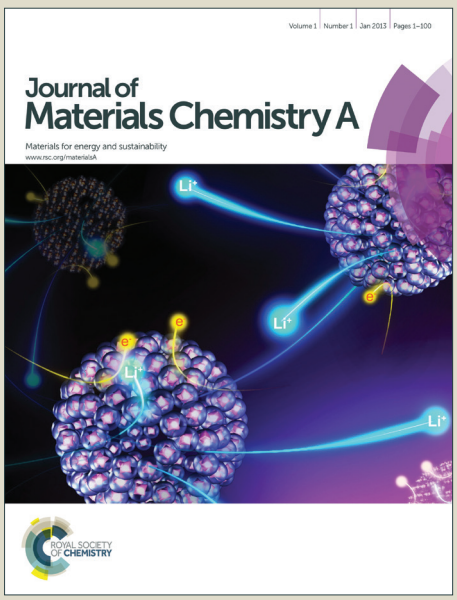
Journal of Materials Chemistry A

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsA

Easy-to-implement methods were realized with glucose-based gelators for the efficient removal of aniline/nitrobenzene, and toxic dyes from contaminated water.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Phase-selective gelators based on closed-chain glucose derivatives: their applications in the removal of dissolved aniline/nitrobenzene, and toxic dyes from contaminated water

Xin Zhang,‡ Jiefang Song,‡ Wei Ji, Ning Xu, Ning Gao, Xuhong Zhang, and Haitao Yu*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Several effective PSGs have been developed out of a series of glucose-based compounds for the removal of aniline and nitrobenzene from their biphasic mixtures with water via a simple shaking strategy at room temperature within 1 min. The morphologies of the gels formed in aniline and nitrobenzene in the absence or presence of a large amount of water have been examined by field emission scanning electron microscopy (FE-SEM). The dominant factors that drive gelation in the case of the gelator and aniline or nitrobenzene have been studied using FT-IR, concentration-dependent ^{1}H NMR, and XRD. Besides, the efficient purification of toxic dye solutions has been realized by using one of these gelators as the adsorbent in the applied form of gel column. And the corresponding xerogel can also be used for the efficient dye removal. HPLC and UV/vis spectroscopy provide the quantification means for the estimation of the purification efficacy. The easy-to-implement performance and high removal efficiency of the organic pollutants from water indicate the potential and promising applicability of these organogelators in water purification.

Introduction

Two explosion incidents followed by the spillage of some materials of organic chemistry industry such as benzene, nitrobenzene, and aniline from chemical plants have recently been reported in China.[1] Benzene is prone to be burnt out into carbon dioxide and water during the explosion and fire, but this is impossible for nitrobenzene and aniline, leading to the spill of a large amount of these toxic organic liquids into the local river, which not only threatened the fresh water ecology but also polluted the local sources of drinking water. What's even worse is that these aromatic hydrocarbon pollutants are too hard to be degraded naturally. In response to this austere situation, apart from strict maintenance of the industrial safety in production and operation, people are drived to develop powerful approaches for the simple and efficient treatment of similar spill cases. Currently, the optional materials or methods for the treatment of such organic liquid pollutants involve adsorbents, polymeric solidifiers, chemical dispersants, and microbials.[2] These approaches, however, have some limitations in practice. Activated carbons, for instance, are very efficient for the organic pollutants as adsorbing materials due to their high ratio surface area, but the post-treatment of this method is very expensive.[2a] Polymeric solidifiers are difficult to be mixed with the viscous organic liquids, and the post-process intricacy is disadvantageous to the recovery of the organic pollutants from polymer gels.[2b] The use of chemical dispersants is usually time-consuming, and sometimes tends to cause the secondary pollution on the aquatic organisms.[2b, 2c] The bioremediation based on microbials is promising but immature, in which the spread of the microbials needs to be accompanied with a large amount of phosphates, and how to securely control them is a problem.[2d]

Phase-selective gelators (PSGs) that prefer to gelate one solvent rather than gel the other in a given biphasic mixture, have been actively studied on water purification and the oil spill recovery from water. Since Bhattacharya and co-workers published their pioneering findings in this research area in 2001,[3] a few more elegant results regarding phase-selective molecular systems based on amino acids/peptides,[4] carbohydrates,[5] cholesteryl derivatives,[6] organic salts,[7] and calixarene derivative,[8] have also been reported in recent decade. However, most of the results in the literature were subjected to the heating-cooling process or the addition of co-solvent for the realization of the phase-selective gelation, which limited their applications in practice. The reports related to phase-selective gelation for the oil spill recovery without the need of the heating-cooling process or the addition of co-solvent, to the best of our knowledge, are very few in number.[6] In addition, the research on the phase-selective gelation of some important organic industrial resources such as aniline and nitrobenzene, which may be spilled into freshwater, is rarely reported. Recently, our group reported a series of gallic ester-based organogelators for the selective gelation of aniline and its derivatives in the presence of excess water, however, in which heating and cooling cycles were still required to complete phase-selective gel formation.[9]

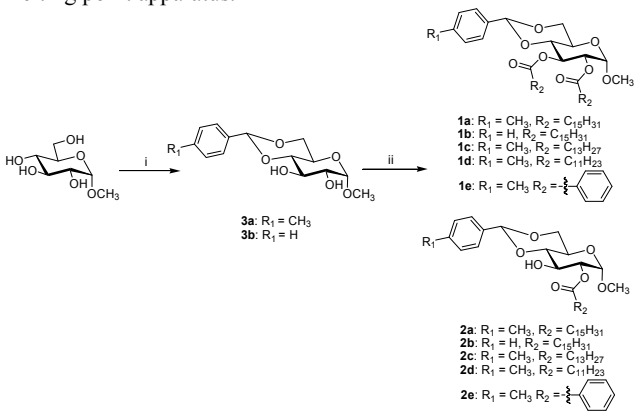
In general, an ideal and suitable phase-selective gelator for the practical application should have advantageous features as

follows: i) the gelator can be obtained in large quantities by simple synthesis from easily available and cheap starting materials, ii) it must be non-toxic and eco-friendly materials, and prone to be degraded naturally into harmless species, iii) the formed gel can be isolated from water readily, iv) the implementation process should be feasible and efficient at room temperature, v) the organic liquid pollutants can be recovered easily, and vi) the gelator can be restored for cyclic utilization. The development of such gelators that can satisfy all the demands mentioned above still remains a major challenge and is desired very much. To this end, we develop a series of glucose-derived organogelators (Scheme 1) in the present work as PSGs for specific gelation of aniline and/or nitrobenzene from their two-phase mixtures with water.

Experimental section

Materials and methods

All the materials for synthesis were obtained from commercial suppliers. All organic solvents of analytical grade for synthesis were obtained commercially and were used without further purification. All reactions were monitored by thin-layer chromatography (TLC) with 0.25-mm Merck silica gel plates (60F-254) under irradiation by UV-lamp (254 nm). Merck Millipore silica gel (300-400 mesh) was used in the column-chromatography purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance AVIII-500Q spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured using AB SCIEX 3200Q TRAP LC/MS/MS system united with Agilent 1260 Infinity HPLC. Elemental analyses were performed using an Elementar Vario EL III elemental analyzer (Germany). Melting points were determined by a X-4 melting point apparatus.



Scheme 1 i) p-Tolualdehyde/benzaldehyde, zinc chloride, N_2, room temperature, 6 h, 73 %-82.5 %; ii) R_2COOH, DCC, DMAP, CH_2Cl_2, room temperature, 24 h, 65 %-87.5 %.

Gelation test for compounds

Method. The gelation abilities of these closed-chain glucose based esters were estimated by mixing a tentative amount of the gelator (30 mg) with 0.3 mL of a pure liquid in a septum-capped vial, heating until solids were dissolved completely, and then cooling to room temperature. As a defining characteristic, the gelation was confirmed upon upending the vial in which the gels stay where they are, after several thermoreversible tests.[10]

Minimum gelation concentration (MGC) test. The MGCs of the tested gelators were determined by a dilution method. Firstly, 30 mg of each gelator was added into 0.3 mL of a known liquid in a septum-capped vial. Then the formed gel system was diluted gradually by small amount of the tested liquid and the heating/cooling process was repeated until gel state could not be kept any more. The last mass percentage concentration at which gel state could be remained was recorded as the MGC with wt% as the unit. More than three times for each assay have been done and stable values were determined to be the MGC.

