

NANO EXPRESS

Open Access



Smart Materials for Environmental Remediation Based on Two-Component Gels: Room-Temperature-Phase-Selective Gelation for the Removal of Organic Pollutants Including Nitrobenzene/O-Dichlorobenzene, and Dye Molecules from the Wastewater

Jing Zhang^{1,2,3}, Jiahui Liu⁴, Ciqing Tong⁵, Shipeng Chen^{1,2}, Baohao Zhang^{1,2}, Bao Zhang^{1,2*}  and Jian Song^{1,2*}

Abstract

Novel two-component gel systems based on aliphatic acid–hydroxy/base interaction were developed as smart materials for environmental remediation. The *G1-A16* gelator could be used directly as a powder form to selectively gel aromatic solvents (nitrobenzene and o-dichlorobenzene) from their mixtures with wastewater (containing 0.5 M sodium nitrate and 0.5 M sodium sulfate) via a simple shaking strategy at room temperature without employing co-solvents and a heating–cooling process. Meanwhile, the two-component gel system can efficiently remove the toxic dyes from the aqueous solution. The dominant factors that drive gelation in the case of the gelator and nitrobenzene or water have been studied using FT-IR, ¹H NMR, and XRD. Overall, our research provides an efficient two-component approach for facilely tuning the properties of one-component gel for the realization of high-performance functionalities of gels. At the same time, our study demonstrates potential industrial application prospect in removing pollutants efficiently (such as aromatic solvents and toxic dye removal).

Keywords: Room-phase-selective-gelator (RPSG), Self-healing, Dye removal

Background

The multicomponent supramolecular gel systems, as intriguing soft materials formed via H-bonding, donor–acceptor, metal ion coordination, and acid–base interactions, provide a flexible method to realize the functionalities of gels [1–3]. They have attracted more and more attention owing to their potential applications in the fields such as pollutant collection [4–6], oil spill treatment [5, 7], and advanced materials.

Nowadays, much attention has been paid to environmental problems raised from the rapid industrial development [5, 8, 9]. When the hazardous waste such as industrial waste water, toxic dyes, and petroleum products are discharged as untreated effluents into rivers, lakes, and oceans, these pollutions threaten the fresh water ecology, affect aquatic life, and pollute the local sources of drinking water. For instance, the 2005 Jilin chemical plant explosions in Jilin City caused a large discharge of nitrobenzene into the Songhua River, which polluted the local sources of drinking water and the environment (https://en.wikipedia.org/wiki/2005_Jilin_chemical_plant_explosions). How to remove the toxic organic liquids which are heavier than

* Correspondence: baozhang@tju.edu.cn; songjian@tju.edu.cn

¹School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China

Full list of author information is available at the end of the article

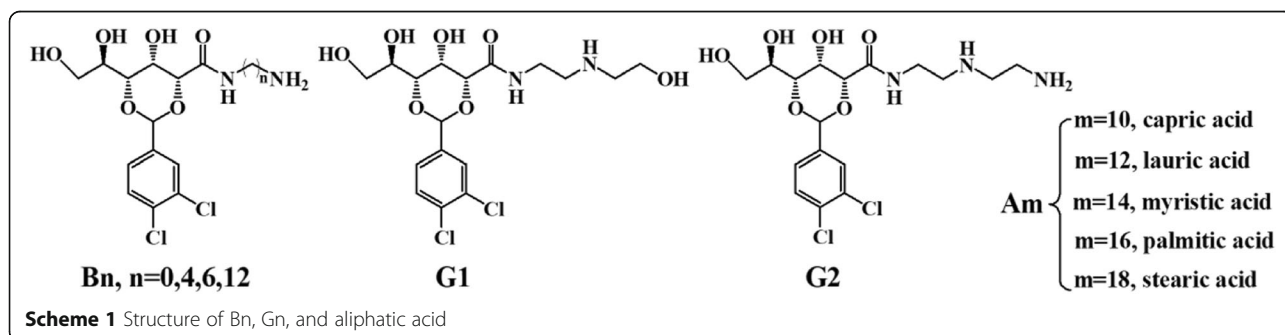
water (e.g., nitrobenzene, *o*-dichlorobenzene) from their biphasic mixtures with industrial waste water easily and efficiently is a great challenge. At present, the possible materials for the treatment of such organic liquid pollutants involve adsorbents, chemical dispersants, polymeric solidifiers, and engineering bacteria [10–18]. However, all materials have some limitations in practice. For example, adsorbents are very efficient for the organic pollutants due to their high surface area, but the post-treatment is very expensive. Polymeric solidifiers cannot be mixed easily with organic pollutants, and the recovery of organic liquid from polymer gels is troublesome. Nowadays, the study of phase-selective gelation towards toxic organic liquids has become a hot topic [19–22]. For example, the first example of phase-selective gelator (PSG) was found by Bhattacharya and Krishnan-Ghosh with amino acid amphiphiles [23]. Vemula et al. Synthesized PSGS based on open-chain sugars [24]. Zeng et al. declared that leucine derivatives could gel crude oils in the presence of seawater at room temperature and a conceptually novel polar solvent-assisted approach to substantially boost the gelling capacities of different types of organogelators without resorting to any structural alteration [25, 26]. Our group previously reported the multifunctional gel systems B6-A18 based on the amine-acid two-component systems which showed room-temperature-phase-selective gelation and could simultaneously gel aromatic solvents (Scheme 1) [27, 28]. Furthermore, a majority of phase-selective gelators necessitated a heating–cooling process or a toxic co-solvent to obtain solutions before use. It was reported that an effective and ideal phase-selective gelator for practical applications must (1) be synthesized easily and at a low cost; (2) selectively, feasibly, and efficiently gel the organic phase in the presence of water at room temperature; (3) be environment-friendly; (4) be easily recovered from the gel involving the organic liquid pollutants; and (5) be recyclable and reusable [29]. So far, research on room-temperature-phase-selective gelation of the toxic organic liquids from their biphasic mixtures with water such as nitrobenzene is still limited [29].

Dyes are useful in the textile industry (e.g., paints, printing, drugs, and cosmetics). Most dyes are non-biodegradable

and even at low concentrations, dyes still threaten the environment and the ecosystem [30–34]. Eliminating toxic dyes from the polluted water is therefore an important goal.

We recently reported the amine-acid two-component gelators Bn-Am (Scheme 1), which exhibited excellent gelation abilities towards certain organic solvents. Herein, based on these previous works [27, 28, 35], a few novel D-gluconic acetal-based derivatives Gn with a free amino or hydroxy group at the terminal position of a long alkyl chain and amino group in the middle of a long carbon chain were designed and synthesized. The amino or hydroxy group provides sites for H-bond interaction with aliphatic acids and for the formation of two-component gelators (Scheme 1).

