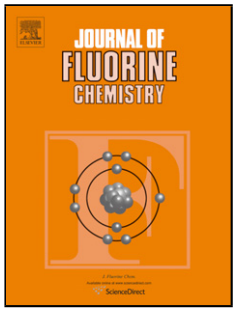

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Full Length Article

Synthesis, liquid crystalline and gelation properties of 4-semifluoroalkoxybiphenyl derivatives

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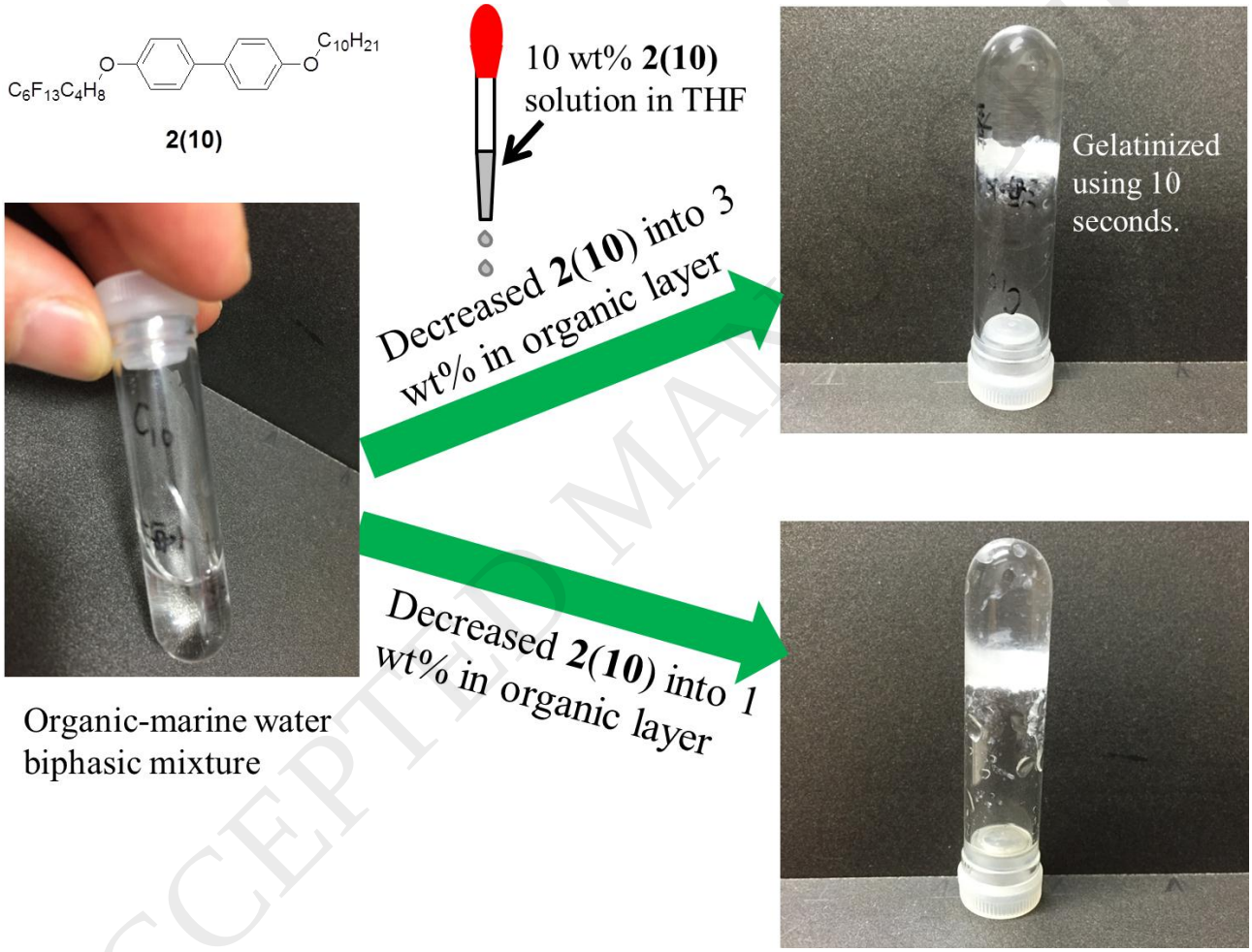
Graphical abstract



Highlights

- Not only the linking group which the structural unit is between perfluoroalkyl and biphenyl core but also the terminal alkoxyl group plays an important role in their liquid crystalline properties and gelation abilities.
- 4-Semifluoroalkoxybiphenyl derivatives solution in THF can selectively gelatinize from aqueous-oil biphasic mixtures about 10 seconds at room temperature even at 3 wt% in the organic layer.

- Formalin as homogeneous organic-aqueous mixtures also can be selectively gelatinized by 4-semifluoroalkoxybiphenyl derivatives solution in THF.

Abstract

4-Semifluoroalkoxybiphenyl derivatives **1** and **2(n)** (n = 4-6, 8 and 10) were designed, synthesized and their physic-chemical properties were examined. The effects of chemical structure on liquid crystalline and gelation properties were investigated. The clear point for **2(n)** declines as the carbon number of terminal alkoxyl chain enlarges from 4 to 10. The clear point for **2(4)** is 172 °C while **2(10)** is 135 °C. The gelation properties for **2(n)** are superior to those for **1**, where the linking group of gelators **2(n)** between a perfluoroalkyl group and biphenyl core are longer than that of **1**. In compounds **2(n)**, the longer alkoxyl chain at the terminal position, the better gelation properties. The phase selective property of compound **2(10)** in THF solution is better than in toluene. 10 wt% **2(10)** solution in THF can selectively gelatinize oils and amines from aqueous-organic biphasic mixtures. Interestingly, 10 wt% **2(10)** solution in THF also selectively gelatinize organic compound from homogeneous aqueous-organic mixtures. Gels formed by compounds **2(n)** as supramolecular gels were investigated their thermoreversible and rheological property.