Gel-to-sol transition temperatures (*T*g) test. The gel-to-sol transition temperatures (*T*g) of the formed gels in various organic liquids were determined by a traditional "dropping ball" method.[10] In practice, a small glass ball of 100 mg was carefully placed on the surface of the gel in a sealed vial, which was slowly heated (1 ^{o}C/min) in a thermostated oil bath until the ball fell to the vial bottom. The temperature of this moment was recorded and determined as *T*g of this gel system.

Instrumentation for gel characterization

Study of scanning electron microscopy (SEM). SEM imaging was carried out on a Hitachi S4800 FE-SEM microscope. The samples for SEM images were fabricated by drying the gels on glass sheets via slow evaporation of the solvents under vacuum for 24 h, followed by a freeze in liquid nitrogen.

Study of FT-IR spectroscopy. IR spectra were performed on a FTIR-8900 spectrometer (Shimadzu Corporation) with KBr pellets. The xerogels were prepared by drying aniline-gels or nitrobenzene-gels of the gelators at their MGCs on glass slices under vacuum for 24 h, followed by a freeze in liquid nitrogen.

Powder X-ray diffraction (PXRD) study. The PXRD spectra of neat gelators and xerogels which were prepared from aniline or nitrobenzene gels, frozen in liquid nitrogen, and finally dried under vacuum, were determined by Bruker D8 ADVANCE (Cu Kα radiation, λ = 1.546 Å). The resulting data were processed by Origin 7.5 with curve smoothing operations. The *d* spacing values were calculated by Bragg's law ($n\lambda = 2d\sin\theta$, *d* is the distance between atomic layers in a crystal or a molecular aggregate; λ is the wavelength of the incident X-ray beam; n is an integer which is generally adopted as 1).[11]

Phase-selective gelation test

Implementary method. Only mechanical shaking as an implementary means in the present work was employed for the realization of the phase-selective gelation of aniline or nitrobenzene in their water mixtures using gelators **1a**, **1b** and **2b** (Figure 5a, and S6 in the ESI†). In a typical manipulating procedure, a required amount of the tested gelator (the concentration is above its MGC in the corresponding organic phase) was directly added to a mixture of aniline or nitrobenzene and water in a glass vial. Then a vigorous shaking was performed to ensure the sufficient dispersion of the gelator in the corresponding organic phase. After the resulting feculent mixture was rested at room temperature for several minutes, the bulk gel formed, leaving the water phase in fluid state.

Determination of removal efficiency. The removal efficiency of aniline or nitrobenzene from water, which reflected the phase-

selective gelation efficacy by using gelators **1a**, **1b** and **2b** as PSGs, was determined by high performance liquid chromatography (1100 America Agilent) with ZORBAX SB-C18 (150 mm × 4.6 mm, 5 μm). The working condition was optimized as follows: flow rate was 1 mL/min, mobile phase was methanol/water with 50 : 50 (v/v) ratio, each sample was injected with 5μl, the operation temperature was 25 °C, pH = 7.0. The absorption wavelengths of aniline and nitrobenzene were recorded at 230 nm and 268 nm, respectively.

Test for dye adsorption

Estimation of removal capacity. The removal efficiency of a dye from its aqueous solution was estimated by UV/vis spectroscopy on a Perkin-Elmer Double Beam UV/vis Spectrometer. And the final concentration of the dye in solution was calculated according to the Beer-Lambert law ($A = \varepsilon bc$, A is the absorbance of the dye at a certain absorption wavelength in solution, ε means the molar extinction coefficient with the unit as $mol \cdot L^{-1} \cdot cm^{-1}$, b is the path length of the incident light with the unit as cm, c is the concentration of the dye in solution with the unit as $mol \cdot L^{-1}$).[12] The molar extinction coefficients of CV (A_{583}) and Rhodamine B (A_{553}) in their aqueous solutions were calculated with $b = 1.0$ cm as 2.53×10^4 and 1.76×10^4. Thus, the final concentration of the dye in solution could be obtained by the Beer-Lambert's equation, which finally determined the removal efficiency (RE) of the dye via the equation as follows: RE = (Ci-Cf)/Ci, in which Ci represents the initial concentration of the dye in solution; Cf is the final concentration of the dye in the presence of an adsorbing agent.

Gel column. In general, 2 mL of **1a**-benzyl alcohol gel was filled into a plastic syringe with some degreased cotton at the bottom of the syringe. And an aqueous solution of the dye could be added from the top of the column, and then an outflow of clear water from the bottom of the column was observed with the flow velocity as one drop per 10-15 seconds under atmospheric pressure and room temperature.

Results and discussion

Synthesis and gelation capability of the target compounds

The synthesis of the target derivatives was carried out only in two steps which are outlined in Scheme 1. Firstly, methyl-α-D-glucopyranoside as the starting material which can be available commercially and cheaply was reacted with p-Tolualdehyde or benzaldehyde to give acetals **3a** and **3b**, respectively. Then acetals **3** were reacted with 2 equivalents of corresponding carboxylic acids to give diester derivatives **1a-e** in good yields of 65 %-87.5 %. While the esterification was carried out with 1 equivalent of carboxylic acid reactants, 2-monoesters **2a-e** were mainly separated out of the crude products in satisfying yields (67 %-77.5 %) for further property tests. All the synthesized compounds were fully characterized by ^1H and ^{13}C NMR spectra, mass spectrometry, and elemental analysis, as collected in the ESI†.

The gelation abilities of these target compounds were estimated by the heating-and-cooling method and determined by a sealed-vial inversion characteristic,[13] which are summarized in Table S1 (ESI†). As observed, long alkyl chain bearing esters **1a-d** and **2a-d** can gelate some organic liquids (polar/non-polar and protic/aprotic), such as aromatic solvents, straight-chain and cyclic aliphatic hydrocarbons, alcohols, esters, carboxylic acids, and other polar solvents with the minimum gelation concentration (MGC) values in wt% ranging from 1.07-5.10 (Table S2, ESI†). Notably, benzoic acid-derived esters **1e** and **2e** are poor gelators for almost all of the tested solvents, clearly indicating the important roles of the presence of the long alkyl chains in the structures of gelators **1a-d** and **2a-d** play in their gelation behaviours in organic liquids. The gel-to-sol transition temperatures (Tg) for the resulting gels at gelator MGCs were evaluated to be 29-65 °C. Moreover, the heating/cooling cycles could be repeated for more than 50 times in the gelation solvents, indicating that these gels are completely thermo-reversible. Most of the gels are robust and stable for at least one month at room temperature.

Among these glucose-based derivatives, both diesters **1a** and **1b** were found to be effective gelators for aniline, besides stable gels in nitrobenzene were able to be formed by using diester **1b** and 2-monoester **2b** as gelators. Thus, **1b** was found to be able to gelate either aniline or nitrobenzene (Figure S1, ESI†). Furthermore, gel formation of these gelators in aniline or nitrobenzene could be realized not only by heating/cooling cycles, but also by shaking/resting means at room temperature. For instance, a mixture of a tentative amount of **1a** with the corresponding volume of aniline was shaken vigorously until **1a** was dissolved to give a homogeneous solution, and then the solution was rested at room temperature, leading to gel formation spontaneously within 1 min (Figure 1a). The similar behaviours were also observed for gel formation with either **1b** or **2b** in aniline or nitrobenzene (Figure 1b, and Figure S2 in the ESI†). These findings established the basis for the real-life applications of these gelators in phase-selective gelation of aniline and/or nitrobenzene from water at room temperature.

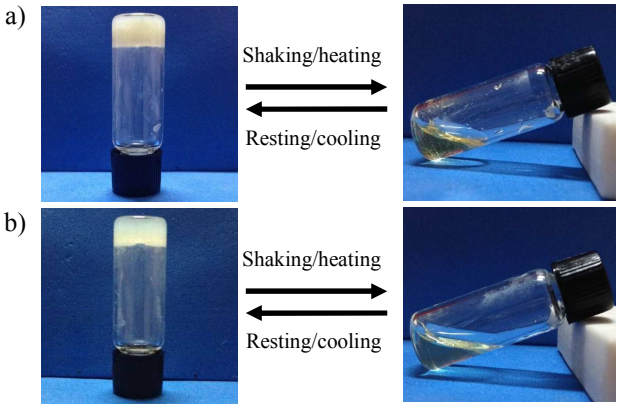


Fig. 1 Reversible sol-to-gel transitions of 1a-aniline gel (a) and 1b-nitrobenzene gel (b) at their MGCs, stimulated by shaking or heating.

