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Instant Room-Temperature Gelation of Crude Oil by Chiral Organogelators

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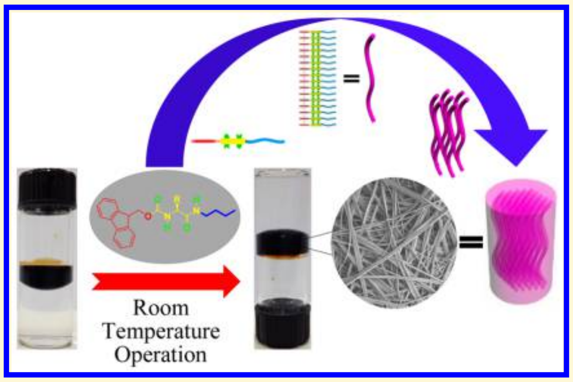
Ⓢ *Supporting Information*



ABSTRACT: Large-scale treatment of oily water arising from frequent marine oil spills presents a major challenge to scientists and engineers. Although the recently emerged phase-selective organogelators (PSOG) do offer very best promises for oil spill treatment, there still exists a number of technical barriers to overcome collectively, including gelators' high solubility, high gelling ability, general applicability toward crude oil of various types, rapid gelation with room temperature operation, low toxicity, and low cost. Here, a denovo-designed unusually robust molecular gelling scaffold is used for facile construction of a PSOG library and for rapid identification of PSOGs with the most sought-after practical traits. The identified gelators concurrently overcome the existing technical hurdles, and for the first time enable instant room-temperature gelation of crude oil of various types in the presence of seawater. Remarkably, these excellent gelations were achieved with the use of only 0.058−0.18 L of environmentally benign carrier solvents and 7−35 g of gelator per liter of crude oil. Significantly, 2 out of 20 gelators could further congeal crude oil in the powder form at room temperature, highlighting another excellent potential of the developed modularly tunable system in searching for more powerful powder-based gelators for oil spill treatment.

■ INTRODUCTION

Including the monstrous BP oil spill of millions of barrels of crude oil in the Gulf of Mexico in 2010,[1] large-scale marine oil spills have occurred more than 50 times and released >5 million tons of crude oil into the ocean over the period of 1965−2010.[2] The devastating and lasting damage caused by spilled oils to the ocean ecosystem and environment as well as the huge socioeconomic losses all call for the urgent development of efficient and sustainable oil spill control technologies. Current oil spill control measures largely rely on *in situ* burning of oil or use of skimmers and booms,[3] sorbents,[4−7] dispersants,[8,9] bioremediation,[10] and solidifiers.[11] None of these approaches, however, are very effective on a large scale either on their own or in combination, especially in rough water.[11−15]

Phase-selective organogelators derived from small organic molecules have recently emerged as candidates as "smart" oil-scavenging materials.[16−24] The majority of the hitherto developed gelators necessitate carrier solvents for their dissolution before being applied to gel organic liquids. For gelators under this category, technical challenges to overcome include gelators' high solubility in environmentally benign solvents, high gelling ability, general applicability toward crude oil of various types, rapid gelation with room temperature operation, low toxicity to marine lives, and low cost. In particular, high solubility in essentially nontoxic carrier solvents such as ethanol and ethyl acetate, which are thousands of times less toxic than crude oil, represents an unsolved issue. Large amounts of carrier solvent[17] or toxic carrier solvent[21] or maintenance of the solution under hot conditions[18,23] was needed for gelling distilled petroleum fractions (e.g, petrol and diesel) whose gelling properties nevertheless are very different from crude oil of complex structures. For a recently elaborated gelator able to gel highly mobile benzene and one type of crude oil of unknown properties in the powder form,[24] it is particularly disadvantaged by a long gelation time even under constant stirring as a result of its low diffusion/dissolution speed into oil. This makes "on-site" collection impossible and increases the risk of pollution by oil during and after gelation. A long gelation time additionally suggests that this powder-based gelator might be incapable of gelling highly viscous heavy crude oil. Prior to our current work, gelators able to instantly solidify crude oil, rather than distilled petroleum fractions, at room temperature still remain elusive. This slow progress with limited practical potential could be attributed to the fact that the *de novo* design of PSOGs, concurrently possessing all the aforementioned desirable practical traits, is an extremely difficult task: the three-dimensional (3D) entangled gelling network stabilized by noncovalent forces cannot be precisely and predictably manipulated at the molecular level.

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Herein, we report a few low-cost low-toxicity gelators that for the first time allow for instant gelation of crude oils of widely ranging densities and viscosities from oily water into water-floating stiff solid with room-temperature operations and with the use of minimum amounts of environmentally benign solvents. The identification of these desired gelators was achieved via a combinatorial screening of a carefully designed PSOG library, possessing an unusually robust molecular gelling scaffold that consistently delivered gelators with high gelling ability regardless of side chains. Such a robust gelling scaffold is rarely seen among the hitherto reported gelling systems of diverse types.[25−28] Another great advantage of our system lies in its modularly tunable nature. It is this unique feature that leads to high tunability in gelators' solubility, eventually culminating in the discovery of commercially viable gelators that concurrently overcome all the major technical barriers including an unprecedentedly high solubility (500 mM in environmentally benign solvents) for large-scale application in mitigating ecosystem damage and environmental pollution caused by oil spills. Significantly, two out of 20 gelators could also gel a light crude oil in the powder form at room temperature, albeit with a long gelation time of 48 h. This very first generation of powder-based gelators sets the groundwork for the evolution of more powerful next-generation gelators for instantly gelling crude oil at room temperature in the powder form for oil spill treatment.

