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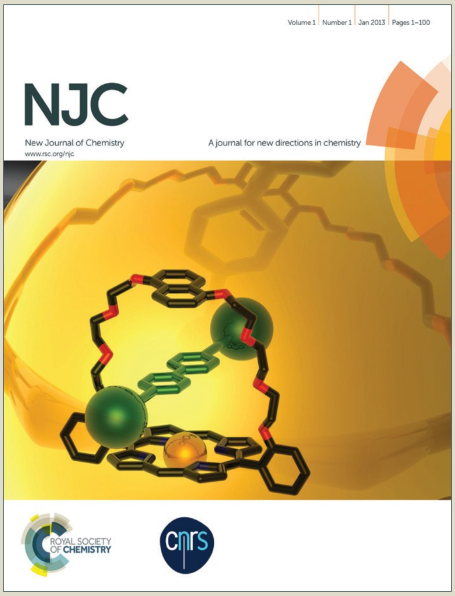

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4-Perfluoroalkylbutoxybenzene derivatives as liquid crystalline organogelators based on phase-selective gelators

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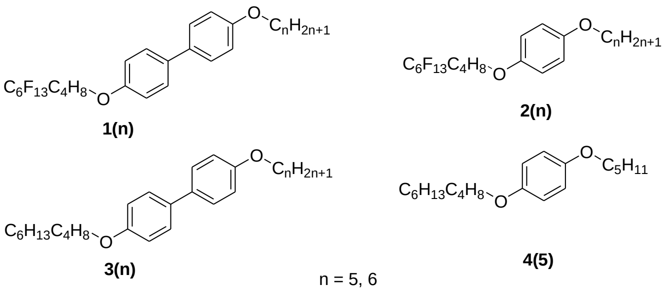
4-Perfluoroalkylbutoxybenzene derivatives 1(n) have been prepared as a new class of thermotropic liquid crystalline organogelators incorporating a perfluoroalkyl group without hydrogen bonding group. Significantly, compounds 1(n) at room temperature as efficient and rapid phase-selective gelators is a kind of method for water purification.

Organogels formed by low molecular weight organogelators (LMWOGs) have attracted amount of interest and are widely used in industry and pharmacy.[1] Research about LMWOGs can be divided into two parts. The first part is that the relationship between molecular structure and gelation property,[2] the second is enlarging LMWOGs' potential applications with novel properties,[3] such as exhibiting liquid crystalline property named liquid crystalline (LC) organogelators, showing phase selective gelation property named phase-selective gelators (PSGs).

PSGs were firstly reported by Bhattacharya and Krishnan-Ghosh.[3] Since then PSGs has become a hot topic because PSGs may be applied in water purification, crude oil and other chemical oil spills recovery.[4] Most of PSGs gelate mainly by hydrogen bonds which have been reported in recently years. The main disadvantages for application in water purification and oil spill recovery is that CH, OH, and NH hydrogen donors usually coordinate to water molecules in many different combinations leading to unstable organogels.[5]

In this context, our intention here is to employ a 4-perfluoroalkylbutoxybenzene fragment as a terminal group to synthesize novel multifunctional materials having not only LC organogelators but also PSGs properties without hydrogen bond. It is to be noted that the modifications of a subtle but significant fluoro substituent are usually discovered in relation to melting point, transitions temperatures, mesophase morphology, and many essential physical properties of soft materials, such as optical, dielectric amphiphilicity and visco-elastic properties.[6] Herein we reported the design and synthesis of 4-perfluoroalkylbutoxybenzene derivatives by combining our past experience in LC and gels.[7] Compounds **1(n)**-**4(5)** are from 4,4'-biphenol or 4-alkoxyphenol with Williamson ether synthesis, free-radical addition and reduction reaction by $LiAlH_4$ (Scheme 1 and Scheme S1).



Scheme 1. Chemical structures of compounds **1(n)**-**4(5)**.

To analyse the influence of core systems and terminal group of perfluoroalkyl group on LC and gels efficiency, compounds **1(n)**-**4(5)**, for comparison, were also synthesized and tested their LC and gelation properties.

Following the general research process about LC organogelators, mesomorphic properties were achieved by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Characteristic textures and defect structures, which change when passing a phase transition, reveal the phase type observed by POM.[8] Compound **2(6)** is in the liquid state at room temperature and compounds **3(5)** and **4(5)** do not show any mesophase on cooling process by POM. Compounds **1(5)** and **1(6)** show similar textures of mesophases (Figure 1 and Figure S1). The phase transition temperatures and thermodynamic data of compounds **1(5)**, **1(6)** and **3(6)** are collected in Figure S2 and Table S1.

