

## Research



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# Peptide-based ambidextrous bifunctional gelator: applications in oil spill recovery and removal of toxic organic dyes for waste water management

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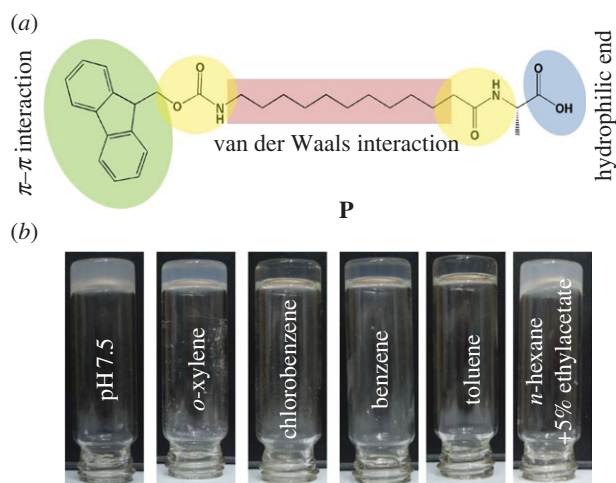
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A low molecular weight peptide-based ambidextrous gelator molecule has been discovered for efficient control of water pollution. The gelator molecules can gel various organic solvents with diverse polarity, e.g. *n*-hexane, *n*-octane, petroleum ether, petrol, diesel, aromatic solvents like chlorobenzene, toluene, benzene, *o*-xylene and even aqueous phosphate buffer of pH 7.5. These gels have been thoroughly characterized using various techniques including field emission scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray powder diffraction analysis, small angle X-ray scattering and rheological experiments. Interestingly, hydrogel obtained from the gelator molecule has been found to absorb toxic organic dyes (both cationic and anionic dyes) from dye-contaminated water. The gelator molecule can be reused for several cycles, indicating its possible future use in waste water management. Moreover, this gelator can selectively gel petrol, diesel, pump oil from an oil–water mixture in the presence of a carrier solvent, ethyl acetate, suggesting its efficient application for oil spill recovery. These results indicate that the peptide-based ambidextrous gelator produces soft materials (gels) with dual function: (i) removal of toxic organic dyes in waste water treatment and (ii) oil spill recovery.

## 1. Introduction

Low molecular weight gelators [1–12] are important systems exploiting molecular assembly [13–17] with many fascinating applications for modern society [18–20]. In this category, peptide- and amino acid-based gels [21–34] are important classes of materials owing to their bioavailability and biocompatibility [24,35]. They are associated with various non-covalent interactions like hydrogen bonding,  $\pi$ – $\pi$  interactions, van der Waals forces and hydrophobic interactions [24]. Amino acid- and peptide-based gels have numerous applications including encapsulation and sustained release of drugs [24,28,36], tissue engineering, dye absorption from waste water [37–40], oil spill recovery [41,42], synthesis of nanoparticles [43,44] and nanoclusters [45] and catalysis [31,46]. Although the old adage of chemists says 'like dissolves like' [47], amphiphilic molecules are somewhat different; within an amphiphilic molecule two different sites are available and this promotes the affinity of these molecules in both polar and non-polar solvents in both aqueous and non-aqueous media. This triggers the self-assembly of these molecules in different solvents like water and organic solvents [48]. Interestingly, some gelators (with amphiphilic character) can gel both polar and non-polar solvents with a diverse polarity profile, including aqueous solutions and various organic solvents with different polarities; these gelators are termed as ambidextrous



**Figure 1.** (a) Gelator molecule with various zones of interactions like  $\pi$ - $\pi$  interactions (green), hydrogen-bonding sites (yellow), van der Waals interactions (red) and the polar head group (blue). (b) Gels formed by **P** in different solvents.

gelator molecules [49–53]. Though there are many examples of hydrogels and organogels in the literature, ambidextrous gels are less reported, because they are generally found by serendipitous discoveries. Though there are some examples of ambidextrous amphiphilic gelators, peptide-based ambidextrous gelators are limited to only a few [54]. So, there is a real need to create an ambidextrous gelator that can not only gel both aqueous and organic solvents but also exhibit different functions in two different types of solvents (aqueous and organic) in which it can form gels.

In our current piece of work, we have synthesized a peptide-based amphiphilic molecule **P** (figure 1a) which was found to form a gel in a versatile range of solvents. **P** can efficiently gelate water with a pH value ranging from 7.5 to 8, and aromatic solvents like benzene, toluene, chlorobenzene, *o*-xylene as well as aliphatic solvents like *n*-hexane, *n*-octane and petroleum ether (figure 1b). Therefore, **P** is a perfect example of an ambidextrous gelator which can gelate numerous solvents with diverse polarity. Dyes have been known as colouring agents since the early days of civilization and dyes are now produced in a diversity of types and in large quantities by chemical industries. Dyes are common materials used in colourful clothes and accessories; therefore, the corresponding industrial waste contains a lot of unused dyes. However, most of these dyes are toxic and under degradation they produce many carcinogenic pollutants [55]. Materials like activated carbon and other nonconventional adsorbents such as zeolites, mineral clays, sawdust and waste biomatter are frequently used to remove toxic dyes from waste water, but they have many shortcomings, including the production of volumes of solid waste, low absorption efficiency and costly regeneration processing [20]. In this context, it is worth noting that hydrogels are good candidates for the removal of toxic organic dyes from waste water in an eco-friendly manner. Gels are basically porous materials with huge interstitial spaces within their matrices which can absorb dye molecules from waste water [20,37–40,56–61]. Numerous hydrogels have been reported in the scientific literature to absorb organic dyes from waste water. Chitosan-based hydrogels mixed with folic acid have been found to absorb Eosin yellow, Methyl orange and Methylene

blue from waste water [60]. Recently, a dibenzylidene sorbitol gelator functionalized with hydrazides has been developed for pH-dependent selective absorption of organic dyes [59]. A small dipeptide superhydrogelator has also been introduced for efficient removal of toxic organic dyes with a high grade of absorption efficacy and reusability [61]. Interestingly, it was found that the hydrogel formed by **P** can absorb a number of toxic organic dyes including Acid black-1, Congo red, Direct red-80, Malachite green and Rhodamine B from waste water. Moreover, it shows reusability of up to three cycles of recovery, which indicates its promising future application in waste water management.

Oil spills are one of the major causes of pollution in sea water; the last few decades have witnessed dangerous oil spill events like the Exxon Valdez disaster that damaged the marine ecosystem of the Prince William Sound area [62]. There is a wide range of materials for remediation of spilled oil by employing dispersants, absorbents, solidifiers, booms and skimmers. Dispersants accelerate the dispersion of oil and separate it from water by absorption. Absorbents simply separate the oil by absorption, whereas solidifiers are dry granular hydrophobic polymers which facilitate oil solids to float in water. Booms and skimmers confine spilled oil in a particular area and stop its free flow [63]. However, these methods have shortcomings, sometimes due to inherent toxicity and sometimes due to difficulty in the recovery of oil from the separated substances [64]. Gels are emerging materials for phase-selective oil spill recovery [65–67]. Ambidextrous gelator **P** has been successfully used to remove fuel oil from an oil–salt water biphasic mixture. Moreover, this compound can be reused several times without a significant loss of activity.