Keywords: 4-Semifluoroalkoxybiphenyl derivatives; Liquid crystal; Phase selective gelator; Aqueous-organic biphasic mixtures; Homogeneous aqueous-organic mixtures.

1. Introduction

Phase selective gelator (PSG) as a kind of low molecular weight gelator (LMWG) selectively gelatinizes one component of mixed solvents by self-assembling into three-dimensional networks, generally, through weak non-covalent interactions such as hydrogen bond, π-π stacking, van der Waals, coordination and so on [1-3].

The first example of PSG was reported by Bhattacharya and Krishnan-Ghosh [4]. Since then, there has been rapidly growing interest in PSGs because supramolecular gels formed by PSGs enlarge their potential applications from drug delivery, catalysis of organic reactions, solid-state electrolytes to environment recoveries and so on [5-13]. Up to now, most PSGs reported are made up of two parts. One is protic functional groups, for instance, hydroxyl, amino, and carboxyl groups, and the other is aprotic ones, bulk aromatic core and/or long alkyl chains [14]. The main driving force for gelation of PSGs consists of the protic intermolecular hydrogen bond [8,15]. In this system, therefore, intermolecular hydrogen bonds forming with not only themselves but also water molecules lead supramolecular gels to unstable [16].

Although it has been difficult to predict the gelation efficiency from the molecular structure, without doubt, the intermolecular interactions play a key role in gelation property [17]. In the past few years, several LMWGs having per- and/or semifluoroalkyl chains (R_f) without hydrogen bond groups were published [8-20]. It is well proved that soft materials containing R_f can show particular properties by the interplay of structural variations, such as the lengthening arms, the type and orientation of the linking groups and the terminal chains [21-23]. R_f groups characteristic showing properties of hydrophobic or fluorophilic/solvophobic interactions have been widely used in the design of soft materials, but they are always as terminal groups [24-29].

We have previously reported that R_f as terminal group affects their gelation ability [19-20], and also investigated 4-semifluoroalkoxybiphenyl derivatives **2(5)** and **2(6)** (Figure 1) incorporating neither protic functional group nor so long alkyl chain as PSGs in aqueous-organic liquid biphasic mixtures [30]. The weaker intermolecular interactions around perfluoroalkyl chains and π-π stacking interactions which were the essential driving force for gelation of compounds **2(5)** and **2(6)** were analyzed by IR and NMR.

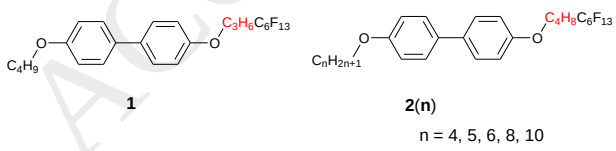
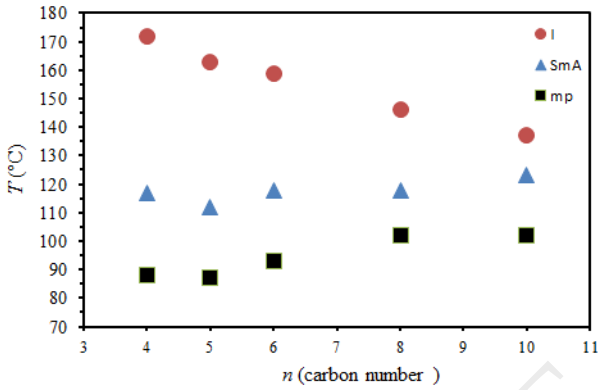


Figure 1. Molecular structures of 4-semifluoroalkoxybiphenyl derivatives

In this paper, we prepared 4-semifluoroalkoxybiphenyl derivatives **1** and **2(n)** (n = 4-6, 8 and 10) in order to investigate the influence of terminal alkoxyl chain and liking group between a perfluoroalkyl group and biphenyl core on their physic-chemical properties such as liquid crystalline properties and gelation properties. Of special interest to us is whether compounds **2(n)** have efficient selective gelation ability at room temperature or not. Particular gelation properties of gelator which shows the best gelation properties among **1** and **2(n)** will be investigated. The properties of gels such as aggregation mode, thermoreversible, the rheological property will be also investigated.

2. Results and Discussion



2.1 Synthesis

Synthesis of **1** was carried out by a similar route to compounds **2(5)** and **2(6)**, showing in Scheme 1. 4,4'-Biphenol was reacted with 1-bromobutane and then 3-bromopropene according to the Williamson ether synthesis in a low yield [31]. The medial product was reacted with 1-iodoperfluorohexane under free-radical addition condition and then reduced by $LiAlH_4$ to give compound **1** in a general yield. Compounds **2(n)** (n = 4, 8 and 10) were also synthesized in a similar route to compound **1**. The products were characterized by NMR, IR spectroscopy and HR-MS.

Scheme 1. Synthesis of 4-semifluoroalkoxybiphenyl derivative **1**

2.2 Liquid crystalline properties

Liquid crystalline properties of compounds **1** and **2(n)** were determined by means of DSC measurements and polarized microscope observations, the enthalpies of transitions and polarized photomicrographs are shown in Figure S1 and Figure S2 respectively [30].

The DSC thermogram for **1** shows endotherms at 76 °C, 107 °C, 110 °C, 116 °C, and 171 °C on the heating process. Because **1** has three transition phases at a narrow temperature range from 107-116 °C, the enthalpies were calculated together. While **2(4)** shows endotherms at 87 °C, 98 °C, 113 °C, 118 °C, and 172 °C on the heating process. For **1** and **2(4)**, type focal conic fan textures and homeotropic texture were observed at 160 °C during a cooling process. Therefore, the mesophases were assigned to be smectic A phase (SmA). The enthalpies for the SmA-I transition also support the characterization, where the value for **1** was determined to be 10.7 kJ/mol and that for **2(4)** was 11.9 kJ/mol. Maybe the carbon number is bigger enough, the clear point (from SmA to isotropic liquid, I) and melt point for **1** and **2(4)** nearly the same with each other are free from odd-even effect.

