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PAPER

Acid-responsive organogel mediated by arene–perfluoroarene and hydrogen bonding interactions†

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A phenyl and a 2,3,5,6-tetrafluorophenyl ring, each bearing a tris(*n*-dodecyloxy)benzylamine moiety *via* an amide bond, were tethered together through an imine linkage to give a non-covalent synthon (imine **1**) with a strong capacity of supramolecular self-assembly. Gelation was observed in several organic solutions, within which fibrous aggregate morphologies were visualized by SEM and AFM. Both arene–perfluoroarene stacking and amide–amide hydrogen bonding interactions were responsible for such self-assembly behaviours, as evidenced by ^{1}H NMR studies. Hydrolysis of the imine linkage catalyzed by acid strongly weakened the intermolecular interactions, resulting in dissociation of the low molecular weight gelator and giving rise to an acid-mediated gel–sol transition.

Introduction

The development of low molecular weight gelators (LMWGs) has been attracting great interest in the past 10 years.[1–15] As an example of "soft matter", an organogel based on molecular assembly exhibits numerous appealing properties: well-defined nanoscale one-dimensional molecular alignment, ease of fabrication, thermo-reversibility, and external physical/chemical stimuli-responsive ability, *etc.* These features promise organogels with various potential applications in areas such as drug delivery,[1,2] sensors,[3–12] light-harvesting systems,[13] electronic devices,[14,15] molecular logic gates,[16] and templates.[17] Gelation of small molecules is speculated to rely on the chemical and/or physical cross-linking of supramolecular polymer chains into three-dimensional networks, which can immobilize solvent molecules.[18] Normally, their aggregation into fibrous superstructures is driven by multiple weak noncovalent interactions, such as hydrogen bonding, van der Waals, electrostatic and solvophobic interactions. Although various LMWGs have been reported to date, to our best knowledge, no previous examples have been reported where arene–perfluoroarene interactions were incorporated for organogelator design.

Arene–perfluoroarene interaction has been extensively studied, since Patrick and Prosser first reported a 1 : 1 mixture of benzene (m.p. = 5 °C) and hexafluorobenzene (m.p. = 5 °C) gave rise to a co-crystal with a much higher melting point (m.p. = 25 °C) than either of the components.[19] In contrast to the edge-to-face molecular packing fashion adopted by pure benzene or hexafluorobenzene in the solid state, an alternating face-to-face stacking arrangement was observed for these two molecules in their co-crystals.[20] The face-to-face stacking motif is stabilized by both electrostatic[21] and van der Waals interactions between the two different phenyl rings. Specifically, the former is a quadrupolar interaction, which originated from opposite charge distributions in the aromatic planar structure of benzene and hexafluorobenzene.[20] A similar alternating stacking motif has also been observed for complexes of aromatic and perfluorinated aromatic compounds.[22–33] Because of this interesting molecular stacking fashion, extensive attention has been paid to the application of arene–perfluoroarene interactions in the field of crystal engineering in past decades to generate unique crystal structures,[22–26] for instance, with molecular arrangements feasible for topochemical reactions (*e.g.* butadiyne polymerizations,[27] olefin photodimerization and 1,3-diene photopolymerization,[28] 1,3-dipolar cycloaddition between azides and alkynes,[29] *etc.*). It has also been used to achieve specific liquid crystalline (LC) behaviours of materials.[30–33] However, when stepping beyond the field of crystal engineering, for instance, in a solution self-assembly system, examples that harness this interaction to construct superstructures are relatively rare, and only a few precedents of bio-related molecules are reported.[34,35] One possible reason for why this interaction is rarely used to modulate molecular assembly in the solution state is that its strength is relatively low, which is usually not enough to outweigh the counteracting entropic effect caused by solvation.[36] In the limiting examples where arene–perfluoroarene interactions were still effective in dilute solutions, aromatic and perfluorinated aromatic moieties were prearranged carefully into peptides[34] and oligonucleotides,[35] with the assistance of backbone hydrogen bonding and/or dipole–dipole interactions, the

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† Electronic supplementary information (ESI) available: Corey–Pauling–Koltun (CPK) modeling of imine **1**; pictures of the gel in testing organic solvents; ^{1}H NMR monitoring the result of the hydrolysis reaction; SEM images of the 1 : 1 mixture of **3** and **4**; and NMR spectra of new compounds. See DOI: 10.1039/c2sm07281e