These kinds of bi-functional gels are very important materials to study as they are cost-effective systems with important application in waste remediation. Here, we have shed light on the design, synthesis and characterization of new gelator molecules for multiple functional uses including selective remediation of organic solvents including oil compounds.

## 2. Experimental details

The peptide **P** was synthesized by a simple *N*-hydroxy-succinimide-assisted coupling of two segments, Fmoc-ADDA and  $\text{H}_2\text{N-Ala-COOH}$ , and was purified by simple column chromatography to get the final product (synthetic details and characterization details are given in the electronic supplementary material).

### 2.1. Gelation experiments

To check the gelation ability in different solvents, a definite weighed amount of gelator peptide was taken in a screw-capped machine-made vial with a total volume of 5 ml. Into this vial, 500  $\mu\text{l}$  of a desired solvent (in which the gelation will be checked) was added, followed by heating on a hot plate. At higher temperature, the solubility of a solute was increased significantly, therefore the vial was subjected to repetitive heating and then cooling at room temperature (27–30°C) to dissolve the entire mass of the peptide in that particular solvent. Finally, the vial was kept at room temperature. After a few minutes (depending upon the solvent),

the vial was examined to find out whether a stable gel was formed or not.

## 2.2. Dye absorption studies

To check the dye absorption ability of hydrogels, different sets of hydrogels were prepared by dissolving 5 mg of the gelator peptide **P** in 1 ml of pH 7.5 phosphate buffer solution. Solutions (8  $\mu$ M) of different dyes were prepared by proper weighing and subsequent dilution; 1 ml of as-prepared solutions was then placed over the hydrogel matrix (net volume 1 ml). The concentration of dye that remained in the solution was monitored from time to time by using a Varian Cary 50 Bio UV–visible (UV–Vis) absorption spectrophotometer.

## 2.3. Reusability of **P** after the absorption of dyes

After absorption of a mixture of dyes, namely Acid black 1, Malachite green and Rhodamine B, the coloured gel was taken out of the vial and treated with a minimum volume of 1(N) HCl solution in the presence of ethyl acetate. The gelator molecules are insoluble in acidic pH, therefore these molecules go into the organic layer. The organic layer was then dried with anhydrous sodium sulfate and ethyl acetate was removed under vacuum to get the solid gelator compound back. The final weight of the extracted compound was measured after each cycle and then it was gellified again to absorb new batches of dye solution.

## 2.4. Oil spill recovery

Different sets of salt water and oil biphasic mixture were prepared with different types of oils including petroleum ether, diesel, petrol and pump oil. A weighed amount of gelator peptide **P** was then dissolved in a minimum volume of ethyl acetate (10% w/v) and then it was injected (100  $\mu$ l of the stock solution was used for injection in each set) into 4 ml of a 1:1 salt water–oil mixture. The time of gelation was recorded for each set.

## 2.5. Recovery of the spilled oil

The gellified oil part was taken out of the vial with the help of a spatula and placed in a round bottom flask. The gellified oil was then subjected to distillation in a rotor evaporator to get the spilled oil in a collector and the gelator compound in the round bottom flask (electronic supplementary material, figure S7). This gelator was used for the recovery of another set of oil spill. Details of instrumentation are given in the electronic supplementary material.

# 3. Results and discussion

## 3.1. Gelation studies

A dipeptide amphiphilic molecule **P** (figure 1a) has been designed in such a way that it contains a free carboxylic acid end in the C-terminus and the N-terminus is protected by a 9-fluorenylmethyloxycarbonyl (Fmoc) group, containing a bulky aromatic unit, to provide  $\pi$ – $\pi$  interaction in self-association. Moreover, the oligomethylene unit of the 12-aminododecanoic acid (ADDA) residue contributes van der Waals interactions and sufficient hydrophobicity in the molecule. In addition to that, the intervening peptide linkage (CO–NH) and the urethane (O–CO–NH) unit can participate in hydrogen bonding, so that these amphiphilic

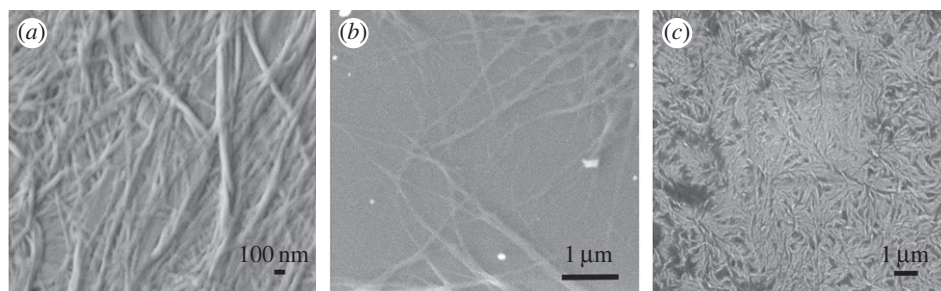
**Table 1.** Gelation behaviour of **P**. G stands for gel, S stands for solution and MGC means minimum gelation concentration.

solvent	gelation activities
pH 7.5 buffer solution	G (MGC 0.5 wt%)
chlorobenzene	G (MGC 0.6 wt%)
toluene	G (MGC 0.8 wt%)
<i>o</i> -xylene	G (MGC 0.5 wt%)
benzene	G (MGC 1 wt%)
<i>n</i> -hexane (with 5% ethyl acetate)	G (MGC 1.5 wt%)
dimethylsulfoxide	S
methanol	S
ethyl acetate	S