RESULTS AND DISCUSSION

Design and Features of the Gelator Library. The PSOG library (**F-AA-Cn**, Figure 1), accessible in a single synthetic step from Fmoc-protected amino acids, was designed to incorporate three key features that define the overall molecular framework of the resultant gelators: (i) two secondary amide bonds carrying two pairs of carbonyl O atoms and amide H atoms to possibly produce, via intermolecular H-bonds, a one-dimensionally (1D) aligned H-bonded β-sheet-like columnar structure, (ii) a rigid planar conjugated aromatic Fmoc group to enhance the stability of the H-bonded 1D structure via robust aromatic $\pi-\pi$ stacking forces, and (iii) a defined chirality that might help to lock the molecular backbone into a conformation predisposed toward forming the H-bonded 1D structure with reduced entropic penalties. In addition, we envisioned that the stabilities of the H-bonded 1D structures and the resultant higher order fibrous structures (i.e., nanofibers), their corresponding gelling ability, and solubility can be further tuned by systematically and combinatorially varying R_1 and R_2 groups. These constant and variable structural features would combine collectively to facilitate the formation of H-bonded 1D structures from which 1D nanofibers could be formed, which further associated with one another to create a 3D entangled nanofiber-based gelling network for extensive solvent entrapment and oil solidification. To test the effect of these three molecular features on the oil-gelling ability of the designed PSOG molecules, a total of 20 library compounds derived from 5 R_1 and 4 R_2 groups was prepared by coupling the corresponding Fmoc-protected amino acids with four types of alkyl amines that differed in the length of hydrophobic carbon chains. Two types of control compounds, i.e., **F-Gly-C4** and **F-Gly-C8** that both lacked a chiral center, as well as **F-Pro-C4** that lacked both the chiral center and two H-bond donor/acceptor sites, were also prepared to substantiate the intended roles played by these two structural features.

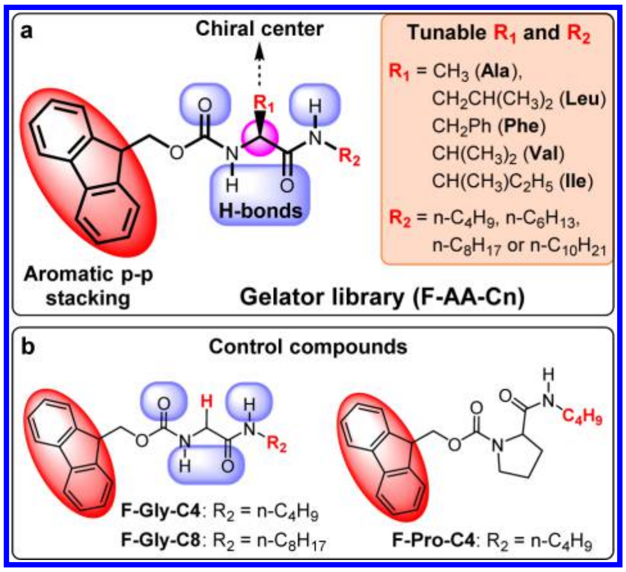

Figure 1. Structural features of the gelator library **F-AA-Cn** and three control compounds: (a) The library is derived from Fmoc-protected amino acids and designed to contain three constant (Fmoc, H-bonds, and chiral center) and two variable (R_1 and R_2) structural features. (b) The three control compounds were made to elucidate the important roles played by the constant structural features, i.e., H-bonds and chiral center, in oil gelation.

Crystal Structures of F-Phe-C4 and F-Gly-C4. To elucidate the above possible roles played by Fmoc, H-bonds, and the chiral center in the formation of fibrous structures, growth of single crystals for the 20 gelators and 3 nongelators (**F-Gly-C4**, **F-Gly-C8**, and **F-Pro-C4**) was attempted. A combinatorial screening of hundreds of crystal growth conditions finally yielded X-ray quality single crystals for **F-Phe-C4** and **F-Gly-C4**, which were obtained after 2−3 weeks by slowly diffusing 2.0 mL of *n*-hexane into 1.0 mL of **F-Phe-C4**-containing chloroform solution or by evaporating a **F-Gly-C4**-containing solvent mixture (acetonitrile/tetrahydrofuran = 3:1, v:v). In both structures, both Fmoc group and H-bonds provided the primary directional driving forces, instructing the molecules to stack along axis b to produce well-organized H-bonded 1D columnar stacks as envisaged (Figure 2). Because of the chiral center, one key difference between the two structures was manifested in the relative orientation of the two amide groups. In **F-Phe-C4**, the two amide groups were aligned in parallel with each other, and both participated in forming the 1D columnar stacks. In **F-Gly-C4**, they were roughly perpendicular to each other with only one of them contributing to the columnar stacking. As a result, the intercolumnar packing in **F-Phe-C4** was exclusively mediated by weak van der Waals (VDW) forces, which might work together with oil molecules to produce a 3D entangled fibrous gelling network in a hydrophobic oil environment, whereas that of **F-Gly-C4** was additionally stabilized by extensive well-aligned intermolecular H-bonds to produce planar ensembles that were not easily interrupted by weak VDW forces from oil molecules, indicating the poor solubility or precipitate-forming nature of **F-Gly-C4** in oil. Indeed, **F-Gly-C4** is poorly soluble in petrol, diesel, and crude oil.[27]