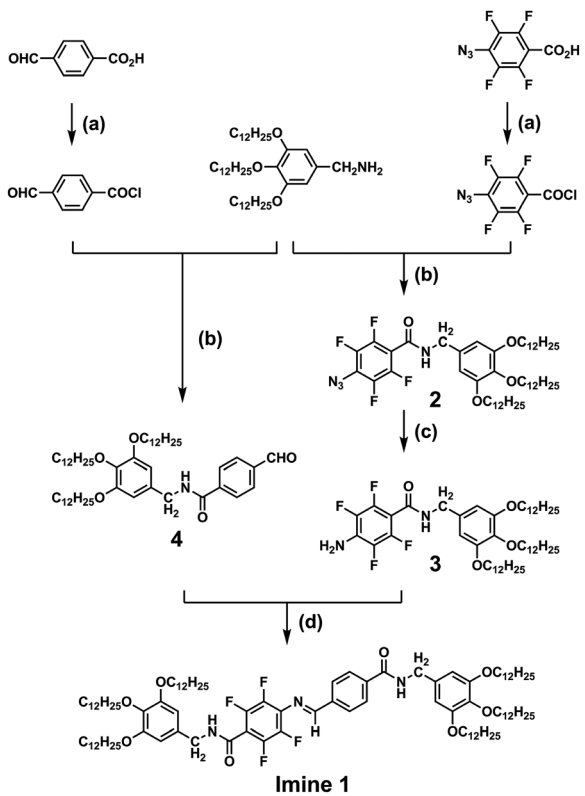
arene–perfluoroarene interaction was able to modulate the stability and the arrangement of these biologically important structures.

We are particularly interested in introducing arene–perfluoroarene interactions into solution self-assembly systems. To this end, we attached a tris(*n*-dodecyloxy)benzylamine segment, which is a promising gel-formation unit, to both ends of a Schiff base consisting of phenyl and 2,3,5,6-tetrafluorophenyl rings, through an amide group. Previously, we have shown that molecules containing a similar Schiff base structure would pack into columns where phenylene–tetrafluorophenylene alternating face-to-face stacking was observed in the crystalline state.[29] The amide group is used here to further stabilize the face-to-face packing of the Schiff base structure in solution by hydrogen bonding,[24] while the tetrafluorinated aniline based imine is highly acid sensitive. Herein, we present self-assembly behaviours of this carefully designed molecule, named imine **1**, as well as its gelation behaviours and gel–sol transition under catalytic amounts of acid.

Results and discussion

Synthesis

The synthesis of imine **1** is shown in Scheme 1. The preparation of 3,4,5-tridodecyloxybenzylamine[37] and 4-azidotetrafluorobenzoic acid[38] were according to literature procedures. A condensation reaction between amine **3** and aldehyde **4** was accomplished by refluxing the reactants in toluene with *p*-$MeC_6H_4SO_3H$ as the catalyst to give imine **1** as a glassy solid with a yield of 30%.



Scheme 1 Synthesis of imine **1**. (a) $(COCl)_2$, CH_2Cl_2, r. t., 24 h. (b) Et_3N, CH_2Cl_2, 0 °C, 20 min. (c) $SnCl_2{\cdot}2H_2O$, CH_2Cl_2/MeOH (1 : 1, v : v), r. t., overnight. (d) *p*-$MeC_6H_4SO_3H$, toluene, reflux, overnight.

Self-association of imine 1 in solution

The ^1H NMR spectroscopy not only helped confirm the molecular structure, but also provided insight into the molecular self-assembly in solution. A set of ^1H NMR spectra of imine **1** in $CDCl_3$ was collected at varied concentrations, ranging from 2.0×10^{-3} mol L^{-1} to 2.7×10^{-2} mol L^{-1} (Fig. 1). The concentration-dependence of the chemical shift revealed that this molecule underwent self-association in solution. Specifically, the increase of concentration caused an upfield shift for nuclei resonances of the aromatic and imine protons (in the range of 7.7 to 8.6 ppm), suggesting face-to-face stacking occurred between the Schiff base structures.[39] Meanwhile, a downfield shift was observed for the resonance of amide NH protons (with chemical shifts of 6.2–6.9 ppm), serving as evidence for intermolecular hydrogen bonding interactions between amide groups. Overall, these data suggested that both the arene–perfluoroarene stacking among the Schiff base moieties and the hydrogen bonding interaction among amide groups were both contributing to the self-assembly of imine **1** in solution.