molecules can be self-assembled in water as well as non-aqueous organic media by using these non-covalent interactions. Figure 1a shows the chemical structure of the gelator molecule **P**, indicating different parts of the molecule that participate in various non-covalent interactions. To check the gelation ability of dipptide **P**, a weighed amount of compound was placed in a capped vial and then a measured amount of the desired solvent was added into it, followed by repeated heating and cooling cycles for a few times, followed by cooling to room temperature to get the gel. The compound was found to form a hydrogel in phosphate buffer medium of pH 7.5–8, and organogels with aromatic solvents including toluene, *o*-xylene, chlorobenzene, benzene and aliphatic solvents like *n*-hexane and octane (figure 1b) including crude solvents like petroleum ether, diesel, pump oil and petrol. The minimum gelation concentrations were found to be 1.6, 0.6, 0.8, 0.5, 1 and 1.5% (w/v) in pH 7.5 buffer solution, chlorobenzene, toluene, *o*-xylene, benzene and *n*-hexane, respectively (table 1). In phosphate buffer solution, gelation occurs immediately after cooling to room temperature (27–30°C), whereas in aromatic solvents gelation was observed after 5–10 min of cooling. For *n*-hexane, gelation took longer, about 2–3 h. However, dissolving the gelator molecule in a minimum volume of ethyl acetate followed by addition of *n*-hexane reduced the gelation time significantly and, in that case, gelation was observed within a few seconds (approx. 15 s). The amount of ethyl acetate is only 5% (v/v) with respect to *n*-hexane. In this situation, the gelator has poor solubility in *n*-hexane, and dissolving it first in ethyl acetate and then adding *n*-hexane leads to instantaneous gelation, making it an example of anti-solvent-induced gelation [68]. All kinds of gels, except the gel in aliphatic organic solvents, show thixotropic behaviour, that is the gel is broken by mechanical shaking and it undergoes gelation upon free standing. This kind of gelation of a range of solvents ranging from water to petroleum ether is quite rare in the literature and the gel can be exploited for multiple functions. The vials containing gels obtained from phosphate buffer solution at a pH of 7.5, and organic solvents *o*-xylene, chlorobenzene, benzene, toluene and *n*-hexane (in the presence of 5% ethyl acetate) are shown in figure 1b.

## 3.2. Morphology

The morphologies of the gels formed with different solvents were investigated by field emission scanning electron



**Figure 2.** FE-SEM images of gels in (a) phosphate buffer of pH 7.5, (b) chlorobenzene and (c) *n*-hexane.

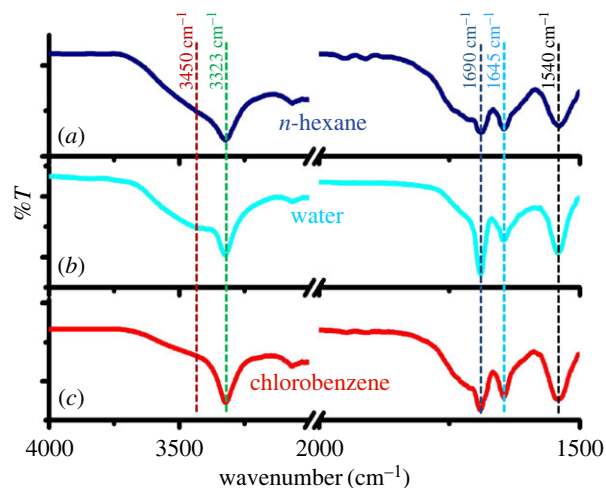
microscopy (FE-SEM). Figure 2 shows a network of fibrils from the dried gel obtained from water at a pH of 7.5 in phosphate buffer (figure 2a). Gels formed in chlorobenzene (figure 2b) and *n*-hexane (figure 2c) are also composed of a fibrillar network structure. There is a difference between the morphologies of gels obtained from chlorobenzene and *n*-hexane; this may arise due to the different structural arrangement of the gelator molecules resulting from the time difference of drying of the gel samples, as the gelator concentration was the same in all cases.

### 3.3. Fourier transform infrared analysis

Fourier transform infrared (FT-IR) spectroscopy is a powerful technique to elucidate the nature of intermolecular interactions in the gel phase. **P** has an ability to gel a large number of solvents. So the FT-IR analyses were done for dried gels obtained from *n*-hexane, water and chlorobenzene. The spectra are shown in figure 3. In all cases, characteristic peaks at 1540 (indicated with a black dotted line), 1645 (cyan dotted line) and 1690 (blue dotted line)  $\text{cm}^{-1}$  appear due to N–H bending, hydrogen-bonded C=O stretching of the amide and hydrogen-bonded C=O stretching of the urethane carbonyl attached to the Fmoc group, respectively. Therefore, it can be said that the gelator molecules in all cases are present in a sheet-like extended backbone structure [24]. The intensity of the peak at 1690  $\text{cm}^{-1}$  is almost the same for organogels obtained from chlorobenzene and *n*-hexane, whereas it is different (higher) for the hydrogel. So, the urethane C=O is more strongly hydrogen-bonded in the hydrogel network structure than in organogels obtained from chlorobenzene or *n*-hexane. Peaks near 3323 (green dotted line) and 3450 (red dotted line)  $\text{cm}^{-1}$  appear due to hydrogen-bonded and free N–H stretching of amide, respectively [69]. It can be seen from figure 3 that the shoulder at 3450  $\text{cm}^{-1}$  is stronger for the hydrogel than the organogels; therefore, it can be concluded that more amide N–Hs are free in the hydrogel compared with the organogels.

### 3.4. X-ray diffraction analysis

Small angle X-ray scattering (SAXS) analysis is an efficient technique to study the aggregation of gelator molecules in the gel phase. From SAXS data of the hydrogel, a peak corresponding to a *d*-spacing of 39 Å (figure 4a) has been found. This observation indicates that the aggregates have a size greater than a molecular length of 28 Å (calculated from the Chemdraw 3D software), but less than the double of the molecular length, i.e. 56 Å. Based on this observation, it can be stated that the molecules form an intercalated hydrogen-bonded structure (for details of SAXS fitting, see the

