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Monopeptide-based powder gelators for instant phase-selective gelation of aprotic aromatics and for toxic dye removal

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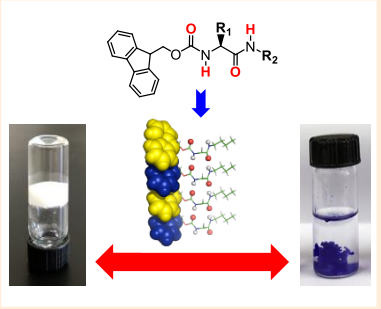
ABSTRACT: Through a combinatorial screening of 35 possible phase-selective monopeptide-based organogelators readily made at lost cost, we identified five of them with high gelling ability toward aprotic aromatic solvents in the powder form. The best of them (**Fmoc-V-6**) is able to instantly and phase-selectively gel benzene, toluene and xylenes in the presence of water at room temperature at gelator loading of 6% w/v. This enables the gelled aromatics to be separated by filtration and both aromatics and the gelling material to be recycled by distillation. We also identified **Fmoc-I-16** as the best gelator for benzyl alcohol, and the corresponding organogel efficiently removes toxic dye molecules by 82 - 99% from their highly concentrated aqueous solutions. These efficient removals of toxic organic solvents and dyes from water suggest their promising applications in remediating contaminated water resources.



INTRODUCTION

Toxic organic solvents and dyes, having carcinogenic and mutagenic effects, are widely found and used in various industry sections (petrochemicals,[1] paints,[2] printing,[3] pharmaceuticals,[4] papermaking,[5] textiles,[6] chemical industry, garment industry, cosmetics, etc). Both intentional and unintentional discharges of organic or dye-containing waste solutions without appropriate treatments have kept happening,[1] not to mention accidental discharges, plant fires or explosions.[7] In particular, around 50000 tons of dyes are released into environment annually.[8] These toxic solvents or dye molecules, discharged into land or rivers but hard to degrade in the natural environment, greatly threaten the terrestrial aquatic systems by such as polluting local drinking water.[9]

At the present, some common strategies to remove these toxic pollutants from the environment include combustion,[10] biochemical treatment,[11] chemical decomposition,[12] membrane separation[13] and physical adsorption.[14] However, these methods have some varying limitations in practical applications. More specifically, a simple burning not only causes environmental pollution but also is difficult and costly on the large scale. While the biochemical treatment is not matured at present, with pending biosafety issues and highly variable treatment outcomes to be addressed,[15] chemical decomposition method is time-consuming and also may cause secondary pollution as a result of introduced chemical reagents. Thus, there is a need to develop alternative technologically simple yet environmentally friendly approaches that offer practically valuable features not seen in the existing methods.

Use of mostly hydrophobic phase-selective organogelators (PSOGs) to achieve selective gelation of oil component from an oil-water mixture was first proposed and demonstrated by Bhattacharya and his co-workers in 2001.[16] In principle, the gelator-containing gelled oil, which stays afloat in water, can be separated from water near-quantitatively by a simple filtration. This certainly enables not only near-complete elimination of toxicity caused by either oil or gelator molecules immiscible with water, but also possible reclamation of treated oil. This noteworthy advantage both intrinsic and unique to PSOGs has aroused intensive interests from researchers worldwide, resulting in rapid development of diverse types of PSOGs that have now emerged as promising oil-scavenging and dye-removing materials.[17-54]

A critical prerequisite for any gelator to find practical applications in spilled oil treatment especially on the large scale is its ability to gel the oil with room temperature operations. This was first achieved by our group in 2016 using a carefully devised monopeptide-based gelator library,[38] with their gelling ability and particularly high solubility in environmentally friendly solvents (e.g., ethanol and ethyl acetate) combinatorially optimizable. The identified gelator is generally applicable to six types of (un)weathered crude oils of varying viscosities. Still, these solution-based gelators require flammable solvents for their dissolution before application for oil gelation. In the effort to minimize or even eliminate the use of flammable carrier solvents, Sureshan,[43] Zeng,[38,44-45] Chaudhuri,[46] and Song[47] reported powder gelators derived from sugar, monopeptide or naphthalene diimide scaffolds for phase-selective room-temperature gelation of crude oils.

Adding into this growing list of recently reported yet limitedly available powder gelators,[7, 43-47] in this work, we describe our systematic efforts toward the discovery of some powerful powder gelators for instant phase-selective gelation of aprotic aromatics (e.g., benzene, toluene, xylene and nitrobenzene) at room temperature. These aromatics, which are one important source of environmental pollutions, nevertheless have remained much less studied so far,[7,47-52] especially when compared to more widely studied petroleum oils.[26-46] Additionally, we have also

demonstrated their usefulness in efficiently removing highly concentrated dyes from dye-contaminated water.