Exceedingly High and Broad Spectrum Oil-Gelling Abilities. The intended oil-gelling abilities for the designed monopeptide-based gelators and nongelators were then

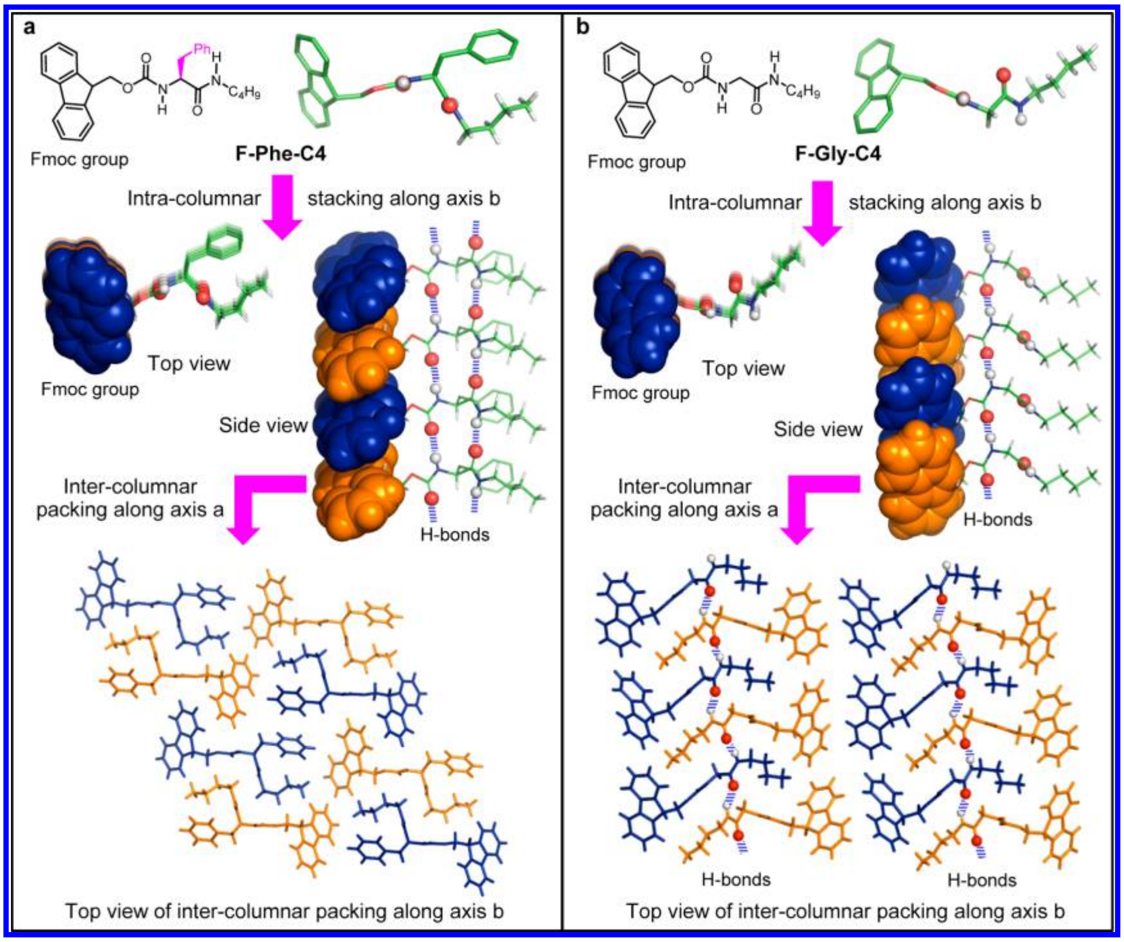

Figure 2. Crystal structures of gelator **F-Phe-C4** and nongelator **F-Gly-C4**. (a) The existence of a chiral center in **F-Phe-C4** induces the two amide bonds to be vertically aligned and in parallel with each other, enabling efficient H-bond-mediated columnar stacking that is further assisted by aromatic $\pi-\pi$ forces among Fmoc groups. (b) A lack of chiral center makes the two amide bonds in **F-Gly-C4** roughly perpendicular to each other, with one participating in forming 1D columnar stacks and the other forming extensive intermolecular H-bonds that act collectively with numerous weak van der Waals forces to allow the 1D columns formed to tightly associate with one another. In contrast, the intercolumnar associations in **F-Phe-C4** rely on only weak van der Waals (VDW) interactions, which can be easily disrupted by other hydrophobic molecules.

