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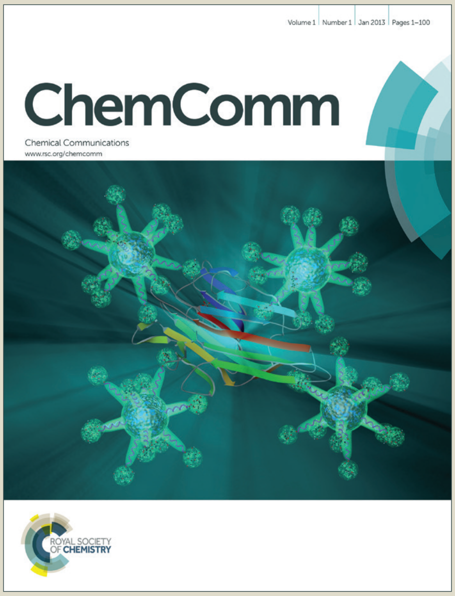

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Communication

N-acetylglucosamine-based efficient phase-selective organogelators for oil spill remediation

Somnath Mukherjee, Congdi Shang, Xiangli Chen, Xingmao Chang, Kaiqiang Liu, Chunmeng Yu and Yu Fang*

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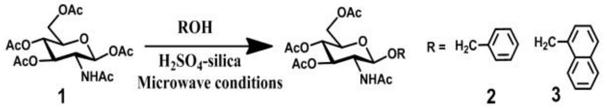
Two simple, eco-friendly and efficient phase-selective gelators were developed for instant (<45 s) gelation of oil (either commercial fuels or pure organic liquids) from oil-water mixture at room temperature to combat marine oil spills.

During recent years, world has experienced many environmental disasters due to oil spills. Marine oil spill is the leakage of oil in the sea water, and causes irrecoverable damage to the marine eco-system. Oil spill is difficult to clean up. Therefore, proper treatment of crude oil spillage is a burning challenge for scientists and a grave concern for the survival of the aquatic life.[1] Till now, the most commonly used techniques for cleaning up oil spills are: (a) bioremediation,[2] (b) dispersion,[3] (c) absorption,[4] and (d) solidification.[5] Each of these methods, however, proved to be incapable of managing the real scenario well due to their own drawbacks.

Low-molecular mass gelators[6] (LMMGs) have gained huge attention over the last few decades owing to their many potential applications from material to medicinal science.[7,8] Such small molecules (MW< 3 000) can immobilize a large volume of liquids by the formation of self-assembled 3D superstructures driven by several non-covalent interactions. Recently, LMMGs that can selectively solidify oils from their biphasic mixtures with water at room temperature (phase-selective gelators, PSGs) have become much more popular and demanding materials as ideal solidifying systems for oil spill recovery.[9] Importantly, they are superior to polymeric solidifiers because of their recoverability from their gels.

Bhattacharya and Ghosh first reported the selective gelation of oil from oil/water mixtures using amino acid amphiphile and really shared an excellent idea to treat the oil spill problem using LMMGs.[9a] Afterward, a number of PSGs have been reported in the literature. In 2010, John and co-workers demonstrated a new class of open chain sugar based gelators as model oil-solidifier for oil spill remediation, and in the model system they first showed the recovery of oil and reuse of the gelator.[9f] In their study, gelators were really efficient to congeal oil part selectively from oil-water mixtures but it took much more time to form a strong gel.

However, instant selective gelation is really very important when their practical use in oil spill recovery is concerned, and also it prevents the spreading of oils in the sea or river water. Therefore, there is a true need to develop some gelators which solidify oils selectively, quickly and efficiently from their mixtures with water. Interestingly, recent work by Arindam et al. mentioned the instant gelation (within 90 s) of oils by using aromatic amino acid based gelators.[9h] Despite of the some recent progress in the field, there is still a great need to develop much more examples of smart, environment-benign and economically cheap LMMGs for instantaneous, efficient, and selective gelation of fuel oils to handle the real situation of marine oil spill.[9] In this communication, we report two sugar-derived new LMMGs, capable of gelling fuel oils selectively and very quickly (within 45 s, the best record so far) from their oil/water mixtures at room temperature.



