptadecafluoro-1-decene, perfluorooctyl iodide, 1,1,2,2-tetrahydroperfluorododecanol and methyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate which are PFOAs.

As discussed in our previous report, the gelation behavior of the 1,3-substituted cholesterol gelator in common organic solvents could not be confirmed because of its kinked and poor symmetrical structure.[1] Similarly, the normal alkyl homologue **1m'** was not gelated in almost all organic and fluorinated solvents. However, interestingly, 1,3-diperfluoroalkyl-substituted gelator **1m** formed gels in hexadecafluoroheptane and 1*H*,1*H*-nonafluoro-1-pentanol, and partial gels in ethanol, tetrahydrofuran (THF), 1,2-difluorobenzene, and heptacosafluorotributylamine. The result was attributed to the relatively stronger aggregation ability of perfluoroalkyl moieties compared to those of cholesteryl and normal alkyl groups. Also, **1p** effectively gelated fluorinated solvents such as 1,2-difluorobenzene, nonafluorobutyl iodide, 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene, hexadecafluoroheptane, 1*H*,1*H*-nonafluoro-1-pentanol, and heptacosafluorotributylamine. Notably, **1p** belated heptacosafluorotributylamine at room temperature (25°C) even when the concentration was reduced to 3.0% (w/v). On the other hand, **1p'** did not gelate fluorinated solvents, but it gelated ethanol and dimethylformamide (DMF), reflecting the higher symmetrical structure than that of **1m'**. The C_3-symmetrical gelator **2** gelated well 1,2- and 1,4-difluorobenzenes, methyl 2,2,3,3,4,4,5,5,5-nonafluoropentanoate and heptacosafluorotributylamine at 25°C. Additionally, compound **2** was gelated in methyl 2,2,3,3,4,4,5,5,5-nonafluoropentanoate and heptacosafluorotributylamine at 25°C even at a 1.0% (w/v) gelator concentration, as described in Table 1. Moreover, the stability of gels prepared from **2** was higher than those of similarly shaped cholesteric gels as they did not collapse for several months. Compound **2** also gelated 1,3-difluorobenzene, nonafluorobutyl iodide, and 1*H*,1*H*-nonafluoro-1-pentanol at 5°C. On the other hand, its homologue **2'** did not gelate common organic and fluorinated solvents.

Yoshida et al. reported that aprotic 4-[2-(perfluoroalkyl)ethylsulfanyl]phenoxy derivatives in DMSO show very low critical gel concentrations of up to 0.1% (w/v).[33] Meanwhile, they also found that when sulfide bonds were oxidized to sulfonyl groups, gels were not formed. This suggests that the non-covalent interaction between the sulfide bonds as well as perfluoroalkyl aggregation is important for gelation in this system. This result from Yoshida et al. strongly indicates that other strong attractive interactions such as lone pair−*d* orbital interactions are required in order to increase the gelation ability of a system without hydrogen bond moieties.

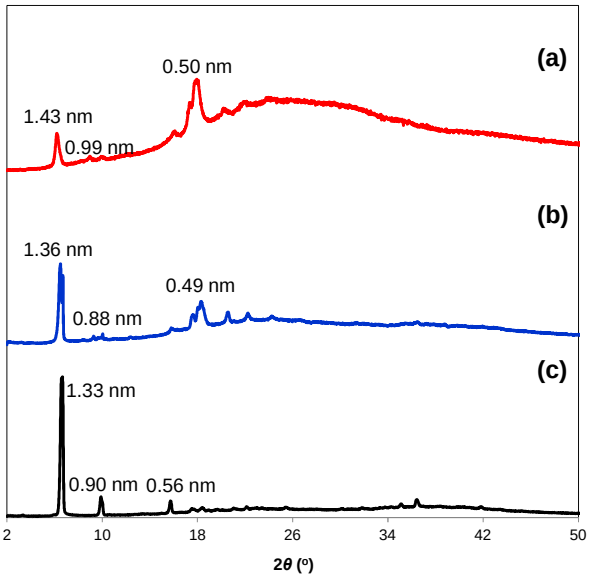


Figure 3. XRD patterns of the xerogels of **2** in (a) heptacosafluorotributylamine, (b) 1*H*,1*H*-nonafluoro-1-pentanol, and (c) 1,2-difluorobenzene.