examined by the "stable to inversion" method (see the Supporting Information) in eight oils, including four types of crude oil (Grissik, Arab Light, Arab Heavy and Ratawi; Table S1, Supporting Information). These four crude oils cover wider ranges in physical properties (density, sulfur content, and viscosity) than the world's most actively traded oils (West Texas Intermediate, Brent Crude, and Dubai Crude) and many others (Tables S2 and S3) and should constitute a good representation of the majority of the world's actively traded oils. (Table S2). Except for some limited cases for which the gelators were soluble in oil (Table S3), these 20 gelators could gel all eight oils with minimum gelation concentrations (MGCs in % w/v, mg/100 μL) ranging from 0.15 to 0.53% w/v for petrol, 0.11 to 0.32% w/v for diesel, 0.06 to 0.28% w/v for mineral oil, 0.08 to 1.85% w/v for silicone oil, 0.29 to 0.75% w/v for Grissik, 0.32 to 1.65% w/v for Arab Light, 0.75 to 3.10% w/v for Arab Heavy, and 0.62 to 1.65% w/v for Gratawi. All the gels were thermoreversible, easily filterable/scoopable, and stable for several months at room temperature, indicating their excellent temporal stability. The solid-state morphologies of the as-formed gels by the 15 gelators in petrol were visualized via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 3a and Figures S1–S4 illustrate the extensive formation of nanofibers of 40 to 800 nm in diameter, which intertwine to produce a 3D entangled network able to trap oil molecules and form the gels through surface tension and capillary forces.

Gelators able to immobilize solvents to ≥100 times their own weight are defined as supergelators. By this conventional criteria, all the 20 gelators acted as supergelators for these oils, except for three cases (**F-Leu-C8** and **F-Phe-C6** with silicone oil and **F-Phe-C8** for Grissik). For instance, **F-Val-C8** gelled mineral oil with a MGC value of 0.06% w/v (= 0.06 mg/100 μL of mineral oil), which corresponds to an ability to immobilize mineral oil >1200 times its own weight, ranking among the best organogelators ever reported. The denser and more viscous Arab Light, Arab Heavy, and Gratawi were more difficult to solidify with average MGC values of 0.95% w/v, 1.50% w/v and 1.12% w/v, respectively. In comparison, the three control compounds, **F-Gly-C4**, **F-Gly-C8**, and **F-Pro-C4** could not gel any of the eight oils examined, demonstrating a necessity to have both the chiral center and H-bonds in the molecular backbone of gelator molecules.

Room-Temperature Phase-Selective Gelation of Crude Oil. The possibility of using these gelators to selectively gel oil from oily water was explored in the presence of seawater. As the typical "stable to inversion"-based method required heating to dissolve the gelators in the liquid to be gelled, which

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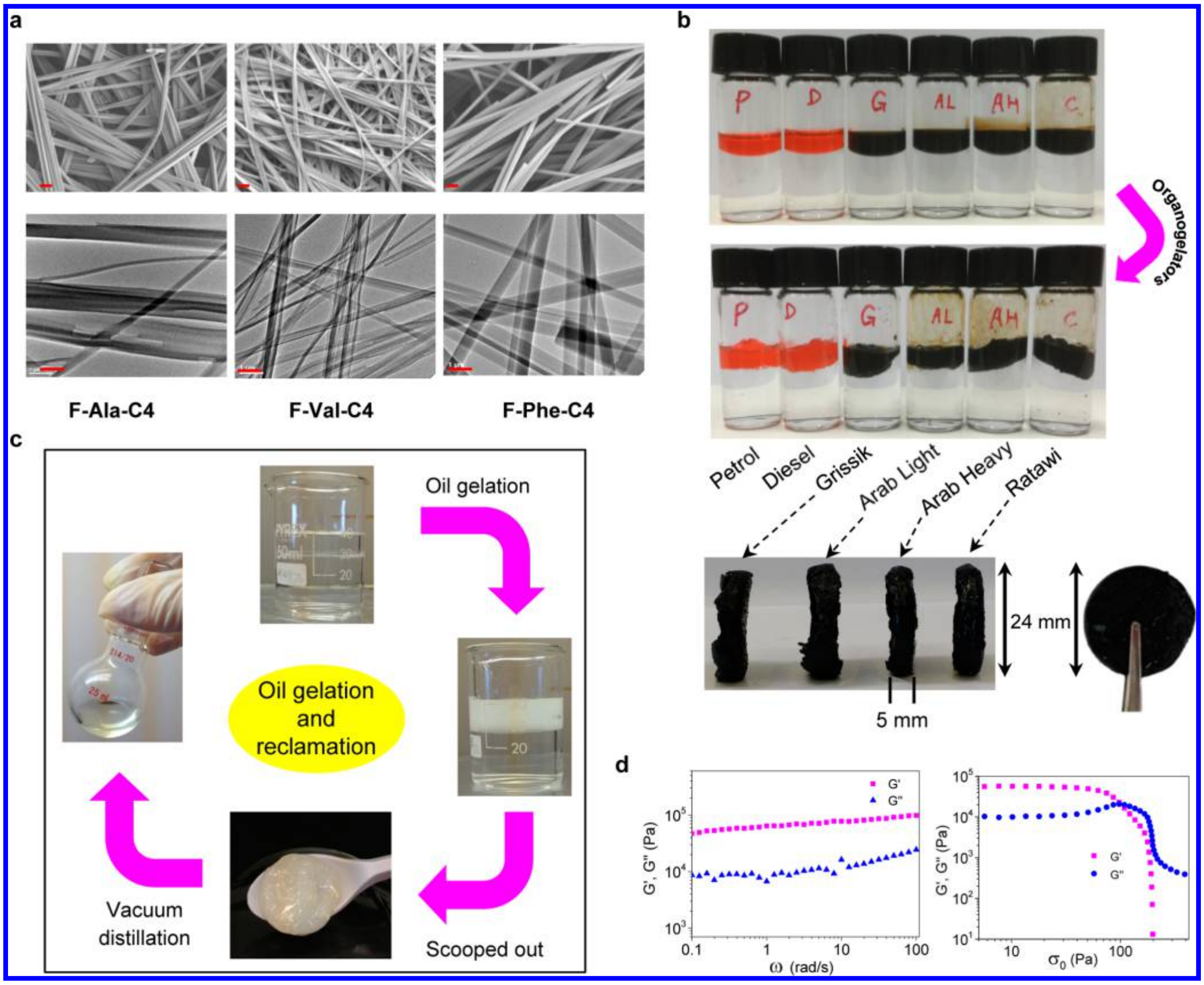