EXPERIMENTAL PROCEDURES

Reagents and compound characterizations. All the reagents were obtained from commercial suppliers and used as received unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance HD400 spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured using an SHIMADZU LCMS-8030. The solvent signal of $CDCl_3$ was referenced at δ = 7.26 ppm or 77 ppm for ^{1}H and ^{13}C NMR, respectively. Coupling constants (*J* values) were reported in Hertz (Hz).

Typical synthetic procedure. Fmoc-Ala-OH (311 mg, 1.00 mmol), *n*-dodecylamine (185 mg, 1.0 mmol) and BOP (486 mg, 1.10 mmol) were dissolved in CH_2Cl_2/DMF (20 mL/10 mL) to which DIEA (0.39 ml, 2.20 mmol) was added. The reaction mixture was stirred for 20 h at room temperature. Solvent was removed in *vacuo* and the crude product was dissolved in CH_2Cl_2 (50 mL), washed with water (2 x 50 mL) and dried over Na_2SO_4 to give the crude product, which was subject to flash column chromatography (MeOH:CH_2Cl_2 = 1:25, v:v) to yield pure product **F-A-12** as a white solid. Yield: 445 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 6.35 (s, 1H), 5.67 (d, *J* = 6.1 Hz, 1H), 4.37 (d, *J* = 6.3 Hz, 2H), 4.29-4.13 (m, 2H), 3.28-3.14 (m, 2H), 1.50-1.42 (m, 2H), 1.38 (d, *J* = 5.0 Hz, 3H), 1.32-1.18 (m, 18H), 0.92-0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.28, 156.12, 143.76, 141.32, 127.79, 127.12, 125.08, 120.03, 67.08, 50.57, 47.12, 39.67, 31.94, 29.67, 29.62, 29.57, 29.48, 29.38, 29.30, 26.89, 22.72, 18.89, 14.16. MS-ESI: calculated for $[M+Na]^+$ ($C_{30}H_{42}O_3N_2Na$): m/z 501.31, found: m/z 501.26.

Stable to inversion method for minimum gelation concentration (MGC) determination. The MGCs of the peptide gelators were determined using a dilution method. First, 10 mg of each gelator was added to 0.2 mL of a known organic solvent in a screw-capped glass vial. Then the formed gel system was progressively diluted with a small amount of the tested solvent and the heating-cooling process was repeated until no gel was formed. The last concentration at which the gel state remained with no flow observed within 30 s after inverting the sample vial was recorded as the MGC value in the unit of % w/v (mg/100 µL). This process was repeated more than three times for each gelator and the average values were reported as the average MGC value.

Stable to inversion method for gelation in the powder state. The gelation abilities of the powder gelators were determined by adding a small amount of each gelator (10 mg) into an aromatic solvent (0.2 mL) in a screw-capped glass vial, followed by gentle shaking for 6 s and then resting at room temperature. The sample was regarded as a gel if no flow was observed after inverting the sample vial.

Method for phase-selective gelation by powder gelators. Generally, a weighted amount of each peptide gelator was added to a biphasic mixture of an appropriate organic solvent (0.5 mL) and water (2.0 mL) in dry powder form *via* simple shaking at gelator loading of 5% w/v at room temperature. Selective gelation of the organic phase was achieved upon resting the sample at room temperature. Gel was confirmed by complete absence of flow of the aromatics by visual inspection.

Scanning electron microscopy (SEM). SEM images were obtained using a field-emission scanning electron microscope (JEOL JSM-6700F, Japan). A small amount of petrol gel was placed on copper tape attached aluminum stub, and allowed to dry overnight under ambient conditions. Sample was then sputter-coated with a thin layer of Pt, and subjected to SEM observation at an accelerating voltage of 20 kV.

Rheological study: Rheological studies of gels at biphasic MGCs (BMGCs) were performed using an ARES-G2 rheometer (TA Instruments, U.S.A.) equipped with a plate (8 mm diameter). The gels were equilibrated at 25ºC between the plates that were adjusted to a gap of 2.0 mm. The storage modulus (G') and loss modulus (G") of gels were first measured in strain sweep (0.01–100%) modes at a constant frequency of 1 Hz, followed by a frequency scan of 1.0 to 100 rad/s under the controlled strain of 0.1%. Experiments were repeated twice to ensure the reproducibility.

Dye adsorption measurement. The capacities by gels to absorb dye from their aqueous solutions were determined using UV/vis spectroscopy. And the final concentrations of the dyes in the aqueous solutions were calculated following the Beer–Lambert law ($A = \alpha lc$, *A* is the absorbance of the dye at a certain absorption wavelength, α is the extinction coefficient in the unit of $L \cdot mg^{-1} \cdot cm^{-1}$, *l* is the path length of the incident light in the unit of cm, and *c* is the concentration of the dye in solution). Crystal violet (CV), rhodamine B and methylene blue were selected for investigation, and the maximum absorption wavelengths for monitoring the absorption process were 585, 555 and 664 nm, respectively. The absorption efficiency (AE) was calculated using equation of RE = $(C_1 - C_0)/C_0$, in which C_0 represents the initial concentration of the dye in solution and C_1 is the final concentration of the dye in the presence of an adsorbing agent.