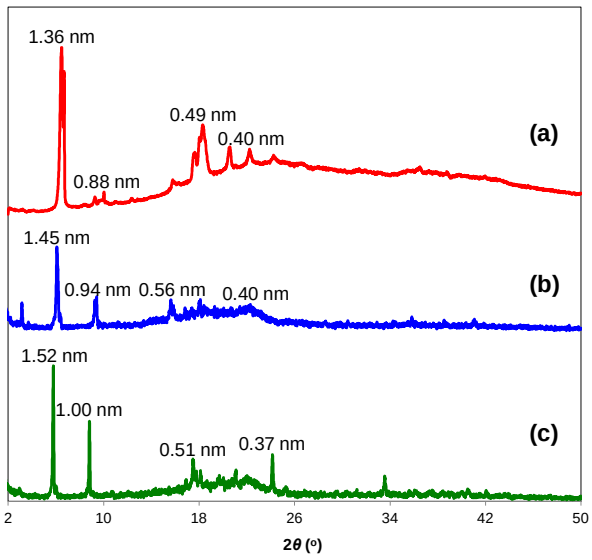


Figure 4. XRD patterns of the xerogels of (a) **2**, (b) **1m**, and (c) **1p** in 1*H*,1*H*-nonafluoro-1-pentanol.

2.4. XRD Studies. Figure 3 shows the XRD patterns of the xerogels prepared from the organogels of **2** in heptacosafluorotributylamine (a), 1*H*,1*H*-nonafluoro-1-pentanol (b), and 1,2-difluorobenzene (c). The xerogel of **2** in 1,2-difluorobenzene (c) exhibited sharper XRD peaks than those of (a) and (b), suggesting that the organogel partially crystallized after the solvent was evaporated. As shown in Figure 3 (a)−(c), the xerogels of **2** displayed intense peaks at 2θ = 6.16° (in heptacosafluorotributylamine), 6.48° (in 1*H*,1*H*-nonafluoro-1-pentanol) and 6.66° (in 1,2-difluorobenzene) corresponding to *d* values of 1.43 (a), 1.36 (b), and 1.33 nm (c), respectively. Moreover, these xerogels also displayed sharp peaks at 2θ = 17.9° (in heptacosafluorotributylamine), 18.3° (in 1*H*,1*H*-nonafluoro-1-pentanol) and 15.7° (in 1,2-difluorobenzene) corresponding to *d* values of 0.50, 0.49, and 0.56 nm, respectively. These values are indicative of face-to-face distances between the gelator molecules. Generally, for a hexagonal columnar packing, the ratio of the *d*-spacing of small angle peaks should be 1 : 1/√3 : 1/2 : 1/√7 etc. The lattice of the xerogels of **2** can be indexed to be a hexagonal one, with the third (1/2) peak absent, in a similar manner to the previous reports, wherein such a feature of certain peaks was found missing.[45]

Figure 4 shows the comparison of XRD patterns of the xerogels prepared from the organogels of **2** (a), **1m** (b), and **1p** (c) in 1*H*,1*H*-nonafluoro-1-pentanol. The XRD patters of xerogels prepared from **1m** and **1p** were similar to each other (Figure 4 (b) and (c)). However, the xerogel of **2** displayed a broader XRD pattern, indicating the crystallinity is lower than those of **1m** and **1p** (Figure 4 (a)). The xerogels of **2**, **1m**, and **1p** displayed intense peaks at 2θ = 6.48° (a), 6.08° (b), and 5.80° (c) corresponding to *d* values of 1.36, 1.45, and 1.52 nm, respectively. Also, the xerogels showed peaks at 2θ = 17.9° (a), 15.6° (b), and 17.5° corresponding to *d* values of 0.49 (a), 0.56 (b), and 0.51 nm (c), respectively. These values are probably the interplanar distances in the gelators. The ratio of the corresponding *d*-spacings of the xerogels of **2**, **1m**, and **1p** in 1*H*,1*H*-nonafluoro-1-pentanol is also roughly1 : 1/√3 : 1/2 : 1/√7, it may be corresponding to a hexagonal columnar packing.[45]