The gelation properties and the gel performance could be flexibly tuned by changing the chain length of the alkyl group in aliphatic acid. Surprisingly, compared with Bn-Am, the two-component gel system Gn-Am could gel not only some organic solvents but also water at room temperature. Moreover, as shown in Additional file 1: Table S5, Bn-Am could gel organic solvents which have smaller densities than water (e.g., toluene, *o*-xylene, 1, 3, 5-trimethylbenzene and ethylbenzene) and Gn-Am showed strong gelation properties towards organic solvents which are heavier than water (e.g., nitrobenzene, *o*-dichlorobenzene, dichloromethane). Additionally, Gn-Am showed strong abilities to selectively gel nitrobenzene/*o*-dichlorobenzene from the mixture with wastewater (containing 0.5 M sodium nitrate and 0.5 M sodium sulfate) without employing co-solvents and a heating-cooling process. Moreover, the gel system Gn-Am at room temperature displayed high-efficiency self-healing properties. To the best of our knowledge, it was the very few examples of two-component gelators reported to be excellent room-temperature PSGs that could gel organic solvents and water. It was also the first example of a two-component gel system reported as excellent room-temperature PSGs used to remove nitrobenzene/*o*-dichlorobenzene from the wastewater directly in a powder form. Furthermore, other excellent functions of two-component gels including dye removal are also demonstrated. These



findings provide a simple method for the design of multifunctional supramolecular gelators via an effective two-component gel strategy.

Methods/Experimental

Materials

D-Gluconic acid, 3, 4-dichlorobenzaldehyde, and β -hydroxyethylenediamine were purchased from Shanghai Jingchen Scientific Co., Ltd. The chemical reagents were commercially available and directly utilized without further purification. 2, 4-(3, 4-Dichloro) benzylidene methyl-D-gluconate was synthesized by the methods reported previously. [27]. Characterizations of a new compound *Gn* are provided in Additional file 1. Synthetic routes of *Gn* are shown in Additional file 1: Scheme S1. The detailed synthetic procedures and characterization data of *Gn* are given in Additional file 1.

Preparation of the Two-Component Hydrogels

Gn (5 mmol) and aliphatic acid (5 mmol) were simultaneously added to 10 mL methanol. The resultant mixture was subsequently heated to reflux for 10 min leading to a clear solution and finally a white or faint yellow solid via vacuum evaporation. A certain amount of the two-component gelator was weighed in a test tube. The corresponding solvents was subsequently added, which was shook for 1 min and then the test tube stood for 8 h. Finally, the test tube was inversed to observe whether the solution inside could still flow [36]. Gelation was considered to have occurred when a homogeneous substance was obtained which exhibited no gravitational flow, and it was denoted by “G”. Solution and solid-like gel may coexist within a system as “partial gels (PG)”. Systems, in which only solution was obtained, were referred to as solution (S). In an insoluble system (I), gelators could not be dissolved. The critical gelation concentrations (CGCs) mean the minimum amount of gelators required to immobilize 1 mL of solvent.

Field-emission scanning electron microscope (FESEM)

The morphologies of the xerogels were obtained by a Hitachi S-4800 SEM instrument operating at 3–5 kV. Samples were prepared by dropping the diluted solution of gels on the thin aluminum sheets and then dried under vacuum for 24 h. We coated the samples with a thin layer of Au before the experiment.

FT-IR

IR spectra were collected by a FTS3000 spectrometer with KBr pellets. The xerogels were prepared by drying chlorobenzene gels on glass slides under vacuum for 24 h.

Powder X-Ray Diffraction (PXRD)

PXRD diagrams of xerogels which were prepared from hydrogels were obtained by using a Bruker D8-S4 (CuK α radiation, $\lambda = 1.546 \text{ \AA}$). The d spacing values were calculated by Bragg's law ($n\lambda = 2d \sin\theta$).

Rheology Measurements

Rheology experiments were carried out with a strain-controlled rheometer (Anton Paar Physica MCR 301) equipped with steel-coated parallel-plate geometry (15 mm diameter). The gap distance was fixed at 0.5 mm. A solvent trapping device was placed above the plate and measurement was set at 20 °C in order to avoid solvent evaporation. The frequency sweep at a constant strain of 0.1% was obtained from 0.1 to 100 rad s⁻¹. Strain sweep was performed in the 0.01–1000% range at a constant frequency (1 Hz). The time sweep was conducted to observe the recovery property of the gel. First, a constant strain of 0.1% was applied on the sample. Then a constant strain of 100% was applied to destroy the sample. And then a constant strain (0.1%) was applied again. The storage modulus G' and the loss modulus G'' of the sample were monitored as functions of time in this experiment.

Dye Removal Experiments

Five milligrams of the xerogels (*G1-Am*) prepared from the hydrogels by freeze drying was immersed in a single dye solution (5 mL, 0.1 mM) for 24 h containing the anionic dyes (e.g., acid fuchsin (AF), eosin Y (EY), methyl orange (MO)) or cationic dyes (e.g., malachite green (MG), methylene blue (MB), Rhodamine (RB)). The resultant mixture was subsequently centrifuged, and the concentration of dyes in the supernatant was monitored by UV-vis spectroscopy. The removal rate was calculated as $(C_0 - C_e)/C_0$, where C_0 (mg L⁻¹) was the initial concentration of dye in the solution and C_e (mg L⁻¹) was the equilibrium concentration. The maximum amount of dyes adsorbed at equilibrium q_e (mg g⁻¹) was calculated as $q_e = (C_0 - C_e) \times V/W$, where V (L) was the solution volume and W (g) was the mass of xerogels. The changes in the dye concentration were also monitored by UV-vis spectroscopy. The adsorption isotherm was determined by immersing 5 mg of the xerogel into a MO or CV solution with varying concentrations for a week, and subsequently calculating the equilibrium adsorption capacity and concentration.