Gel characterization

The morphologies of the xerogels obtained from gels **1a**, **1b**, and **2b** in aniline or nitrobenzene were examined by scanning electron microscopy (SEM). As shown in Figure 2, well-defined three dimensional (3D) network structures involving in the entanglement of tape-like (Figure 2a), plank-like (Figure 2b), petal-like (Figure 2c), and strip-like (Figure 2d) aggregates were observed from **1a**-aniline, **1b**-aniline, **1b**-nitrobenzene, and **2b**-nitrobenzene xerogels, respectively. Further magnified SEM

images (Figure S3, ESI†) illustrated that these bulk aggregates emanate from the agglomeration of countless one-dimensional (1D) supramolecular fibres of different thicknesses which were self-assembled by gelator molecules. Such 3D networks with the entanglement of bundles of fibres should be responsible for the entrapment and fixation of organic liquid molecules to form a gel.

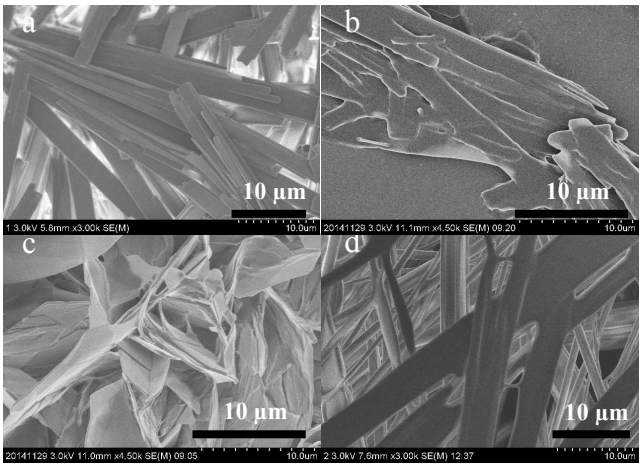


Fig. 2 SEM images of xerogels prepared by **1a**-aniline gel (a), **1b**-aniline gel (b), **1b**-nitrobenzene gel (c), and **2b**-nitrobenzene gel (d) at their MGCs.

In view of the similar structural features, **1b** and **2b** were exemplified as the representative gelators of the diester series and the 2-monoester series, respectively, for the investigation of the driving forces for the self-assembly of the gelators in organic liquids. For this purpose, FT-IR spectroscopic studies were performed on the inducement that can drive the gelators to self-assemble into nanofibers in aniline or nitrobenzene. It was found in Figure 3 that the absorption bands at 2922 cm^{-1} and 2859 cm^{-1} assigned to the asymmetric ($\nu_{as}CH_2$) and symmetric (ν_sCH_2) stretching vibrations of the alkyl chains were observed in the neat solid of **1b**, whereas the peaks at 2920 cm^{-1} and 2851 cm^{-1}, and 2918 cm^{-1} and 2849 cm^{-1} appeared in **1b**-aniline xerogel and **1b**-nitrobenzene xerogel, respectively. Besides, the absorption band arising from the deformation vibration (δCH_3) of the alkyl chains appeared at 1460 cm^{-1} in the neat solid of **1b**, which showed slight shifts to 1465 cm^{-1} and 1468 cm^{-1}, respectively, in **1b**-aniline xerogel and **1b**-nitrobenzene xerogel. These findings clearly demonstrated that van der Waals interaction between the alkyl chains which can decrease the mobility of the alkyl chain may play important role in the self-assembly of gelator **1b** in either aniline or nitrobenzene.[14] The similar changes were also observed in the IR spectrum of **2b**-nitrobenzene xerogel, as compared with the case of the neat solid of **2b** (Figure S4, ESI†). As no forming conditions of the hydrogen bond existing in the **1b** structure, hydrogen bonding was not considered to be a driving force for the self-assembly of **1b**, furthermore, no changes were observed in the absorption band at 1738 cm^{-1} ascribed to the C=O stretching vibration of the ester groups in either **1b**-aniline or **1b**-nitrobenzene xerogel, as compared with that in the neat solid of **1b**, revealing that the ester groups did not participate in the gelator self-assembly at all.[15]

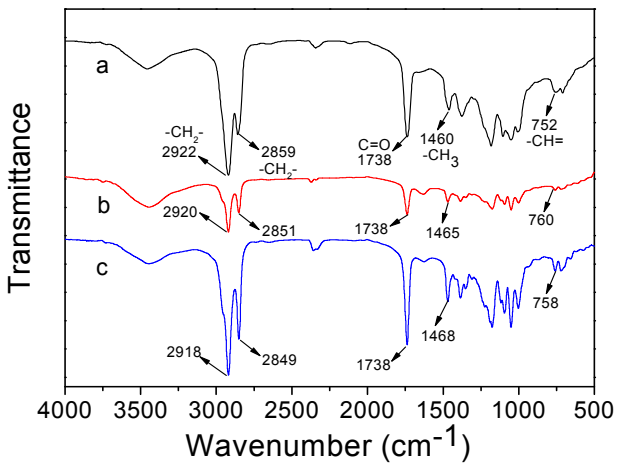


Fig. 3 FT-IR spectra of **1b**: (a) neat solid, (b) xerogel from aniline at its MGC, and (c) xerogel from nitrobenzene at its MGC.

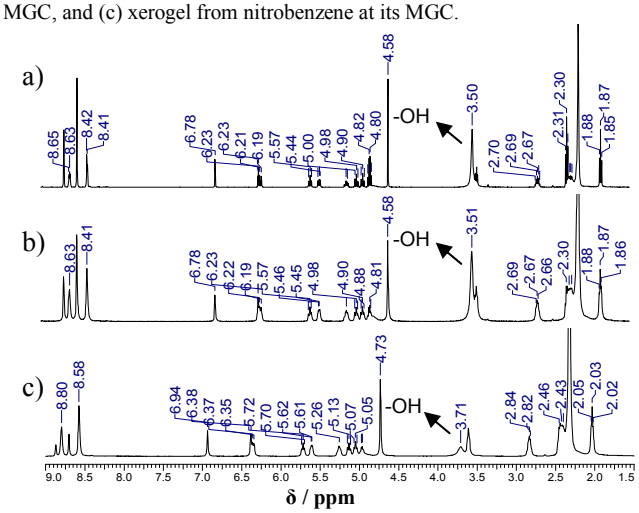


Fig. 4 Changes in the ^{1}H NMR (500 MHz) spectra of **2b** at different concentrations in nitrobenzene-d5 at 25 °C: (a) 5 mg/ml (solution), (b) 30 mg/ml (solution), (c) 50 mg/ml (4.0 wt%, gel state).

In order to gain further understanding on the possible role that hydrogen bonding may play in the self-assembly of gelator **2b** for gel formation, concentration-dependent ^{1}H NMR spectroscopic studies were also undertaken in nitrobenzene-d5. As shown in Figure 4, no significant changes were observed in the chemical shift of **2b** protons in solutions with different concentrations, however, gel formation of gelator **2b** lead to a downfield shift (from δ = 3.51 to 3.71 ppm) for the signals ascribed to the protons of the hydroxyl groups, and the sharp signals in solution become broad in gel state. This is taken as an indication that intermolecular hydrogen bonding may participate in gel formation.[5b] In addition, the aromatic proton signals corresponding to the phenyl rings showed a downfield shift in gel state as compared to the cases in solutions, which provided the support for the existence of π-π interactions between phenyl groups of **2b** in gel state. Concurrently, the ^{1}H NMR spectral signals of the alkyl chain protons were seen to shift downfield (*e. g.* from δ = 1.87 ppm in solution to 2.03 in gel). Accordingly, these results lead us to suggest that gel formation of **2b** in nitrobenzene resulted from the associated interactions of hydrogen bonding, π-π, and van der Waals.

Also, X-ray diffraction analysis was conducted for the further understanding of gelator self-assembly properties in the gel phase. It can be seen from Figure S5 (ESI†) that xerogels **1b** prepared from aniline and nitrobenzene should possess similar packing mode that is evidently different from that of xerogel **2b** obtained from its nitrobenzene-gel. Additionally, intense reflections with *d* spacings of 0.45 nm and 0.42 nm were observed in xerogels **1b** and **2b**, respectively, which are usually corresponding to disordered alkyl chains.[16] And a *d* spacing value of 0.37 nm which is close to the typical π-π stacking distance (0.35 nm) of the phenyl rings was observed in either xerogels **1b** or xerogel **2b**.[17] In addition, the proposed π-π interactions could be also testified by the fact that the red shift of the UV absorption spectra of **1b** solutions was induced by the increase of **1b** concentration (Figure S12 in the ESI†), which indicated the possible presence of J-type aggregation of the gelator.[5b, 13f] As analyzed above, the van der Waals interaction between the alkyl chains was thus considered to be the major driving force for supramolecular self-assembly of **1b** in either aniline or nitrobenzene, sequentially, the π-π stacking interaction between the phenyl moieties also offered the contribution in gel formation.