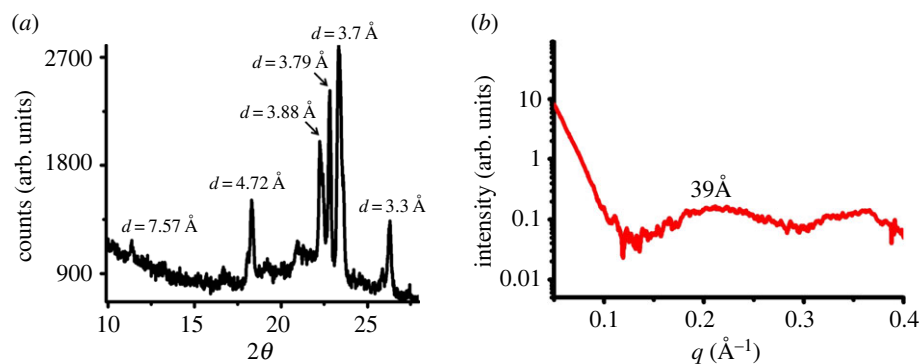


**Figure 3.** FT-IR analysis of xerogels obtained from (a) *n*-hexane gel, (b) hydrogel and (c) gel in chlorobenzene.

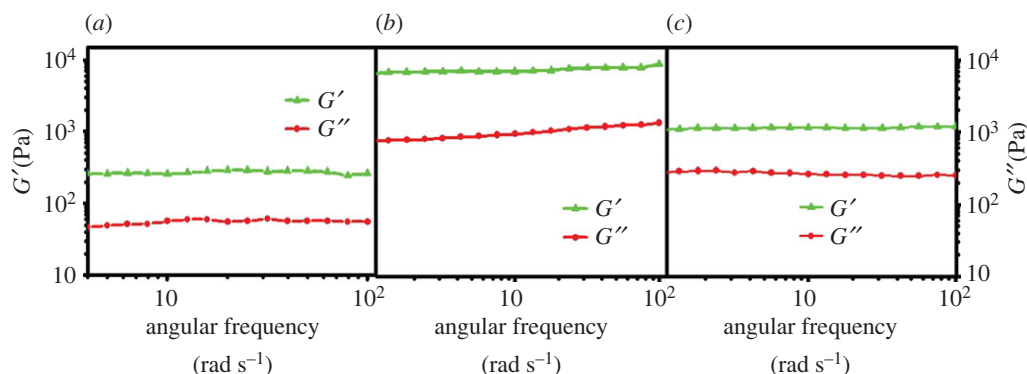
electronic supplementary material). On the other hand, X-ray diffraction of the freeze-dried hydrogel in powder form shows sharp peaks in the  $2\theta = 10\text{--}30^\circ$  region (figure 4), indicating a well-defined arrangement of the molecules in the gel phase. The peaks corresponding to the *d* values of 4.72 Å and 3.88 Å can be due to the hydrogen-bonded  $\beta$  sheet-like arrangement of the gelator molecules in the assembled gel state, whereas the peak at  $d = 3.7$  Å corresponds to the distance between two  $\pi$ -stacked layers formed by Fmoc groups in the self-assembled state [24]. From the SAXS, X-ray powder diffraction and FT-IR data a tentative model of molecular arrangement of these gelator molecules in the assembled state is proposed, as shown in the electronic supplementary material, figure S5.

### 3.5. Rheological experiments

Rheological experiments are an important tool to confirm the gelation behaviour of gels. Rheological experiments deal with two parameters: storage modulus ( $G'$ ) or elastic component, and loss modulus ( $G''$ ) or viscous component. A value of  $G'$  higher than  $G''$  and essentially independent of frequency is observed for the gel phase, and is a defining measure of gelation. Rheological experiments were carried out by using gels obtained from different solvents including pH 7.5 phosphate buffer solution, chlorobenzene and *n*-hexane, keeping the concentration of gelator at 19.6 mM in all cases. Figure 5 shows that in all cases  $G'$  is greater than  $G''$  over a range of angular frequency values and they are almost frequency-independent with no crossover, indicating the viscoelastic behaviour of the gel phase. Interestingly,



**Figure 4.** (a) X-ray powder diffraction analysis of the freeze-dried hydrogel of **P**. (b) Small-angle X-ray scattering analysis of the hydrogel **P**. (Online version in colour.)



**Figure 5.** Frequency sweep rheological experiments for gels formed by **P** in (a) pH 7.5 phosphate buffer solution, (b) chlorobenzene and (c) *n*-hexane in the presence of 5% ethyl acetate. (Online version in colour.)

it has been found that organogels are stronger (having more stiffness) than hydrogels. Moreover, the organogel obtained from chlorobenzene is more mechanically strong than the organogel obtained from *n*-hexane. So, the stiffness of the gel lies in the order: gel in chlorobenzene > gel in *n*-hexane > gel in aqueous medium at pH 7.5.

It is found that the hydrogel at a pH of 7.5 and organogels in aromatic solvents are mechanosensitive (thixotropic) in nature. This means that these gels undergo a gel-to-sol transition upon the application of mechanical stress (or under mechanical shaking) and the gel phase reappears upon withdrawal of the stress (or under free standing). Time-dependent step strain rheological experiments were performed on the hydrogel and chlorobenzene gel to confirm the thixotropic behaviour in a quantitative manner (electronic supplementary material, figure S6). In this experiment, a constant strain of 0.5% was maintained for the first 100 s, and then the strain was suddenly increased to 30%; at such a high strain the gel ruptures as indicated by the increase of  $G''$  over  $G'$ . Then, suddenly the strain was reduced to 0.5% again after 200 s and the gel was found to be re-formed, as indicated by the increase of  $G'$  over  $G''$  again. This process was repeated over another cycle and gel recovery was observed again after release of the heavy strain. For the hydrogel, 97.8% of gel strength was recovered after 90 s of removal of strain, and for the gel in chlorobenzene 99.4% of gel strength was recovered after 50 s. These experiments confirm that the gels undergo a fast repair after breaking, i.e. they are thixotropic in nature.

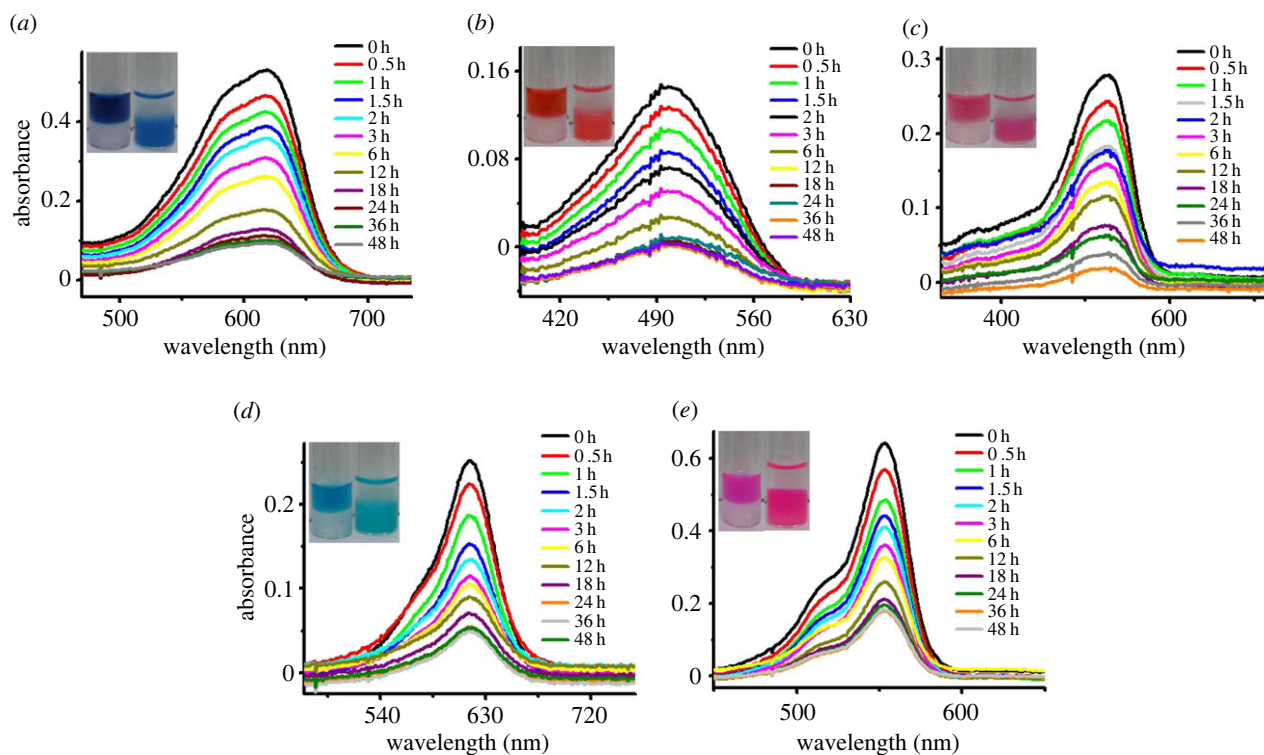
### 3.6. Absorption of toxic dyes from water