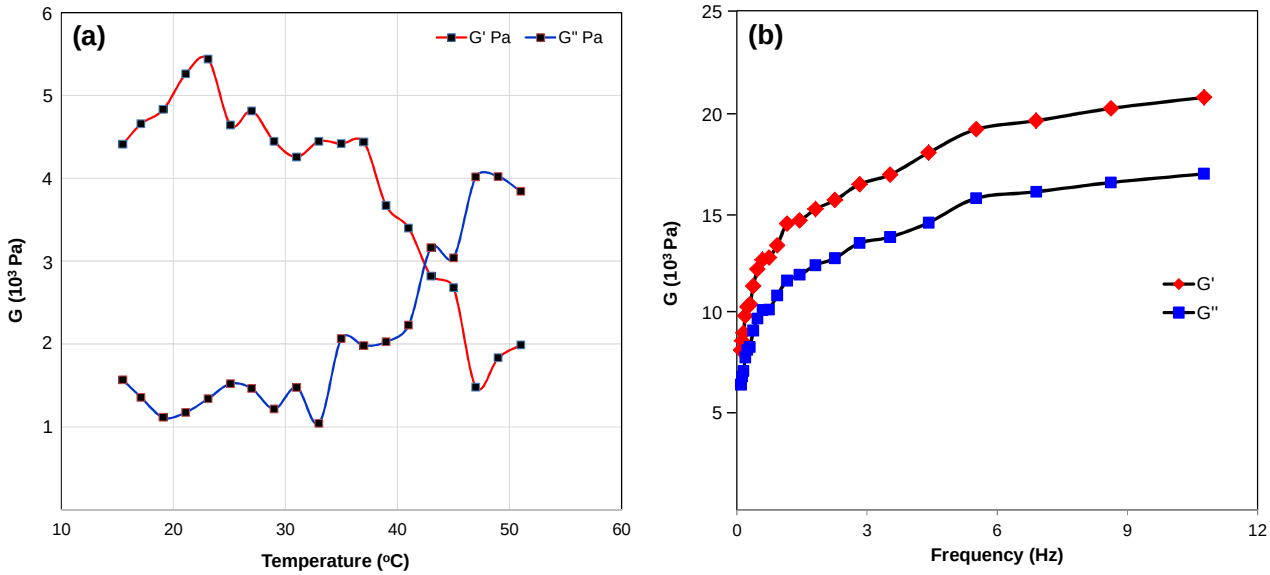


Figure 5. Variation of *G*' and *G*" as a function of temperature (at 1 Hz) (a) and frequency (at 23°C) (b). The sample is a goal of **2** in heptacosafluorotributylamine (1.0% (w/v)).

2.5. Rheological studies. As discussed above, the gel of **2** in heptacosafluorotributylamine (1.0% (w/v)) is spontaneously formed at 23°C. The temperature sweep of shear storage and loss moduli (*G*' and *G*") at a heating rate of 1°C min^{-1} for the organogel is shown in Figure 5 (a). The *G*' and *G*" measure the stored energy, representing the elastic portion, and the energy dissipated as heat, representing the viscous portion. When *G*' > *G*", the material is in a gel state, and when *G*' < *G*", the material is in a sol state. The temperature dependence revealed that the sample of **2** in heptacosafluorotributylamine (1.0% (w/v)) remains a gel state from 15°C upto 42°C, then it is transformed to a sol state at around 43°C. On the other hand, in the frequency sweep experiments of **2** in heptacosafluorotributylamine (1.0% (w/v)), *G*' was always higher than *G*" over the frequency range of 0.1–10 Hz as shown in Figure 5 (b), suggesting the formation of a gel with good tolerance toward the shear stress.

2.6. Morphological Studies. Figure 6 (a) and (b) show the SEM images of xerogels prepared from the organogels of **1p** and **2** in heptacosafluorotributylamine. Irregularly layered morphologies were observed for the xerogels of **1p**, while the xerogel of **2** was composed of thin layers with straight and sharp edges. In contrast to the difference in shapes of xerogels of **1p** and **2** in heptacosafluorotributylamine, all the xerogels of **1m**, **1p**, and **2** in 1*H*,1*H*-nonafluoro-1-pentanol displayed complicatedly layered morphologies, as shown in Figure 6 (c)−(e). This trend is in agreement with the results of XRD analysis. This result indicates that the type of fluorinated solvent significantly influences the gelation and aggregation behavior of LMOGs having perfluoroalkyl substituents. As a whole, we could not confirm the formation of fibrillar networks for the xerogels of **1m**, **1p** and **2** in heptacosafluorotributylamine and 1*H*,1*H*-nonafluoro-1-pentanol by FE-SEM images. This fact strongly suggests that in the gelation event of a fluorinated