For **2(8)** and **2(10)**, mesophases before isotropic liquid were judged by a method which is similar to **1** and **2(4)** and the mesophases fitted the characterization of SmA were found. The temperatures of clear point (I), SmA-mesophase (from other mesophases to smectic A phase, SmA) and melting point (mp) were plotted against the carbon number of a terminal alkoxyl chain (n) for **2(n)** shown in Figure 2. The clear point for **2(n)** declines as the carbon number of terminal alkoxyl chain enlarges from 4 to 10. The clear point for **2(4)** is 172 °C while **2(10)** is 135 °C. The transition temperature from other mesophases to SmA and melt point increases slightly on increasing the carbon number of the terminal alkoxyl chain.

Figure 2. Plots of transition temperature (*T*) vs. carbon number (*n*) for compounds 2(n)

2.3 General gelation properties

The gelation properties of **1** and **2(n)** with organic solvents were tested in a heating-cooling cycle by the "stable to inversion in a test tube" method at room temperature [32], and the results are shown in Table 1. The results indicate that **1** can't gelatinize any tested organic solvents, while **2(4)** is able to form gels with octane, γ-butyrolactone (GBL), 1-octanol and propylene carbonate (PC). According to odd-even effects in organic self-assemble [33-34] and the different gelation property between **1** and **2(4)** means that the linking groups between perfluoroalkyl and biphenyl core have an important role in gelation ability.

We elongated the terminal alkoxyl chain of **2(n)** to clarify the relationship between gelation ability and the terminal alkoxyl chain length. Critical gelation concentrations (CGCs) are summarized in Table 1. Compounds **2(n)** are dissolved in THF and toluene, and precipitated from ethanol. Compound **2(10)** gelatinizes most of the organic solvents which were tested in this paper. In some cases, the critical gelation concentrations value of compound **2(10)** range between 0.7-1.0 wt%. Among all the gelators, the lowest CGC value (0.5 wt%) is observed by PC gelatinized by **2(8)** and **2(10)**. The result shown in Table 1 indicates that the elongation of the terminal alkoxyl chains may increase gelation property.

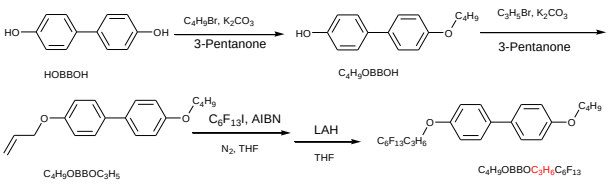


Table 1. Critical gelation concentration of compounds **1** and **2(n)** (wt%) at room temperature [a],[b]

Solvents	**1**	**2(4)**	**2(5)**[c]	**2(6)**[c]	**2(8)**	**2(10)**
PE	P(5.0)	P(5.0)	P(5.0)	P(5.0)	P(5.0)	G(5.0)
DPMNP	P(5.0)	P(5.0)	G(4.0)	G(4.0)	G(3.0)	G(2.0)
THF	S(5.0)	S(5.0)	S(5.0)	S(5.0)	S(5.0)	S(5.0)
Toluene	S(5.0)	S(5.0)	S(5.0)	S(5.0)	S(5.0)	S(5.0)
Cyclohexane	S(5.0)	S(5.0)	G(4.0)	G(4.0)	G(5.0)	G(3.0)
Octane	P(5.0)	G(3.0)	G(3.0)	G(2.0)	G(2.0)	G(1.0)
Acetone	S(5.0)	P(5.0)	P(5.0)	P(5.0)	P(5.0)	P(5.0)
3-Pentone	S(5.0)	S(5.0)	S(5.0)	S(5.0)	S(5.0)	G(5.0)
Ethanol	P(5.0)	P(5.0)	P(5.0)	P(5.0)	P(5.0)	P(5.0)
1-Octanol	P(5.0)	G(4.0)	G(0.7)	G(0.6)	G(0.8)	G(0.7)
Ethyl acetate	S(5.0)	P(5.0)	S(5.0)	S(5.0)	P(5.0)	G(5.0)
GBL	P(5.0)	G(4.0)	G(0.5)	G(0.5)	G(0.8)	G(0.8)
PC	P(5.0)	G(4.0)	G(0.6)	Ins(5.0)	G(0.5)	G(0.5)
DMF	P(5.0)	P(5.0)	G(2.0)	G(1.0)	G(4.0)	G(1.0)
DMSO	P(5.0)	P(5.0)	G(2.0)	Ins(5.0)	G(1.0)	G(0.7)
HMPA	S(5.0)	S(5.0)	S(5.0)	G(5.0)	G(5.0)	G(4.0)

[a] G: gel, P: precipitate, S: soluble, Ins: insoluble; for gels, the critical gelation concentrations at room temperature were shown in parentheses; for P, S and Ins, compounds **1** and **2(n)** were precipitated, soluble and insoluble respectively at the concentrations in parentheses; [b] PE, DPMNP, THF, DMF, DMSO and HMPA indicated petroleum ether, dipropylene glycol methyl propyl ether, tetrahydrofuran, *N*,*N*-dimethyl formamide, dimethyl sulfoxide and hexamethylphosphoric triamide, respectively; [c] CGCs of **2(5)** and **2(6)** cited from our previous work.[11]

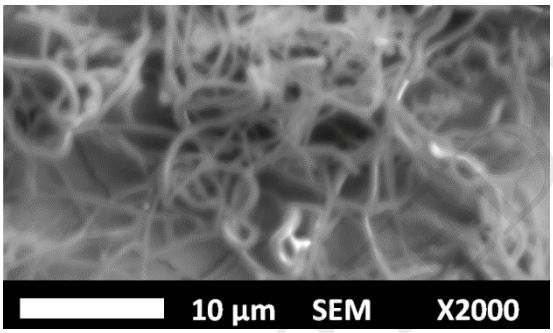


Figure 3. SEM image of PC xerogel system formed by compound **2(10)** (scale bar = 10 µm)

To gain visual insights into the aggregation mode, we investigated the fibril of gel which formed by **2(10)** with PC at 1 wt% using scanning electron microscopy (SEM) (Figure 3). The SEM image means that three-dimensional (3D) nanofiber networks formed by self-assembly of **2(10)** molecules. The average diameters of nanofiber are a range of 250-600 mm. Interestingly the X-ray profile for solid power of compound **2(10)** at 25 °C shows two broad reflections at 2θ = 18.0 ° and 19.5 ° shown in Figure S3. From the characteristic feature, only a little crystalline structure was found in solid power of compound **2(10)** and the lateral interaction was very weak were proved.