Phase-selective gelation of aniline and nitrobenzene in their water mixtures

The feasibility of actualizing methods is the key for the practical application of a PSG in the treatment of spillage event. The use of co-solvent is a popular approach in the literature. However, some of the reports were involved in the use of water-soluble toxic solvent like tetrahydrofuran or methanol which may introduce the secondary pollution to water, limiting the applied values of the reported PSGs.[5b, 5e, 7a] For the gelators reported in this work, simple mechanical shaking could realize the homogeneous dispersal of the gelators in organic phase and further facilitate to complete gel formation in water. For instance, compound **1a** with the concentration above its MGC in aniline was directly added to an aniline/water (0.5 mL/2.0 mL) mixture in a glass vial, and then a vigorous concussing was carried out to cause the sufficient dissolution of **1a** in aniline. The resulting feculent mixture was rested at room temperature, giving rise to a gel-like chunk within 1 min. The mixture was then filtered by common filter paper, leaving the water clear, as shown in Figure 5a. It is worth mentioning that the morphology (Figure 6a) of the xerogel obtained from the separated gel from water looks almost the same to that of the xerogel that was prepared from the gel formed in pure aniline (Figure 2a), indicating the presence of a large amount of water did not impact the formation of 1a-aniline gel. The similar phenomena were also observed for other xerogels, as shown in Figure 2b-2d and Figure 6b-6d. Furthermore, the gelator and aniline could be recycled via simple distillation, and the restored gelator could be purified by recrystallization for its reuse (Figure 5b). The similar results could be also obtained using **1b** or **2b** for the phase-selective gelation of aniline or nitrobenzene in their water mixtures (Figure S6, ESI†). In addition, if the homogeneous sols of **1a** and **1b** in aniline formed via the shaking process were dropped slowly on the surface of water in vials, the resulting gels could seal water in vials and support their own weights plus the weight of water when the vials were inverted. Since the density of nitrobenzene is much higher than that of water, the nitrobenzene gels formed in nitrobenzene/water biphasic mixtures by using **1b** and **2b** as PSGs could remain at the bottom of the vials when they were inverted, leaving water at the top of the vials. These findings, as shown in Figure S7 (ESI†), indicated that these phase-selectively formed gels possess relatively high mechanical strength, which is beneficial to the real-life applications of these gelators in the treatment of water pollution.

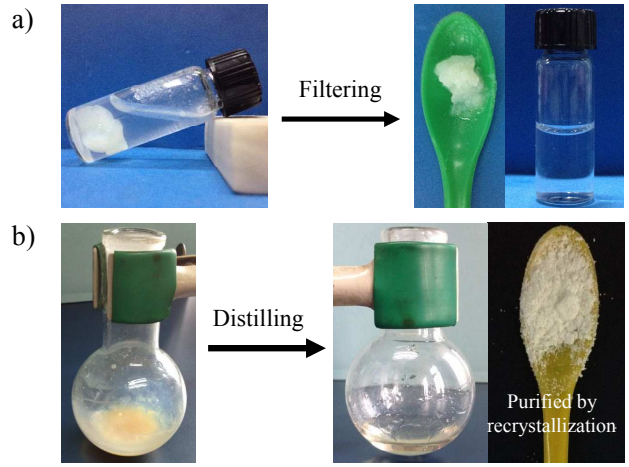


Fig. 5 (a) Specific gelation of the aniline phase by using **1a** (concentration of **1a** is 45 mg/ml in aniline phase) as PSG in a two-phase mixture of aniline and water (0.5 mL/2.0 mL) by mechanical shaking, and separation of the formed gel-water mixture into the aniline gel and clear water via simple filtration. (b) Recovery of aniline from 1a-aniline gel via distillation, and purification of the restored gelator by recrystallization.

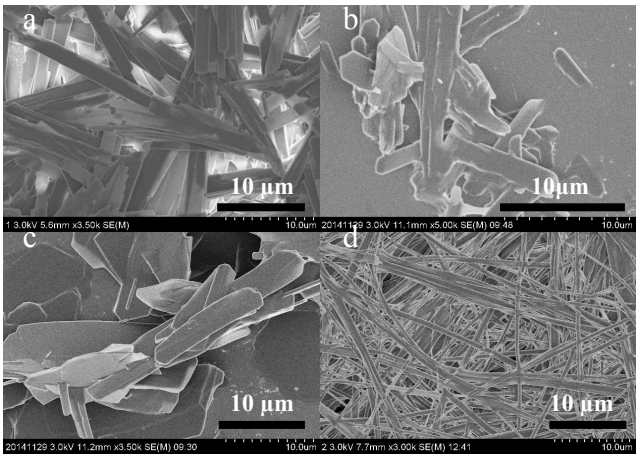


Fig. 6 SEM images of xerogels obtained from the gels which were formed in water mixtures of aniline/nitrobenzene: (a) **1a**-aniline gel, (b) **1b**-aniline gel, (c) **1b**-nitrobenzene gel, and (d) **2b**-nitrobenzene gel at their MGCs.

The removal efficiency of an organic pollutant in water is the most critical performance parameter for the application of a PSG in the water purification. In this work, efforts to quantify the removal efficiency of aniline or nitrobenzene were made by high performance liquid chromatography (HPLC) with **1a**, **1b**, and **2b** as the PSGs. First of all, the removal efficiencies of aniline and nitrobenzene were investigated by alternating the gelator concentrations in organic phases with the volume ratio as 0.5 mL/2.0 mL between the organic phase and water phase. Consequently, a much higher efficiency of 98 % was achieved with **1a** (4.2 wt% in aniline phase) as the PSG for aniline as

compared with the value of 94 % with **1b** (5.4 wt% in aniline phase) tested under the same condition (Table S3, ESI†). Besides, relatively high efficiencies of 88 % and 85 % for nitrobenzene were also obtained by using **1b** (4.7 wt% in nitrobenzene phase) and **2b** (5.6 wt%) as the PSGs, respectively, with the same volume ratio of 0.5 mL/2.0 mL between nitrobenzene and water (Table S4, ESI†). Next, based on the optimum removal concentrations of the gelators, we further probed the removal abilities of **1a** and **1b** for aniline and nitrobenzene in their biphasic mixtures of different volume ratios between the organic phase and water phase (Table S5, ESI†). A similar removal efficiency of 98 % for aniline was obtained with **1a** (4.2 wt%) as the PSG in aniline/water mixture with the volume ratio as 0.1 mL/2.0 mL. The removal efficiency has been raised by about 17 % compared to the reported value (81 %).[9] Finally, in view of the ability of **1b** to gelate both aniline and nitrobenzene, 0.25 mL of aniline and 0.25 mL of nitrobenzene were mixed with 2.0 mL of water to mimic the case of simultaneous spillage of these two toxic liquids for the investigation of the removal efficiencies of them (Table S6, ESI†). The efficiencies were found to be up to 94 % and 87 %, respectively, for the removal of aniline and nitrobenzene when 5.1 wt% of **1b** was used in the organic phase, indicating **1b** can be employed to deal with the simultaneous spillage case.

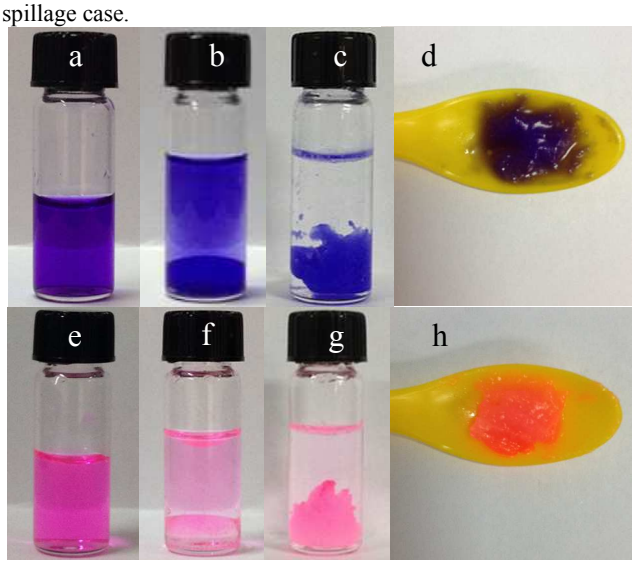


Fig. 7 Photographs of (a) CV (0.098 mmol·L^{-1}) aqueous solution (2.0 mL), (b) CV aqueous solution + 0.2 mL of benzyl alcohol, (c) CV aqueous solution + **1a**-benzyl alcohol gel (2.3 wt% of **1a** in 0.2 mL of benzyl alcohol), (d) CV-adsorbed gel, (e) rhodamine B (0.17 mmol·L^{-1}) aqueous solution (2.0 mL), (f) rhodamine B aqueous solution + 0.2 mL of benzyl alcohol, (g) rhodamine B aqueous solution + **1a**-benzyl alcohol gel (2.3 wt% of **1a** in 0.2 mL of benzyl alcohol), (h) rhodamine B-adsorbed gel.