Scheme 1 Synthetic route of two β-glycosides of *N*-acetyl glucosamine (**2** and **3**) and their chemical structures

Our target compounds were synthesized in a single step from easily accessible per-*O*-acetylated β-D-GlcNAc by following the experimental protocol reported in the literature (Scheme S1, ESI†).[10] The gelling abilities of compound **2** and **3** were tested in several polar and nonpolar organic liquids and the results are summarized in Table S1(ESI†). Both compounds showed remarkable gelation ability in various organic liquids including some commercial fuels such as diesel, petrol and kerosene with critical gelation concentrations (CGCs) ranging from 0.23 to 3.5% (w/v). It is interesting to note that the CGC's for diesel gel of compound **2** and petrol gel of **3** were found to be 0.23 and 0.35% (w/v) respectively. The very low CGC's of the two LMMGs raise them to the category of super-gelators. All gels as prepared were stable at room temperature and were almost unaltered when stored in a closed container for 3 months, pointing out their temporal stability. The gelation process was thermo-reversible in nature, and the gelation abilities of the LMMGs as created remained unchanged after several times repetition of the sol-gel cycle. As expected, T_{gel} values of both the gelators were found to increase in an approximately linear way upon increasing gelator concentration, showing the enhancement in gel stability at high concentration (Fig. S1, ESI†)

Mechanical strength study of these organogels is extremely important for their real life applications. In our work, we should think about both the strength and stability of these solidified oils as far as the proposed use is concerned, because these solidified gels have to face tides, waves etc. and have to be stable for a long time so that such floating solids can be collected well either from the sea surface or from the seashore.

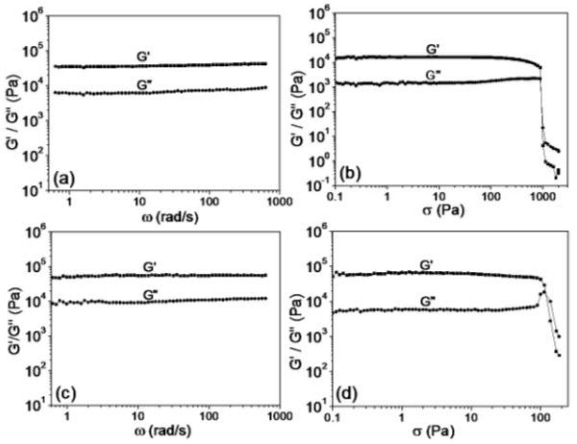


Fig. 1 Rheological studies for diesel gel of **2** (2%, w/v) (a) frequency sweep, (b) stress sweep; and for petrol gel of **3** (1.5% w/v) (c) frequency sweep, (d) stress sweep

In our study, for both the frequency sweep measurements (Figs. 1 a and c), storage modulus, G', predominates over the loss modulus, G", and furthermore, the storage modulus are invariant with frequency throughout the experimental region. This observation is as expected of soft solid like gels and points out their good tolerance towards external forces. The value of G' is in the order of 10^4, clearly indicates the higher stiffness and strength of these gels. In stress sweep experiments (Figs. 1 b and d), G' is more than one order magnitude higher than G", demonstrating dominate elastic nature of the samples. Both G' and G" remain roughly constant initially and in a definite stress value they cross each other and at which a sharp decrease in moduli happens. This definite value of stress is called yield stress and after that gel starts to flow. Higher yield stress value points to higher mechanical strength of the gel system. Yield stress values for diesel gel of **2** and petrol gel of **3** are 903 Pa and 115 Pa respectively, supporting their enough ability to bear up own weights in inverted vial.