The gels formed by **2(n)** were thermoreversible. Hence the gel to sol transition temperature (T_{gel}) was plotted against the gelator weight concentration (wt%) in DMSO, GBL or PC (Figure 4). Figure 4 shows that in GBL at the same concentration the T_{gel} values of **2(10)** is similar to those of **2(8)**, on the other hand, in DMSO the T_{gel} values of **2(10)** is about 20 °C higher than those of **2(8)**. The T_{gel} values of **2(8)** show the order of PC > GBL > DMSO at the same concentration. For **2(10)**, the T_{gel} values in DMSO are similar to those in PC, and both of them are higher than in GBL. The T_{gel} values rapidly decreased below 2 wt% concentration.

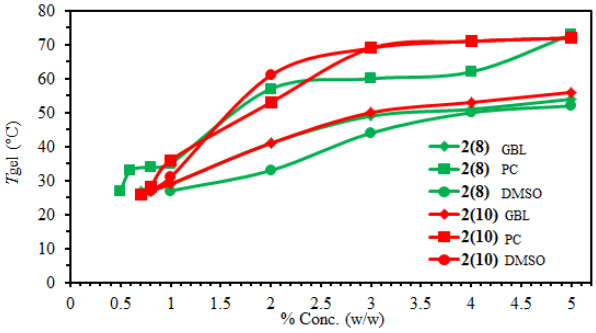


Figure 4. Plots of concentration for **2(8)** and **2(10)** vs. T_{gel} in GBL, PC, and DMSO

2.4 Phase selective gelation properties

2.4.1 Phase selective gelation properties under heating-cooling process

Amines are widely used as industrial chemicals and may exist in the environment as pollution sources [35]. Although amines themselves maybe not the major risk for the environment, from the past researches, amines as a precursor of toxic compounds can destroy the environment through degradation reactions [36]. In order to protect human health and environmental safety, it is important to reduce amines in the environment, especially in water. So, representative examples of amines were chosen and investigated with compounds **1** and **2(n)** by the "stable to inversion in a test tube" method firstly. The results of CGCs are shown below Table 2. Except for some cases (i.e. CGCs of **2(6)** with *N*,*N*-diisopropylethylamine (DIEA), **2(8)** with benzylamine or piperidine), for gelators **2(n)** with the long alkoxyl chains, gelation properties have become strong.

We investigated the selective gelation ability of **2(5)** and **2(6)** with aniline, benzylamine, 2-PEA, piperidine, DIEA and pyridine at CGC. 1 g Water was dropped into a sealed tube containing gel at CGC and the mixture was heated until the gel dissolved. Then, the aqueous-oil biphasic mixture was shaken about 1 min with heating and then cooled to room temperature. The tube was subsequently inverted to judge the gel formation.

The gels gelatinized by **2(5)** and **2(6)** could selectively gelatinize some kinds of amines phase from the aqueous-amines biphasic mixture (Figure S4). After cooling the mixture to room temperature, compound **2(5)** could selectively gelatinize the aniline, benzylamine, and 2-phenylethylamine in aqueous-amines biphasic systems. While compound **2(6)** could only selectively gelatinize with aniline in aqueous-aniline again.

Table 2. Gelation properties of compounds **1** and **2(n)** (wt%) with amines at room temperature [a],[b]

Solvents	**1**	**2(4)**	**2(5)**	**2(6)**	**2(8)**	**2(10)**
Aniline	P(5.0)	G(4.0)	G(1.0)	G(1.0)	G(1.0)	G(0.2)
Benzylamine	P(5.0)	G(5.0)	G(1.0)	G(1.0)	G(2.0)	G(0.6)
1-PEA	P(5.0)	P(5.0)	G(2.0)	G(2.0)	G(1.0)	G(1.0)
2-PEA	P(5.0)	G(5.0)	G(1.0)	G(1.0)	G(1.0)	G(0.6)
Piperidine	P(5.0)	P(5.0)	G(1.0)	G(1.0)	G(5.0)	G(3.0)
DIEA	P(5.0)	G(3.0)	G(5.0)	S(5.0)	G(5.0)	G(3.0)
DMA	P(5.0)	P(5.0)	G(5.0)	G(5.0)	G(5.0)	G(4.0)
Pyridine	P(5.0)	G(5.0)	G(5.0)	G(5.0)	G(5.0)	G(5.0)

[a] G: gel, P: precipitate, S: soluble, for gels, the critical gelation concentrations at room temperature were shown in parentheses, for P and S, compounds **1** and **2(n)** were precipitated and soluble respectively at the concentrations in parentheses; [b] 1-PEA, 2-PEA and DMA indicated 1-phenylethylamine, 2-phenylethylamine and *N*,*N*-dimethyl- aniline, respectively.

Oil is one of the important materials not only in our daily life but also in industry. For example, the synthetic lubricant is used in automobile engines, generators and other machines; mineral oil is used in biomedicine, veterinary medicine, mechanical and electrical industries [37-39]. So every year many tons of oils are used and even threw into the environment [40]. In here gelation ability of **1** and **2(n)** with synthetic lubricant, mineral oil, lamp oil, polyolefin or rape oil were investigated. The results are shown in Table 3.