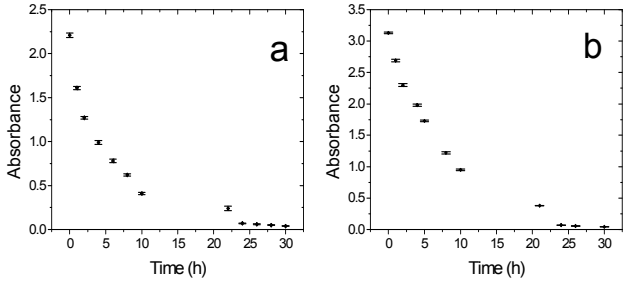


Fig. 8 Absorbance changes of the dye solutions with **1a** gel as the adsorbing agent (2.3 wt% of **1a** in 0.2 mL of benzyl alcohol) recorded at 583 nm for CV (0.098 mmol·L^{-1}) (a), and at 553 nm for rhodamine B (0.17 mmol·L^{-1}) (b).

Dye adsorption

The industrial and life discharge of water-soluble toxic dyes to groundwater is another environmental and economical hazard, so the treatment of such pollutants has also been an focused research area recently.[18] In our case, compound **1a** as a typical adsorbing agent was found to be able to remove the toxic dyes such as crystal violet (CV) and rhodamine B from their aqueous solutions. And two actualizing avenues were available for **1a** to realize the adsorption of the dyes by the gel formed in a certain solvent, and via the xerogel. And the capacity of **1a** to remove the dye was estimated by UV/vis spectroscopy. For the former method, taking the high toxicity of aniline or nitrobenzene into account, benzyl alcohol, a relative safe solvent which is usually permitted to be food flavor (GB2760-2014, Chinese National Food Safety Standards), was employed as the gelation solvent in this work. In a given amount, the efficient removal behaviors, as described in Figure 7, were observed based on this method after 24 h for both CV and rhodamine B with the efficiencies as 97 % (Table S7 in the ESI†), and after 30 h the intensities of the absorption of the dyes almost disappeared (Figure 8a and 8b). It is worth mentioning that although benzyl alcohol could extract the dyes from water to the organic layer, the efficiency was much lower (Figure S9, ESI†), indicating the presence of **1a** enhanced the adsorption capacity for the dyes due to the formation of the supramolecular 3D networks comprised of countless nanofibers with high adsorbing surface areas. And the adsorption driving forces may ascribe to the existence of both of the hydrophilic glucose head and the hydrophobic alkyl chains in **1a** structure, which is advantageous for the accommodation of the organic dyes out of water.[18a, 18c] However, the separation process was inconvenient, and the adsorption rate was very slow (the pseudo second-order adsorption constants for CV and Rhodamine B were 1.1 × 10^{-2} and 2.9 × 10^{-2} g/mg h, respectively)[18e] by only using gel **1a** as the adsorbent. In order to facilitate the practical application in water purification, gel column was made by filling **1a**-benzyl alcohol gel in a plastic syringe, as shown in Figure 9a and Figure S10a (ESI†). Excitingly, the one-time removal efficiencies using **1a**-gel column (2.3 wt% of 1a in 2.0 mL of benzyl alcohol) could reach up to 99 % and 98 % for CV (0.098 mmol·L^{-1}, 2.0 mL) and rhodamine B (0.17 mmol·L^{-1}, 2.0 mL), respectively (Figure 9b, and Figure S10b and Table S7 in the ESI†). Interestingly, when 1.5 mmol·L^{-1} of CV and 1.3 mmol·L^{-1} of rhodamine B passed through the gel column under the same condition mentioned above, the removal efficiencies could be 99 % although there were 0.0056 mmol·L^{-1} of CV and 0.0075 mmol·L^{-1} of rhodamine B left in the purified water. Accordingly, the saturated amount of the dye uptake using the gel column for both CV and rhodamine B were estimated as 24 mg/g (mass of the uptake dye per unit mass of gelator). And the purification process could be completed within 20 min under atmospheric pressure and room temperature. It should be pointed out that although this is an efficient removal means, trace amount of benzyl alcohol could remain in the clear water during the purification process at room temperature. And the increase of the

gelator concentration in the gel phase could decrease the leakage of benzyl alcohol to the purified water. For instance, when the concentration of **1a** was 2.3 wt%, the concentration of benzyl alcohol in the purified water was 1.1 mg/mL, whereas the use of 3.7 wt% of **1a** could result in only 0.33 mg/mL of benzyl alcohol remaining in the purified water. In addition, it was found that scarcely any benzyl alcohol remained in the purified water when the purification process was operated at low temperature (below 10 °C).

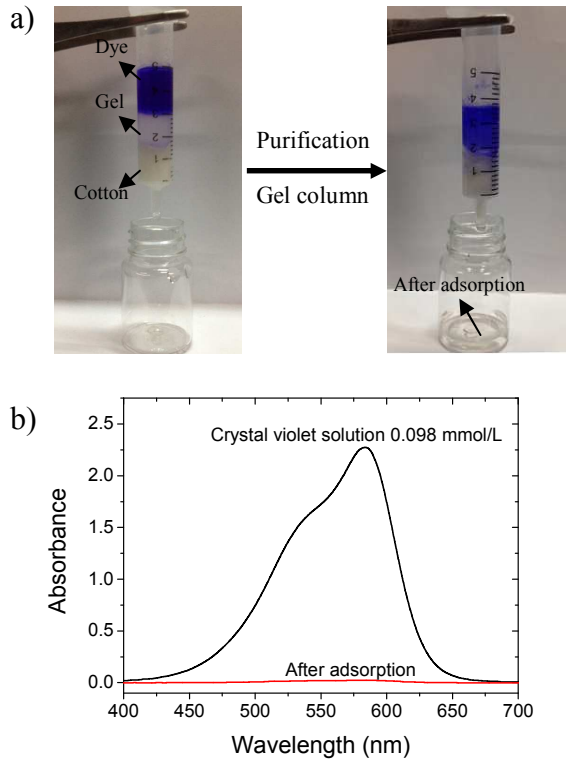


Fig. 9 (a) Removal of crystal violet from its aqueous solution by **1a**-benzyl alcohol gel (2.3 wt% of **1a** in 2.0 mL of benzyl alcohol) column. (b) UV/vis spectral changes of the aqueous solution of crystal violet (0.098 mmol·L^{-1}) before and after purification by gel column.

On the other hand, the xerogel prepared from the **1a**-benzyl alcohol gel could also undertake the task for the adsorption of the dyes (Figure 10a-b, and Figure S11a-b in the ESI†), and the removal capacities using the xerogel obtained from 4.6 wt% of **1a**-benzyl alcohol gel for CV and rhodamine B from their aqueous solutions could reach to 98 % and 97 %, respectively (Figure 10d, and Figure S11d in the ESI†). Furthermore, the adsorbent could be recovered by eluting the dye-adsorbed xerogel with methanol, as depicted in Figure 10c, and S11c (ESI†). These findings indicate **1a** is an excellent water purification agent for the toxic dyes.

Conclusions

In summary, a series of glucose-based organogelators have been synthesized with relatively high synthesis yields, which may satisfy the need of mass production. These gelators are able to gel a wide range of organic liquids, and some of them are particularly effective phase-selective gelators for aniline and/or nitrobenzene in their biphasic mixtures with water with the advantages of harmlessness to natural environment, feasible and easy-to-implement method via mechanical shaking, high removal capacity (~98 %), easy recycle of the gelator and organic liquids by simple distillation. In addition, gelator **1a** can be used to effectively remove crystal violet and rhodamine B from their aqueous solutions with the removal efficiencies more than 97 % by either gel form or xerogel. Especially, the use of the gel column can aid the real-life application of **1a** in water purification and enhance the removal efficiency to ~99 % for one-time purification. The impressive study in this work lead us to believe that these organogelators will be promising water purification agents for the future applications.