Figure 3. Phase-selective gelation of oils, physical characterizations of gels and diesel recovery from solidified diesel gels. (a) SEM (top) and TEM (bottom) images of gelled petrol via the "heating and cooling" method in the presence of **F-Ala-C4**, **F-Val-C4**, and **F-Phe-C4**. Red scale bars = 1 μm. (b) Phase-selective gelation of petrol by **F-Ala-C6** (1.4% w/v), diesel by **F-Leu-C4** (1.6% w/v), Grissik by **F-Ala-C4** (1.0% w/v), Arab Light by **F-Leu-C4** (1.8% w/v), Arab Heavy by **F-Leu-C4** (2.8% w/v), and Ratawi by **F-Leu-C4** (3.0% w/v) in the presence of seawater at room temperature. Both diesel and petrol were dyed with 0.01% red Sudan III for clarity in visualization. The vertically aligned gels (24 mm diameter and 5−7 mm thick) shown at the bottom were prepared from the larger vials. (c) Phase-selective gelation of bulk diesel in the presence of seawater and its quantitative recovery through vacuum distillation. (d) Dynamic rheological studies of Arab Heavy in phase-selective gelation by **F-Leu-C4** (2.5% w/v). G' = storage modulus, G'' = loss modulus, frequency sweep = ω, and stress amplitude = σ_0.

would be impractical for the treatment of large-area oil spills, an alternative room-temperature gelation protocol was examined. After screening all the routinely used organic solvents and their various combinations, we found that 4 out of the 20 gelators, **F-Ala-C4**, **F-Ala-C6**, **F-Leu-C4**, and **F-Leu-C6**, were sufficiently soluble in solvent mixtures containing ethyl acetate/ethanol or acetone/ethanol. Accordingly, a high concentration of the gelator, e.g., 200 mg/mL of **F-Leu-C4**, was prepared in a solvent mixture containing ethyl acetate and ethanol (3:2, v:v), an aliquot of which (0.04 mL) was then added to a biphasic system containing 0.5 mL of oil, such as diesel, and 2 mL of seawater. Upon gentle shaking to simulate the choppy wave motion, spontaneous partitioning of the gelator into diesel and selective gelation of the oil phase occurred instantaneously, while leaving the aqueous layer intact. In less than 90 s, diesel was fully gelled and stayed afloat on the seawater surface (Figure 3b). By this protocol, the corresponding biphasic MGC (BMGC in % w/v, mg/100 μL) value for **F-Leu-C4** against diesel was determined to be 1.2% w/v, indicating that **F-Leu-C4** was able to solidify diesel at 69 times its own weight. The full testing of all the 4 gelators against the 6 representative oils (diesel, petrol, Grissik, Arab Light, Arab Heavy, and Ratawi) was then conducted. With the exception of **F-Leu-C4** and **F-Leu-C6** against petrol, all the other 22 combinations yielded stable phase-selective water-floating gels within 28−97 s (more vigorous shaking of oily water after addition of gelator solution significantly shortened the gelation time to within 6−28 s for all cases) and excellent BMGC values of 0.7−2.8% w/v (Table S4). These BMGC values corresponded to oil/gelator mass ratios of 32.5−107. The longest gelation time of 97 s was observed for **F-Leu-C4** against Ratawi. Generally, crude oil with higher density and viscosity requires more gelator to attain full gelation. The robustness of the phenomenon can be established by the fact that both the phase-selective gelation and the

BMGC value remain minimally affected by the type of water (e.g., plain water, groundwater, and seawater) and pH (0−14). The gels' high thermal and temporal stabilities were demonstrated by the fact that these four gelators have thermal decomposition temperatures of 171−190 °C (Figure S5) and that the 18 gels exhibited a $T_{\text{gel-sol}}$ value of ≥44 °C and remained stable at room temperature for more than 6 months. Our additional testing of all 20 gelators showed that, under very vigorous shaking, both **F-Leu-C6** and **F-Leu-C8** in the powder form can fully gel Grissik at room temperature after 48 h at 2.5% w/v. They, however, cannot congeal the other three types of crude oils (e.g., Arab Light, Arab Heavy, and Ratawi).