On cooling process of compound **1(5)**, a typical focal conic fan texture was observed at 163 °C under homogeneous alignments (Figure 1-A), and then the texture changed to a

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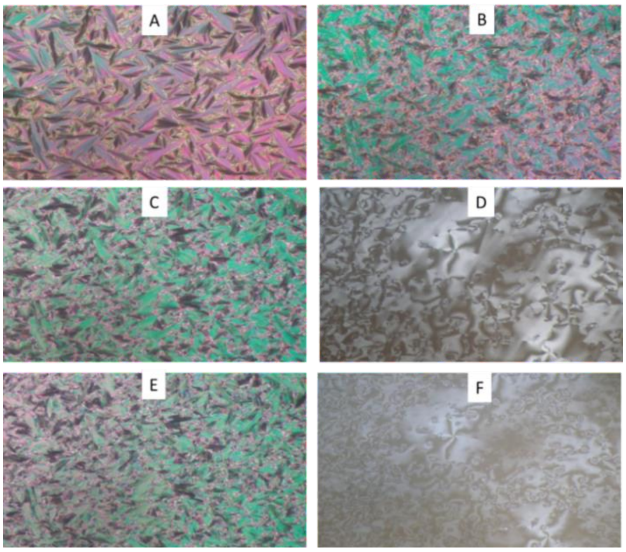

Figure 1. Polarized photomicrographs of compound **1(5)** on cooling process at: A 120 °C, B 110 °C, C & D 100 °C, E & F 90 °C.

broken-fan texture at 112 °C (Figure 1-B). Both mesophases have an orthogonal characteristic. These results suggest that compound **1(5)** shows two kinds of smectic A phases (SmA) which was named SmA(2) and SmA(1), respectively. The enthalpy change of SmA(1)-SmA(2) also supports the assignment of the SmA.[9] At 100 °C, a schlieren texture was observed under homeotropic alignment (Figure 1-D), suggesting the mesophase is assigned to be smectic C phase (SmC). The enthalpy change is agreed to the assingnment of SmC-SmA.[10] However, the lower tilted phase was unidentified. The similar results of compound **1(6)** showed in table S1 and compound **3(6)** only shows SmA with a narrow range of temperature from 106 °C to 108 °C.

To clarify a relationship between molecular structure and the gelation ability, the gelation ability of compounds **1(n)**-**4(5)** as LMWOGs in various organic solvents (polar and non-polar) and H_2O were investigated in a heating-cooling cycle by the“stable to inversion in a test tube” method.[11] Compounds **1(5)** and **1(6)** as LMWOGs can gelate solvents like cyclohexane, octane, 1-octanol, DMF and butyrolactone. Compounds **1(5)** and **1(6)** tend to precipitate in petroleum ether, acetonitrile, acetone, methanol and ethanol, while dissolve in ethyl acetate, 3-pentanone, chloroform, 1,2-dichloromethane, toluene and tetrahydrofuran, and insoluble in H_2O. Unfortunately, except compounds **1(n)**, others such as **2(n)**, **3(n)** and **4(5)** can’t form gel in test organic solvents (Table S2). Although chemical structures of compound **1(5)** and **1(6)** are similar, gelation ability are different from each other. In DMSO and propylene carbonate (PC), compound **1(5)** can respectively form gels even critical gel concentrations (CGCs) at 2.0 wt% and 1.0 wt%, and meanwhile compound **1(6)** can’t gelate at 5.0 wt% in DMSO and PC.

To gain visual insights into the aggregation mode, we selected the gel which was formed by compound **1(5)** in PC system as a sample to study by scanning electron microscope

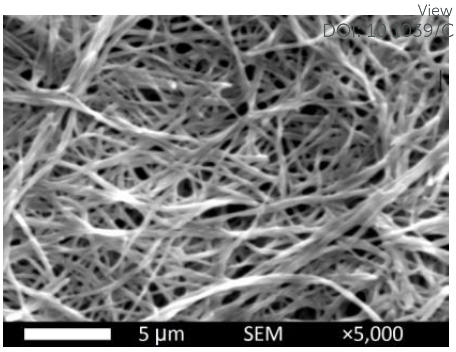

Figure 2. SEM image of in PC xerogel system formed by compound **1(5)** (scale bar = 5 μm)

(SEM) (Figure 2). The SEM image showed that three-dimensional (3D) nanofiber networks are formed by self-assembly of compound **1(5)** molecules.