Subsequently, the gelation capability of imine **1** was investigated. This molecule was speculated to be an organogelator as it has structural features very favourable for gelation: (a) arene–perfluoroarene interaction is capable of inducing infinite supramolecular polymerization, (b) 3,4,5-tris(*n*-dodecyloxy) benzylamine units can further stabilize the fibrous aggregates by amide–amide hydrogen bonding and enable the formation of three-dimensional networks *via* van de Waals interaction between the long dodecyloxy sidechains. As expected, thixotropic gels were observed at room temperature in a variety of organic solutions of imine **1**, including *n*-alkanes, ethyl acetate, 1,4-dioxane, and some combinations of solvents such as ethyl acetate–*n*-alkanes and 1,4-dioxane–*n*-alkanes. Gelation properties and respective minimum gelation concentrations are summarized in Table 1. It was noted that in aromatic solvents, such as toluene and benzene, gelation process were not observed. Given that hydrogen bonding interaction should not be severely affected by these aromatic solvents, we reasonably suggested that

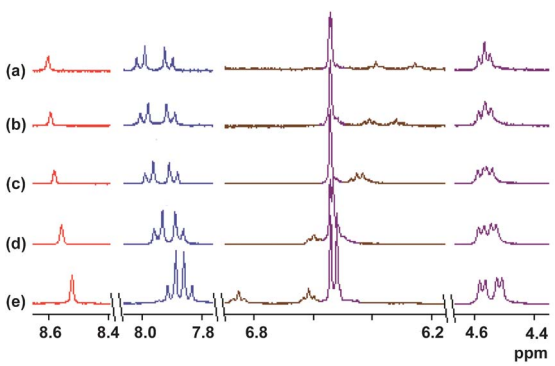


Fig. 1 ^1H NMR spectra of imine **1** in $CDCl_3$ at (a) 2.0×10^{-3} mol L^{-1}; (b) 3.2×10^{-3} mol L^{-1}; (c) 5.9×10^{-3} mol L^{-1}; (d) 1.4×10^{-2} mol L^{-1}; (e) 2.7×10^{-2} mol L^{-1}.

Table 1 Results of gelation tests in different organic solvents

Solvent	Imine **1**	**3** and **4** (1 : 1[e])
n-Dodecane	TG[a](1.8[b])	S
n-Hexane	TG(0.6)	S
Ethyl acetate–*n*-hexane (1 : 3, v : v)	TG(1.3)	S
1,4-Dioxane–*n*-dodecane (1 : 3, v : v)	OG[c](3.7)	S
1,4-Dioxane	OG(5.5)	S
Ethyl acetate	OG(2.5)	S
Benzene	S[d]	S
Toluene	S	S

[a] Transparent gel. [b] Minimum gelation concentration (mmol L^{-1}). [c] Opaque gel. [d] Solution. [e] Molar ratio.

the disruption of arene–perfluoroarene stacking interaction, mainly by the competing aromatic interaction from solvent molecules, was most likely to be the reason for the failure of gelation.

The viscoelastic nature of a gel can be characterized by rheological measurements if the storage modulus G' exceeds the loss modulus G'' and if there is no dependence of G' on the oscillatory frequency.[40,41] To assess the viscoelasticity of the gel rheologically, a gel of imine **1** was prepared at a concentration of 8.2×10^{-3} mol L^{-1} in 1,4-dioxane–*n*-dodecane (1 : 3, v : v) on a parallel plate (diameter = 25 mm) and was stood at 20 °C for 24 h before being subjected to testing. The rheological results, including dynamic strain sweep (DSS), dynamic frequency sweep (DFS), and dynamic time sweep (DTS) patterns, are shown in Fig. 2. DSS was performed at a frequency of 6 rad s^{-1} as a function of strain, ranging from 0.01 to 100%, to examine the linear viscoelastic strain regime. Both moduli, G' and G'', remained roughly constant below 0.2% strain, implying the upper limit of the linear regime corresponds to a critical strain value of 0.2%. G'' was observed to increase when subjected to a higher strain, indicating local rearrangements taking place in the gel.[42,43] Mechanically-induced fracture resulted when the gel was subjected to a strain above 0.6%, which was evidenced by a decrease in the absolute values of both G' and G''. The gel was then subjected to a nondestructive DFS experiment performed at a constant strain of 0.1% to obtain the linear viscoelastic frequency regime. Data collected with frequencies ranging from 100 to 0.5 rad s^{-1} showed that G' was constantly greater than respective G'', suggesting that the gel was viscoelastic in the testing frequency range. Based on the DSS and DFS results, a constant strain of 0.1% and frequency of 6 rad s^{-1} were chosen as the linear viscoelastic conditions for DTS test, which were carried out as a function of time. Within the investigated regime, storage moduli G' ($\sim 10^5$ Pa) were found to be an order of magnitude larger than respective loss moduli G'' ($\sim 10^4$ Pa), and both G' and G'' remained constant over 3000 s, implying that the gel was quite rigid and stable.