Here, the peptide-based thixotropic hydrogel shows great ability in absorbing different toxic organic dyes (cationic, anionic

and neutral) from water. The dye absorptions were checked by adding dye solutions of a known concentration over the hydrogel matrix and then measuring the concentration of the remaining dye of the supernatant solution from time to time by using UV-Vis spectrophotometry. It was found that the hydrogel obtained from **P** absorbs both cationic and anionic toxic organic dyes from water, namely Acid black 1, Congo red, Direct red 80, Malachite green and Rhodamine B with 82%, 98%, 93%, 79% and 71% of removal efficiency, respectively, within 48 h (calculated from UV-Vis absorption curves shown in figure 6; see also table 2). Moreover, the hydrogel can remove a mixture of dyes (Acid black 1, Malachite green and Rhodamine B) from water, indicating its potential use in waste water management (electronic supplementary material, figure S7).

### 3.7. Reusability

From the practical viewpoint, reusability of a functional soft material is needed. Textile industries release gallons of waste water containing toxic dyes; therefore a large amount of gelator would be necessary to remove dyes from such a huge amount of waste water. Therefore, in order to meet the demand, the gelator should be reusable several times. The reusability of the gelator was checked as follows: after absorption of a mixture of dyes, namely Acid black 1, Malachite green and Rhodamine B, the gel was taken out of vial and treated with minimum volume of 1(N) HCl solution in the presence of ethyl acetate. The gelator molecules are insoluble in acidic pH and these molecules go into the organic layer. Then the organic layer was dried with anhydrous sodium sulfate and ethyl acetate was removed under vacuum to get back the solid gelator. Figure 7 shows a bar diagram illustrating the reusability of gelator **P** and it has



**Figure 6.** Dye absorption assay by UV–Vis absorption spectroscopy for (a) Acid black 1, (b) Congo red, (c) Direct red 80, (d) Malachite green and (e) Rhodamine B; insets show gels before and after dye absorption. (Online version in colour.)

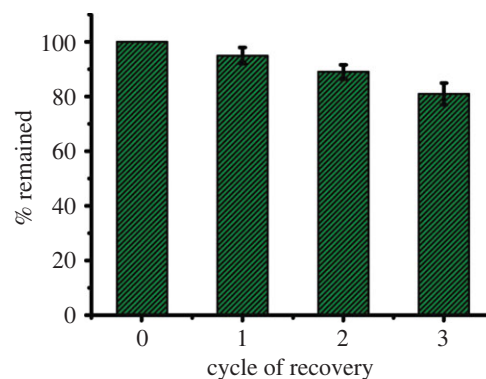
**Table 2.** Details and amount of dyes absorbed by the hydrogel.

dye	nature	% absorbed	amount of dyes absorbed (per g of gelator P) (mg)
Acid black 1	anionic	82	350
Congo red	neutral	98	720
Direct red 80	anionic	93	680
Malachite green	cationic	79	580
Rhodamine B	anionic	71	410

been found that the gelator can be reused for three cycles of dye removal.

### 3.8. Oil spill recovery

Low molecular weight gelators are useful materials for selective recovery of spilled mineral oil from oil spill recovery [70]. The first reported example of phase-selective gelation of crude oil from an oil–water biphasic mixture was urea-based supramolecular gelators [71]. An amino acid-containing amphiphile with a long fatty acyl chain in the N-terminus showed phase-selective gelation of various mineral oils from an oil–water mixture, indicating possible use in oil spill recovery [41]. It has been mentioned that **P** can gelate mineral oil instantaneously from an oil–salt water biphasic mixture. So it can be a good soft material for the recovery of spilled mineral oil in the ocean. In this study, the gelator **P** was first dissolved in a minimum volume of ethyl acetate (10% w/v) and then it was injected (100  $\mu$ l of the stock solution was used for injection in each set) into 4 ml of a 1:1 salt water–oil mixture, and gelation of the oil part was

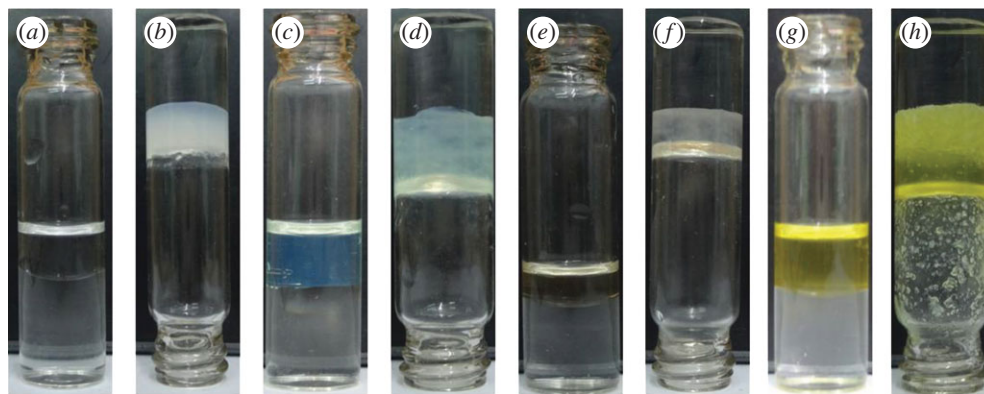


**Figure 7.** Bar diagram (with error bar) of the reusability of gelator molecules after absorption of a mixture of dyes (Acid black 1, Malachite green and Rhodamine B).

observed within 20 s after addition of the gelator solution (figure 8; also see the video in the electronic supplementary material). The gelled oil can be recovered by the simple distillation of the gel as shown schematically in electronic supplementary material, figure S8. To the best of our knowledge, this is the first example of a simple dipeptide-based gelator able to selectively gel fuel oil from a salt water–oil biphasic mixture within less than 20 s.

### 3.9. Conclusion

The discovery of new functional gels to carry out multiple applications is needed in modern society. The discovery of a new ambidextrous gelator that can gel both organic solvents as well as water is reported in this study. Interestingly, the hydrogel is endowed with an important application of absorbing toxic organic dyes from waste water; moreover, the gelator can be used several times. The gelator molecule can gel various organic



**Figure 8.** Gelation of oil from biphasic mixtures of different oils and water: (a) and (b) with petroleum ether; (c) and (d) with diesel; (e) and (f) with petrol; (g) and (h) with pump oil. (Online version in colour.)

solvents including fuel oils from an oil–salt water biphasic mixture, indicating its possible use in oil spill recovery. The easy synthesis procedure and the use of cheap starting materials for the synthesis suggest its possible use for waste water treatment in future.