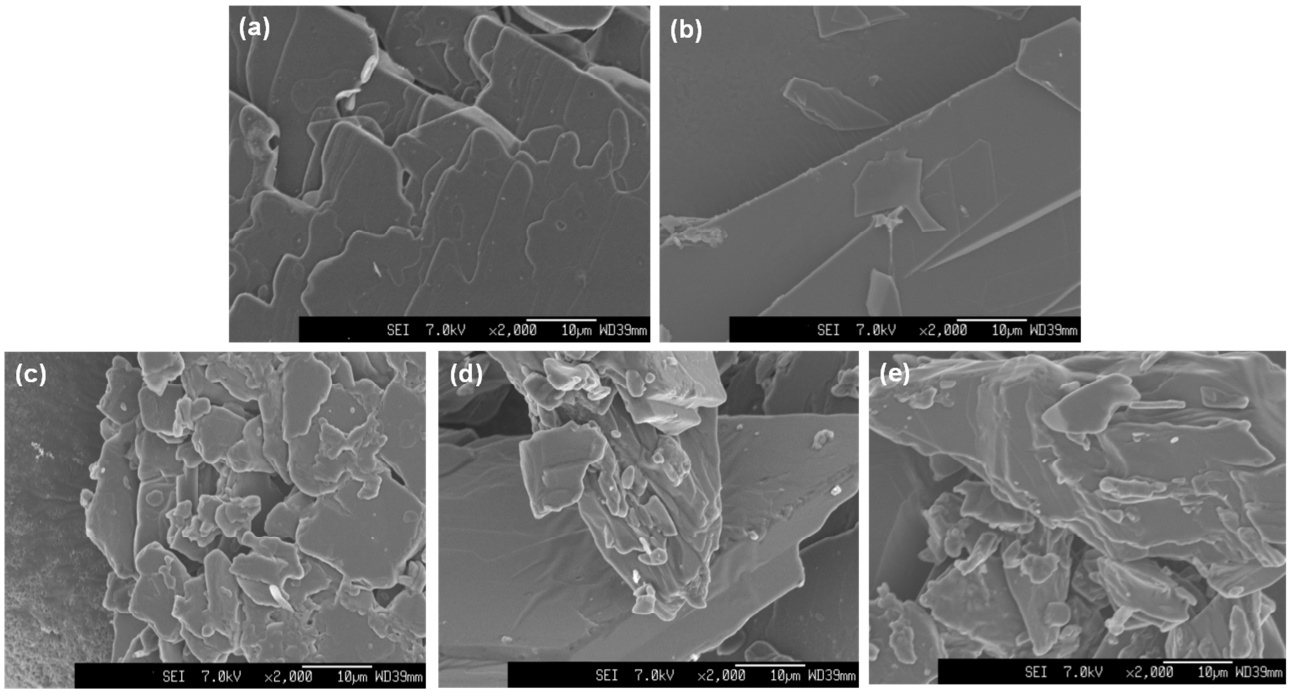


Figure 6. SEM images of xerogels: (a) **1p** (b) **2** in heptacosafluorotributylamine (c) **1m** (d) **1p** (e) **2** in 1*H*,1*H*-nonafluoro-1-pentanol.

solvent by perfluoroalkyl gelators, the large hexagonal aggregates were precipitously formed without forming fibrillar networks upon gelating, probably because the affinity between the perfluoroalkyl gelator and fluorinated solvent is almost same as or stronger than that between the perfluoroalkyl LMOGs.

3. Conclusions.

Three novel LMOGs (**1m**, **1p**, and **2**) having perfluoroalkyl moieties were synthesized by typical esterification reactions of acid chlorides with 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol, giving modest yields. Their structural details were investigated by ^{1}H NMR, FT-IR spectroscopy, high-resolution mass spectrometry, and DFT simulations. As a result of gelation testing, the perfluoroalkyl gelators, **1m**, **1p**, and **2** were efficiently gelated in fluorinated solvents such as difluorobenzenes, nonafluorobutyl iodide, 1*H*,1*H*-Nonafluoro-1-pentanol, and heptacosafluorotributylamine, whereas their normal alkyl homologues (**1m'**, **1p'**, and **2'**) were not gelated. Notably, compound **2** displayed the lowest critical gel concentration (1.0% (w/v)) in methyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate and heptacosafluorotributylamine at 25°C, attributable to the fact that both compound **2** and heptacosafluorotributylamine have high degrees of symmetry. The gel of **2** in heptacosafluorotributylamine (1.0% (w/v)) remains a gel state from 15°C upto 42°C, then it is transformed to a sol state at around 43°C. The xerogels of **1p** and **2** in heptacosafluorotributylamine showed different morphologies, whereas the microstructures for **1m**, **1p**, and **2** in 1*H*,1*H*-nonafluoro-1-pentanol were similar to each other. We found that the type of solvent significantly affected the morphology of the xerogel of **2**.