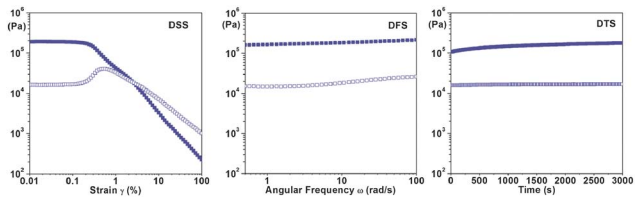


Fig. 2 DSS, DFS and DTS plots of imine **1** tested on a 8.2×10^{-3} mol L^{-1} gel in 1,4-dioxane–*n*-dodecane (1 : 3, v : v) at 20 °C. Storage modulus G': ■; loss modulus G'': □. DSS was tested at $\omega = 6$ rad s^{-1}; DFS was tested at strain = 0.1%; DTS was tested at $\omega = 6$ rad s^{-1} and strain = 0.1%.

The morphology of the gel was examined by scanning electron microscopy (SEM). Fig. 3 shows the representative SEM image of the xerogel obtained after solvent evaporation. As expected, a three-dimensional network with an extended fibrous structure was observed. The width of individual fibers ranged from 40 nm to 200 nm, suggesting that the individual fibers were likely to be composed of bundles of stacking arrays of imine molecules.

Additionally, aggregates of imine **1** were visualized by atomic force microscopy (AFM) in tapping mode (Fig. 4). A dilute solution of imine **1** in *n*-hexane (1.4×10^{-5} mol L^{-1}) was drop-cast on to a fresh mica substrate and allowed to dry in air before imaging. The observed fibrous structures indicate aggregation of **1** occurred upon solvent evaporation. The average height of the fibers measured from the AFM images was 3.5 ± 0.2 nm, which was in accordance with the extended molecular width estimated by the CPK model (Fig. S1†). Morphologies observed by SEM and AFM revealed that imine **1** underwent anisotropic aggregation in solution, as a result of both face-to-face arene–perfluoroarene interaction and hydrogen bonding interaction.

Self-association behaviors of a 1 : 1 mixture of 3 and 4 in solution

Note that in the molecular design, we purposely fused the phenyl ring to the 2,3,5,6-tetrafluorophenyl ring *via* an imine linkage to facilitate the alternating face-to-face molecular stacking of imine **1**. In order to justify that covalently fusing these two moieties into one molecule is indispensible for molecular self-assembly to occur, we investigated the self-assembly behaviors of a mixture of imine **1**'s synthetic precursors, compounds **3** and **4**, in solution. A set of ^{1}H NMR spectra of a mixture of compounds **3** and **4** at a molar ratio of 1 : 1 was collected in $CDCl_3$ within a similar concentration range as Fig. 1. In contrast to the concentration-dependent ^{1}H NMR spectra of imine **1**, no evident chemical shift changes of the aromatic resonances were detected in this mixture system upon concentration variation (Fig. 5), indicating the absence of face-to-face aromatic stacking interactions between **3** and **4** in solution. Moreover, upon increasing the concentration,

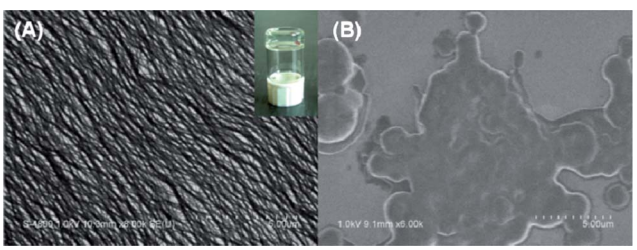


Fig. 3 (A) SEM image of a xerogel of imine **1** from ethyl acetate–*n*-hexane (1 : 3, v : v) with a concentration of 8.2×10^{-3} mol L^{-1}. Insert: photo of the gel. (B) SEM image of the gel sample made from ethyl acetate–*n*-hexane (1 : 3, v : v, 8.2×10^{-3} mol L^{-1}) after undergoing gel–sol transition triggered by adding a catalytic amount of acidic stimuli (*p*-$MeC_6H_4SO_3H$).