RESULTS AND DISCUSSION

Molecular design of the gelator library. As illustrated in Fig 1, the gelator library is derived from commercially available Fmoc-protected (Fmoc = fluorenylmethyloxycarbonyl) amino acids (**A**, **V**, **L**, **I** and **F**) with their N-terminus amidated via one step reaction using straight alkyl chains of 4 to 16 carbon atoms (Fig. 1). Combinations among five types of amino acids and seven types of alkyl chains generate 35 simple monopeptide molecules. The potential of these monopeptides to act as the gelator stems from the ability of the two amide bonds to cross-link, via intermolecular H-bonds, the molecules into one dimensionally aligned structures, which further entangle with each other to produce 3D gelling network for entrapment of liquid to be gelled. In fact, molecules containing straight alkyl chains of 4 to 10 carbon atoms recently

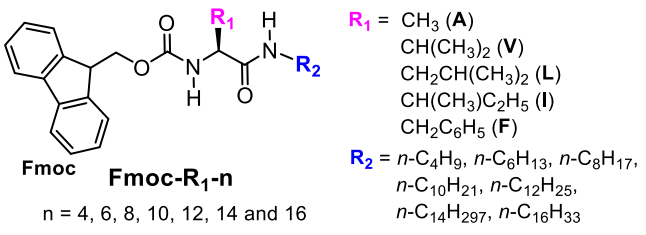


Fig. 1 Structures of monopeptide-based PSOGs, with groups of R_1 and R_2 combinatorially variable to generate 35 library members.

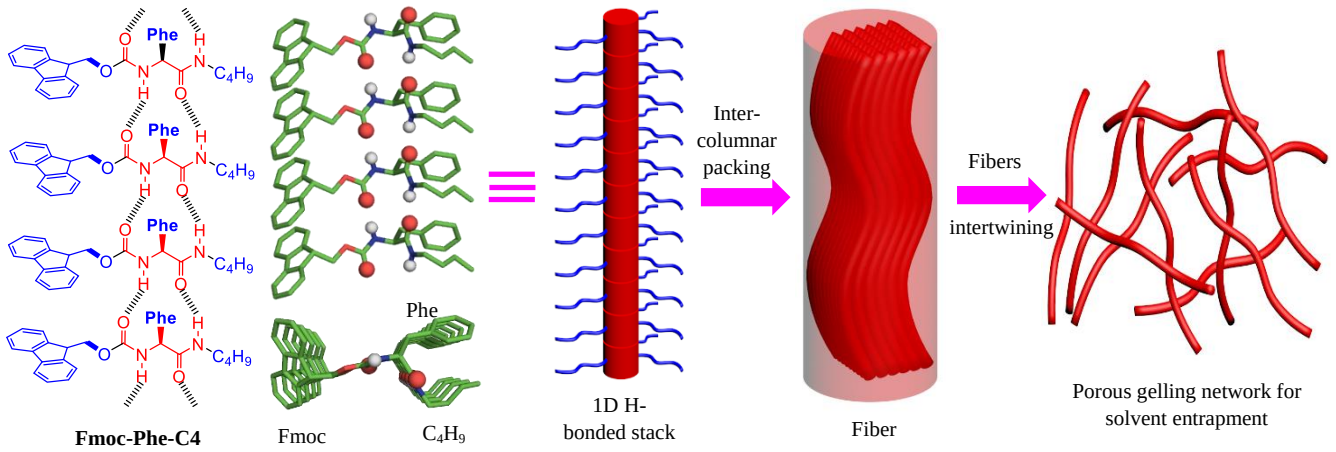


Fig.2 Hypothetic hierarchical formation of supramolecular gelling network by one-dimensionally aligned H-bonded gelator molecules. Crystal structure of **Fmoc-Phe-C4**, revealing the formation of well-defined 1D columnar structure, was recently reported by us.[38]

have been demonstrated to gel crude oils, via a hierarchically formed supramolecular gelling network (Fig. 2), with moderate to excellent gelling capacities, i.e., minimum gelation concentrations (MGCs) to range from 0.29% w/v to 3.10% w/v (mg/100 μL), .[38]

Moreover, this simple modularly tunable molecular monopeptide-based gelling scaffold turns out to be exceptionally robust in that aromatic Fmoc can be replaced by a variety of both aromatic[39,41] and non-aromatic[44] groups, invariably producing high capacity PSOGs after a combinatorial screening of R_1 and R_2 groups.