4. Experimental Section.

4.1 General Experimental Methods. Column chromatography and plug filtrations were performed on silica gel 60. TLC was performed on aluminum sheets that were coated with silica gel 60 F_{254}; visualization was performed with a lamp (λ = 254 or 365 nm). Melting points are uncorrected. IR spectra were recorded by using the attenuated total reflectance (ATR) method. ^{1}H NMR spectra for **1m**, **1p**, and **2** were determined in $CDCl_3$ containing C_6F_6. Chemical shifts (d) are given in ppm relative to tetramethylsilane (TMS). Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), and m (multiplet). The surface morphology of the xerogel samples was observed by a field emission scanning electron microscope (FE-SEM). The samples were coated with gold prior to the observation, and the accelerating voltage was 1 kV. X-ray diffraction (XRD) analysis was performed at ambient temperature on an X-ray diffractometer at a scanning rate of 2.0 min^{-1}, using Cu Kα radiation (wavelength, λ = 0.154 nm) at 40 kV and 14 mA. All scans were in the range $5° \leq 2\theta \leq 50°$ at a scanning rate of 1.0 min^{-1} and a step size of 0.01°. FAB-MS spectra for **1m**, **1p** and **2** were recorded in CH_2Cl_2 containing C_6F_6 with *m*-nitrobenzyl alcohol as a matrix. Rheological measurements were performed on a using a plate type rotor of diameter of 20 mm. All the theoretical calculations were performed by using the Gaussian program package.[46] The geometry optimizations were performed by the Becke's three-parameter hybrid functional (B3),[47] the Lee, Yang, and Parr (LYP) correlation,[48,49] and the correlation consistent cc-pVDZ basis set of Dunning.[50]

4.2. Materials. Terephthaloyl dichloride (purity >99.0% by gas chromatography), isophthaloyl dichloride (purity >99.0% by gas chromatography), trimesoyl trichloride (benzene-1,3,5-tricarbonyltrichloride, purity >98.0% by gas chromatography), 1*H*,1*H*-pentadecafluoro-1-octanol (purity >98.0% by gas chromatography), 1-octanol (purity >99.0% by gas chromatography) and 4-dimethylaminopyridine (DMAP, purity >99.0% by gas chromatography) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Triethylamine and toluene were purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan). All of the commercially available reagent was used without further purification.

4.3. Synthesis.

Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) isophthalate (1m). Dimethylaminopyridine (DMAP) (36.1 mg, 0.30 mmol) was slowly added to a stirred solution of 1*H*,1*H*-pentadecafuluoro-1-octanol (1.74 g, 2.69 mmol) in toluene (10 mL) at room temperature under N_2. After 10 min, isophthaloyl chloride (229 mg, 1.13 mmol) and Et_3N (5 mL) were added in sequence and stirred at 100°C for 48 h. The mixture was then cooled to room temperature and the volatile materials were removed under reduced pressure, dissolved in CH_2Cl_2 (30 mL), and washed several times with H_2O. The crude material was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 1:20) to obtain the compound **1m** as a white solid. Yield, 530 mg (0.570 mmol), 50%; mp, 65.0−66.0°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85 (4H, t, *J* = 13.0 Hz), 7.64 (1H, t, *J* = 7.9 Hz), 8.32 (2H, dd, *J* = 1.8 and 7.9 Hz), 8.73 (1H, t, *J* = 1.6 Hz); IR (ATR, cm^{-1}) $\tilde{\nu}$ = 723, 781, 957, 989, 1007, 1103, 1140, 1196, 1229, 1296, 1325, 1369, 1443, 1611, 1738, 1751; HRMS (FAB+): m/z calcd for $C_{24}H_9F_{30}O_4$: 931.0022; found: 931.0018 [(M + H)$^+$].

Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) terephthalate (1p).[51] DMAP (35.2 mg, 0.28 mmol) was slowly added to a stirred solution of 1*H*,1*H*-pentadecafuluoro-1-octanol (1.85 g, 2.69 mmol) in toluene (10 mL) at room temperature under N_2. After 10 min, terephthaloyl chloride (224 mg, 1.10 mmol) and Et_3N (5 mL) were added in sequence and stirred at 100 °C for 48 h. The mixture was then cooled to room temperature and the volatile materials were removed under reduced pressure, dissolved in CH_2Cl_2 (30 mL), and washed several times with H_2O. The crude material was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 3:1) to obtain the compound **1p** as a white solid. Yield, 375 mg (0.403 mmol), 37%; mp, 66.5−67.5°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (4H, t, *J* = 16.8 Hz), 8.17 (4H, s); IR (ATR, cm^{-1}) $\tilde{\nu}$ = 719, 874, 966, 988, 1016, 1034, 1103, 1138, 1200, 1325, 1369, 1400, 1452, 1732; HRMS (FAB+): m/z calcd for $C_{24}H_9F_{30}O_4$: 931.0022; found: 931.0052 [(M + H)$^+$].

Tris(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) benzene-1,3,5-tricarboxylate (2). DMAP (41.3 mg, 0.34 mmol) was slowly added to a stirred solution of 1*H*,1*H*-pentadecafuluoro-1-octanol (2.67 g, 6.68 mmol) in acetonitrile (5 mL) and hexafluorobenzene (1 mL) at room temperature under N_2. After 10 min, benzene-1,3,5-tricarbonyl trichloride (522 mg, 1.97 mmol) and Et_3N (10 mL) were added in sequence and stirred at 80 °C for 120 h. The mixture was then cooled to room temperature and the volatile materials were removed under reduced pressure, and added to CH_2Cl_2 (30 mL). The white powder, which was insoluble in CH_2Cl_2, was collected by filtration, and washed with CH_2Cl_2, acetonitrile, and H_2O several times to obtain the compound **2** as a white solid. Yield, 953 mg (0.70 mmol), 36%; mp, 114.5.0−115.5°C; ^{1}H NMR (500 MHz, $CDCl_3$ in the presence of hexafluorobenzene) δ 4.98 (6H, t, *J* = 13.0 Hz), 9.01 (3H, s); IR (ATR, cm^{-1}) $\tilde{\nu}$ = 723, 779, 870, 959, 974, 1009, 1103, 1142, 1198, 1231, 1296, 1327, 1443, 1611, 1737, 1751; HRMS (FAB+): m/z calcd for $C_{33}H_{10}F_{45}O_6$: 1356.9759; found: 1356.9743 [(M + H)$^+$].

Trioctyl benzene-1,3,5-tricarboxylate (2'). DMAP (37.0 mg, 0.30 mmol) was slowly added to a stirred solution of 1-octanol (861 mg, 6.61 mmol) in toluene (5 mL) at room temperature under N_2. After 10 min, benzene-1,3,5-tricarbonyl trichloride (290 mg, 1.09 mmol) and Et_3N (5 mL) were added in sequence and stirred at 100 °C for 72 h. The mixture was then cooled to room temperature and the volatile materials were removed under reduced pressure, dissolved in CH_2Cl_2 (30 mL), and washed several times with H_2O. The crude material was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 20:1) to obtain the compound **2'** as a colorless oil. Yield, 317 mg (5.81 mmol), 53%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (9H, t, *J* = 7.1 Hz), 1.27−1.39 (25H, m), 1.41−1.47 (5H, m), 1.79 (6H, quin, *J* = 7.9 Hz), 4.37 (6H, t, *J* = 6.7 Hz), 8.84 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.9, 28.6, 29.16, 29.20, 31.8, 65.8, 131.5, 134.4, 165.1; IR (ATR, cm^{-1}) $\tilde{\nu}$ = 723, 741, 779, 870, 957, 972, 1009, 1132, 1142, 1198, 1233, 1294, 1327, 1369, 1443, 1609, 1738, 1751, 2853, 2928; HRMS (FAB+): m/z calcd for $C_{33}H_{55}O_6$: 547.3999; found: 546.3999.