FT-IR studies showed the strong involvement of NH proton in hydrogen bonding interaction, where NH stretching bands shifted to the lower frequencies in the gel state ((Fig. S2, ESI†). Concentration dependent proton NMR studies for the gelators exhibited consistent and significant downfield shift of the NH proton signals with increase in the gelator concentration, providing another evidence for the formation of strong hydrogen bonding in the self-assembly of the gel state (Fig. S3, ESI†). Therefore, intermolecular hydrogen bonding plays an important role in the self-assembly of these gelators. In addition, further fluorescence studies revealed π-π stacking between naphthyl units also plays a role in the formation of the gels, where excitation spectrum of compound **3** significantly shifted to longer wavelengths with increasing the gelator concentration, in particular when it closes to the CGC of the system (Fig. S4, ESI†). Scanning Electron Microscopy (SEM) images displayed cross linked fibre network and this morphology was again confirmed by Atomic Force Microscopy (AFM) studies (Fig. 2a-d and Fig. S5, ESI†). XRD experiments suggested the similar type of molecular packing in the xerogel and powder state, and analysis of the XRD traces resulted in a tetragonal packing arrangement ((Fig. S6, ESI†).

Excellent gelation ability of gelator **2** and **3** in fuel oils made us curious to know whether they are good candidate for efficient phase-selective gelation of oil from oil/water mixture at room temperature for realistic applications like oil spill recovery. Interestingly, both were found to be suitable for selective gelation of organic liquids (organic solvents and fuel oils) from their corresponding mixtures with water.

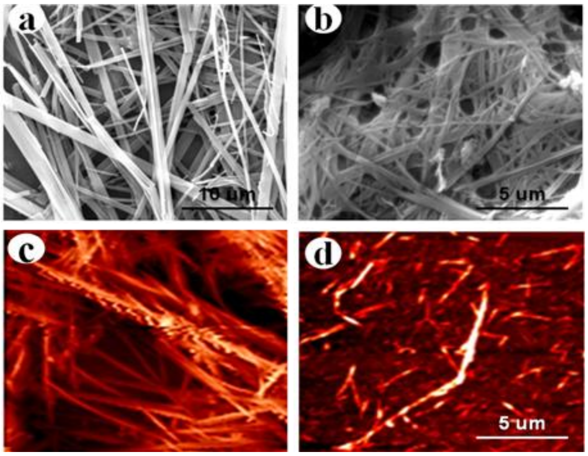


Fig. 2 SEM images of **2** (a) and **3**(b), and AFM images of **2** (c) and **3** (d) in toluene at their CGCs

At first, we investigated PSG process by conventional heating-cooling method. In a typical experiment, compound **2** (6 mg) was added in a mixture of water (2 mL) and toluene (0.8 mL) in a vial and solubilized by heating. Then the resultant mixture was allowed to cool to room temperature. Interestingly, the toluene layer was gelated selectively leaving the water layer intact in its free flowing state. However, this method is impractical in the situation of oil spill recovery from sea. Therefore, PSG at room temperature using the solution of gelator in co-solvent was studied. Although there are some reports of PSG at room temperature using sonication,[9b] a change in the pH of the medium[9c] and shaking,[9d] using solution of the gelator in co-solvent is quite practicable in real life applications to clean up oil spill. A concentrated solution of compound **2** (16 mg in 0.1 mL THF) was added by syringe in the interface of a 0.8: 2 mixture of diesel and water in a glass vial. It is worth noting that within 10 s, gelator **2** selectively gelled the diesel layer leaving water phase unaffected and within 45 s, the diesel gel was stiff enough to hold up its own weight plus weight of the water with the inversion of vial. Finally, the gel was scooped out using a spatula and placed in a round bottom flask and vacuum distilled to recover diesel. The isolated diesel gel melted upon heating it to 91 ℃ (above T_{gel}) and diesel subsequently distilled off in a round bottom flask (Fig. 3). The residue in the round bottom flask was characterized by mass spectrometry and thin layer chromatography and gelator was found to be intact for further use. The recovered gelator was used for selective gelation studies three more times and after each cycle, its gelling ability was retained. PSG of **3** in petrol at room temperature was carried out in a similar process stated above, and in this case the biphasic CGC (BCGC), gel melting temperature and selective gelation time in inverted vial condition were 1.5 % w/v, 56 ℃ and 50 s respectively (Fig. S7, ESI†).