The essential driving force for gelation of compounds **1(n)** was also studied by IR and ^{1}H NMR. Infrared spectra of the xerogels of compounds **1(n)** in cyclohexane and pure compounds **1(n)** were carried out and showed in Figure S3. Pure compounds and xerogels present the same Infrared spectra images. At the same time, from ^{1}H NMR spectra of compound **1(5)** in *d*-DMSO at different temperatures and concentrations in Figure S4, we thought that hydrogen bonds do not play any significant role in gel self-assembly. As reported in the past, the presence of long alkyl chains and rigid rodlike aromatic segments has been considered to be essential for the stable LMOG assemblies.[12] In compounds **1(n)**-**4(5)**, only compounds **1(n)** showed gelation ability means that the gelation by compounds **1(n)** with 4-perfluoroalkylbutoxy-benzene derivatives results primarily from not only the formation of π-π stacking interactions, but also the weaker intermolecular interaction between perfluoroalkyl chains.[13]

Gelation ability of compounds **1(n)** at concentration changing from 5 to 1 wt% in amines and oils was also tested (Table S3, Figure S5 and Figure S6). Compounds **1(5)** and **1(6)** could rapidly gelate primary amines (e.g. aniline, benzylamine, β-phenylethlamine). The time of secondary amine (e.g. piperidine) forming gel at 1 wt% were longer than those of primary amines’s in heating-cooling cycle at room temperature. Hexamethylphosphoric triamide (HMPA) could be gelated only by compound **1(6)** at 5 wt% while N-ethyldiisopropy amine only by compound **1(5)** at the same concentration. In the gelation test of oil, we chose synthetic lubricant, mineral oil, lamp oil, polyolefin and rape oil to study gelation ability of **1(5)** and **1(6)**. Except lamp oil at 5 wt%, compounds **1(5)** and **1(6)** gelated others at 1 wt%.

Amines as an important organic base are widely used in industry and may spill into nature and pollute our rivers and ocean.[14] Meanwhile almost every year, accidents of oil spills happen in oceans and rivers.[15] Removal pollutants from water is arduously but obligatorily needed. Though approaches (e.g. adsorbents, chemical dispersants) which remove pollutants out of environment have been researched, those approaches have some limitations in practice.[16] PSGs that can selectively

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solidify organic layer from a biphasic mixture of water and organic layer are studied to offer a potential and effective solution to this pollution problem. Generally PSGs with CGCs at 5 wt% show phase-selective property.[17] In the meantime compound **1(5)** and **1(6)** are showing efficient gelation ability even at 1 wt% to encourage us to analyze their phase-selective property. We dropped water (1 mL) into each test tube containing gel formed by compounds **1(5)** and **1(6)** in amines at CGCs. The mixture were heated and shaken sharply to ensure homogeneous dispersion of amine in water. After cooling the mixture to room temperature, compound **1(5)** could selectively gelate the aniline, benzylamine and β-phenylethlamine in aqueous-amine biphasic systems (Figure S7). The gels formed by compound **1(6)** in benzylamine, β-phenylethlamine and HMPA were destroyed, but that in aniline gelated again.

The ability of phase selectively gelation in aqueous-oil biphasic systems was also tested. Because oil spills often happen in ocean and pH of seawater is about 8.0, we replaced water with 1 mL of saturated solution in which NaCl was added into a saturated solution of $NaHCO_3$ until NaCl was undissolved. Similar test like the test in aqueous-amine biphasic systems was carried out. All of those gels formed by compounds **1(n)** at CGCs in synthetic lubricant, mineral oil, lamp oil, polyolefin and rape oil selectively solidified in the aqueous-oil biphasic systems after heating-cooling cycle process (Figure S8). We adjusted the aqueous from basic to acidic by 0.5 mL of 1M HCl(aq.) and found that compound **1(n)** still can selectively solidify oil layer (Figure 3).