4.4. Methods. In a typical procedure, the weighed sample was mixed with the specified solvent in a sealed sample tube, and then the mixture was heated until the solid was completely dissolved. The resulting solution (concentration 10.0% (w/v)) was cooled to 5 °C for 10 min, and finally the test tube was inverted to determine whether the sample inside could still flow. Gelation was considered to have occurred when a homogeneous substance was obtained and exhibited no gravitational flow. In such cases, the sample was denoted as 'G' (gel). In other cases, solution and gel might coexist in a system; these samples were denoted as 'PG' (partial gel). Systems in which only the solution remained were denoted as 'S' (solution). The label 'P' (precipitation) was used for systems in which a precipitate was obtained at the end of the tests. Finally, systems in which the samples could not be dissolved, even at the boiling point of the solvent, were denoted as 'I' (insoluble).

Acknowledgements

This work was supported by the Grant-in-Aid for Young Scientists (B) from JSPS (Grant Number 17K14452). We thank Mr. Kaito Sugane of Chiba Institute of Technology for the XRD measurements.

5. References and notes.

1. Part 2 of ''C_3-symmetric gelators without hydrogen bond moiety.'' For Part 1, see: T. Shimasaki, Y. Okamiya, R. Sato, K. Hara, T. Nakamura, N. Teramoto, M. Shibata *Tetrahedron*, **2016**, *72*, 1517−1523.
2. A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith *Angew. Chem., Int. Ed.* **2008**, *47*, 8002−8018.
3. L. Maggini, D. Bonifazi, *Chem. Soc. Rev.* **2012**, *41*, 211−241.
4. S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* **2014**, *114*, 1973−2129.
5. L. Sun, W. M. Huang, Z. Ding, Y. Zhao, C. C. Wang, H. Purnawali, C. Tang, *Mater. Des.* **2012**, *33*, 577−640.
6. T. Kato, Y. Hirai, S. Nakaso, M. Moriyama, *Chem. Soc. Rev.* **2007**, *36*, 1857−1867.
7. M. Hasegawa, M. Iyoda, *Chem. Soc. Rev.* **2010**, *39*, 2420−2427.
8. J. H. Van Esch, B. L. Feringa, *Angew. Chem., Int. Ed.* **2000**, *39*, 2263−2266.
9. N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821−836.
10. P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133−3159.
11. X. Yang, G. Zhang, D. J. Zhang, *Mater. Chem.* **2012**, *22*, 38−50.
12. H. Svobodová, V. Noponen, E. Kolehmainen, E. Sievänen, *RSC Adv.* **2012**, *2*, 4985−5007.
13. A. Ajayaghosh, V. K. Praveen *Acc. Chem. Res.* **2007**, *40*, 644–656.
14. V. K. Praveen, S. S. Babu, C. Vijayakumar, R. Varghese, A. Ajayaghosh *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1196–1211.
15. V. K. Praveen, C. Ranjith, N. Armaroli *Angew. Chem. Int.*