**Authors' contributions.** K.B. carried out the synthesis, analysis, all experiments, data interpretation of the work and initially drafted the manuscript. N.N. helped in the experiments regarding the XRD, dye absorption studies and in taking the digital photographs and videos. B.M. purified the final peptide compound several times and did NMR and mass experiments. A.D. did the

SAXS experiments. I.W.H. explained the SXAS and XRD data and added valuable and important comments in the manuscript. A.B. conceived, designed and coordinated the study, and composed the manuscript to its final form. All the authors gave their final approval for publication.

**Competing interests.** We declare we have no competing interests.

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## References

- Du X, Zhou J, Shi J, Xu B. 2015 Supramolecular hydrogelators and hydrogels: from soft matter to molecular biomaterials. *Chem. Rev.* **115**, 13 165–13 307. (doi:10.1021/acs.chemrev.5b00299)
- Mallia VA, Weiss RG. 2016 Correlations between thixotropic and structural properties of molecular gels with crystalline networks. *Soft Matter* **12**, 3665–3676. (doi:10.1039/c6sm00377j)
- Kaufmann L, Kennedy SR, Jones CD, Steed JW. 2016 Cavity-containing supramolecular gels as a crystallization tool for hydrophobic pharmaceuticals. *Chem. Commun.* **52**, 10 113–10 116. (doi:10.1039/c6cc04037c)
- Kumari H, Kline SR, Kennedy SR, Garvey C, Raston CL, Atwood JL, Steed JW. 2016 Manipulating three-dimensional gel network entanglement by thin film shearing. *Chem. Commun.* **52**, 4513–4516. (doi:10.1039/c6cc00171h)
- Sajisha VS, Maitra U. 2014 Remarkable isomer-selective gelation of aromatic solvents by a polymorph of a urea-linked bile acid–amino acid conjugate. *RSC Adv.* **4**, 43 167–43 171. (doi:10.1039/c4ra08957j)
- Balk S, Maitra U, König B. 2014 Terbium(III)-cholate functionalized vesicles as luminescent indicators for the enzymatic conversion of dihydroxynaphthalene diesters. *Chem. Commun.* **50**, 7852–7854. (doi:10.1039/c4cc03724c)
- Deng M, Zhang L, Jiang Y, Liu M. 2016 Role of achiral nucleobases in multicomponent chiral self-assembly: purine-triggered helix and chirality transfer. *Angew. Chem. Int. Ed.* **55**, 15 062–15 066. (doi:10.1002/anie.201608638)
- Lee H, Lee JH, Kang S, Lee JY, John G, Jung JH. 2011 Pyridine-based coordination polymeric hydrogel with  $\text{Cu}^{2+}$  ion and its encapsulation of a hydrophobic molecule. *Chem. Commun.* **47**, 2937–2939. (doi:10.1039/c0cc05555g)
- Lalitha K, Prasad YS, Sridharan V, Maheswari CU, John G, Nagarajan S. 2015 A renewable resource-derived thixotropic self-assembled supramolecular gel: magnetic stimuli responsive and real-time self-healing behavior. *RSC Adv.* **5**, 77 589–77 594. (doi:10.1039/c5ra14744a)
- Feldner T, Häring M, Saha S, Esquena J, Banerjee R, Díaz Díaz D. 2016 Supramolecular metallogel that imparts self-healing properties to other gel networks. *Chem. Mater.* **28**, 3210–3217. (doi:10.1021/acs.chemmater.6b01144)
- Grijalvo S, Puras G, Zárate J, Pons R, Pedraz JL, Eritja R, Díaz Díaz D. 2016 Nioplexes encapsulated in supramolecular hybrid biohydrogels as versatile delivery platforms for nucleic acids. *RSC Adv.* **6**, 39 688–39 699. (doi:10.1039/c6ra01005a)
- Draper ER, Adams DJ. 2016 Photoresponsive gelators. *Chem. Commun.* **52**, 8196–8206. (doi:10.1039/c6cc03485c)
- Hamley IW, Hutchinson J, Kirkham S, Castelletto V, Kaur A, Reza M, Ruokolainen J. 2016 Nanosheet Formation by an anionic surfactant-like peptide and modulation of self-assembly through ionic complexation. *Langmuir* **32**, 10 387–10 393. (doi:10.1021/acs.langmuir.6b02180)
- Kirkham S, Hamley IW, Smith AM, Gouveia RM, Cannon CJ, Reza M, Ruokolainen J. 2016 A self-assembling fluorescent dipeptide conjugate for cell labeling. *J. Colloids Surf. B Biointerfaces* **137**, 104–108. (doi:10.1016/j.colsurfb.2015.04.062)
- Aytun T, Santos PJ, Bruns CJ, Huang D, Koltonow AR, de la Cruz MO, Stupp SI. 2016 Self-assembling tripodal small-molecule donors for bulk heterojunction solar cells. *J. Phys. Chem. C* **120**, 3602–3611. (doi:10.1021/acs.jpcc.5b10064)
- Pellach M, Mondal S, Shimon LJW, Adler-Abramovich L, Buzhansky L, Gazit E. 2016 Molecular engineering of self-assembling diphenylalanine analogues results in the formation of distinctive microstructures. *Chem. Mater.* **28**, 4341–4348. (doi:10.1021/acs.chemmater.6b01322)
- Zhang HV, Polzer F, Haider MJ, Tian Y, Villegas JA, Kiick KL, Pochan DJ, Saven JG. 2016 Computationally designed peptides for self-assembly of nanostructured lattices. *Sci. Adv.* **2**, e1600307. (doi:10.1126/sciadv.1600307)
- Babu SS, Praveen VK, Ajayaghosh A. 2014 Functional  $\pi$ -gelators and their applications. *Chem. Rev.* **114**, 1973–2129. (doi:10.1021/cr400195e)
- Nair VS, Mukhopadhyay RD, Saeki A, Seki S, Ajayaghosh A. 2016 A  $\pi$ -gel scaffold for assembling fullerene to photoconducting supramolecular rods. *Sci. Adv.* **2**, e1600142. (doi:10.1126/sciadv.1600142)