With an aim to identify good PSOGs for room-temperature gelation of aromatics,[7,47] we have additionally included alkyl chains having 12 to 16 carbon atoms for a systematic examination of side chain effect on phase-selective gelling properties. The syntheses and characterizations (i.e., ^{1}H and ^{13}C NMR spectra and mass spectrometry) of these 15 new compounds can be found in the Supporting Information.

Gelation properties determined by a heating-cooling process. The gelation capacities of these 35 monopeptides were determined by the conventional stable-to-inversion method via a heating-cooling process. That is, after cooling to room temperature, gel formation was confirmed by complete absence of gravitational flow within 30 s when the gelling-containing glass vial was turned upside-down. From the experimental results summarized in Table 1, at least two trends can be identified. For one, leucine-based monopeptides tend to have a good solubility in aromatics, and only the ones containing alkyl chains of 14 or 16 carbon atoms can function as the gelators. For the other, protic aromatics (e.g., benzyl alcohol and aniline) are more difficult to gel than aprotic ones (e.g., benzene, toluene, xylenes and nitrobenzene). This is because aprotic solvents such as benzene won't interfere with H-bonded 1D columnar structure formed among gelator molecules, which subsequently associated with each other to generate fibers of various sizes. Further intertwining of fibers results in the formation of gelling network. In protic solvents such as benzyl alcohol and aniline that contain H-bond-competing hydroxyl groups, H-bonded 1D stacks are more difficult to form and their stabilization requires additional assistance from aromatic π-π stacking as seen in phenylalanine-derived gelators (e.g., **Fmoc-F-n**, n = 6, 8, 12, 14 and 16, Table 1) or enhanced VDW forces among elongated alkyl chains as seen in gelators that carry long $C_{14}H_{29}$ or $C_{16}H_{32}$ alkyl groups (e.g., **Fmoc-aa-14** or 16, **aa** = **A**, **V**, **I** and **L**, Table 1).

The MGCs of the remaining 31 gelators (except for four leucine derivatives) are 1.01% w/v - 4.23% w/v for benzene, 0.65% w/v - 3.69% w/v for toluene, 0.70% w/v - 4.02% w/v for xylenes and 1.11% w/v - 4.53% w/v for nitrobenzene. Among five types of amino acids, valine appears to perform generally better than other amino acids, with isoleucine derivatives the second best. In particular, **Fmoc-V-n** (n = 4, 6, 8 and 10) display high gelling capacities of 0.73% w/v - 1.21% w/v toward benzene, toluene and xylenes.

Gelation properties determined in the powder form. The potential of these gelators to gel the aromatics in the powder state was then examined via shaking 0.2 mL aromatic solvent containing gelator at 5% w/v loading for 6 s at room temperature, followed by resting the solution for observing gel formation within a restrict time frame of 1 h at room temperature. 7 out of 35 monopeptides tested show room-temperature gelling abilities to varying extents in the powder form (Table 2). Among them, **Fmoc-A-6**, **Fmoc-V-6**, **Fmoc-I-6** and **Fmoc-I-8** all are able to gel benzene, toluene, xylenes (a mixture of isomeric *ortho*, *meta* and *para*-forms) and nitrobenzene within 10 min at room temperature. The gelling times for the best powder gelator **Fmoc-V-6** to gel benzene, toluene, xylenes and nitrobenzene are 2, 2, 2 and 8 min, respectively.

With **Fmoc-V-6**, we have also investigated the impact of the gelator loading amounts on the gelling time, and we compared four loading amounts from 3% w/v to 6% w/v. The data presented in Fig. 3 clearly point to dramatic effects by minute increases in gelator loading amount. More specifically, in all four aromatics studied, an increase in gelator loading amount from by 3% w/v to by 6% w/v shortens the gelling time by more than 88 times, and gelling times for gelling benzene, toluene and xylenes are shortened to 6 s, 6 s, 6 s and 3 min, respectively. These indicate instant gelation of these three aromatics at room temperature in the presence of **Fmoc-V-6**.

In further detail and take benzene as the example, the gelling times are shortened from 125 min to 7 min by 16 times, from 7 min to 2 min by 3.5 times, and from 2 min to 0.1 min by 20 times upon respective increases of the loading amounts from 3% w/v to 6 % w/v at an increment of 1% w/v. Similar drastic enhancements are seen for both toluene and xylenes (Fig. 3). It might be worth mentioning that powder-based PSOGs for gelling aromatics are very limited.[7,42-27] Recently, Yu[7] and Song[47] reported glucose- and

Table 1. Gelation abilities (MGC values in % w/v, mg/100 µL) of gelators in five types of aromatics.[a,b]