Results and Discussion

The Gelation Abilities of the Two-Component Gel System at Room Temperature

Initially, the gelation tests for *Gn-Am* in some solvents were summarized in Additional file 1: Table S1-S4. All the gels reported here were generated by using a 1:1 or

1:2 (the molar concentration of the two-component gel) ratio of Gn/aliphatic acids as the two-component gelators. The gelation abilities of the two-component gelators varied depending upon the structure of the single component. In particular, the gelation abilities of the Gn-Am at room temperature were greatly enhanced compared with that of a single Gn. It was found that G1-Am and G2-A16 were efficient room-temperature gelators in certain solvents such as nitrobenzene, *o*-dichlorobenzene, dichloromethane, toluene, and water, while G1 and G2 cannot gelate any testing solvent at room temperature. Except for G2-A16, G2-Am did not exhibit room-temperature gelation abilities in all the tested solvents (Additional file 1: Table S2 and S4). Intriguingly, the G1-Am gels exhibited high-performance self-healing properties. All the G1-Am room-temperature gels can undergo an instant self-healing process (within 5 s) upon mechanical damage. The self-healing properties of G1-A16 gels were further demonstrated by shaking/resting tests at room temperature. For instance, the G1-A16 hydrogel and nitrobenzene gel (2.0%, *w/v*) were shaken vigorously until a homogeneous solution was resulted, and then the solutions were rested at room temperature, leading to re-formation of gels spontaneously within 1 min (Fig. 1a, b). A similar behavior was also observed for gel formation with G1-A16 in *o*-dichlorobenzene. Meanwhile, G1-A16 can gelate nitrobenzene/*o*-dichlorobenzene at room temperature at a concentration as low as 0.45 wt% and 0.72 wt% respectively. These findings established the basis for the real-life applications of these gelators in the phase-selective gelation of nitrobenzene/*o*-dichlorobenzene from wastewater at room temperature. Also, G1-A16/nitrobenzene gels showed highly transparent and

excellent viscoelasticity that allow it to be easily processed such as extrusion from a syringe (Fig. 1c). The high transparency, enhanced viscoelasticity, and the rapid self-healing properties of these gels make them attractive for developing flexible optical devices [37]. Furthermore, it was shown that G1-A16 xerogels obtained from nitrobenzene/water could adsorb toxic dyes from the polluted water, indicating a promising application in the field of water purification. However, the two-component gel systems obtained by mixing aliphatic acids with G2 except for A16 (palmitic acid), did not show enhanced room-temperature gelation abilities and interesting properties mentioned above. It indicated that the terminal hydroxyl attached to the side alkyl chain in Gn was critical to tune the properties of a two-component gel system.

Rheology of Self-Sealing Two-Component Gel System

Mechanical properties of the two-component gel systems at room temperature were studied by oscillatory rheological measurements. For all the gel samples, the storage modulus G' has a larger magnitude than the loss modulus G'' in the overall range of frequency sweep and the linear viscoelastic region (LVR) of the strain sweep, confirming their gel nature (Additional file 1: Figure S1) [38]. The strain sweep showed that G1-A16/nitrobenzene gels could tolerate a much larger strain (flowing point = 10.9%) than the G1-A16/hydrogel (flowing point = 8.8%) (Fig. 2). The recovery properties of the gels were examined by time scan tests under alternating strain of 0.1% and 100% (Fig. 2 and Additional file 1: Figure S1). Obviously, G1-Am gels exhibited excellent self-healing abilities, and the G' values could recover to their original values immediately after the cessation of the destructive

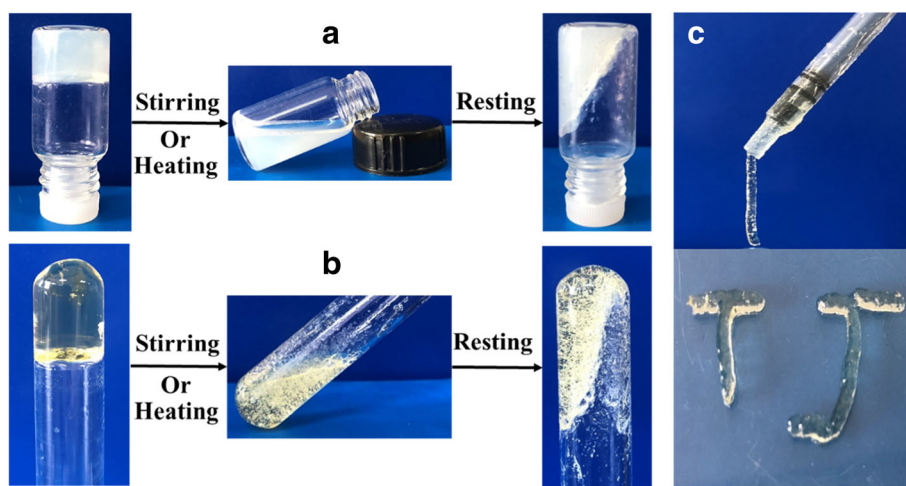
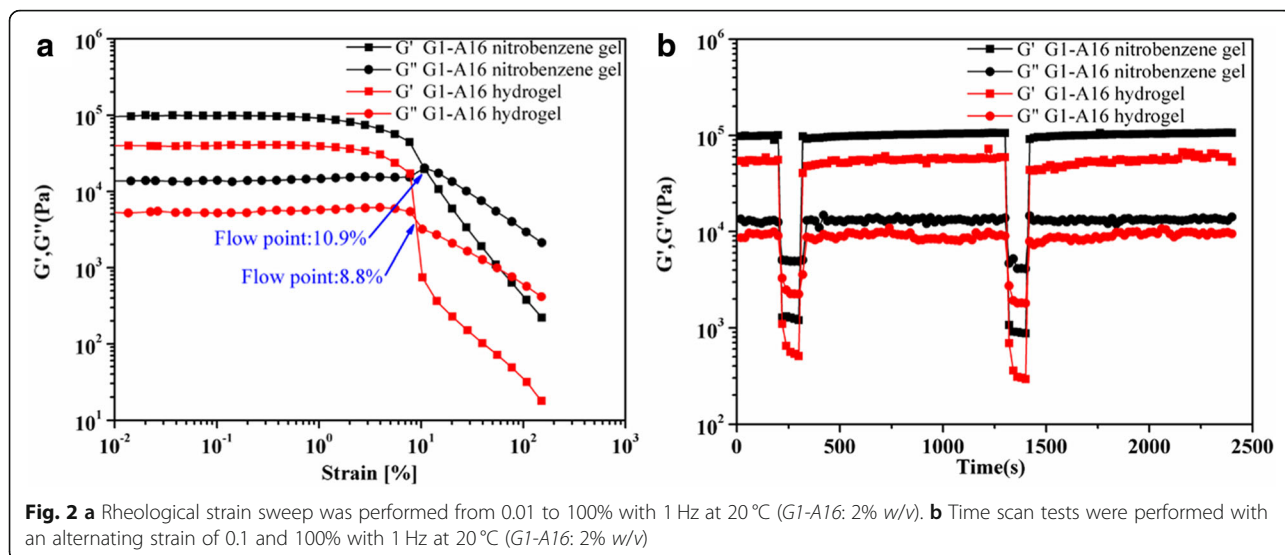