20. Okesola BO, Smith DK. 2016 Applying low-molecular weight supramolecular gelators in an environmental setting—self-assembled gels as smart materials for pollutant removal. *Chem. Soc. Rev.* **45**, 4226–4251. (doi:10.1039/c6cs00124f)
21. Gupta JK, Adams DJ, Berry NG. 2016 Will it gel? Successful computational prediction of peptide gelators using physicochemical properties and molecular fingerprints. *Chem. Sci.* **7**, 4713–4719. (doi:10.1039/c6sc00722h)
22. Bhattacharya S, Samanta SK. 2016 Soft-nanocomposites of nanoparticles and nanocarbons with supramolecular and polymer gels and their applications. *Chem. Rev.* **116**, 11 967–12 028. (doi:10.1021/acs.chemrev.6b00221)
23. Adhikari B, Banerjee A. 2011 Self-assembling peptides: from molecules to nanobiomaterials. *J. Ind. Inst. Sci.* **91**, 471–483.
24. Basu K *et al.* 2016 Peptide based hydrogels for cancer drug release: modulation of stiffness, drug release and proteolytic stability of hydrogels by incorporating D-amino acid residue(s). *Chem. Commun.* **52**, 5045–5048. (doi:10.1039/c6cc01744d)
25. Choe S, Veliceasa D, Bond CW, Harrington DA, Stupp SI, McVary KT, Podlasek CA. 2016 Sonic hedgehog delivery from self-assembled nanofiber hydrogels reduces the fibrotic response in models of erectile dysfunction. *Acta Biomater.* **32**, 89–99. (doi:10.1016/j.actbio.2016.01.014)
26. Liyanage W, Nilsson BL. 2015 Substituent effects on the self-assembly/coassembly and hydrogelation of phenylalanine derivatives. *Langmuir* **32**, 787–799. (doi:10.1021/acs.langmuir.5b03227)
27. Swanekamp RJ, Welch JJ, Nilsson BL. 2014 Proteolytic stability of amphipathic peptide hydrogels composed of self-assembled pleated  $\beta$ -sheet or coassembled rippled  $\beta$ -sheet fibrils. *Chem. Commun.* **50**, 10 133–10 136. (doi:10.1039/c4cc04644g)
28. Sun JEP, Stewart B, Litan A, Lee SJ, Schneider JP, Langhans SA, Pochan DJ. 2016 Sustained release of active chemotherapeutics from injectable-solid  $\beta$ -hairpin peptide hydrogel. *Biomater. Sci.* **4**, 839–848. (doi:10.1039/c5bm00538h)
29. Tao K, Levin A, Adler-Abramovich L, Gazit E. 2016 Fmoc-modified amino acids and short peptides: simple bio-inspired building blocks for the fabrication of functional materials. *Chem. Soc. Rev.* **45**, 3935–3953. (doi:10.1039/c5cs00889a)
30. Sasselli IR, Pappas CG, Matthews E, Wang T, Hunt NT, Ulijn RV, Tuttle T. 2016 Using experimental and computational energy equilibration to understand hierarchical self-assembly of Fmoc-dipeptide amphiphiles. *Soft Matter* **12**, 8307–8315. (doi:10.1039/c6sm01737a)
31. Tena-Solsona M, Nanda J, Díaz-Oltra S, Chotera A, Ashkenasy G, Escuder B. 2016 Emergent catalytic behavior of self-assembled low molecular weight peptide-based aggregates and hydrogels. *Chem. Eur. J.* **22**, 6687–6694. (doi:10.1002/chem.201600344)
32. Frederix PWJM, Scott GG, Abul-Hajja YM, Kalafatovic D, Pappas CG, Javid N, Hunt NT, Ulijn RV, Tuttle T. 2015 Exploring the sequence space for (tri-)peptide self-assembly to design and discover new hydrogels. *Nat. Chem.* **7**, 30–37. (doi:10.1038/NCHEM.2122)
33. Yu Q, Fan M, Li D, Song Z, Cai M, Zhou F, Liu W. 2014 Thermoreversible gel lubricants through universal supramolecular assembly of a nonionic surfactant in a variety of base lubricating liquids. *ACS Appl. Mater. Interfaces* **6**, 15 783–15 794. (doi:10.1021/am502832z)
34. Boothroyd S, Saiani A, Miller AF. 2013 Controlling network topology and mechanical properties of co-assembling peptide hydrogels. *Biopolymers* **101**, 669–680. (doi:10.1002/bip.22435)
35. Baral A, Roy S, Dehsorkhi A, Hamley IW, Mohapatra S, Ghosh S, Banerjee A. 2014 Assembly of an injectable noncytotoxic peptide-based hydrogelator for sustained release of drugs. *Langmuir* **30**, 929–936. (doi:10.1021/la4043638)
36. Li F, He J, Zhang M, Tam KC, Ni P. 2015 Injectable supramolecular hydrogels fabricated from PEGylated doxorubicin prodrug and  $\alpha$ -cyclodextrin for pH-triggered drug delivery. *RSC Adv.* **5**, 54 658–54 666. (doi:10.1039/c5ra06156c)
37. Ray S, Das AK, Banerjee A. 2007 pH-responsive, bolaamphiphile-based smart metallo-hydrogels as potential dye-adsorbing agents, water purifier, and vitamin B<sub>12</sub> carrier. *Chem. Mater.* **19**, 1633–1639. (doi:10.1021/cm062672f)
38. Adhikari B, Palui G, Banerjee A. 2009 Self-assembling tripeptide based hydrogels and their use in removal of dyes from waste-water. *Soft Matter* **5**, 3452–3460. (doi:10.1039/b905985g)
39. Dutta S, Das D, Dasgupta A, Das PK. 2010 Amino acid based low-molecular-weight ionogels as efficient dye adsorbing agents and templates for the synthesis of TiO<sub>2</sub> nanoparticles. *Chem. Eur. J.* **16**, 1493–1505. (doi:10.1002/chem.200901917)
40. Debnath S, Shome A, Dutta S, Das PK. 2008 Dipeptide-based low-molecular-weight efficient organogelators and their application in water purification. *Chem. Eur. J.* **14**, 6870–6881. (doi:10.1002/chem.200800731)
41. Bhattacharya S, Krishnan-Ghosh Y. 2001 First report of phase selective gelation of oil from oil/water mixtures. Possible implications toward containing oil spills. *Chem. Commun.* 185–186. (doi:10.1039/b007848o)
42. Basak S, Nanda J, Banerjee A. 2012 A new aromatic amino acid based organogel for oil spill recovery. *J. Mater. Chem.* **22**, 11 658–11 664. (doi:10.1039/c2jm30711a)
43. Palui G, Nanda J, Ray S, Banerjee A. 2009 Fabrication of luminescent CdS nanoparticles on short-peptide-based hydrogel nanofibers: tuning of optoelectronic properties. *Chem. Eur. J.* **15**, 6902–6909. (doi:10.1002/chem.200900149)
44. Wu J, Tian Q, Hu H, Xia Q, Zou Y, Li F, Yi T, Huang C. 2009 Self-assembly of peptide-based multi-colour gels triggered by up-conversion rare earth nanoparticles. *Chem. Commun.* 4100–4102. (doi:10.1039/b907517h)
45. Adhikari B, Banerjee A. 2010 Short-peptide-based hydrogel: a template for the in situ synthesis of fluorescent silver nanoclusters by using sunlight. *Chem. Eur. J.* **16**, 13 698–13 705. (doi:10.1002/chem.201001240)
46. Escuder B, Rodriguez-Llansola F, Miravet JF. 2010 Supramolecular gels as active media for organic reactions and catalysis. *New J. Chem.* **34**, 1044–1054. (doi:10.1039/b9nj00764d)
47. Sanger MJ, Badger II SM. 2001 Using computer-based visualization strategies to improve students' understanding of molecular polarity and miscibility. *J. Chem. Educ.* **78**, 1412–1416. (doi:10.1021/ed078p1412)
48. Lombardo D, Kiselev MA, Magazù S, Calandra P. 2015 Amphiphiles self-assembly: basic concepts and future perspectives of supramolecular approaches. *Adv. Condens. Matter Phys.* **2015**, 151683. (doi:10.1155/2015/151683)
49. Makarevič J, Jokić M, Perić B, Tomišić V, Kojić-Prodić B, Žičić M. 2001 Bis(amino acid) oxalyl amides as ambidextrous gelators of water and organic solvents: supramolecular gels with temperature dependent assembly/dissolution equilibrium. *Chem. Eur. J.* **7**, 3328–3341. (doi:10.1002/1521-3765(20010803)7)
50. Imura Y, Matsue K, Sugimoto H, Ito R, Kondo T, Kawai T. 2009 Ambidextrous gel property and pH-responsive sol-gel transition of low molecular mass gelator based on a long-chain amide derivative. *Chem. Lett.* **38**, 778–779. (doi:10.1246/cl.2009.778)
51. Miravet JF, Escuder B. 2005 Pyridine-functionalised ambidextrous gelators: towards catalytic gels. *Chem. Commun.* 5796–5798. (doi:10.1039/b510874h)
52. Pal A, Dey J. 2013 L-cysteine-derived ambidextrous gelators of aromatic solvents and ethanol/water mixtures. *Langmuir* **29**, 2120–2127. (doi:10.1021/la3042764)
53. Mandal D, Kar T, Das PK. 2014 Pyrene-based fluorescent ambidextrous gelators: scaffolds for mechanically robust SWNT-gel nanocomposites. *Chem. Eur. J.* **20**, 1349–1358. (doi:10.1002/chem.201303401)
54. Duan P, Liu M. 2009 Design and self-assembly of L-glutamate-based aromatic dendrons as ambidextrous gelators of water and organic solvents. *Langmuir* **25**, 8706–8713. (doi:10.1021/la8043335)
55. Ratna, Padhi BS. 2012 Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. *Int. J. Environ. Sci.* **3**, 940–955.
56. Okesola BO, Smith DK. 2013 Versatile supramolecular pH-tolerant hydrogels which demonstrate pH-dependent selective adsorption of dyes from aqueous solution. *Chem. Commun.* **49**, 11 164–11 166. (doi:10.1039/c3cc45969a)
57. Chakraborty P, Roy B, Bairi P, Nandi AK. 2012 Improved mechanical and photophysical properties of chitosan incorporated folic acid gel possessing