The above BMGC values show that, to gel one volume of weathered or unweathered crude oil, only 0.058−0.18 volume of solvents of extremely low toxicity was needed for dissolution of the required amount of gelators. This was much lower when compared to two reported examples, whereby 0.8 volume of ethanol or 0.33 volume of toxic hot petrol were needed to dissolve gelators for solidifying one volume of diesel[17] or crude oil,[20] respectively. For additional comparisons, other gelators able to gel one or a few refined oils (petrol, diesel, etc.) are disadvantaged by their inability to gel some refined oils[19,22] or a need to use toxic or hot cosolvent[18,21,23] for dissolution of gelators.

Very recently, Sureshan and his co-workers reported a sugar-based gelator able to gel crude oil in the powder form.[24] Compared to the existing solution-based method, powder-based gelation is more advantageous in that no carrier solvents are needed and represents a significant advance in the field. Nevertheless, gelators of this type in general are greatly disadvantaged by (1) difficulty to treat large-scale marine oil spill as powders cannot be evenly sprayed from aircraft over large sea surface and (2) low diffusion/dissolution speed into oil (it took, under constant stirring, about an hour alone for the reported gelator to fully gel highly mobile benzene with a low viscosity of 0.6 mPa s at 25 °C). Such a long gelation time makes "on-site" collection impossible, thereby increasing the risk of pollution by the oil during and after gelation. In analogue to solidifiers generally suffering from an inability to satisfactorily solidify viscous medium or heavy crude oil and in view of the fact that only one type of crude oil of unknown property has been tested with no mentioning of exact gelation time, the powder-based approach might not be sufficiently general toward gelling various kinds of weathered and unweathered crude oils, particularly heavy crude oils (e.g., Arab Heavy and Ratawi). Our present investigation lends support to this perspective, suggesting both powder form and solution method have its own pros and cons, and neither is significantly better than the other. For the powder-based gelators, the major challenge is to shorten gelation time needed for light, rather than heavy, crude oil to within minutes such that on-site collection becomes possible to prevent secondary pollutions resulting from treated oil.

Oil weathering on the sea surface begins as soon as oil is spilled. To test if the gelators can achieve similarly efficient gelation of weathered oil, crude oil (4 mL each) was placed in an open vial of 22 mL in the presence of 2 mL of seawater, left in fume hood with an air flow speed of ~0.5 m/s at room temperature for 3 weeks, and further subjected to oxidation via direct exposure to the tropical sunlight in Singapore at room temperatures of 26−31 °C for 3 days. Despite weight losses of 7−62% and huge increases in viscosity across the four crude oils (Table 1), the determined BMGC values using gelator **F-Leu-C4** confirm its outstanding ability to achieve instant room-temperature gelation of both weathered and unweathered crude oils.

Table 1. Changes in Physical Properties of Weathered Crude Oils and BMGC Values Determined Using F-Leu-C4[a]

crude oil	weight loss (%)	density (kg/L)	viscosity at 25 °C (mPa s)	BMGC (% w/v)
Grissik	62	0.77 (0.75)	2.2 (0.66)	1.6 (1.3)
Arab Light	32	0.85 (0.83)	12.2 (2.7)	2.3 (1.4)
Arab Heavy	12	0.92 (0.89)	171.3 (42.5)	3.2 (2.5)
Ratawi	7	0.93 (0.91)	330.5 (81.9)	3.5 (2.8)

[a] 200 mg/mL of **F-Leu-C4** in ethyl acetate and ethanol (3:2, v:v). The values shown in parentheses are for unweathered oils.

The ease of removal and reclamation of treated oils is an important practical aspect that would help to permanently eliminate possible damage of the spilled oil to the chemical, physical, and biological integrity of the ecosystem. First, a biphasic solution containing Ratawi (2.00 g) and water (10.00 g) was prepared to which 0.09 g of gelator dissolved in 0.18 mL (0.14 g) of ethanol and 0.27 mL (0.25 g) of ethyl acetate (2:3, v:v) was added, and the resultant solution was vigorously shaked for 20 s. Assuming water-immiscible ethyl acetate and gelator molecules both remain 100% in gelled oil, the gelled oil should weigh 2.34 g. After filtration and from the weight of ethanol-containing water, total mass of collected solidified oil containing gelator and ethyl acetate was calculated to be 2.44 g, which is 0.10 g more than the theoretically allowed value. Visual inspection of the water solution confirms no visible oil droplets or oil slick remains in water, thereby confirming that majority of crude oil has been separated from water upon solidification. Second, to examine reclamation of treated oil, gelation experiment in a larger scale was conducted using 120 mg of **F-Leu-C4**, 10 mL of diesel, and 30 mL of seawater (Figure 3c). The fully solidified diesel, which was stiff enough to be easily scooped out using a spatula, was transferred to a round-bottom flask and subjected to vacuum distillation, which resulted in a quantitative recovery of the diesel. Although the gelators could be recycled and reused, the recyclability was limited to light oils (petrol or diesel) and not heavy crude oil containing components of high boiling points.