	Benzyl alcohol	Benzene	Toluene	Xylenes[c]	Nitro-benzene	Aniline
Fmoc-F-4	S	4.15	3.59	1.82	2.41	4.53
Fmoc-F-6	2.75	3.12	3.68	2.51	1.65	4.50
Fmoc-F-8	3.50	PG	3.60	1.93	2.07	3.60
Fmoc-F-10	S	4.23	3.69	S	4.56	S
Fmoc-F-12	2.51	3.09	3.63	S	4.35	1.49
Fmoc-F-14	1.92	3.25	2.03	3.11	1.22	1.49
Fmoc-F-16	1.75	2.50	3.61	4.02	2.93	2.60
Fmoc-A-4	S	1.85	2.15	0.75	4.92	S
Fmoc-A-6	S	2.19	1.65	1.56	S	S
Fmoc-A-8	S	2.23	2.03	0.73	S	S
Fmoc-A-10	S	2.39	2.39	1.65	S	S
Fmoc-A-12	S	3.12	2.26	2.23	S	S
Fmoc-A-14	2.50	2.86	1.86	2.11	S	3.43
Fmoc-A-16	1.61	2.50	1.50	1.15	2.88	2.78
Fmoc-V-4	S	0.90	1.21	0.89	2.07	S
Fmoc-V-6	S	1.04	0.94	0.70	2.33	S
Fmoc-V-8	S	1.03	0.65	0.81	1.77	S
Fmoc-V-10	S	0.92	0.81	0.73	2.49	4.34
Fmoc-V-12	S	1.01	1.58	1.85	2.49	2.51
Fmoc-V-14	2.40	0.90	1.36	1.69	1.06	1.71
Fmoc-V-16	1.52	1.21	1.12	1.58	1.48	1.15
Fmoc-I-4	S	1.35	0.95	0.85	1.75	S
Fmoc-I-6	S	1.25	0.85	0.79	1.72	4.80
Fmoc-I-8	S	1.16	0.76	0.70	1.68	S
Fmoc-I-10	S	2.01	1.29	1.55	1.99	S
Fmoc-I-12	S	2.10	1.20	0.85	1.29	3.34
Fmoc-I-14	1.63	2.03	1.13	1.13	1.95	1.43
Fmoc-I-16	1.08	1.45	1.15	1.10	1.60	1.11
Fmoc-L-4	S	S	S	S	S	S
Fmoc-L-6	S	S	S	S	S	S
Fmoc-L-8	S	S	S	S	S	S
Fmoc-L-10	S	S	S	S	S	S
Fmoc-L-12	S	S	S	S	3.33	S
Fmoc-L-14	2.63	2.13	2.10	1.75	2.61	3.01
Fmoc-L-16	1.88	2.10	2.02	2.13	3.55	2.44

[a] All the MGC values were determined by using a heating-cooling (stable-to-inversion) method. [b] S = soluble and PG = partial gel at gelator loading of 5% w/v. All gels formed at room temperature are stable at least for one month. [c] A mixture of isomeric *ortho*, *meta* and *para*-forms of xylene commercially available from Sigma

D-gluconic acetal-based powder PSOGs that can phase-selectively solidify aniline/nitrobenzene (> 4.5% wt) and benzene/toluene/xylene (1.8 – 2.3% wt), respectively, at room temperature within minutes. In other words, our work reported here represents the 3rd type of powder gelators for room-temperature phase-selective gelation of aromatic solvents.

Phase-selective gelation of aromatics in the presence of water. The ability to phase selectively gel aromatics in the presence of water is one of key requirements for the practical application of

Table 2. Gelling times (min) for achieving room-temperature gelation of aromatics by peptide gelators in the powder form at gelator loading of 5% w/v.

	Benzyl alcohol	Benzene	Toluene	Xylenes[c]	Nitro-benzene	Aniline
Fmoc-A-6	N	5	8	12	N	N
Fmoc-V-6	N	2	2	2	8	N
Fmoc-V-12	N	5	5	6	60	PG
Fmoc-V-16	PG	T	23	12	T	T
Fmoc-I-4	N	35	PG	3	PG	N
Fmoc-I-6	N	6	2	2	10	T
Fmoc-I-8	N	4	2	2	10	N

[a] All the gelling times were determined by shaking the gelator-containing solution for 6 s, followed by resting the sample at room temperature; gelling times beyond 1 h were not recorded. [b] N = no gel formed, PG = partial gel and T = turbid fluid state. [c] We have also determined the room-temperature gelation of *ortho*, *meta* and *para*-xylenes using four gelators **Fmoc-A-6**, **Fmoc-V-6 Fmoc-I-6**, and **Fmoc-I-8** at the same gelator loading of 5% w/v. And we found that the gelling capacities of the four gelators toward xylenes are near-identical to those toward ortho, meta and para-xylenes.