Table 3. Gelation properties of compounds **1** and **2**(**n**) (wt%) with oils at room temperature [a],[b]

Solvents	**1**	**2(4)**	**2(5)**	**2(6)**	**2(8)**	**2(10)**

Synth. Lub.	G(5.0)	G(1.0)	G(1.0)	G(1.0)	G(1.0)	G(0.7)
Mineral oil	G(5.0)	G(1.0)	G(1.0)	G(1.0)	G(1.0)	G(0.7)
Lamp oil	G(5.0)	G(5.0)	G(5.0)	G(5.0)	G(3.0)	G(2.0)
Poly-α-olefin	G(5.0)	G(4.0)	G(0.8)	G(1.0)	G(0.7)	G(0.7)
Rapeseed oil	G(5.0)	G(4.0)	G(0.8)	G(0.8)	G(0.7)	G(0.7)

[a] G: gel, for gels, the critical gelation concentrations at room temperature were shown in parentheses; [b] Synth. Lub. indicated synthetic lubricant.

As can be seen from Table 3, it proves that the longer terminal alkoxyl chains, the better gelation properties again. Compound **2(10)** performs the best gelation ability among **1** and **2(n)**. At the same time, oil pollution usually happens in lake and sea [41]. So we also investigated the selective gelation ability of **2(8)** and **2(10)** with tested oil at CGC. The steps were the same with **2(5)** and **2(6)** except water replaced by marine water. The results showed that gels gelatinized by **2(8)** and **2(10)** can selectively gelatinize tested oil phase from the aqueous-oil biphasic mixture (Figure S5).

2.4.2 Phase selective gelation properties with cosolvent

The process of forming gels through heating-cooling process limits gel potential applications in practice, and the addition of a co-solvent to prepare gelator solution is a quite feasible method to cover the disadvantage [9]. Compound **2(10)** was inspiring us to explore selective gelation property at room temperature. From Table 1, 10 wt% **2(10)** solutions in toluene or THF were prepared and investigated their gelation properties in other organic liquid at room temperature.

In our previous work, we found that the gelation property of **2(6)** solution in toluene was disturbed about its temperature [30]. So in here, we prepared 10 wt% **2(10)** solution by ultrasonic wave without heating at room temperature in a sealed tube. The selective gelation properties of **2(10)** solution in toluene or THF were studied with aqueous-aniline biphasic mixtures as follows. Firstly, aqueous-aniline biphasic mixtures (0.1 g aniline and 1 g marine water) was put into a sealed tube and mixed by ultrasonic wave without heating about 1 min. Secondly, **2(10)** solution was dropped into the tube then shook it to make them intensive mixing. After 1 min, we found that 10 wt% **2(10)** solution in THF could selectively gelatinize aniline layer, while the same concentration solution in toluene gelatinized a part of aniline, and liquid aniline was easily found by visual observation (Figure S6). For that, we selected 10 wt% **2(10)** solution in THF to explore gelation property in further examinations at room temperature.

The selective phasic ability of 10% **2(10)** solution in THF was also studied with synthetic lubricant at room temperature. We prepared two different kinds of aqueous-oil mixtures (A and B). Mixture A contained 1g marine water and 0.1 g synthetic lubricant and B contained 1g marine water and 0.2g synthetic lubricant. Aqueous-oil mixtures A and B were mixed respectively by ultrasonic wave without heating at room temperature of about 1 min. Then, the solution of **2(10)** was added into A and B to make the weight concentration of **2(10)** decreased into 3% and 1% in organic components (Figure S7). The synthetic lubricant was gelatinized at 3 wt% about 10 seconds. The organic component of aqueous-oil mixtures was selectively gelatinized at a weight concentration of 1% overnight.

2.4.3 Phase selective gelation properties with homogeneous aqueous-organic mixtures

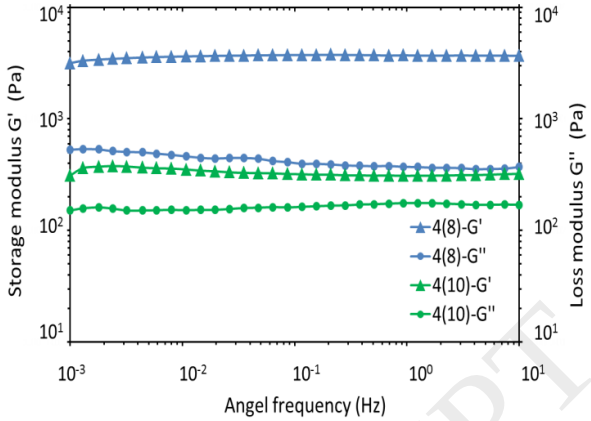
Formalin is widely used in the chemical industry as an important precursor for many chemical compounds and other materials, especially for polymers [42]. Formalin is toxic and allergenic, according to the US National Toxicology Program described formalin as "known to be a human carcinogen". Gelation ability of a10 wt% **2(10)** solution with formalin (40 wt%, containing 7-8 wt% CH_3OH) was investigated (Figure S8). Formaldehyde was selectively gelatinized out of formalin, and water in formalin was still liquid. The residues of formaldehyde in water after gelation was determined using Hantzsch reaction shown in Figure S9.

The test sample was prepared as follow: first, 0.2671 g formalin was weighed and added to a tube; second, 0.1109 g 10 wt% **2(10)** THF solution was added to the tube; third, in order to concentrate the residues of formaldehyde, 1.9978 g water was added; at last, the mixture was filtered to remove gel, and the filtrate was tested as a sample.

As shown in Figure S9, a linear calibration curve can be found between the absorbance changes at 412 nm and the concentration of formaldehyde in range of 0.5 to 2.5 μg/mL (R^2 = 0.99926). The residues of formaldehyde after gelation was measured to be about 0.4112 mol/L while the concentration of formaldehyde in formalin is about 14.4 mol/L.

2.5 Particular gelation properties of 2(10)

Gelation ability of **2(10)** was investigated with organic acids and some particular organic compounds. Acetic acid is one of the simplest carboxylic acids and is classified as a weak acid. At the same time, acetic acid has not only a distinctive sour taste and



pungent smell but also a corrosive effect. If acetic acid can be gelatinized, it maybe decreases its criticality. Compound **2(10)** showed effective gelation ability in acetic acid (Table 4). Caproic acid as a precursor for the synthesis of fine chemicals was investigated and even gelatinized at a general CGC value (2.0 wt%) [43].