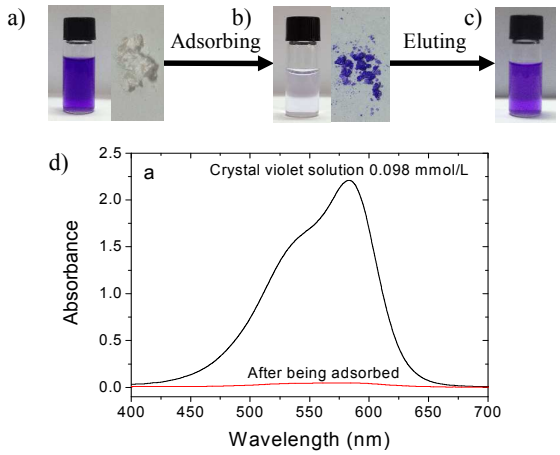


Fig. 10 Photographs of (a) an aqueous solution (2.0 mL) of CV (0.098 mmol·L^{-1}) and the xerogel obtained from **1a**-benzyl alcohol gel (4.6 wt% of **1a** in 0.2 mL of benzyl alcohol), (b) CV-adsorbed xerogel and the clear water, (c) the xerogel after being eluted by methanol and the CV solution in methanol. (d) UV/vis spectral changes of an aqueous solution of CV before and after adsorption (~24 h) of the dye by the xerogel obtained from **1a**-benzyl alcohol gel (4.6 wt% of **1a** in 0.2 mL of benzyl alcohol) at 25 °C. The removal efficiency under this condition was determined to be 98 %.

Procedure for synthesis

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-α-D-glucopyranoside (3a). A mixture of p-tolualdehyde (6.2 mL, 49.5 mmol) and methyl-α-D-glucopyranoside (2.0 g, 10.3 mmol) was stirred with zinc chloride (1.5 g, 11.0 mmol) under a nitrogen atmosphere. The reaction was continued at room temperature for 6 h. After the reaction mixture was poured into water (50 mL), the product was precipitated then collected by filtration. The resulting precipitate was washed with water and n-hexane, and then re-precipitated by chloroform/n-hexane to give a white solid of 2.35 g, yield: 73 %. M. p. 118-121℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.49 (s, 1H), 4.77 (d, J = 4.0 Hz, 1H), 4.27 (dd, J = 5.0, 4.5 Hz, 1H), 3.90 (t, J = 9.0 Hz, 1H), 3.76-3.82 (m, 1H), 3.72 (t, J = 10.0 Hz, 1H), 3.61 (dd, J = 4.5, 4.5 Hz, 1H), 3.47 (d, J = 9.0 Hz, 1H), 3.45 (s, 3H), 2.46 (d, J = 9.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1, 128.9, 126.2, 102.0, 99.9, 81.0, 72.8, 71.6, 68.9, 62.4, 55.5, 21.3. EPI-MS $C_{15}H_{20}O_6$ ([M-H]$^-$) calcd. 295.1, found 295.0. Elem. Anal. for $C_{15}H_{20}O_6$: calcd. C 60.80, H 6.80; found C 63.29, H 6.19.

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (3b). Compound **3b** was synthesized according to the method described in the literature.[19]

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2,3-di-*O*-hexadecanoyl-α-D-glucopyranoside (1a). Compound **3a** (1.48 g, 5 mmol) and palmitic acid (2.56 g, 10 mmol), and anhydrous dichloromethane (DCM, 80 mL) were mixed in a round-bottom flask. The flask was cooled to 0-5 ℃ in an ice bath. DMAP (0.2 g, 1 mmol) and DCC (3.0 g, 12 mmol) were added to the reaction mixture, which then was warmed to room temperature and stirred for 24 h. Then the reaction mixture was filtered, and the filtrate was washed with hydrochloric acid solution (1 mol·L^{-1}, 2 × 30 mL) and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography on silica gel using various gradients of petroleum ether and ethyl acetate (30-10 : 1). Compound **1a** was isolated as white solid in 85 % yield. M. p. 82-84 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.59 (t, *J* = 10.0 Hz, 1H), 5.47 (s, 1H), 4.93 (d, *J* = 3.5 Hz, 1H), 4.90 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.29 (dd, *J* = 5.0, 4.5 Hz, 1H), 3.92 (t, *J* = 10.0 Hz, 1H), 3.75 (t, *J* = 10.0 Hz, 1H), 3.63 (t, *J* = 9.5 Hz, 1H), 3.40 (s, 3H), 2.34 (d, *J* = 12.5 Hz, 4H), 2.22-2.31 (m, 3H). 1.56 (t, *J* = 4.0 Hz, 4H), 1.25-1.28 (m, 48H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 172.5, 138.8, 134.2, 128.8, 126.0, 101.6, 97.7, 79.4, 71.5, 68.9, 68.6, 62.4, 55.4, 34.3, 34.1, 29.5, 29.1, 25.1, 24.9, 22.7, 14.1. EPI-MS $C_{47}H_{80}O_8$ ($[M+H]^+$) calcd. 773.5, found 773.4. Elem. Anal. for $C_{47}H_{80}O_8$: calcd. C 73.01, H 10.43; found C 73.17, H 10.38.