Ed. **2014**, *53*, 365–368.
16. R. K. Mishra, S. Das, B. Vedhanarayanan, G. Das, V. K. Praveen, A. Ajayaghosh *Molecular Gels: Structure and Dynamics*: *Structure and Dynamics, Monographs in Supramolecular Chemistry Series*, RSC, **2018**; Chapter 7.
17. A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George *Angew. Chem. Int. Ed.* **2006**, *45*, 456–460.
18. For review, see; M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed *Chem. Rev.* **2010**, *110*, 1960–2004.
19. For a recent example, see; C. Kulkarni, K. K. Bejagam, S. P. Senanayak, K. S. Narayan, S. Balasubramanian, S. J. George *J. Am. Chem. Soc.* **2015**, *137*, 3924−3932.
20. M. Hird *Chem. Soc. Rev.* **2007**, *36*, 2070–2095.
21. E. Krieg, H. Weissman, E. Shimoni, A. Bar On (Ustinov), B. Rybtchinski *J. Am. Chem. Soc.* **2014**, *136*, 9443−9452.
22. A. Riccobono, R. R. Parker, A. C. Whitwood, J. M. Slattery, D. W. Bruce, I. Pibiri, A. Pace *Chem. Commun.* **2018**, *54*, 9965−9968.
23. Y. Morita, T. Tasaka, K. Kawabe, H. Okamoto, S. Takenaka, and H. Kita, *Mol. Cryst. Liq. Cryst.* **2005**, *435*, 813–822.
24. A. Iuchi, Y. Morita, T. Hirakawa, K. Kasatani, H. Okamoto *ESC Trans*. **2009**, *16*, 65–70.
25. J. Loiseau, M. Lescanne, A. Colin, F. Fages, J.-B.Verlhac, J.-M.Vincent *Tetrahedron* **2002**, *58*, 4049–4052.
26. M. George, S. L. Snyder, P. Terech, C. J. Glinka, R. G. Weiss, *J. Am. Chem. Soc.* **2003**, *125*, 10275–10283.
27. M. George, S. L. Snyder, P. Terech, R. G. Weiss, *Langmuir* **2005**, *21*, 9970–9977.
28. E. Faggi, R. Maria Sebastian, A. Vallribera, *Tetrahedron* **2010**, *66*, 5190–5195.
29. J. Gan, M. El Bakkari, C. Belin, C. Margottin, P. Godard, J.-L. Pozzo, J.-M. Vincent, *Chem. Commun.* **2009**, 5133–5134.
30. H. Kumari, S. E. Armitage, S. R. Kline, K. K. Damodaran, S. R. Kennedy, J. L. Atwood, J. W. Steed *Soft Matter* **2015**, *11*, 8471–8478.
31. T. Yoshida, T. Hirakawa, T. Nakamura, Y. Yamada, H. Tatsuno, M. Hirai, Y. Morita, H. Okamoto *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1447–1452.
32. H. Sato, T. Yajima, A. Yamagishi *Phys. Chem. Chem. Phys.* **2018**, *20*, 3210–3215.
33. T. Yoshida, T. Nakamura, Y. Morita, H. Okamoto *Chem. Lett.* **2015**, *44*, 512–514.
34. S. S. Babu, V. K. Praveen, S. Prasanthkumar, A. Ajayaghosh *Chem. Eur. J.* **2008**, *14*, 9577–9584.
35. B. Cao, Y. Kaneshige, Y. Matsue, Y. Morita, H. Okamoto *New J. Chem.* **2016**, *40*, 4884–4887.
36. T. Yajima, E. Tabuchi, E. Nogami, A. Yamagishi, H. Sato *RSC Adv.* **2015**, *5*, 80542–80547.
37. I. T. Horváth, J. Rábai *Science*, **1994**, *266*, 72–75.
38. D. -W. Zhu *Synthesis*, **1993**, *10*, 953–954.
39. I. Klement, H. Lütjens, P. Knochel *Angew. Chem. Int. Ed.* **1997**, *36*, 1454–1456.
40. Stockholm Convention **2005**; Decision POPRC-1/7: Perfluorooctanesulfonate. http://www.pops.int/documents/meetings/poprc/docs/chem_review.htm.
41. Y. Zhai, X. Xia, X. Zhao, H. Dong, B. Zhu, N. Xia, J. Dong *J. Hazard. Mater.* **2016**, 302, 404−414.
42. M. D. Taylor, J. Beyer-Robson, D. D. Johnson, N. A. Knott, K. C. Bowles *Mar. Pollut. Bull.* **2018**, *131*, 303–313.
43. H. Omorodion, M. Palenzuela, M. Ruether, B. Twamley, J. A. Platts, R. J. Baker *New J. Chem.* **2018**, *42* , 7956−7968.
44. M. Yano, T. Taketsugu, K. Hori, H. Okamoto, S. Takenaka *Chem. Eur. J.* **2004**, *10*, 3991–3999.
45. A. Sandeep, V. K. Praveen, D. S. S. Rao, S. K. Prasad, A. Ajayaghosh *ACS Omega* **2018**, *3*, 4392–4399.
46. All calculations were performed using: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Son-nenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
47. A. D. Becke *J. Chem. Phys.*, **1993**, 5648−5652.
48. C. Lee, W. Yang, R. G. Parr *Phys. Rev. B*, **1988**, *37*, 785−789.
49. B. Miehlich, A. Savin, H.Stoll, H. Preuss *Chem. Phys. Lett.*, **1989**, *157*, 200−206.
50. J. T. H. Dunning *J. Chem. Phys.* **1989**, *90*, 1007−1023.
51. Chemical data of **1p** (bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl) terephthalate) was reported recently; M. Vandamme, L. Bouchard, A. Gilbert, M. Keita, J.-F. Paquin *Org. Lett.* **2016**, *18*, 6468–6471.