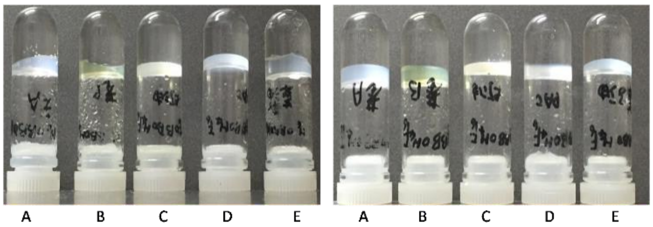

Figure 3. Photograph of gel formed at acidic solution using compound **1(5)** (left) and **1(6)** (right) as gelators. A: synthetic lubricant, B: mineral oil, C: lamp oil, D: polyolefin, E: rape oil.

Compounds **1(n)** perform excellent selective gelation ability even with CGCs at 1% in the aqueous-aniline and aqueous-oil biphasic systems by heating-cooling process that was inspiring us to research their selective gelation ability at room temperature. We prepared solution of 10 wt% of compound **1(5)** in toluene by heating. The warm toluene solution was dropped into aqueous-aniline biphasic mixture until weight percentage of compound **1(5)** in organic layer decreasing to 5 wt%. Then the mixture was shaken sharply to make sure that aniline can mix with the solution. To our surprise, the solution of compound **1(5)** can fast selectively solidify aniline from a biphasic mixture. Compound **1(6)** present the same result as compound **1(5)** (Figure S9).

Biphasic systems (aqueous/synthetic lubricant = 4:1) were also researched with the same process. The organic layer was quickly and selectively gelated in 1 min. Unfortunately there was a sharp slowdown in gelation speed when the toluene solution of compound **1(5)** was at room temperature. We proposed that the warm toluene solution of 10 wt% of compound **1(5)** was dropped into the biphasic systems. It seems that rapid-cooling process makes 3D nanofiber networks quickly formed.[18] We replaced compound **1(5)** with compound **1(6)** and found the same result as compound **1(5)**. All of gels formed by dropping toluene solutions could keep gel states for at least three months.

Compound **1(5)** successfully gelated in toluene overnight storage at 10 wt%, but it failed to gelate at 5 wt%. The morphology of xerogel gelated by compound **1(5)** at 10 wt% was investigated by SEM. There were many 3D nanofiber networks (Figure 4-A), at the same time, clusters (Figure 4-B) and zero-dimensional (0D) nano dots (Figure 4-C) also were found in the same sample at different place. We proposed that the stability of gel gelated by compound **1(5)** at 10 wt% is not very good.

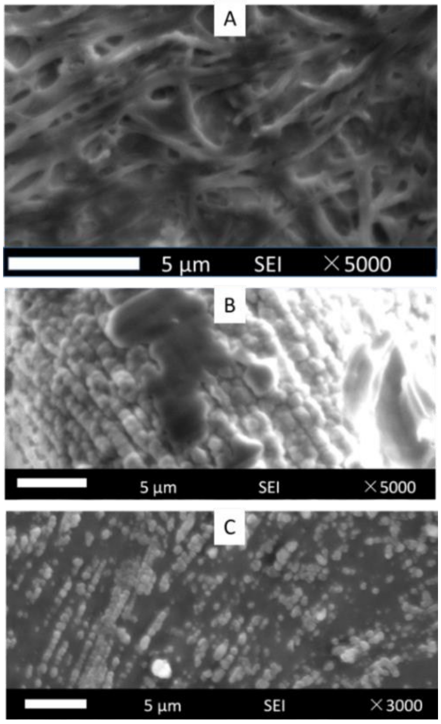

Figure 4. SEM image of compound **1(5)** in toluene (10 wt%)

In summary, to our best knowledge, a new liquid crystalline organogelator by low molecular weight organogelators based on 4-perfluoroalkylbutoxybenzene derivatives without hydrogen bond have been synthesized for the first time. The gelation ability of compound **1(n)** owes to π-π stacking interactions and the weaker intermolecular interaction around the perfluoroalkyl chains. Interestingly and importantly, the gelators can selectively gelate organic layer not only in aqueous-amine but also in aqueous-oil system, especially efficient and rapid by toluene solution of compound **1(n)** in biphasic systems at room temperature. In aqueous-oil system, compound **1(n)** can show phase-selective property at extremes of pH. 4-Perfluoroalkylbutoxybenzene derivatives as liquid crystalline physical gels could expand application field to environment recovery.

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4-Perfluoroalkylbutoxybenzene derivatives as a smart soft material show efficient and rapid phase-selective gelation ability from water at extremes of pH.