Volatile organic compounds (VOCs) such as alkanes, arenes, phosphines, ketones, amines, carboxylic acids, esters, and aldehydes may have toxic effects on the human host after intestinal absorption and delivery to the liver via the portal vein [44]. Fatty acid esters as a kind of VOCs are widely used in food, textile, cosmetic, rubber and metal processing, synthetic lubricant industries, and so on [45]. From the results showed in Table 1, we know that **2(10)** gelatinize ethyl acetate at CGC of 5 wt%. Gelation test was carried out with dibutyl oxalate, methyl laurate or dibutyl adipate using **2(10)**, and the results were shown in Table 4.

Table 4. Gelation properties of **2(10)** (wt%) solution with VOCs at room temperature [a]

Solvents	Acetic acid	Caproic acid	Dibutyl oxalate	Methyl laurate	Dibutyl adipate
2(10)	G(0.4)	G(2.0)	G(2.0)	G(2.0)	G(2.0)

[a] G: gel, for gels, the critical gelation concentrations (CGC) at room temperature were shown in parentheses.

Some VOCs are not very stable when they are heated in air. For example, methacrylic acid may be polymerized, phenols and aldehydes are easily oxidized. **2(10)** Solution was dropped into VOCs until the weight concentration of **2(10)** declined from 10% into 3%. All of the tested VOCs were quickly gelatinized at room temperature (Table 5, Figure S10).

Table 5. Gelation properties of **2(10)** solution with some particular VOCs at room temperature [a],[b]

Solvents	MAA	C6:O	2LP	Guaiacol
2(10)/wt%	G(3.0)	G(3.0)	G(3.0)	G(3.0)
Solvents	HEXANAL	Decanal	BzH	
2(10)/wt%	G(3.0)	G(3.0)	G(3.0)	

[a] G: gel, for gels, the critical gelation concentrations (CGC) at room temperature were shown in parentheses; [b] C6:O, MAA, 2LP, HEXANAL, and BzH indicated *n*-caproic acid, methacrylic acid, 2-allylphenol, *n*-hexylaldehyde, and benzaldehyde.

2.6 Rheological property of gels

The supramolecular gel characterization is principally related to the rheological properties, even defined [46]. The rigidity and flow behaviors show in rheological measurement by storage modulus (G') and loss modulus (G") respectively. As a supramolecular gel, G' should behold the line with frequency up to a particular yield point and should be stronger than G".

Figure 5 Frequency sweep rheometry data for supramolecular gels were gelatinized by **2(8)** and **2(10)** at 1 wt% with PC at room temperature.

From Figure 5, we know that G' of gels formed by **2(8)** and **2(10)** are nearly a line, and the values of storage modulus and G" of gel formed by **2(8)** are larger than formed by **2(10)** respectively. The results mean that gels are showing rigidity and elastic characters and different gels formed by different gelators are showing different strength of the gel networks in the same solvents.

3. Conclusion

In summary, we have synthesized 4-semifluoroalkoxy- benzene derivatives **1** and **2(n)**, and demonstrated their liquid crystalline properties and gelation properties clearly related to the linking group and terminal alkyl group once more.

Moreover, the selective gelation ability of 10 wt% **2(10)** solution in THF is more powerful than that in toluene at room temperature. Compound **2(10)** solution in THF can selective gelatinize with synthetic lubricant from aqueous-oil biphasic mixture about 10 seconds at room temperature even **2(10)** at 3 wt% in the organic layer. Formalin as homogeneous aqueous-organic mixture also can be selectively gelatinized by 10 wt% **2(10)** solution.

4. Experimental

4.1 General materials and methods

4,4'-Biphenol was purchased from wako Industries, Ltd. reagent chemicals; 1-iodoperfluorohexane was purchased from Daikin Industries Ltd. reagent chemicals; 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Tokyo Chemical Industry Co., Ltd. reagent chemicals and recrystallized from cold ethanol. Rapeseed oil was purchased from Nisshin oillio group Ltd. Other reagents and solvents were obtained from general commercial sources. Synthetic lubricant and mineral oil were provided by Cosmo oil lubricants co. Ltd. and formalin was provided by Meiwa Plastic Industries Ltd. Marine water (ρ = 1.0198 g mL^{-1}, pH ≈ 8) which picked up from Tokiwa beaches in Yamaguchi prefecture of Japan was used.

Melting point was obtained with a Yanaco MP-J3 micro melting point apparatus. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer using KBr disc. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded with JMN-LA500 (500 MHz) spectrometer, where tetramethylsilane was used as an internal standard. High resolution mass spectra (HRMS) were recorded with a Waters LCT Premier™ XE. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). Scanning electron microscope (SEM) images were observed with a JEOL JSM-6510LA. X-ray diffraction (XRD) experiment was performed with a Rigaku-denki RINT 2000 diffractometer equipped with Rigaku PTC-20A thermo-controller. The rheological properties of a sample with high viscosity were measured using a Dynamic Viscoelasticity Measurement Apparatus (Reogel-G1000, UBM Co., Ltd.) equipped with cone and plate geometry of 40 mm diameter and 2° angle.

4.2 General procedure for preparation of 4-alkoxy-4'-hydroxybiphenyl

4,4'-Biphenol (1.86 g, 10 mmol) was dissolved in 3-pentanone (10 mL), potassium carbonate (2.07 g, 15 mmol) was added, and then 1-bromoalkane (10 mmol) was dropped into the reaction mixture. The reaction mixture was stirred at 80 °C for one day and separated by filtration. Filtrate was concentrated in *vacuo*, the residue was purified by silica gel column chromatography, and the eluent was recrystallized from CH_3OH to give a pure product, as a colorless crystalline solid.