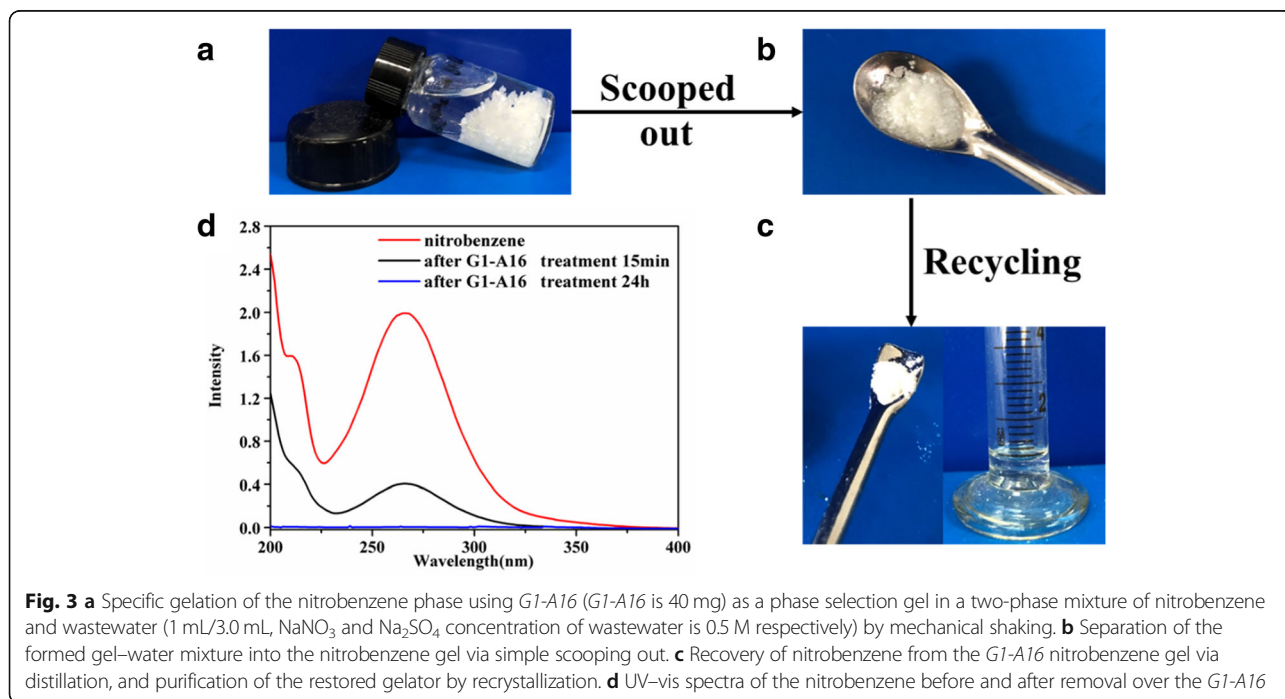
Fig. 1 a Reversible sol-to-gel transitions of G1-A16 room-temperature hydrogel stimulated by shaking or heating at 20 mg mL⁻¹. b Reversible sol-to-gel transitions of G1-A16 room-temperature nitrobenzene gel stimulated by shaking or heating at 20 mg mL⁻¹. c Extrusion of G1-A16 room-temperature nitrobenzene gel from a syringe



strain. The damage recovery process could be repeated for at least two cycles without any reduction in the value of G' and G'' . Almost all *G1-Am* gels could repair themselves within 5 s. As shown in the Additional file 1: Figure S1 (g), the G' values of *G1-A10*, *G1-A12*, *G1-A16*, and *G1-A18*/nitrobenzene gels were 1460, 5300, 100,000, and 107,000 Pa. These results revealed the mechanical properties of two-component gel systems at room temperature can be regulated via the finely tuning of the alkyl chain length of *Am*.

Room-Temperature-Phase-Selective Gelation in the Removal of Nitrobenzene

For the *G1-A16* gel system at room temperature reported in this work, via simple mechanical shaking, the two-component gelators were fully dispersed in the nitrobenzene phase, which further facilitated complete gel formation in wastewater (containing 0.5 M sodium nitrate and 0.5 M sodium sulfate). For example, as shown in Fig. 3, 40 mg *G1-A16* powders were directly added to a mixture of nitrobenzene/water (1