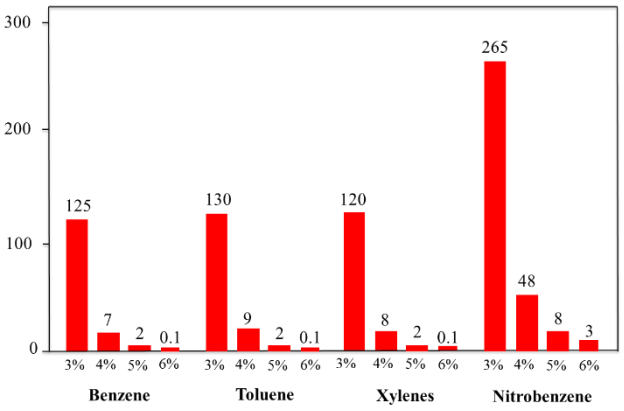


Fig. 3 Times (min) taken for **Fmoc-V-6** to gel benzene, toluene, xylenes and nitrobenzene at room temperature in the powder form at gelator loading amounts of 3% w/v to 6% w/v. Gelator-containing solution was first shaken for 6 s before resting at room temperature until gel was formed.

a PSOG in the treatment of an oil spillage. To demonstrate this feasibility, the best powder gelator **Fmoc-V-6** was taken for further study at 5% w/v loading amount. Procedurewise, 25 mg of **Fmoc-V-6** was added into a biphasic systems comprising 0.5 mL benzene and 2.0 mL water, and the resultant mixture was shaken for 6 s to facilitate dispersion or dissolution in aromatics. Upon resting the mixture for < 2 min, a gel was not only formed but also sufficiently strong to support water that is 4.6 times of its own weight (Fig. 4a). In the same way, toluene, xylenes and nitrobenzene can be gelled within 2 min by 5% w/v of **Fmoc-V-6** and, except for nitrobenzene gells, are also able to support water 4.6 times of their own weights (Fig. 4b-d). Since the density of nitrobenzene (1.2 g/cm^3) is greater than that of water, the nitrobenzene gel formed remained at the bottom of the vial when the vial was inverted (Fig. 4d). We have further studied three more volumetric ratios of benzene (0.25, 0.75 and 1.0 mL) over water (2 mL). In all three cases, instant phase-selective gelation within 2 min were similarly observed. We have

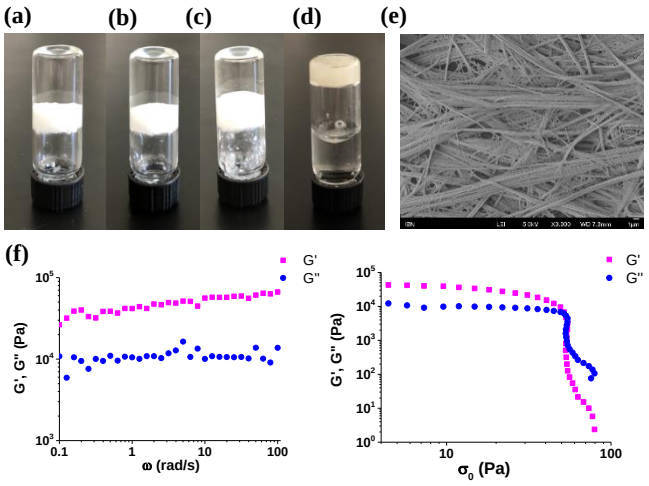


Fig. 4 (a)-(d) depict the gels phase-selectively formed from benzene, toluene, xylenes and nitrobenzene at room temperature in the presence of **Fmoc-V-6** at 5% w/v. (e) SEM image of the as-formed benzene gels. (f) Dynamic rheological studies of the as-formed benzene gels; G' = storage modulus, G" = loss modulus, frequency sweep = ω, and stress amplitude = σ_0.

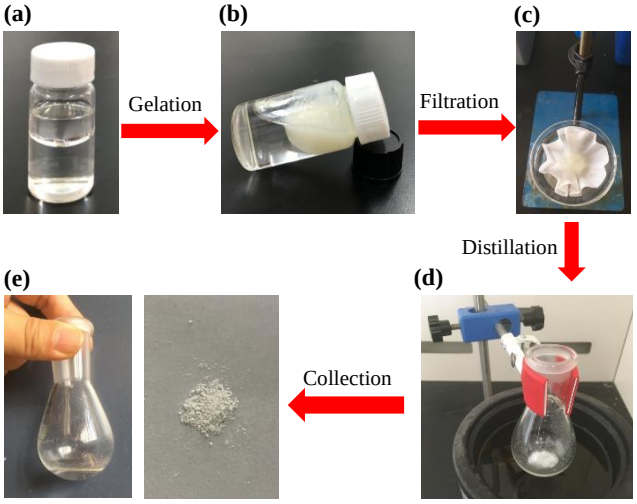


Fig. 5 Schematic illustration of recovery of gelled xylenes and gelator through filtration and distillation. (a) A mixture of water (10 mL) and xylenes (5 mL). (b) Gel formation by **Fmoc-V-6** (250 mg). (c) Separation of the gels from water by filtration. (d) Distillation to recycle both xylenes and gelator (e).

also further studied the possibility of using 5% wt of the powder gelator to gel the emulsified aromatics (0.5 mL of benzene, toluene or xylene) in water (2 mL). Again, in all three cases, we observed instant gelation of emulsified aromatics within seconds (Supporting movies 1-3). Additionally, such instant gelation was not affected by pH (3, 7 or 11) or presence of NaCl at high concentration (35 g, 0.6 M), suggesting potential of its uses in real environment.