Physical data of 4-butoxy-4'-hydroxybiphenyl

Yield = 35%, mp = 167-168 °C, IR (KBr, cm^{-1}) ν = 2956.8, 2933.7, 1506.4, 1286.2, 817.8. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.7-1.66 (m, 2H), 1.52-1.35 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.51, 132.63, 130.78, 127.22, 127.00, 115.65, 114.76, 67.14, 30.81, 18.79, 13.74 ppm.

Physical data of 4-octyloxy-4'-hydroxybiphenyl

Yield = 40%, mp = 152-153 °C, IR (KBr, cm^{-1}) ν = 2955.0, 2920.2, 1500.6, 1261.5, 814.0. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.44 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.79-1.60 (m, 2H), 1.40 (dd, *J* = 14.4, 6.8 Hz, 2H), 1.36-1.16 (m, 8H), 0.86 (t, *J* = 6.6 Hz, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.57, 156.52, 132.63, 130.79, 127.22, 127.00, 115.66, 114.76, 67.45, 31.30, 28.81, 28.73, 25.59, 22.14, 14.01 ppm.

Physical data of 4-decyloxy-4'-hydroxybiphenyl

Yield = 44%, mp = 145-147 °C, IR (KBr, cm^{-1}) ν = 2929.9, 2854.7, 1506.4, 1251.8, 817.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.38 (m, 4H), 7.03-6.73 (m, 4H), 4.73 (s, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.90-1.70 (m, 2H), 1.46 (m, 2H), 1.40-1.23 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.56, 156.51, 130.78, 127.21, 126.99, 115.65, 114.75, 67.44, 31.34, 29.06, 29.00, 28.82, 28.75, 25.56, 22.14, 14.00 ppm.

4.3 General procedure for preparation of 4-alkenyloxy-4'-alkoxybiphenyl

4-Alkoxy-4'-hydroxybiphenyl (10 mmol) was dissolved in 3-pentanone (10 mL), potassium carbonate (2.07 g, 15 mmol) was added, and then 1-bromoalkane (10 mmol) was dropped into the reaction mixture. The reaction mixture was stirred at 80 °C for one day and separated by filtration. Filtrate was concentrated in *vacuo*, the residue was refined by silica gel column chromatography, and the eluent was recrystallized from CH_3OH to give a pure product, as a colorless crystalline solid. Due to dissolve in *d*-substituted solvent, except 4-(but-3-enyloxy)-4'-decyloxybiphenyl, the ^{13}C NMR data are not described.

Physical data of 4-allyloxy-4'-butoxybiphenyl

Yield = 70%, mp = 146-147 °C, IR (KBr, cm^{-1}) ν = 2956.9, 2933.7, 2873.9, 1500.6, 1273.0, 1246.0, 825.5. ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.49-7.29 (m, 4H), 6.95-6.80 (m, 4H), 6.01 (ddt, *J* = 17.2, 10.5, 5.1 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.50 (t, *J* = 5.1 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 1.74-1.69 (m, 2H), 1.49-1.39 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm.

Physical data of 4-(but-3-enyloxy)-4'-butoxybiphenyl

Yield = 50%, mp = 133-135 °C, IR (KBr, cm^{-1}) ν = 2949.2, 2883.6, 2357.0, 1500.6, 1273.0, 1246.0, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.38 (m, 4H), 7.04-6.84 (m, 4H), 5.92 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 2.59-2.54 (m, 2H), 1.81-1,76 (m, 2H), 1.55-1.46 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm. ESI-TOF-MS: m/z calculated for $C_{20}H_{24}O_2$, $[M+H]^+$: 297.1855, found: 297.1853.

Physical data of 4-(but-3-enyloxy)-4'-octyloxybiphenyl

Yield = 46%, mp = 108-110 °C, IR (KBr, cm^{-1}) ν = 2933.7, 2922.2, 2864.3, 1500.6, 1176.6, 1043.5, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.34 (m, 4H), 7.04-6.87 (m, 4H), 5.93 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.57 (q, *J* = 6.7 Hz, 2H), 1.87-1.74 (m, 2H), 1.52-1.41 (m, 2H), 1.41-1.17 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm. ESI-TOF-MS: m/z calculated for $C_{24}H_{32}O_2$, $[M+H]^+$: 353.2481, found: 353.2481.

Physical data of 4-(but-3-enyloxy)-4'-decyloxybiphenyl

Yield = 45%, mp = 107-108 °C, IR (KBr, cm^{-1}) ν = 3437.2, 2955.0, 2931.8, 2850.8, 1820.8, 1510.3, 1275.0, 1246.0, 827.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.33 (m, 4H), 7.02-6.85 (m, 4H), 5.92 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.59-2.54 (m, 2H), 1.89-1.67 (m, 2H), 1.47 (dt, *J* = 15.2, 7.0 Hz, 3H), 1.41-1.13 (m, 13H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.40, 158.11, 134.61, 133.70, 133.38, 127.82, 127.80, 117.18, 114.95, 68.23, 67.43, 33.82, 29.74, 29.56, 29.47, 29.45, 26.21, 22.83, 14.27 ppm. ESI-TOF-MS: m/z calculated for $C_{26}H_{36}O_2$, $[M+H]^+$: 381.2793, found: 381.2793.

4.4 General procedure for preparation of compound 1 and 2(n)

4-Alkenyloxy-4'-alkoxybiphenyl (3 mmol), 1-iodoper- fluorohexane (1.35 g, 3 mmol), and AIBN (0.50 g, 3 mmol) were dissolved in THF and stirred at 70 °C under a nitrogen atmosphere for one day. The reaction was quenched with Na_2CO_3 (aq.), diluted with ethyl acetate and rinsed with water and then with brine. After the organic layer was dried using anhydrous magnesium sulphate, the solvent was evaporated in *vacuo*. The residue without any other refined was dissolved in THF (anhydrous) to the next step. The mixture with $LiAlH_4$ (1 *eq*.) stirred at room temperature for one day. The reaction quenched with NH_4Cl (aq.). The mixture was filtered and the filtrate was concentrated in *vacuo*. The residue was purified by silica gel column chromatography, and the eluent was recrystallized from CH_3OH to give a pure product, as a colorless solid. Due to significant multiple couplings, carbon atoms with fluorine atoms are not described.