Methyl 4,6-*O*-benzylidene-2,3-di-*O*-hexadecanoyl-α-D-glucopyranoside (1b). The procedures used for the preparation of **1b** are similar to that for **1a**. Compound **1b** was isolated as white solid in 87.5 % yield. M. p. 92-94 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 6.5 Hz, 3H), 5.59 (s, 1H), 5.00 (d, *J* = 3.5 Hz, 1H), 4.84 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.34 (dd, *J* = 4.5, 4.5 Hz, 1H), 4.22(d, *J* = 9.5 Hz, 1H), 3.83-3.92 (m, 1H), 3.81 (t, *J* = 10.0 Hz, 1H), 3.61 (t, *J* = 9.5 Hz, 1H), 3.44 (s, 3H), 2.34 (d, *J* = 12.5 Hz, 4H), 2.22-2.31 (m, 3H). 1.56 (t, *J* = 4.0 Hz, 4H), 1.25-1.28 (m, 48H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 138.8, 134.2, 128.9, 126.1, 101.6, 100.2, 78.7, 72.1, 71.9, 68.9, 62.8, 55.6, 34.4, 31.9, 29.6, 25.1, 22.7, 21.2, 14.1. EPI-MS $C_{46}H_{78}O_8$ ($[M+H]^+$) calcd. 759.6, found 759.6. Elem. Anal. for $C_{46}H_{78}O_8$: calcd. C 72.78, H 10.36; found C 72.15, H 10.23.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2,3-di-*O*-tetradecanoyl-α-D-glucopyranoside (1c). The procedures used for the preparation of **1c** are similar to that for **1a**. Compound **1c** was isolated as white solid in 77 % yield. M. p.76-78 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.60 (t, *J* = 9.5 Hz, 1H), 5.47 (s, 1H), 4.94 (d, *J* = 3.5 Hz, 1H), 4.90 (dd, *J* = 4.0, 3.5 Hz, 1H), 4.29(dd, *J* = 4.5, 5.0 Hz, 1H), 3.92 (td, *J* = 5.0, 4.5, 4.5 Hz, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.63 (t, *J* = 9.5 Hz, 1H), 3.40 (s, 3H), 2.33 (s, 3H), 2.18-2.29 (m, 4H), 1.53-1.56 (m, 4H), 1.22-1.30 (m, 40H), 0.88 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 172.5, 138.8, 134.2, 128.8, 126.0, 101.6, 97.7, 79.3, 71.5, 68.9, 68.6, 62.4, 55.4, 34.3, 34.1, 29.5, 29.0, 25.1, 24.9, 22.7, 14.1. EPI-MS $C_{43}H_{72}O_8$ ($[M+H]^+$) calcd. 717.5, found 717.4. Elem. Anal. for $C_{43}H_{72}O_8$: calcd. C 72.03, H 10.12; found C 72.51, H 10.18.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2,3-di-*O*-dodecanoyl-α-D-glucopyranoside (1d). The procedures used for the preparation of **1d** are similar to that for **1a**. Compound **1d** was isolated as white solid in 73.3 % yield. M. p.73-74 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.60 (t, *J* = 9.5 Hz, 1H), 5.47 (s, 1H), 4.94 (d, *J* = 3.5 Hz, 1H), 4.90 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.29 (dd, *J* = 5.0, 5.0 Hz, 1H), 3.89-3.94 (m, 1H), 3.75 (t, *J* = 10.0 Hz, 1H), 3.63 (t, *J* = 9.5 Hz, 1H), 3.40 (s, 3H), 2.33 (s, 3H), 2.20-2.32 (m, 4H), 1.57 (d, *J* = 6.5 Hz, 4H), 1.17-1.25 (m, 36H) ,0.88 (t, *J* = 6.5 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 172.5, 138.8, 134.1, 128.8, 126.0, 101.6, 97.7, 79.3, 71.5, 68.8, 68.6, 62.4, 55.4, 34.3, 34.1, 31.9, 29.5, 29.0, 25.1, 24.9, 22.7, 14.1. EPI-MS $C_{39}H_{64}O_8$ ($[M+H]^+$) calcd. 661.4, found 661.3. Elem. Anal. for $C_{39}H_{64}O_8$: calcd. C 70.87, H 9.76; found C 70.55, H 9.83.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2,3-di-*O*-benzoyl-α-D-glucopyranoside (1e). The procedures used for the preparation of **1e** are similar to that for **1a**. Compound **1e** was isolated as white solid in 65 % yield. M. p.160-161 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 4H), 7.46-7.52 (m, 2H), 7.30 -7.39 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.04 (t, *J* = 10.0 Hz, 1H), 5.53 (s, 1H), 5.23 (dd, *J* = 3.5, 3.5 Hz, 1H), 5.17 (d, *J* = 3.5 Hz, 1H) 4.36 (dd, *J* = 4.5, 5.0 Hz, 1H), 4.05-4.07 (m, 1H), 3.84-3.88 (m, 1H), 3.72 (d, *J* = 7.0 Hz, 1H), 3.44 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 165.6, 138.9, 134.1, 133.4, 133.0, 130.0, 129.8, 128.9, 128.5, 128.3, 126.1, 101.8, 97.8, 79.4, 72.6, 69.6, 68.9, 62.6, 55.5, 21.3. EPI-MS $C_{29}H_{28}O_8$ ($[M+H]^+$) calcd. 505.2, found 505.1. Elem. Anal. for $C_{29}H_{28}O_8$: calcd. C 69.04, H 5.59; found C 68.91, H 5.71.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2-*O*-pencadecanoyl-α-D-glucopyranoside (2a). Compound **3a** (1.48 g, 5 mmol) and hexadecanoic acid (1.28 g, 5 mmol), and anhydrous dichloromethane (DCM, 80 mL) were mixed in a round-bottom flask. The flask was cooled to 0-5 ℃ in an ice bath. DMAP (0.1 g, 0.5 mmol) and DCC (1.5 g, 6 mmol) were added to the reaction mixture, which then was warmed to room temperature and stirred for 24 h. Then the reaction mixture was filtered, and the filtrate was washed with hydrochloric acid solution (1 mol·L^{-1}, 2 × 30 mL) and saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography on silica gel using various gradients of petroleum ether and ethyl acetate (30-10 : 1). Compound **2a** was isolated as white solid in 70 % yield. M. p.79-82 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.47 (s, 1H), 4.92 (d, *J* = 3.5 Hz, 1H), 4.76 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.24 (dd, *J* = 4.5, 5.0 Hz, 1H), 4.10 (t, *J* = 9.5 Hz, 1H), 3.79 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.70 (t, *J* = 10.0 Hz, 1H), 3.47 (t, *J* = 9.5 Hz, 1H), 3.35 (s, 3H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.59-1.65 (m, 2H) ,1.25-1.33 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 139.0, 134.3, 128.9, 126.3, 102.0, 97.7, 81.4, 73.4, 68.8, 68.5, 62.1, 55.3, 34.1, 31.9, 29.6, 29.1, 24.9, 22.7, 14.2. EPI-MS $C_{31}H_{50}O_7$ ($[M+H]^+$) calcd. 535.4, found 535.3. Elem. Anal. for $C_{31}H_{50}O_7$: calcd. C 69.63, H 9.42; found C 69.00, H 9.67.

Methyl 4,6-*O*-benzylidene-2-*O*-hexadecanoyl-α-D-glucopyranoside (2b). Compound 2b was synthesized according to the method described in the literature.[20]

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2-*O*-tetradecanoyl-α-D-glucopyranoside (2c). The procedures used for the preparation of **2c** are similar to that for **2a**. Compound 2c was isolated as white solid in 73.8 % yield. M. p. 92-94 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 4.99 (d, J = 4.0 Hz, 1H), 4.83 (dd, J = 4.0, 3.5 Hz, 1H), 4.32 (dd, J = 5.0, 4.5 Hz, 1H), 4.20 (t, J = 9.5 Hz, 1H), 3.83-3.93 (m, 1H), 3.78 (t, J = 10.5 Hz, 1H), 3.58 (t, J = 9.5 Hz, 1H), 3.43 (s, 3H), 2.44 (t, J = 7.5 Hz, 2H), 2.38 (s, 3H), 1.68 (dd, J = 7.0, 7.5 Hz, 2H), 1.20-1.43 (m, 20H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 139.2, 134.2, 129.0, 126.2, 102.1, 97.6, 81.4, 73.4, 68.9, 68.7, 62.0, 55.4, 34.2, 31.9, 29.5, 29.0, 24.9, 22.7, 14.1. EPI-MS $C_{29}H_{46}O_7$ ($[M+H]^+$) calcd. 507.3, found 507.3. Elem. Anal. for $C_{29}H_{46}O_7$: calcd. C 68.74, H 9.15; found C 68.98, H 9.39.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2-*O*-dodecanoyl-α-D-glucopyranoside (2d). The procedures used for the preparation of **2d** are similar to that for **2a**. Compound **2d** was isolated as white solid in 67 % yield. M. p. 97-98 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.46 (s, 1H), 5.32 (t, J =9.5 Hz, 1H), 4.80 (t, J = 3.5 Hz, 1H), 4.29 (dd, J = 4.5, 4.5 Hz, 1H), 3.85 (dd, J = 5.5, 5.5 Hz, 1H), 3.74 (t, J = 10.5 Hz, 1H), 3.62-3.67 (m, 1H), 3.57 (t, J = 9.5 Hz, 1H), 3.47(s, 3H), 2.37 (d, J = 7.5 Hz, 2H), 1.60-1.63 (m, 2H), 1.20-1.30 (m, 16H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 136.9, 129.0, 128.2, 126.1, 101.5, 97.7, 79.4, 71.4, 70.8, 69.7, 68.6, 67.3, 58.4, 34.3, 31.9, 29.7,25.1, 24.9, 22.7, 14.1. EPI-MS $C_{27}H_{42}O_7$ ($[M+H]^+$) calcd. 479.3, found 479.2. Elem. Anal. for $C_{27}H_{42}O_7$: calcd. C 67.76, H 8.84; found C 67.43, H 8.79.

Methyl 4,6-*O*-[(4-methylphenyl)methylene]-2-*O*-benzoyl-α-D-glucopyranoside (2e). The procedures used for the preparation of **2e** are similar to that for **2a**. Compound **2e** was isolated as white solid in 77.5 % yield. M. p. 130-132 ℃.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 5.08 (d, J =3.5 Hz, 1H), 5.04 (d, 1H), 4.34-4.36 (m, 1H), 4.05-4.07 (m, 1H), 4.32 (dd, J = 4.5, 5.0 Hz, 1H), 3.79 (d, J =10.5 Hz, 1H), 3.63 (t, J = 9.5 Hz, 1H), 3.40 (s, 3H), 2.54 (s, 1H), 2.35(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 139.2, 134.2, 133.4, 133.0, 130.0, 129.0, 128.5, 126.2, 102.2, 97.8, 81.5, 74.1, 68.9, 62.1, 55.5, 21.3. EPI-MS $C_{22}H_{24}O_7$ ($[M+H]^+$) calcd. 401.1, found 401.1. Elem. Anal. for $C_{22}H_{24}O_7$: calcd. C 65.99, H 6.04; found C 65.74, H 6.27.

Acknowledgements

We thank the support of the National Natural Science Foundation of China (No. 21272054, 21072043 and 20772022), the Youth Foundation of Hebei Provincial Department of Education (No. 2010142), Youth Top-notch Talent Foundation of the Education Department of Hebei Province (No. BJ2014039), Nature Science Foundation of Hebei Province (B2010000362, B2007000242, B2011205037), the Key Project of Chinese Ministry of Education (No. 207012), and Startup Foundation of Hebei Normal University (No. L2015B08, L2015B09, L2015k02).