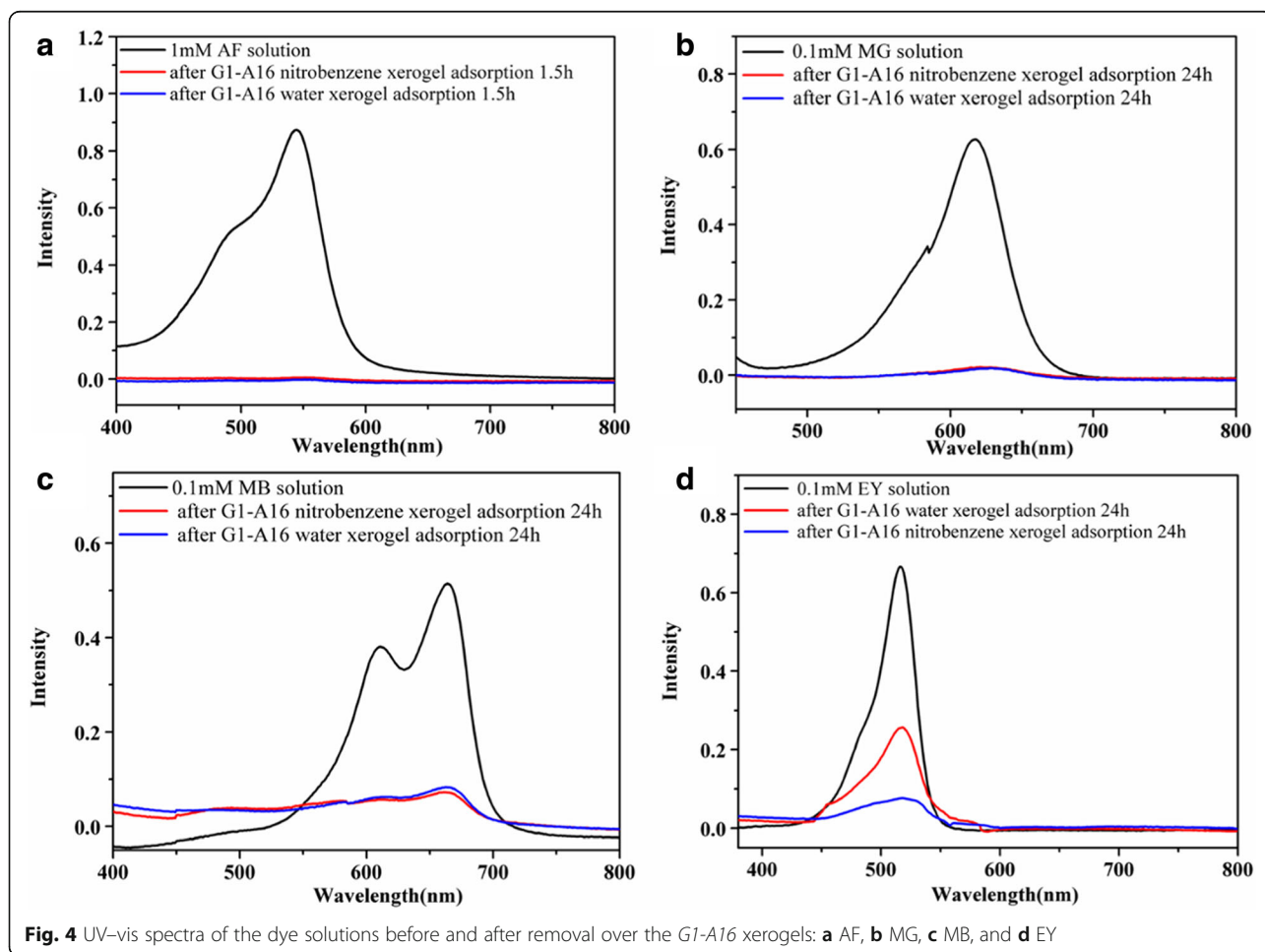


mL/3 mL containing 0.5 M sodium nitrate and 0.5 M sodium sulfate) in a glass vial. Further vigorous shaking was carried out to facilitate the sufficient dissolution of *G1-A16* powders in nitrobenzene. As shown in Fig. 3a, at room temperature, the resulting feculent mixture was rested for 15 min leading to a gel-like chunk (Fig. 3a). The gel-like chunk was scooped out easily by a spoon (Fig. 3b). Furthermore, the two-component gelators could be recycled via a simple distillation process and the nitrobenzene solvents recovered (the average recovery ratio was 85%). The restored two-component gelators could be purified by recrystallization (Fig. 3c). As shown in Fig. 3d, the treated water by *G1-A16* only contained trace amounts of nitrobenzene. Similarly, Additional file 1: Figure S3 shows that *G1-A16* could be used to remove *o*-dichlorobenzene. To the best of our knowledge, this is the first example of the two-component gelators that had the potential application in the real-life recovery of nitrobenzene/*o*-dichlorobenzene.

Removal of Dyes

The industrial wastewater containing dye molecules are classical refractory organic pollutants. These effluents

cause serious pollution to the environment, and the treatment of such pollutants has also been a field of focused research recently. In our case, *G1-A16* xerogels obtained from nitrobenzene or water were further explored for the removal of toxic dyes (anionic dyes: acid fuchsin (AF), eosin Y (EY), methyl orange (MO); cationic dyes: malachite green (MG), methylene blue (MB), rhodamine (RB), structures shown in Additional file 1: Figure S3) from water in detail. Interestingly, the xerogels showed excellent adsorption capacity for all testing dyes except for MO (Fig. 4 and Additional file 1: Figure S4). For instance, 5 mg *G1-A16* xerogel obtained from nitrobenzene were poured into the aqueous solution of MG (5 mL, the concentration at 0.1 mmol/L) at room temperature. The adsorption behavior of the xerogel was monitored by UV-vis spectroscopy measurement of the aqueous solution. In Fig. 4b, after 24 h, about 99.73% of MG were adsorbed. It was shown in Fig. 4a that *G1-A16* xerogel was the efficient sorbents for AF (the concentration is 1 mM). AF was completely absorbed only 1.5 h. In addition, about 86.02% MB was absorbed by *G1-A16* xerogels even after 24 h (Fig. 4c). Furthermore, the



maximum adsorption capacity of the two types of xerogels was examined (Additional file 1: Table S6). Encouragingly, the maximum amount of AF adsorbed for the *G1-A16*/nitrobenzene and *G1-A16*/water xerogels reached 610.75 and 594.09 mg g⁻¹, respectively (Additional file 1: Table S6). This large dye-removal amount is very rare for supramolecular gel systems [5]. Figure 4d and Additional file 1: Figure S4 and Table S6 indicate that the adsorption capacity of the *G1-A16* nitrobenzene xerogels was stronger than that of the *G1-A16* xerogels obtained from hydrogel for some toxic dye (e.g., EY, RB). Interestingly, the anionic dye-adsorption abilities of *G1-A16* xerogels were stronger than those of *B6-A16* xerogels. In contrast, *B6-A16* xerogels showed strong adsorption properties of the cationic dyes (Additional file 1: Table S6).