The SEM images of the as-formed benzene gels (Fig. 4e) as well as toluene and xylene gels (Fig. S1) reveal extensive formation of the fibrous structures, further assembling into a 3D gelling network that trap the benzene molecules, via surface tension and capillary forces, to turn liquid aromatics into a semi-solid gel state.

As shown in Fig. 4f, the facts that the storage modulus G' of the as-formed benzene gels is largely independent of frequency while remaining much larger than loss modulus G'' across the whole frequency sweep range studied suggest excellent elasticity of the gels. A relative high value of 7.0×10^3 Pa for the storage modulus G', which serves as an indicator of gel strength, demonstrates the remarkable stiffness and strength of the benzene gels. Consistent with the ability of the benzene gels to support the water layer (Fig. 4a), this high mechanic strength, together with facts that these as-formed gels are stable for months and exhibit no thixotropy property at room temperature, makes **Fmoc-V-6** suitable for application in oil spill treatment.

In addition, a likelihood to recycle both gelled aromatics and gelator was demonstrated (Fig. 5). Briefly, 250 mg of **Fmoc-V-6** in the powder form was added into a biphasic system composed of 5 mL of xylenes and 10 mL of water. After shaking the mixture for 6 s and resting at room temperature for 1 min, the formed gels were separated from water by filtration. Subsequent distillation recovers both the gelled xylenes and gelator molecules nearly quantitatively.

Highly efficient dye absorption. With the rapid development of our society, the heavy industrial discharge of water-soluble toxic dyes to groundwater on the daily basis poses a serious environmental and economic problem,[8] and effective removing of

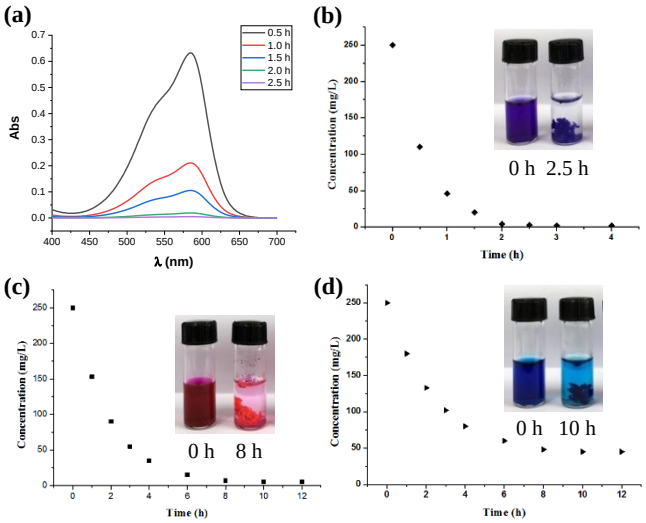


Fig. 6 (a) Time-dependent adsorption spectra recorded at 585 nm for an aqueous solution (2 mL), which contains the crystal violet dye at an initial concentration of 250 mg/L, in the presence of 0.2 mL benzyl alcohol gel formed using 2.0% w/v of **Fmoc-I-16**. (b)-(d) depict the concentration-time correlations for (b) crystal violet at 585 nm, (c) for rhodamine B at 555 nm (c) and (d) for methylene blue at 664 nm.

these toxic dyes from such as the sewage treatments has been a constant focus in recent years.[7,13,15,28,42,52-54] Since aniline, nitrobenzene or other aromatic solvents are more toxic than benzyl alcohol, benzyl alcohol was therefore chosen as a relatively safe liquid for gel formation and as subsequent dye removal medium. In this regard, we have tested all 35 monopeptides toward the gelation of benzyl alcohol, and **Fmoc-I-16** was identified to have the highest gelling ability with a MGC value of 1.08% w/v toward benzyl alcohol (Table 1). Therefore, **Fmoc-I-16** was employed for subsequent dye removal study. In a typical experiment, 0.2 mL

Table 3. Effects of pH and 0.6 M NaCl on the dye absorption efficiency.

	pH =3	pH =7	pH =11
Crystal violet	98%	99% (98%[a])	98%
Rhodamine B	94%	97% (93%[a])	96%
Methylene blue	80%	82% (78%[a])	75%

[a] Measured in the presence of NaCl at high concentration (35 g/L, 0.6 M)

Table 4. Dye absorption efficiencies by benzene gels formed by the best five gelators at 2% wt at pH 7.