Notes and references

College of Chemistry and Materials Science, Hebei Normal University, Shijiazhuang, 050024, China Fax: +86-311-8078-7400; Tel: 86-311-8078-7400; E-mail: haitaoyu@mail.hebtu.edu.cn

† Electronic supplementary information (ESI) available: [Table S1 and S2: gelation ability and properties of the target compounds in various organic liquids; Table S3-S6: removal efficiencies of aniline and nitrobenzene in their biphasic mixtures with water by using **1a**, **1b**, or **2b** as PSGs under various kinds of conditions; Table S7: adsorption efficacy for CV or rhodamine B in their aqueous solutions by using **1a** as the adsorbent in different methods; Fig. S1: photos of the gels formed in aniline or nitrobenzene with gelators **1a**, **1b**, and **2b**; Fig. S2: photos of the reversible sol-to-gel transitions of 1b-aniline gel and **2b**-nitrobenzene gel; Fig. S3: SEM images of the xerogels prepared by aniline and nitrobenzene gels; Fig. S4: FT-IR spectra of **2b** in neat solid and xerogel state; Fig. S5: X-ray diffraction patterns of the xerogels **1b** and **2b** prepared from aniline or nitrobenzene; Fig. S6: photos of the phase-selective gelation of the organic phase in the aniline/water and nitrobenzene/water mixtures; Fig. S7: photos of the inverted vials with the gels formed phase-selectively in the biphasic mixtures with water; Fig. S8: the linear regression results for the correlation between concentrations of aniline and nitrobenzene in water and the peak areas of HPLC. Fig. S9: UV/vis spectra of the CV and rhodamine B solutions in the presence of single benzyl alcohol and gel **1a** in benzyl alcohol; Fig. S10: removal of rhodamine B using **1a**-benzyl alcohol gel column and the removal effect of this method; Fig. S11: process of rhodamine B adsorption using xerogel **1a**, and the elution of the dye-adsorbed xerogel with methanol; Fig. S12: concentration-dependent UV spectral changes of **1b** in ethanol]. See DOI: 10.1039/b000000x/

‡ Both authors contributed equally to this work.

1 (*a*) http://www.ens-newswires.com/ens/jan2006/2006-01-13-05.asp; (*b*) http://en.m.wikipedia.org/wiki/Tianji_Coal_Chemistry_Industry_Group_Chemical_spill#undefined.

2 (*a*) B. Kakavandi, A. J. Jafari, R. R. Kalantary, S. Nasseri, A. Ameri, A. Esrafily, *Iran. J. Environ. Health Sci. Eng.*, 2013, **10**, 19/1–19/9; (*b*) É. Pelletier, R. Siron, *Environ. Toxicol. Chem.*, 1999, **18**, 813–818; (*c*) R. R. Lessard, G. Demarco, *Spill Sci. Technol. Bull.*, 2000, **6**, 59-68. (*d*) R. P. J. Swannell, K. Lee, M. McDonagh, *Microbiol. Rev.*, 1996, **60**, 342–365.

3 S. Bhattacharya, Y. Krishnan-Ghosh, *Chem. Commun.*, 2001, 185–186.

4 (*a*) M. Suzuki, T. Sato, H. Shirai, K. Hanabusa, *New J. Chem.*, 2006, **30**, 1184–1191; (*b*) S. Debnath, A. Shome, S. Dutta, P. K. Das, *Chem. Eur. J.*, 2008, **14**, 6870–6881; (*c*) T. Kar, S. Debnath, D. Das, A. Shome, P. K. Das, *Langmuir*, 2009, **25**, 8639–8648; (*d*) S. Basak, J. Nanda, A. Banerjee, *J. Mater. Chem.*, 2012, **22**, 11658–11664; (*e*) A. Pal, T. Patra, J. Dey, *Chem. Phys. Lett.*, 2013, **556**, 245–250; (*f*) T. Kar, S. Mukherjee, P. K. Das, *New J. Chem.*, 2014, **38**, 1158–1167.

5 (*a*) S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan, G. John, *Angew. Chem. Int. Ed.*, 2010, **49**, 7695–7698; (*b*) S. Mukherjee, B. Mukhopadhyay, *RSC Adv.*, 2012, **2**, 2270–2273; (*c*) A. Prathap, K. M. Sureshan, *Chem. Commun.*, 2012, **48**, 5250–5252; (*d*) Rajkamal, D. Chatterjee, A. Paul, S. Banerjee, S. Yadav. *Chem. Commun.*, 2014, **50**, 12131–12134; (*e*) S. Mukherjee, C. Shang, X. Chen, X. Chang, K. Liu, C. Yu, Y. Fang, *Chem.Commun.*, 2014, **50**, 13940-13943.

6 (*a*) J. Peng, K. Liu, X. Liu, H. Xia, J. Liu, Y. Fang, *New J. Chem.*, 2008, **32**, 2218–2224; (*b*) M. Xue, D. Gao, K. Liu, J. Peng, Y. Fang, *Tetrahedron*, 2009, **65**, 3369–3377.

7 (*a*) D. R. Trivedi, A. Ballabh, P. Dastidar. *Chem. Mater.*, 2003, **15**, 3971–3973; (b) D. R. Trivedi, A. Ballabh, P. Dastidar, B. Ganguly, *Chem. Eur. J.*, 2004, **10**, 5311–5322.

8 C. Tsai, Y. Cheng, L. Shen, K. Chang, I. Ho, J. Chu, W. Chung, *Org. Lett.*, 2013, **15**, 5830–5833.

9 H. Yu, B. Liu, Y. Wang, J. Wang, Q. Hao, *Soft Matter*, 2011, **7**, 5113–5115.

10 T. Tu, W. Fang, X. Bao, X. Li, K. H. Dötz, *Angew. Chem. Int. Ed.*, 2011, **50**, 6601–6605.

11 M. George, R. G. Weiss. *J. Am. Chem. Soc.*, 2001, **123**, 10393–10394.
12 N. G. James, A. B. Mason, *Anal. Biochem.*, 2008, **378**, 202-207.
13 (*a*) O. Gronwald, S. Shinkai, *Chem. Eur. J.*, 2001, **7**, 4328–4334; (*b*) J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686–3699; (*c*) M. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960–2004; (*d*) M. George, R. G. Weiss, *Acc. Chem. Res.*, 2006, **39**, 489–497; (*e*) S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973–2129; (*f*) X. Zhang, S. Lee, Y. Liu, M. Lee, J. Yin, J. L. Sessler, J. Yoon, *Sci. Rep.*, 2014, **4**, 4593/1–4593/8.
14 M. Masuda, V. Vill, T. Shimizu. *J. Am. Chem. Soc.*, 2000, **122**, 12327–12333.
15 M. F. Abreu, V. T. Salvador, L. Vitorazi, C. E.N. Gatts, D. R. dos Santos, R. Giacomini, S. L. Cardoso, P. C.M.L. Miranda, *Carbohydr. Res.*, 2012, **353**, 69–78.
16 F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.*, 2001, **7**, 2245–2253.
17 H. Xu, A. K. Das, M. Horie, M. S. Shaik, A. M. Smith, Y. Luo, X. Lu, R. Collins, S. Y. Liem, A. Song, P. L. A. Popelier, M. L. Turner, P. Xiao, I. A. Kinloch, R. V. Ulijn, *Nanoscale*, 2010, **2**, 960–966.
18 (*a*) V. Bekiari, P. Lianos, *Chem. Mater.*, 2006, **18**, 4142–4146; (*b*) S. Ray, A. K. Das, A. Banerjee, *Chem. Mater.*, 2007, **19**, 1633–1639; (*c*) E. J. Cho, I. Y. Jeong, S. J. Lee, W. S. Han, J. K. Kang, J. H. Jung, *Tetrahedron Lett.*, 2008, **49**, 1076–1079; (*d*) S. Huang, L. Yang, M. Liu, S. L. Phua, W.A. Yee, W. Liu, R. Zhou, X. Lu, *Langmuir*, 2013, **29**, 1238–1244. (*e*) B. O. Okesola, D. K. Smith, *Chem. Commun.*, 2013, **49**, 11164–11166.
19 K. Yoza, N. Amanokura, Y. Ono, T. Akao, H. Shinmori, M. Takeuchi, S. Shinkai, D. N. Reinhoudt, *Chem. Eur. J.*, 1999, **5**, 2722–2729.
20 J. Guiard, A. Collmann, M. Gilleron, L. Mori, G. De Libero, J. Prandi, G. Puzo, *Angew. Chem. Int. Ed*., 2008, **47**, 9734–9738.