- the characteristics of dye and metal ion absorption. *J. Mater. Chem.* **22**, 20 291–20 298. (doi:10.1039/c2jm33995a)
58. Sengupta S, Mondal R. 2014 A novel gel-based approach to wastewater treatment—unique one-shot solution to potentially toxic metal and dye removal problems. *J. Mater. Chem. A* **2**, 16 373–16 377. (doi:10.1039/c4ta03919j)
  59. Cheng N, Hu Q, Guo Y, Wang Y, Yu L. 2015 Efficient and selective removal of dyes using imidazolium-based supramolecular gels. *ACS Appl. Mater. Interfaces* **7**, 10 258–10 265. (doi:10.1021/acsami.5b00814)
  60. Sukul PK, Malik S. 2013 Removal of toxic dyes from aqueous medium using adenine based bicomponent hydrogel. *RSC Adv.* **3**, 1902–1915. (doi:10.1039/C2RA22988A)
  61. Nandi N, Baral A, Basu K, Roy S, Banerjee A. 2017 A dipeptide-based superhydrogel: removal of toxic dyes and heavy metal ions from waste-water. *Biopolymers* **108**, e22915. (doi:10.1002/bip.22915)
  62. Guterman L. 2009 *Exxon Valdez* turns 20. *Science* **323**, 1558–1559. (doi:10.1126/science.323.5921.1558)
  63. Adebajo MO, Frost RL, Kloprogge JT, Carmody O, Kokot S. 2003 Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. *J. Porous Mater.* **10**, 159–170. (doi:10.1023/A:1027484117065)
  64. Tsai C -C, Cheng Y-T, Shen L-C, Chang K-C, Ho I-T, Chu J-H, Chung W-S. 2013 Biscalix[4]arene derivative as a very efficient phase selective gelator for oil spill recovery. *Org. Lett.* **15**, 5830–5833. (doi:10.1021/ol402898u)
  65. Trivedi DR, Ballabh A, Dastidar P, Ganguly B. 2004 Structure-property correlation of a new family of organogelators based on organic salts and their selective gelation of oil from oil/water mixtures. *Chem. Eur. J.* **10**, 5311–5322. (doi:10.1002/chem.200400122)
  66. Rajkamal, Chatterjee D, Paul A, Banerjee S, Yadav S. 2014 Enantiomeric organogelators from D-/L-arabinose for phase selective gelation of crude oil and their gel as a photochemical micro-reactor. *Chem. Commun.* **50**, 12 131–12 134. (doi:10.1039/c4cc05950f)
  67. Mallia AV, Blair DL, Weiss RG. 2016 Oscillatory rheology and surface water wave effects on crude oil and corn oil gels with (R)-12-hydroxystearic acid as gelator. *Ind. Eng. Chem. Res.* **55**, 954–960. (doi:10.1021/acs.iecr.5b04267)
  68. Sahoo P, Kumar DK, Raghavan SR, Dastidar P. 2011 Supramolecular synthons in designing low molecular mass gelling agents: L-amino acid methyl ester cinnamate salts and their anti-solvent-induced instant gelation. *Chem. Asian J.* **6**, 1038–1047. (doi:10.1002/asia.201000560)
  69. Moretto V, Crisma M, Bonora GM, Toniolo C, Balarum H, Balarum P. 1989 Comparison of the effect of five guest residues on the .beta.-sheet conformation of host (L-Val)<sub>n</sub> oligopeptides. *Macromolecules* **22**, 2939–2944. (doi:10.1021/ma00197a010)
  70. Vibhute AM, Muvvala V, Sureshan KM. 2016 A sugar-based gelator for marine oil-spill recovery. *Angew. Chem. Int. Ed.* **55**, 7782–7785. (doi:10.1002/anie.201510308)
  71. USEPA-Water Quality Office. 1971 Gelling crude oils to reduce marine pollution from tanker oil spills. *Water pollution control research series 15080DJN 1/71*. Washington, DC: US Government Printing Office.