Physical data of 1

Yield = 44%, mp = 95-96 °C, IR (KBr, cm^{-1}) ν = 2939.5, 2873.9, 1500.6, 1251.8, 1192.0, 1180.4, 1145.7, 1031.9, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.45 (m, 4H), 6.96-6,93 (m, 4H), 4.07 (t, *J* = 5.9 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 2.65-2.26 (m, 2H), 2.15-2.09 (m, 2H), 1.82-1.76 (m, 2H), 1.76-1.45 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.43, 157.70, 134.02, 133.16, 127.80, 127.73, 114.80, 114.73, 67.77, 66.39, 31.31, 27.93 (t, *J* = 22.3 Hz), 20.57, 19.21, 13.78 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.70 (t, *J* = 10.3 Hz), -114.30 (dd, *J* = 17.8, 12.0 Hz), -121.86, -122.81, -123.47, -125.63--126.54 (m) ppm. ESI-TOF-MS: m/z calculated for $C_{25}H_{23}F_{13}O_2$, $[M+HCOO]^-$: 647.1467, found: 647.1465.

Physical data of 2(4)

Yield = 37%, mp = 93-95 °C, IR (KBr, cm^{-1}) ν = 2937.6, 2875.9, 1500.6, 1275.0, 1190.1, 1180.5, 1041.6, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.30 (m, 4H), 6.9-6.82 (m, 4H), 3.95 (t, *J* = 5.9 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.15-2.05 (m, 2H), 1.85-1.68 (m, 6H), 1.51-1.25 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.13, 157.67, 133.51, 132.98, 127.51, 127.46, 114.53, 114.47, 67.50, 66.98, 31.06, 30.38 (t, *J* = 22.3 Hz), 28.43, 18.95, 17.00, 13.53 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.71 (tt, *J* = 10.0, 2.6 Hz), -114.38 (dd, *J* = 18.8, 14.1 Hz), -121.86, -122.81, -123.47, -125.53--126.84 (m) ppm. ESI-TOF-MS: m/z calculated for $C_{26}H_{25}F_{13}O_2$, $[M+HCOO]^-$: 661.1624, found: 661.1630.

Physical data of 2(5)[30]

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.37, 157.93, 133.77, 133.23, 127.76, 127.71, 114.78, 114.72, 68.07, 67.24, 30.63, 28.96 (t, *J* = 22.4 Hz), 28.68, 28.17, 22.42, 17.25, 13.95 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.72 (t, *J* = 10.3 Hz), -114.38 (ddt, *J* = 18.6, 14.9, 4.3 Hz), -121.87, -122.31--123.11 (m), -123.47 (d, *J* = 17.0 Hz), -126.08 (td, *J* = 14.3, 6.5 Hz) ppm.

Physical data of 2(6) [30]

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.37, 157.92, 133.76, 133.23, 127.76, 127.71, 114.78, 114.71, 68.08, 67.23, 31.55, 30.64 (t, *J* = 22.1 Hz), 29.23, 28.68, 25.69, 22.56, 17.27, 13.96 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.72 (t, *J* = 10.1 Hz), -114.38 (ddt, *J* = 18.5, 14.2, 4.7 Hz), -121.86 (d, *J* = 20.0 Hz), -122.82, -123.47 (d, *J* = 17.7 Hz), -126.08 (td, *J* = 14.8, 6.7 Hz) ppm.

Physical data of 2(8)

Yield = 35%, mp = 103-104 °C, IR (KBr, cm^{-1}) ν = 2958.8, 2875.9, 1500.6, 1275.0, 1190.1, 1178.5, 1041.6, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.31 (m, 4H), 6.95-6.71 (m, 4H), 3.95 (t, *J* = 5.8 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.15-2.05 (m, 2H), 1.91-1.62 (m, 6H), 1.45-1.33 (m, 2H), 1.33-1.14 (m, 8H), 0.82 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.37, 157.92, 133.76, 133.22, 127.76, 127.71, 114.77, 114.71, 68.08, 67.23, 31.78, 30.63 (t, *J* = 22.3 Hz), 29.33, 29.26, 29.21, 28.68, 26.02, 22.61, 17.25, 14.03 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.76 (t, *J* = 10.3 Hz), -114.44 (td, *J* = 14.0, 3.8 Hz), -121.05--122.38 (m), -122.88 (d, *J* = 19.9 Hz), -123.54 (t, *J* = 15.2 Hz), -126.13 (td, *J* = 14.8, 6.3 Hz) ppm. ESI-TOF-MS: m/z

calculated for $C_{30}H_{33}F_{13}O_2$, $[M+HCOO]^-$: 717.2250, found: 717.2269.

Physical data of 2(10)

Yield = 38%, mp = 105-106 °C, IR (KBr, cm^{-1}) ν = 2922.2, 2852.7, 1500.6, 1275.0, 1190.1, 1179.5, 1143.8, 825.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.36 (m, 4H), 7.03-6.83 (m, 4H), 4.03 (t, *J* = 5.8 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.23-2.13 (m, 2H), 1.98-1.71 (m, 6H), 1.51-1.41 (m, 2H), 1.41-1.20 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.37, 157.91, 133.76, 133.22, 127.76, 127.71, 114.77, 114.71, 68.08, 67.23, 31.86, 30.63 (t, *J* = 22.5 Hz), 29.54, 29.52, 29.37, 29.28, 28.68, 26.01, 22.63, 17.25, 14.05 ppm. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.76 (t, *J* = 10.3 Hz), -114.44 (td, *J* = 14.0, 3.8 Hz), -121.05--122.38 (m), -122.88 (d, *J* = 19.9 Hz), -123.54 (t, *J* = 15.2 Hz), -126.13 (td, *J* = 14.8, 6.3 Hz) ppm. ESI-TOF-MS: m/z calculated for $C_{32}H_{37}F_{13}O_2$, $[M+NH_4]^+$: 718.2930, found: 718.2924.

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