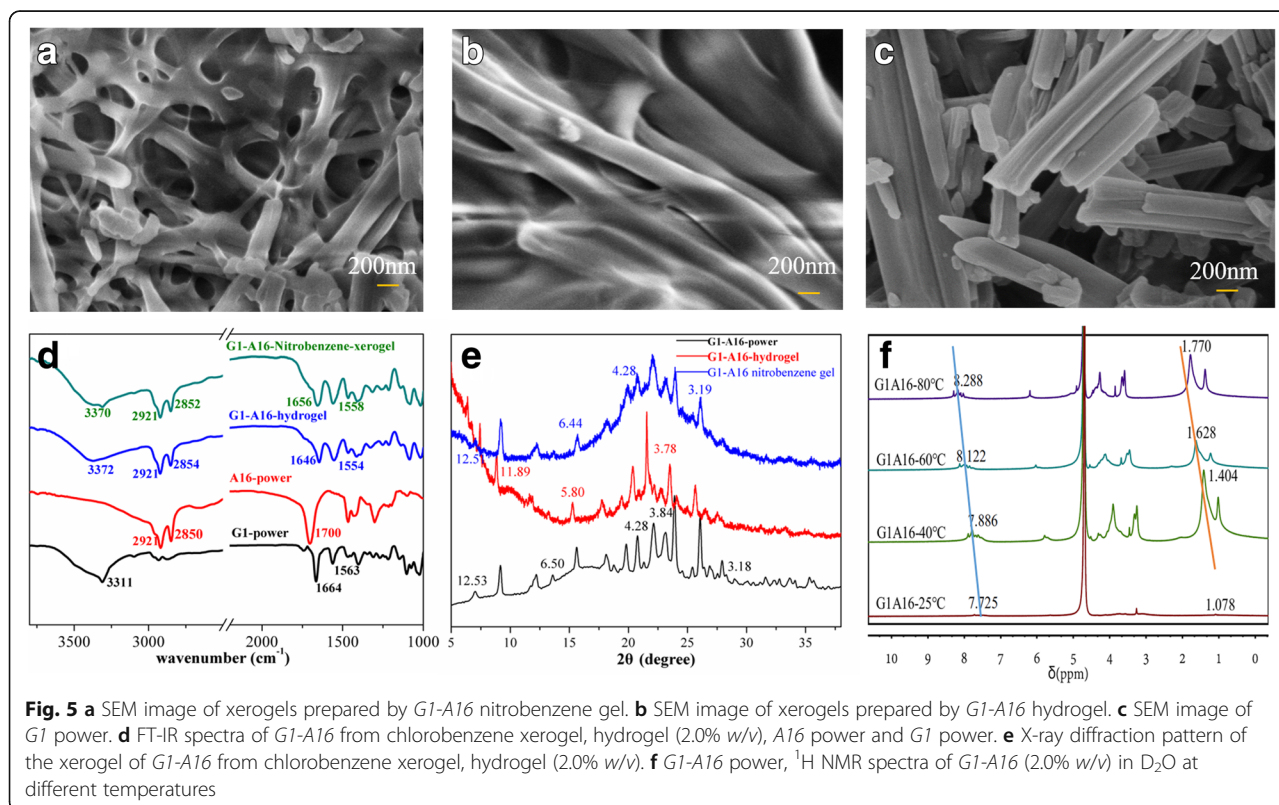
FT-IR

To reveal the mechanism of on the self-assembly of the *G1-Am* gel system, the FT-IR investigations of *G1* powder, *A16* powder, and *G1-A16* xerogels were performed (Fig. 5d). In the FT-IR spectra, the absorption bands of the asymmetric and symmetric CH₂ stretching vibrations of the side alkyl chains of the *G1-A16*/nitrobenzene and *G1-A16*/water xerogels were observed at 2921 cm⁻¹, 2852 cm⁻¹ and 2921 cm⁻¹, 2854 cm⁻¹, respectively, suggesting that the alkyl chains are all in the trans form and

there are strong van der Waals forces between the components [39, 40]. In the FT-IR spectra of *G1-A16*/nitrobenzene and water xerogels, the bands of OH (NH) appeared at 3370 cm⁻¹ and 3372 cm⁻¹ respectively, which were observed at 3311 cm⁻¹ for the *G1* power. Furthermore, for *G1-A16*/nitrobenzene and water xerogels, the band of the carbonyl group of the stearic acid component at 1700 cm⁻¹ disappeared, indicating that all carbonyls participated in H-bonding interaction in the two-component gel system [41–43]. The amide I and II bands of the xerogels were found at 1656 cm⁻¹, 1558 cm⁻¹ and 1646 cm⁻¹, 1554 cm⁻¹ respectively, also implying the formation of the intermolecular hydrogen bonding [43–45].

Powder X-Ray Diffraction (PXRD)

The XRD patterns of *G1-A16* nitrobenzene xerogel showed *d* spacing values of 1.25, 0.64, 0.43, and 0.32 nm (Fig. 5e) in a ratio of 1:1/2:1/3:1/4, indicating the lamellar arrangements [46, 47]. Similarly, the XRD patterns of *G1-A16*/water xerogel and *G1-A16* powder suggested the lamellar arrangements. Additionally, the *d* values of 0.38 nm was the characteristic of π–π stacking force of the benzene rings [48–50]. Moreover, the *d* value of 0.43 nm was ascribed to the packing of the alkyl chains [51, 52]. It reveals that the driving forces for the self-assembly involve the π–π stacking force of the



benzene rings and van der Waals force of the alkyl chains in the solution system.

¹H NMR

In order to gain further understanding of the possible driving force in the self-assembly of *G1-A16* for gel formation, temperature-dependent ¹H NMR spectroscopic studies were also performed in D₂O-d₆. As shown in Fig. 5f, ¹H NMR spectra of the *G1-A16* (2.0% w/v) in D₂O at different temperatures were compared. One of the H-shifts on the benzene ring of *G1-A16* hydrogel appeared at 8.288 ppm in pure D₂O at 80 °C. The aromatic proton signals showed an up-field shift (blue line in Fig. 5f) when the temperature decreased, which provided the support for the existence of π–π interactions between the phenyl groups of *G1-A16* in the gel state. Concurrently, the ¹H NMR spectral signals of the alkyl chain protons were observed to shift up-field when the temperature reduced (orange line in Fig. 5f). Accordingly, these results reveal that the main driving force for the self-assembly of *G1-A16* in water is the combined interactions of π–π and van der Waals.

These results suggested that the excellent properties of the two-component *G1-Am* gels originated from their highly ordered structures which formed based on the synergistic effect of intermolecular hydrogen bonding, van der Waals, and π–π stacking.

Conclusions

In summary, we have designed a novel multifunctional two-component gel system, which exhibited highly efficient self-healing and room temperature-phase-selective properties, and potential applications in the fields of waste water treatment. The viscoelasticity and self-healing properties of gels can be successfully tuned by changing the length of the alkyl chain of the aliphatic acid component. Surprisingly, the *G1-Am* gel system could gel four organic solvents and water at room temperature. Moreover, the powders of the *G1-A16* could directly gel nitrobenzene/o-dichlorobenzene from their biphasic mixtures with wastewater at room temperature via simple mechanical shaking. In addition, the xerogels obtained from *G1-A16* gel can be used to effectively remove toxic dyes (anionic dyes: AF, EY; cationic dyes: MG, MB, RB) from their aqueous solutions. Further studies on the relationship of gel properties and the component structure and exploring applications of these materials are still in progress.

Additional file

Additional file 1: Scheme S1. The synthetic routes of *Gn*. **Table S1.** Gelation behavior of gelators *G1-Am* (the molar ratio is 1:1) in various solvents at room temperature (about 25 °C). **Table S2.** Gelation behavior of gelators *G2-Am* (the molar ratio is 1:1) in various solvents at room

temperature (about 25 °C). **Table S3.** Gelation behavior of gelators *G1-Am* (the molar ratio is 1:2) in various solvents at room temperature (about 25 °C). **Table S4.** Gelation behavior of gelators *G2-Am* (the molar ratio is 1:2) in various solvents at room temperature (about 25 °C). **Figure S1.** Oscillatory rheological study of gel from *G1-Am* (the molar ratio is 1:2, 2%, w/v): (a) *G1-A12* nitrobenzene gel, (b) *G1-A14* nitrobenzene gel, (c) *G1-A16* nitrobenzene gel (d) *G1-A18* nitrobenzene gel (e) *G1-A16* hydrogel, (f) *G1-A16* hydrogel, (g) Frequency sweep of nitrobenzene gel from *G1-Am* with a fixed strain (0.1%) at 20 °C. **Figure S2.** (a) Specific gelation of the o-dichlorobenzene phase using *G1-A16* (*G1-A16* is 40 mg mL⁻¹) as a phase selection gel in a two-phase mixture of o-dichlorobenzene and wastewater (1 mL/3.0 mL, NaNO₃ and Na₂SO₄ concentration of wastewater is 0.5 M) by mechanical shaking. (b) Separation of the formed gel–water mixture into the o-dichlorobenzene gel via simple scooped out. (c) Recovery of o-dichlorobenzene from the *G1-A16* nitrobenzene gel via distillation, and purification of the restored gelator by recrystallization. **Figure S3.** The molecular structures of dyes. **Figure S4.** Time-dependent UV–vis spectroscopy measurement of the *G1-A16* xerogels-treated RB aqueous solution (a), MO (b), AF (c). **Table S5.** Maximum adsorption capacity of xerogels. (DOXC 1791 kb)