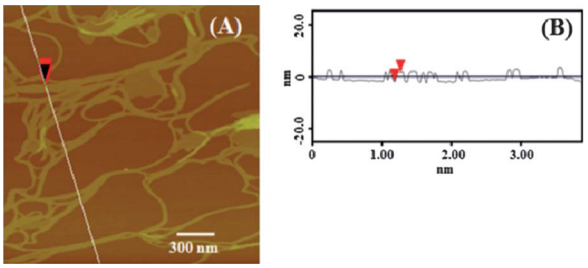


Fig. 4 (A) AFM image of a film cast from *n*-hexane solution of imine **1** (1.4×10^{-5} mol L^{-1}) on mica substrate. (B) The cross section analysis of the white line in (A).

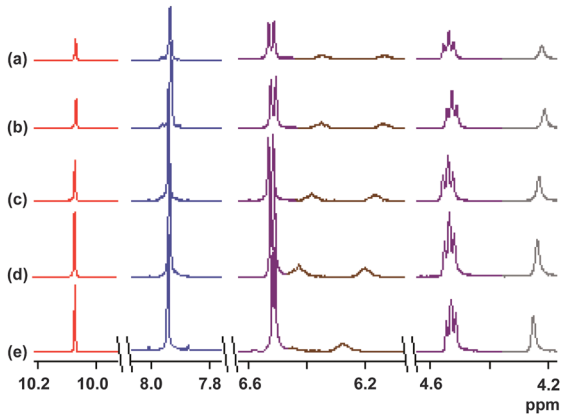


Fig. 5 ^{1}H NMR spectra of a 1 : 1 mixture of **3** and **4** in $CDCl_3$ at (a) 1.4×10^{-3} mol L^{-1}; (b) 2.8×10^{-3} mol L^{-1}; (c) 5.8×10^{-3} mol L^{-1}; (d) 1.4×10^{-2} mol L^{-1}; (e) 2.7×10^{-2} mol L^{-1}.

the downfield shift of the amide NH protons in **3** and **4** was smaller in magnitude, compared to that observed for imine **1**. These results suggested that intermolecular association was greatly weakened when the covalent linkage between the phenyl and tetrafluorophenyl moieties is broken.

The gelation capacity of the mixture of **3** and **4** in organic solvents, shown in Table 1, was also examined. Test solutions of compounds **3** and **4** mixed at a molar ratio of 1 : 1 were prepared at various concentrations, followed by standing at room temperature for a couple of hours to see if gelation occured. However, gelation was not observed, even in solutions with nearly saturated concentrations (~40 mM). These solutions were then subjected to SEM imaging (Fig. S9†), showing that no fibrous aggregate was formed in any case. All these results provided clear evidence that self-assembly capacity of imine **1** was different from that of the 1 : 1 mixture of its synthetic precursors, **3** and **4** (Table 1). Thus, the covalent imine linkage between the phenyl and tetrafluorophenyl moieties employed in our molecular design, indeed, played an essential role in facilitating intermolecular interactions as well as molecular self-assembly.

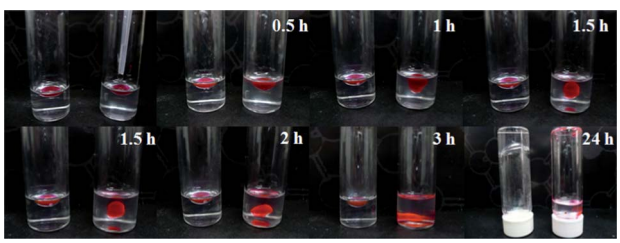


Fig. 6 Gel–sol transition of a gel of **1** in ethyl acetate–*n*-hexane (colorless portion) triggered by adding a drop of HCl (10%) to the colored aqueous droplet on the top of the gel (Rhodamine B was used as dye). Different time intervals after adding the drop of acid are indicated in the photos.

Acid-responsive gels

Acid-catalyzed hydrolysis of imine is known to be a highly efficient reaction. Provided that a rather distinct gelation capability was observed between imine **1** and its precursors, inducing a gel–sol transition process by adding acid to the gel may be achievable with the current system. It is very attractive to explore acid-responsive low molecular weight organogels. To the best of our knowledge, no precedent of such an example has been reported.