Real world applications further require the floating gels to be robust enough under the choppy wave motion in rough seawater and to allow for easy collection and separation. In this regard, the mechanical strength of the organogel formed phase-selectively from oily water using **F-Leu-C4** at its BMGC value was examined in rheological studies at 25 °C. In all four frequency sweep experiments (Figure 3d and Figure S6), the storage modulus G' was essentially independent of frequency and much higher than the viscous modulus G'' over the frequency range, suggesting excellent elasticity of the gels, which would not relax over long time scales. The high G' values (5.0×10^4, 7.4×10^4, 5.5×10^4, and 1.4×10^5 Pa for diesel, Arab Light, Arab Heavy, and Ratawi gels, respectively) pointed to the remarkable stiffness and strength of these gels (Figure 3b). The stress amplitude (σ_0) at which a sharp decrease in moduli occurred corresponded to the yield stress of the gel, and high values of >80 Pa were obtained, demonstrating the ability of these gels to withstand high pressures, i.e., going well beyond supporting their own weight in an inverted vial.

Toxicity of Oils and Gelators. The OECD approved protocol (OECD test guideline 236)[29] with validated intra- and interlaboratory reproducibility[30] was followed to test the

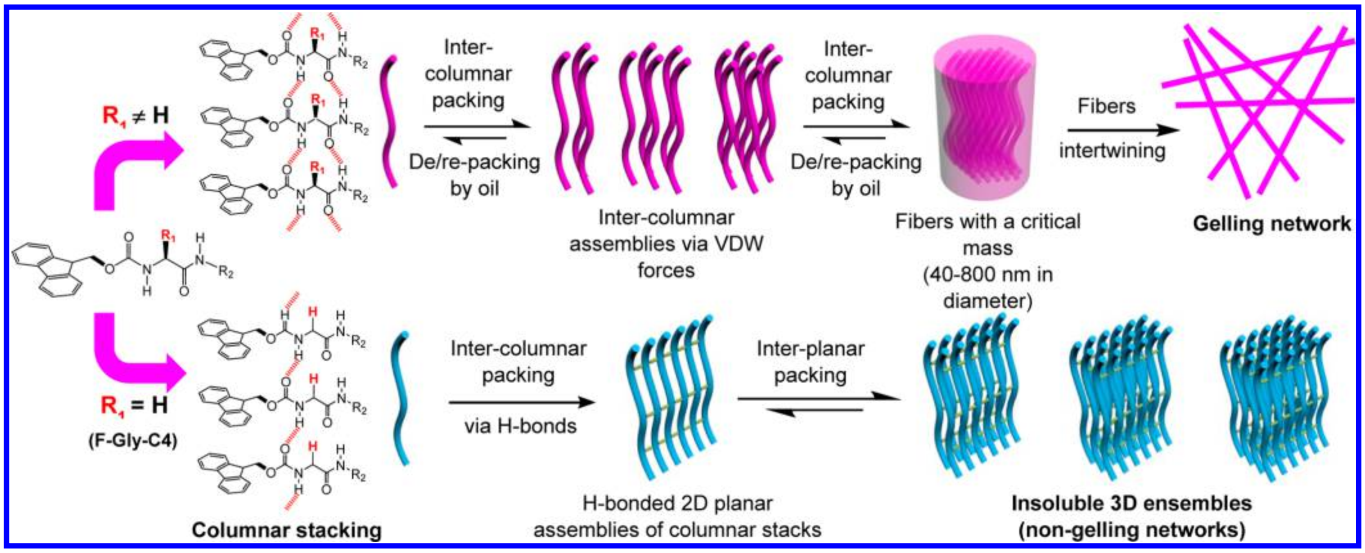

Figure 4. Plausible hierarchies of supramolecular connectivities underscoring a different gelling ability between gelators and nongelling glycine derivatives (**F-Gly-C4** and **F-Gly-C8**). In a hydrophobic environment, aromatic $\pi-\pi$ stacking, H-bonding, and extensive interplanar VDW interactions are not easily disrupted by weak VDW forces. Columnar stacks, H-bonded 2D planar assemblies, and 3D ensembles therefore could be readily formed in solution. Oil molecules, however, do exert variable influences on the sizes and structures of the intercolumnar assemblies facilitated by VDW forces. Since **F-Gly-C4** and **F-Gly-C8** both precipitate out from oil upon cooling, these extensively aggregated 3D ensembles, which are assumed to prevail in solution via strong interplanar VDW forces, should be oil-insoluble too.

aquatic safety of oils and gelator **F-Leu-C4** using freshly fertilized zebrafish embryos and 3-day-old larvae as the test organisms over a time period of 96 h. The data showed the four crude oils to have a high toxicity, causing ~30% death of zebrafish larvae at a concentration as low as 2 ppm after 3 days, while **F-Leu-C4** and **F-Leu-C6** produced no harmful effects toward both zebrafish embryo and larvae after 4 days at concentrations of up to 100 ppm (Table S7 and Figures S7−S12). Surprisingly, structurally similar alanine derivatives were much more toxic with 97% death of zebrafish larvae caused by **F-Ala-C4** after 2 days at 12.5 ppm and 22% death by **F-Ala-C6** after 4 days at 50 ppm (Figure S13).