Abbreviations

¹H NMR: H nuclear magnetic resonance; AF: Acid fuchsin; EY: Eosin Y; FESEM: Field-emission scanning electron microscope; FT-IR: Fourier transform infrared spectroscopy; MB: Methylene blue; MG: Malachite green; MO: Methyl orange; PXRD: Powder X-ray diffraction; RB: Rhodamine

Acknowledgements

All authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (grant nos. 21676185) in the design of the study, collection, and analysis. The fundings from Tianjin science and technology innovation platform program (no. 14TXGCCX00017) and Tianjin municipal education commission scientific research project (no. 2018KJ265) are also acknowledged.

Funding

This research was supported financially by the National Natural Science Foundation of China (grant nos. 21676185), the Tianjin science and technology innovation platform program (no. 14TXGCCX00017) and Tianjin municipal education commission scientific research project (no. 2018KJ265).

Availability of data and materials

All data generated or analyzed during this study are included in this published article and in Additional file 1.

Authors' contributions

JZ conceived and carried out the experiments, analyzed the data, and wrote the manuscript. JL, CT, SC, and BaohaoZ carried out the experiments and analyzed the data. BaoZ and JS designed the study, analyzed the data, and wrote the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Author details

¹School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China. ²The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, Tianjin 300072, China. ³Renai College of Tianjin University, Tianjin 301636, China. ⁴Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. ⁵Department of Supramolecular and Biomaterials Chemistry, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