Hydrolysis reaction of imine **1** with *p*-$MeC_6H_4SO_3H$ as a catalyst was monitored by ^{1}H NMR. The majority of the reactant was decomposed into its two precursors within 30 min (see Supporting Information†), suggesting cleavage of the imine linkage under acidic conditions was facile and effective. The sensitivity of the gels formed by imine **1** towards acid was observed in subsequent study. When a catalytic amount of *p*-$MeC_6H_4SO_3H$ was added onto the top of a gel, gel–sol transition occurred within less than one hour. In another experiment shown in Fig. 6, a colored aqueous droplet could stand steadily on the top of an ethyl acetate–*n*-hexane (1 : 3, v : v) gel for several days. Note that the density of the aqueous droplet was larger than that of the ethyl acetate–*n*-hexane (1 : 3, v : v) gel system, this phenomenon is in accordance with the rheological result that the gel formed by imine **1** was stable and viscoelastic. However, after a drop of HCl (10%) was added to the aqueous droplet, gel–sol transition, resulting from the acid-induced irreversible fracture of the gel, occurred. After this phase transition, the acidic droplet sank to the bottom of the container due to gravitational attraction. Changes of aggregate morphology upon acid-induced gel–sol transition were studied by SEM, which showed the fibrous nanostructures of imine **1** disappeared after treatment with acid (Fig. 3B). Overall, these results unambiguously showed that the organogels formed by imine **1** are acid-responsive.

Conclusion

In summary, a Schiff base molecule, imine **1**, was designed and synthesized to realize for the first time a catalytic acid-responsive organogel system furnished by arene–perfluoroarene interactions. Both arene–perfluoroarene interactions and amide–amide hydrogen bonding were identified as the driving forces for the self-assembly of imine **1**. Additionally, imine **1** was found to be a good gelator in ethyl acetate, 1,4-dioxane, and *n*-alkanes, as well as in ethyl acetate–*n*-alkane and 1,4-dioxane–*n*-alkane mixtures. Whereas in aromatic solvents, where arene–perfluoroarene interactions between the solute molecules were disrupted by the competing aromatic interaction from solvent molecules, gelation was not observed. Gelation did not occur in a solution of a 1 : 1 mixture of Schiff base precursors **3** and **4**

either. On the basis of NMR spectra, no arene–perfluoroarene stacking were observed in this mixture system, only weak hydrogen bonding interactions, providing an explanation for the absence of the gelation process. This interesting result was exploited to realize the first acid-responsive organogel with a gel–sol transition process induced by acid.

Experimental section

General

All solvents were obtained from commercial sources and purified and/or dried according to standard procedures. Unless otherwise indicated, all of the commercial reagents were used as received. All of the reactions were carried out in oven-dried round-bottom flasks. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Mercury plus 300 MHz or Bruker 400 MHz using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported in hertz (Hz). ^{1}H NMR chemical shifts were referenced to TMS (0 ppm), ^{19}F NMR chemical shifts were referenced to CF_3COOH (0 ppm) and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Electro-spray ionization (ESI) mass spectrometry was performed using a Bruker Apex IV FTMS instrument.

Procedures of synthesis

4-Azidotetrafluoro-*N*-(3,4,5-tris(dodecyloxy)benzyl) benzamide (2). 4-Azidotetrafluorobenzoic acid (2.84 g, 12.1 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL), and $(COCl)_2$ (10.4 mL, 121 mmol, 10 equiv.) was injected into the solution. A drop of *N*,*N*-dimethylformamide (DMF) was added to induce the reaction, and the reaction mixture was stirred under anhydrous atmosphere for 24 h at room temperature. The solvent and excessive $(COCl)_2$ was removed under reduced pressure to give 4-azidotetrafluorobenzoyl chloride as a red viscous liquid. It was used in the following reaction without further purification.