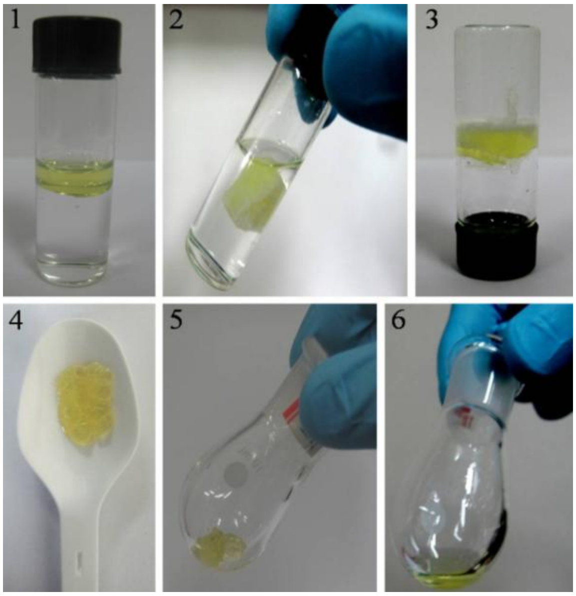


Fig. 3 Selective gelation of the diesel layer in a biphasic mixture of diesel and water at room temperature: (1) mixture of 2 mL water and 0.8 mL diesel, (2) instantaneous selective gelation of diesel layer after addition of the solution of gelator **2** (16 mg in 0.1 ml THF) and the diesel gel floating on water, (3) within 45 s the gel holding up its own weight plus weight of water in inverted vial, (4) scooped organogel in spatula, (5) scooped diesel gel (in several batches) taken in a round bottom flask, and (6) diesel collected in a round bottom flask after distillation

Furthermore, to examine the robustness of that PSG phenomenon, we performed it in several conditions such as in different oil water ratio, different type of aqueous solution (saturated NaCl, saturated $CaCl_2$, $KMnO_4$, $CuSO_4$) but for all these cases selective gelation was really unaltered. In addition, we also examined this selective gelation at low temperature (at 0-5 ℃ using ice bath) and importantly selective gelation time, efficiency and stability of the solidified oils were found same as room temperature method, increasing robustness of our model system for its practical use (Fig. S8, ESI†).

Such effective phase-selective phenomenon was also observed for others fuel oils including pump oil, silicon oil etc. and other pure organic liquids. Considering the practical situation of oil spill treatment, we also checked the selective gelation of a thin layer of diesel (1 mm) floating on a large volume of water in a petri dish, and within 20 s the resulted gel was sufficiently strong so that it could be scooped out by spatula (Fig. S9, ESI†). Subsequently, oil and gelator both could be recovered via distillation and gelator could be reused for further batch of experiment.

In conclusion, we have reported two new sugar derived efficient organogelators for instant selective gelation of some fuel oils from their oil/water mixtures at room temperature. Selective gelation was very fast and to the best of our knowledge, such a fast gelation time has not been reported so far. Our gelators are very attractive as a model system for oil spill recovery because (1) they can be easily prepared in one step from easily accessible and cheap per-*O*-acetylated glucosamine, (2) being sugar derivative they are eco-friendly and biodegradable, (3) they can offer very fast and efficient selective gelation of oils at room temperature, (4) both oil and gelator can be recovered easily and gelator can be reused, and (5) selective gelation efficiency and time were found to be unchanged at low temperature, allowing them in wide range of applications to clean up oil spill. Thus, all these advantages strongly point out their bright future in oil spill recovery.

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Notes and references

[a] *Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China. E-mail: yfang@snnu.edu.cn; Fax: +86-29-81530787; Tel:; +86-29-81530786*

† Electronic Supplementary Information (ESI) available: [Details of the synthesis, characterization, gel preparation, gel characterization (gel melting temperature, SEM, AFM, XRD, IR, and rheology) and selective gelation photographs are included.]. See DOI: 10.1039/b000000x/.

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A Table of Contents Entry

Two simple, eco-friendly and efficient carbohydrate gelators have been created for instant selective gelation of oil from oil-water mixtures to combat marine oil spills.