Received: 30 November 2018 Accepted: 14 January 2019

Published online: 01 February 2019

References

1. He Y, Xu M, Gao R, Li X, Li F, Wu X, Xu D, Zeng H, Yuan L (2014) Two-component supramolecular gels derived from amphiphilic shape-persistent Cyclo 6 aramides for specific recognition of native arginine. *Angew Chem Int Ed* 53(44):11834–11839
2. Raeburn J, Adams DJ (2015) Multicomponent low molecular weight gelators. *Chem Commun* 51(25):5170–5180
3. Nandi N, Basak S, Banerjee A, Kirkham S, Hamley IW (2016) Two-component fluorescent-semiconducting hydrogel from naphthalene diimide-appended peptide with long-chain amines: variation in thermal and mechanical strengths of gels. *Langmuir* 32(49):13226–13233
4. Trivedi DR, Dastidar P (2006) Instant gelation of various organic fluids including petrol at room temperature by a new class of supramolecular gelators. *Chem Mater* 18(6):1470–1478
5. 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(15):4226–4251
6. Edwards W, Smith DK (2012) Cation-responsive silver-selective organogel-exploiting silver-alkene interactions in the gel-phase. *Chem Commun (Camb)* 48(22):2767–2769
7. Yan L, Li G, Ye Z, Tian F, Zhang S (2014) Dual-responsive two-component supramolecular gels for self-healing materials and oil spill recovery. *Chem Commun (Cambridge, U K)* 50(94):14839–14842
8. Sharma R K, Adholeya A, Das M, Puri A. (2013). CHAPTER 2 Green Materials for Sustainable Remediation of Metals in Water. In *Green Materials for Sustainable Water Remediation and Treatment* (pp. 11–29): The Royal Society of Chemistry.
9. Readman JW (2006) An introduction to pollution science. RSC, Cambridge, pp 77–121
10. Kakavandi B, Jafari AJ, Kalantary RR, Nasserli S, Ameri A, Esrafilly A (2013) Synthesis and properties of Fe₃O₄-activated carbon magnetic nanoparticles for removal of aniline from aqueous solution: equilibrium, kinetic and thermodynamic studies. *Iran J Environ Health Sci Eng* 10:19
11. Pelletier E, Siron R (1999) Silicone-based polymers as oil spill treatment agents. *Environ Toxicol Chem* 18(5):813–818
12. Lessard RR, Demarco G (2000) The significance of oil spill dispersants. *Spill Sci Technol Bull* 6(1):59–68
13. Swannell RPJ, Lee K, McDonagh M (1996) Field evaluations of marine oil spill bioremediation. *Microbiol Rev* 60(2):342–365
14. Tanmoy K, Sisir D, Dibyendu D, Anshupriya S, Prasanta Kumar D (2009) Organogelation and hydrogelation of low-molecular-weight amphiphilic dipeptides: pH responsiveness in phase-selective gelation and dye removal. *Langmuir* 25(15):8639–8648
15. Jadhav SR, Vemula PK, Kumar R, Raghavan SR, John G (2010) Sugar-derived phase-selective molecular gelators as model solidifiers for oil spills. *Angew Chem Int Ed* 49(42):7695–7698
16. Prathap A, Sureshan KM (2012) A mannitol based phase selective supergelator offers a simple, viable and greener method to combat marine oil spills. *Chem. Commun* 48(43):5250–5252
17. Wang D, Niu J, Wang Z, Jin J (2015) Monoglyceride-based organogelator for broad-range oil uptake with high capacity. *Langmuir* 31(5):1670–1674
18. Karan CK, Bhattacharjee M (2016) Self-healing and moldable metallogels as the recyclable materials for selective dye adsorption and separation. *ACS Appl Mater Interfaces* 8(8):5526–5535
19. Ohseido Y (2016) Low-molecular-weight organogelators as functional materials for oil spill remediation. *Polym Adv Technol* 27(6):704–711
20. Sun HL, Chuai J, Wei H, Zhang X, Yu H (2018) Multi-functional organic gelator derived from phenylacetic acid for phenol removal and oil recovery. *J Hazard Mater* 366:46–53
21. Yan L, Lv M, Su C, Zheng L, Li J, Ye Z (2017) An efficient supramolecular adsorbent for co-adsorption of dyes and metal ions from wastewater and its application in self-healing materials. *Soft Matter* 13(46):8772–8780
22. Yu HT, Liu B, Wang YH, Wang J, Hao QS (2011) Soft Matter. Gallic ester-based phase-selective gelators 7:5133–5135
23. 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* 2:185–186
24. Vemula PK, John G (2008) Crops: a green approach toward self-assembled soft materials. *Acc Chem Res* 41(6):769–782
25. Ren C, Shen J, Chen F, Zeng H (2017) Rapid room-temperature gelation of crude oils by a wetted powder gelator. *Angew Chem Int Ed* 56(14):3847–3851
26. Li J, Huo Y, Zeng H (2018) Polar solvent-induced unprecedented Supergelation of (un)weathered crude oils at room temperature. *Langmuir* 34(27):8058–8064
27. Guan X, Fan K, Gao T, Ma A, Zhang B, Song J (2016) A novel multi-stimuli responsive gelator based on D-gluconic acetal and its potential applications. *Chem Commun (Camb)* 52(5):962–965
28. Liu J, Li J, Lin P, Zhang N, Han X, Zhang B, Song J (2016) Flexible and highly transparent two-component organogels with enhanced viscoelasticity for self-healing materials and room-temperature phase-selective gelation. *Chem Commun (Camb)* 52(97):13975–13978
29. Zhang X, Song J, Ji W, Xu N, Gao N, Zhang X, Yu H (2015) Phase-selective gelators based on closed-chain glucose derivatives: their applications in the removal of dissolved aniline/nitrobenzene, and toxic dyes from contaminated water. *J Mater Chem A* 3(37):18953–18962
30. Bekiari V, Lianos P (2006) Ureasil gels as a highly efficient adsorbent for water purification. *Chem Mater* 18(17):4142–4146
31. Ray S, Das AK, Banerjee A (2007) pH-responsive, bolaamphiphile-based smart metallo-hydrogels as potential dye-adsorbing agents, water purifier, and vitamin B12 carrier. *Chem Mater* 19(7):1633–1639
32. Cho EJ, Jeong IY, Lee SJ, Han WS, Kang JK, Jung JH (2008) Terpyridine-based smart organic-inorganic hybrid gel as potential dye-adsorbing agent for water purification. *Tetrahedron Lett* 49(6):1076–1079
33. Huang S, Yang L, Liu M, Phua SL, Yee WA, Liu W, Zhou R, Lu X (2013) Complexes of polydopamine-modified clay and ferric ions as the framework for pollutant-adsorbing supramolecular hydrogels. *Langmuir* 29(4):1238–1244
34. Okesola BO, Smith DK (2013) Versatile supramolecular pH-tolerant hydrogels which demonstrate pH-dependent selective adsorption of dyes from aqueous solution. *Chem Commun* 49(95):11164–11166
35. Han X, Liu J, Zhao C, Zhang B, Xu X, Song J (2018) Two-component gelator isomers with different combination of amine and acid: helical/non-helical morphology and selective adsorption of dyes. *J Colloid Interface Sci* 525:177–186
36. Weng W, Jamieson AM, Rowan SJ (2007) Structural origin of the thixotropic behavior of a class of metallosupramolecular gels. *Tetrahedron* 63(31):7419–7431
37. Vidyasagar A, Handore K, Sureshan KM (2011) Soft optical devices from self-healing gels formed by oil and sugar-based organogelators. *Angew Chem Int Ed* 50(35):8021–8024
38. Li C, Rowland MJ, Shao Y, Cao T, Chen C, Jia H, Zhou X, Yang Z, Scherman OA, Liu D (2015) Responsive double Network hydrogels of interpenetrating DNA and CB[8] host-guest supramolecular systems. *Adv Mater* 27(21):3298–3304
39. Luo X, Chen Z, Xiao W, Li Z, Wang Q, Zhong J (2011) Two-component supramolecular organogels formed by maleic N-monoalkylamides and aliphatic amines. *J Colloid Interface Sci* 362(1):113–117
40. Zhan C, Gao P, Liu M (2005) Self-assembled helical spherical-nanotubes from an L-glutamic acid based bolaamphiphilic low molecular mass organogelator. *Chem Commun* 4:462–464
41. Miao W, Qin L, Yang D, Jin X, Liu M (2015) Multiple-stimulus-responsive supramolecular gels of two components and dual chiroptical switches. *Chem Eur J* 21(3):1064–1072
42. Bhattacharjee S, Bhattacharya S (2014) Phthalate mediated hydrogelation of a pyrene based system: a novel scaffold for shape-persistent, self-healing luminescent soft material. *J Mater Chem A* 2(42):17889–17898
43. Zhong D-C, Liao L-Q, Wang K-J, Liu H-J, Luo X-Z (2015) Heat-set gels formed from easily accessible gelators of a succinamic acid derivative (SAD) and a primary alkyl amine (R-NH₂). *Soft Matter* 11(32):6386–6392
44. Martinez-Calvo M, Kotova O, Mobius ME, Bell AP, McCabe T, Boland JJ, Gunnlaugsson T (2015) Healable luminescent self-assembly supramolecular metallogels possessing lanthanide (Eu/Tb) dependent rheological and morphological properties. *J Am Chem Soc* 137(5):1983–1992
45. 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(23):6870–6881
46. Janni DS, Manheri M (2013) Hierarchical preferences of hydroxylated oxanorbornane-based achiral amphiphiles. *Langmuir* 29(49):15182–15190

47. Cui J, Zheng Y, Shen Z, Wan X (2010) Alkoxy tail length dependence of gelation ability and supramolecular chirality of sugar-appended organogelators. *Langmuir* 26(19):15508–15515
48. Liu J-W, Yang Y, Chen C-F, Ma J-T (2010) Novel anion-tuning supramolecular gels with dual-channel response: reversible sol-gel transition and color changes. *Langmuir* 26(11):9040–9044
49. Rajamalli P, Prasad E (2011) Low molecular weight fluorescent organogel for fluoride ion detection. *Org Lett* 13(14):3714–3717
50. Banerjee A, Palui G, Banerjee A (2008) Pentapeptide based organogels: the role of adjacently located phenylalanine residues in gel formation. *Soft Matter* 4(7):1430–1437
51. Cao H, Yuan Q, Zhu X, Zhao Y-P, Liu M (2012) Hierarchical self-assembly of achiral amino acid derivatives into dendritic chiral nanotwists. *Langmuir* 28(43):15410–15417
52. Shen Z, Jiang Y, Wang T, Liu M (2015) Symmetry breaking in the supramolecular gels of an achiral gelator exclusively driven by π - π stacking. *J Am Chem Soc* 137(51):16109–16115

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- ▶ Convenient online submission
- ▶ Rigorous peer review
- ▶ Open access: articles freely available online
- ▶ High visibility within the field
- ▶ Retaining the copyright to your article

Submit your next manuscript at ▶ [springeropen.com](https://www.springeropen.com)