3,4,5-Tridodecyloxybenzylamine (8.0 g, 12.1 mmol) and Et_3N (5.5 ml, 36.4 mmol, 3 equiv) were dissolved in anhydrous CH_2Cl_2 (20 mL) and the solution was cooled to 0 °C under anhydrous atmosphere. 4-Azidotetrafluorobenzoyl chloride (12.1 mmol, 1 equiv.) was dissolved into anhydrous CH_2Cl_2 (5 mL) and the solution was added dropwise to the reaction system. The reaction mixture was stirred under anhydrous atmosphere for 20 min at 0 °C. The solvent was removed under reduced pressure. The solid residue was purified through column chromatography over silica gel with ethyl acetate/petroleum ether (60–90 °C) (1 : 8, v : v) as eluant to afford compound **2** as a white powder: 8.07 g (76.4%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.51 (s, 2H), 6.10–6.19 (b, 1H), 4.54 (d, J = 5.4 Hz, 2H), 3.99–3.89 (m, 6H), 1.85–1.68 (m, 6H), 1.52–1.40 (m, 6H), 1.40–1.16 (m, 48H), 0.88 (t, J = 6.6 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.6, 153.3, 144.0 (J_{C-F} = 251 Hz), 140.4 (J_{C-F} = 249 Hz), 137.4, 131.9, 121.9, 111.4, 105.8, 73.4, 69.0, 44.4, 31.9, 30.3, 29.7, 29.7, 29.6, 29.4, 29.4, 26.1, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ −62.9, −72.7. MS (ESI, *m*/*z*): Calcd: 876.6 (M^+), Found: 899.6 $(M + 23)^+$. Anal. Calcd. for $C_{50}H_{80}F_4N_4O_4$: C, 68.46; H, 9.19; N, 6.39. Found: C, 68.21; H, 9.17; N, 6.64.

4-Aminotetrafluoro-*N*-(3,4,5-tris(dodecyloxy)benzyl) benzamide (3). Compound **2** (8.07g, 9.2 mmol) was dissolved in 50 mL of mixture of CH_2Cl_2/MeOH (1 : 1, v : v), and $SnCl_2 \cdot 2H_2O$ (2.7 g, 12 mmol, 1.3 equiv) was added to the solution. The reaction mixture was stirred overnight at room temperature. After the reaction, the solvents were evaporated under reduced pressure. The solid residue was purified through column chromatography over silica gel with ethyl acetate/petroleum ether (60–90 °C) (1 : 5, v : v) as eluant to afford **3** as a white powder: 5.80 g (74.4%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.52 (s, 2H), 6.17–6.08 (b, 1H), 4.54 (d, J = 5.4 Hz, 2H), 4.24–4.20 (b, 2H), 3.99–3.90 (m, 6H), 1.82–1.70 (m, 6H), 1.50–1.41 (m, 6H), 1.38–1.18 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.0, 153.3, 144.5 (J_{C-F} = 247 Hz), 137.5, 136.1 (J = 238 Hz), 132.4, 128.4, 105.9, 102.9, 73.4, 69.1, 44.3, 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 29.4, 26.1, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ −65.4, −83.3. MS (ESI, *m*/*z*): Calcd: 850.6 (M^+), Found: 873.6 $(M + 23)^+$. Anal. Calcd. for $C_{50}H_{82}F_4N_2O_4$: C, 70.55; H, 9.71; N, 3.29. Found: C, 70.46; H, 9.76; N, 3.38.

4-Formyl-*N*-(3,4,5-tris(dodecyloxy)benzyl)benzamide (4). 4-Formylbenzoic acid (3.42 g, 22.8 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and $(COCl)_2$ (20 mL, 228 mmol, 10 equiv.) was injected into the solution. A drop of DMF was added to induce the reaction and the reaction mixture was stirred under anhydrous atmosphere for 24 h at room temperature. The solvent and excessive $(COCl)_2$ was removed under reduced pressure to afford 4-formylbenzoyl chloride as yellow viscous liquid. It was used in the following reaction without further purification.