Mechanistic Insights into Gelling and Nongelling Networks. To assess whether the three structural features (Fmoc, H-bonds, and a chiral center) designed into the molecular backbone of the gelators work in concert with the expected roles (Figure 1), physical characterizations were conducted in the solution and solid state.

Upon dilution from 100 mM to 0.8 mM in $CDCl_3$, which allowed hydrogen-bonding, concentration-dependent ^1H NMR study at 25 °C revealed significant upfield shifts of the amide H atoms H_a and H_b in **F-Ala-C4** by 0.25 and 0.35 ppm (Figure S14a), respectively, indicating the involvement of H_a and H_b in forming intermolecular H-bonds. Similar concentration-dependent upfield shifts were also observed for gelators **F-Ala-C6**, **F-Leu-C4**, and **F-Leu-C6** and nongelator **F-Gly-C4**, which consisted of two secondary amide bonds but not for **F-Pro-C4**, which has only one such group (Figures S14b,c and S15). These results demonstrated that, except for **F-Pro-C4**, all the (non)gelator molecules carrying two secondary amide groups were capable of self-assembling via intermolecular H-bonds to produce extended H-bonded supramolecular structures. Intermolecular associations among Fmoc groups were also detected in fluorescence emission spectra at various concentrations in a solvent mixture of chloroform and *n*-hexane (1:4, v:v). With an increase in concentration from 0.1 mM to 1 mM and to the gel-forming 10 mM (0.37% w/v), the emission maximum of **F-Ala-C4** was red-shifted by 10 nm (Figure S14a), which was indicative of aromatic $\pi-\pi$ stacking among the Fmoc groups.[32] The fact that such a red shift (9−16 nm) persisted with all the molecules including **F-Pro-C4** (Figures S14 and S16) firmly established the Fmoc group as a robust $\pi-\pi$ stacking moiety that contributed reliably to the formation of oil-gelling fibrous structures. Circular dichroism (CD) experiments (Figures S14 and S17) confirmed chirality in the resultant H-bonded supramolecular structures, which presumably was imparted by the chiral center in the gelator molecules such as **F-Ala-C4**. For **F-Phe-C4**, further analyses of X-ray diffraction (XRD) patterns of its crystal, fibrous gelling aggregates, and solid powder revealed a significant similarity between the crystal structure and the fibers (Figure S18), suggesting the ordered 1D columns of varying lengths, the basic units of the nanofibers, resembled those seen in the crystal structure.

The above findings, combined with the crystal structures presented in Figure 2, led us to propose two hierarchies of supramolecular connectivities to account for the differences in gelling abilities (Figure 4). For gelators containing a chiral center, both the two amide groups participated in forming the columnar stacks, which underwent further self-associations to create intercolumnar assemblies of varying structures and sizes via VDW forces. In a hydrophobic environment, the oil molecules might play an important role in de/repacking these intercolumnar assemblies. Once these assemblies reached a critical mass with a diameter of 40−800 nm, they would intertwine as a 3D entangled fibrous gelling network. As for the nongelling precipitate-forming glycine derivatives (**F-Gly-C4** and **F-Gly-C8**) that lacked a chiral center, only one amide group was involved in forming H-bonded 1D columns with the other cross-linking numerous 1D columns into 2D planar assemblies of varying sizes, giving rise subsequently to the 3D ensembles stabilized by extensive interplanar VDW forces under little influence from the oil molecules. These extensively aggregated 3D ensembles were expectedly oil-insoluble and hence incapable of producing gelling aggregates.[27]

■ CONCLUSION

Our current work demonstrated a robust and modularly tunable molecular gelling scaffold for reliably and combinatorially constructing organogelators with high gelling ability while allowing their solubility in environmentally benign solvents to be highly tunable. Out of 20 library compounds with high gelling ability, only two (e.g., **F-Leu-C4** and **F-Leu-C6**) were found to concurrently possess excellent solubility, likely nontoxicity to marine lives and unprecedented ability to instantly solidify both weathered and unweathered crude oils in the presence of seawater at room temperature. This, together with inexpensive material costs ($0.6−2.5 for leucine derivatives vs current cost of ∼$100 for treating per liter of crude oil[31]) and excellent prospect of eliminating secondary pollutions from treated oil via onsite removal and easy recovery, makes the gelators practical and commercially viable for cleaning up oil spills, while ensuring environmental safety and ecosystem integrity. The fact that both **F-Leu-C4** and **F-Leu-C6** could also gel light crude oil in the powder form points to a high likelihood of finding more powerful powder-based gelators for their eventual uses in oil spill treatment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b01367.

> Synthetic procedures for 20 gelators, minimum gelation concentration data, SEM and TEM images, TGA analysis curves, rheological data, toxicity data, ^{1}H NMR dilution experiments, fluorescence spectra, circular dichroism spectra, powder X-ray diffraction, and ^{1}H NMR and ^{13}C NMR spectra, and (HR)MS data (PDF)
>
> X-ray crystal file/data sheet for **F-Gly-C4** and **F-Phe-C4**(TXT)

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Notes

The authors declare no competing financial interest.

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