	Crystal violet	Rhodamine B	Methylene blue
Fmoc-I-16	99%	97%	82%
Fmoc-F-16	96%	95%	81%
Fmoc-A-16	96%	95%	81%
Fmoc-V-16	97%	96%	82%
Fmoc-L-16	94%	93%	80%

benzyl alcohol gel, formed using **Fmoc-I-16** at loading of 2.0% w/v was loaded into a 2 mL aqueous solution containing three different dyes (i.e., crystal violet, rhodamine B and methylene blue) at a high concentration of 250 mg/mL. The abilities of **Fmoc-I-16** to remove these dyes were monitored at 585 nm, 555 nm and 664 nm, respectively, using UV/vis spectroscopy. The representative time-dependent absorption curves for crystal violet are presented in Fig. 6a and the concentration-time correlations for the three dyes are plotted in Fig. 6b-d. As evidenced from Fig. 6b-d, the dye removal efficiencies from their aqueous solutions by benzyl alcohol gels reach 99%, 97% and 82% for crystal violet, rhodamine B and methylene blue after 2.5, 8.0 and 10.0 h, respectively. It might be worth mentioning that the dye-absorbing capacity for methylene blue plateaus at 82% around 10 h, after which time we observed the same absorption efficiency of 82% at both 18 and 24 h. Moreover, dye absorption efficiency of 97% was obtained at 12 h for a mixture of dyes consisting of crystal violet and rhodamine B in equal weight. Although we are not certain why the absorption times (i.e., 2.5 – 10 h) to reach the maximum absorptions vary substantially among the three dyes, there are a number of preceding examples that suggest dye-absorption process often is a time-consuming process, taking up to 24 h for achieving the maximum absorption[7,28].

Further investigations were then carried out to examine the effects of pH or salt on the absorption capacity of the gelator (Table 3). We found variations in pH or the presence of NaCl at concentration of as high as 0.6 M exert insignificant influence on dye sorption efficiencies, which nevertheless reach the maximum absorption capacities at neutral condition. At pH 7, inclusive of the weight of benzyl alcohol, the maximum dye sorption capacities were determined to be 10.14 mg/g for crystal violet, 10.02 mg/g for rhodamine B, 1.93 mg/g for methylene blue.

Interestingly, we found that either MeOH or EtOH allows the gelators to be recycled after dye absorption. Specifically, addition of 1.0 mL of essentially non-toxic EtOH (or more toxic MeOH) into 0.2 mL of dye-absorbed benzyl alcohol gels turns the gels into solution, dissolving away dye and benzyl alcohol while precipitating the gelator out. A Subsequent filtration near-quantitatively recovers gelator by 96% for re-use.

In addition to these cationic dyes, we have also tested the ability of both benzyl alcohol and aniline-based gels formed by **Fmov-V-6** toward absorbing anion dyes (*i.e.*, Congo red and Trypan blue). For reasons unclear to us, these gels turn out to be incapable of extracting these anionic dyes from water.

Lastly, to check the effect gelators of different types might have on the dye removal efficiency, we have measured and compared the dye removal efficiencies by benzyl alcohol gels formed by the best five gelators (**Fmoc-I-16**, **Fmoc-F-16**, **Fmoc-A-16**, **Fmoc-V-16**, and **Fmoc-L-16**) at pH 7. Results summarized in Table 4 indicates insignificant differences among the five gels across three dyes.

The above findings indicate that **Fmoc-I-16** and its associated benzyl alcohol gels can be used as an alternative sewage treatment agent for removing the toxic dyes, particularly given that small peptides are generally biodegradable.[55]

CONCLUSIONS

In summary, a series of peptide gelators have been synthesized in one step generally with high yields, which may satisfy the cost-effective requirement of mass production in industrial scale for practical applications. A combinatorial screening of a total of 35 candidates allowed us to identify **Fmoc-V-6** as the best powder gelator capable of instantly and phase-selectively gelling toluene, toluene and xylenes in the presence of water in less than one minute at room temperature at gelator loading of 6% w/v. In addition to common advantages associated with phase-selective organogelators (e.g., simple filtration to separate formed gels from water, and distillation to recover gelator for re-use), such a solvent-free approach completely eliminates the toxicities and risks associated with the flammable solvents required by solution-based gelators. As such, **Fmoc-V-6**, which is possibly biodegradable,[53] may offer practical benefits for its possible use in removing organic pollutants from the environment. In addition, the gelator **Fmoc-I-16**, having the highest gelling ability toward benzyl alcohol among 35 gelators studied, could combine with benzyl alcohol to produce gels for efficiently removing dyes (crystal violet, rhodamine B and methylene blue) form their highly concentrated aqueous solutions, with removal efficiencies of 99%, 97% and 82%, respectively. These findings let us to believe that these peptide gelators may find promising use as effective sewage treatment agents in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.

Synthetic scheme, experimental procedures and a full set of characterization data including ^{1}H NMR, ^{13}C NMR and MS as well as SEM images of the as-formed gels and supporting movies 1-3.

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Notes

The authors declare no competing financial interest.

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