3,4,5-Tridodecyloxybenzylamine (15.0 g, 22.8 mmol) and Et_3N (15 mL, 68.3 mmol, 3 equiv.) were dissolved in anhydrous CH_2Cl_2 (20 mL) and the solution was cooled to 0 °C under anhydrous atmosphere. 4-Formylbenzoyl chloride (22.8 mmol, 1 equiv.) was dissolved in anhydrous CH_2Cl_2 (5 mL) and the solution was added dropwise to the reaction system. The reaction mixture was stirred under anhydrous atmosphere for 20 min at 0 °C. Then, the solvent was removed under reduced pressure and the solid residue was purified through column chromatography over silica gel with ethyl acetate/petroleum ether (60–90 °C) (1 : 5, v : v) as eluant to afford compound **4** as a yellow powder: 4.03 g (22.2%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.08 (s, 1H), 7.95 (m, 2H), 6.54 (s, 2H), 6.31–6.39 (b, 1H), 4.55 (d, J = 5.7 Hz, 2H), 3.99–3.90 (m, 6H), 1.84–1.71 (m, 6H), 1.53–1.40 (b, 6H), 1.40–1.16 (b, 48H), 0.88 (t, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.4, 166.1, 153.4, 139.5, 138.2, 137.8, 132.6, 129.8, 127.7, 106.6, 73.5, 69.2, 44.7, 31.9, 30.3, 29.7, 29.7, 29.6, 29.4, 29.4, 26.1, 22.7, 14.1. MS (ESI, *m*/*z*): Calcd: 791.6 (M^+), Found: 814.6 $(M + 23)^+$, 792.6 $(M + 1)^+$. Anal. Calcd. for $C_{51}H_{85}NO_5$: C, 77.32; H, 10.81; N, 1.77. Found: C, 77.30; H, 10.98; N, 1.80.

(*E*)-2,3,5,6-Tetrafluoro-*N*-(3,4,5-tris(dodecyloxy)benzyl)-4-(4-(3,4,5-tris(dodecyloxy)benzyl-carbamoyl)benzylideneamino) benzamide (1). A solution of **3** (0.85 g, 1 mmol), **4** (0.791 g, 1 mmol, 1 equiv.) and *p*-$MePhSO_3H \cdot H_2O$ (1.9 mg, 0.01 mmol) in toluene

(10 mL) was heated to reflux overnight. The solvent was removed under reduced pressure at room temperature and the residue was purified through column chromatography over silica gel with Et_3N/CH_2Cl_2/petroleum ether (60–90 °C) (0.2 : 1 : 3, v : v : v) as eluant to afford **1** as a yellow glassy solid: 0.487 g (30%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.52 (s, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.7$ Hz, 2H), 6.85 (t, $J = 5.6$ Hz, 1H), 6.61 (t, $J = 5.4$ Hz, 1H), 6.54 (s, 2H), 6.52 (s, 2H), 4.57 (d, $J = 5.7$ Hz, 2H), 4.51 (d, $J = 4.5$ Hz, 2H), 4.03–3.84 (m, 12H), 1.90–1.62 (m, 12H), 1.58–1.10 (m, 96H), 0.880 (t, $J = 7.2$ Hz, 9H), 0.875 (t, $J = 6.9$ Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 168.0, 166.4, 158.3, 153.3, 153.2, 143.7 ($J_{C-F} = 245$ Hz), 139.1 ($J_{C-F} = 250$ Hz), 138.3, 137.3, 137.1, 132.7, 132.3, 131.7, 129.7, 129.3, 127.7, 127.5, 112.3, 106.2, 105.7, 73.5, 73.4, 69.0, 44.7, 44.2, 31.9, 30.3, 30.3, 29.7, 29.7, 29.6, 29.4, 29.4, 29.3, 26.1, 26.1, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ −64.3, −74.4. MS (ESI, *m/z*): Calcd: 1625.3 (M^+), Found: 1699.3 (M + 74) $^+$. Anal. Calcd. for $C_{101}H_{165}F_4N_3O_8$: C, 74.63; H, 10.23; N, 2.59. Found: C, 74.30; H, 10.32; N, 2.70.

Scanning electron microscopy (SEM)

SEM measurements were carried out by a field emission scanning electron microscope (FEEM, LEO 1530 VP) operated at an accelerating voltage of 1.0 kV. All samples were applied to a stainless silica wafer and allowed to dry under reduced pressure.

Atomic force microscopy (AFM)

AFM measurements were conducted in tapping mode on freshly stripped mica surfaces by DI Nanoscope IIIa in air. Tap300Al tips (Budget Sensors) with a force constant of 40 N m^{-1} and a resonance frequency of 300 kHz were used.

Rheological measurements

Rheological measurement were carried out by using Physica MCR 301 instrument with a parallel plate (diameter = 25 mm) at 20 °C.

Gelation test

A typical procedure for qualitative gelation testing was as following: in a test tube (diameter = 1 cm), imine **1** was mixed with appropriate amounts of solvent and the mixture was heated until the solid dissolved. The resulting clear solution was cooled to 20 °C and annealed for about 1 h at this temperature. When the test tube could be inverted without change of shape of its content, it was indentified as a gel.

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