ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, **50**, 13940

Received 1st August 2014,
Accepted 2nd September 2014

DOI: 10.1039/c4cc06024e

www.rsc.org/chemcomm

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*

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 an oil–water mixture at room temperature to combat marine oil spills.

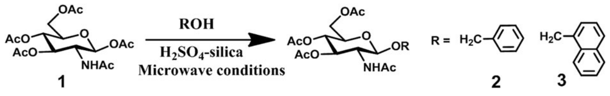
In recent years, the world has experienced many environmental disasters due to oil spills. Marine oil spill is the leakage of oil into seawater and causes irrecoverable damage to the marine ecosystem. An oil spill is difficult to clean up. Therefore, the proper treatment of crude oil spillage is a challenge for scientists and a grave concern for the survival of aquatic life.[1] Till now, the most commonly used techniques for cleaning oil spills are: (a) bioremediation,[2] (b) dispersion,[3] (c) absorption,[4] and (d) solidification.[5] However, each of these methods have proven to be incapable of managing the real scenario due to their own drawbacks.

Low-molecular mass gelators[6] (LMMGs) have attracted significant attention over the last few decades due to their many potential applications from materials to medicinal science.[7,8] Such small molecules (M_W < 3000) can immobilize a large volume of liquid by the formation of self-assembled 3D superstructures driven by several non-covalent interactions. Recently, LMMGs that can selectively solidify oils from their biphasic mixture 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 an amino acid amphiphile and shared an excellent idea to treat the oil spill problem using LMMGs.[9a] Afterward, numerous PSGs have been reported in the literature. In 2010, John and co-workers demonstrated a new class of open chain sugar-based gelators as a 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 efficient in congealing the oil part selectively from oil–water mixtures but it took much more time to form a strong gel.

However, instant selective gelation is very important when their practical use in oil spill recovery is concerned, and also prevents the spreading of oils in sea or river water. Therefore, there is a need to develop gelators that solidify oils selectively, quickly and efficiently from their mixtures with water. Interestingly, recent work by Banerjee *et al.* reported the instant gelation (within 90 s) of oils using aromatic amino acid-based gelators.[9h] Despite some recent progress in the field, there is still a significant need to develop many more examples of smart, environmentally-benign and economically cheap LMMGs for the instantaneous, efficient, and selective gelation of fuel oils to handle the real situation of a marine oil spill.[9] In this communication, we report two new sugar-derived LMMGs, capable of gelling fuel oils selectively and very quickly (within 45 s, the best record so far) from oil–water mixtures at room temperature (Scheme 1).

Our target compounds were synthesized in a single step from easily accessible per-*O*-acetylated β-D-GlcNAc 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 non-polar organic liquids and the results summarized in Table S1 (ESI†). Both compounds showed remarkable gelation ability in various organic liquids including



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

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. See DOI: 10.1039/c4cc06024e

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 the diesel gel of compound **2** and the 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 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 created remained unchanged after several repetitions of the sol–gel cycle. As expected, the T_{gel} values of both gelators were found to increase in an approximately linear way upon increasing the gelator concentration, showing the enhancement in gel stability at high concentrations (Fig. S1, ESI†).

A 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 easily either from the sea surface or from the seashore.

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

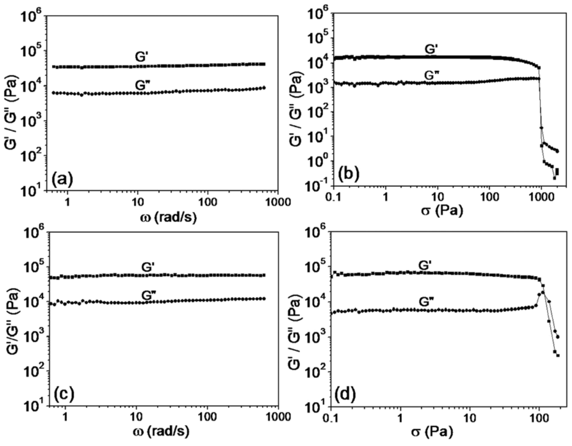


Fig. 1 Rheological studies for the diesel gel of **2** (2%, w/v) (a) frequency sweep, (b) stress sweep; and for the petrol gel of **3** (1.5%, w/v) (c) frequency sweep, (d) stress sweep.

FT-IR studies showed the strong involvement of NH protons in hydrogen bonding interactions, where NH stretching bands shifted to lower frequencies in the gel state (Fig. S2, ESI†). Concentration dependent proton NMR studies for the gelators exhibited a consistent and significant downfield shift of the NH proton signals with an increase in the gelator concentration, providing more evidence for the formation of strong hydrogen bonding during 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 the naphthyl units also plays a role in the formation of the gels, where the excitation spectrum of compound **3** was significantly shifted to longer wavelengths upon increasing the gelator concentration, in particular when it approaches the CGC of the system (Fig. S4, ESI†). Scanning electron microscopy (SEM) images display 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 a 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†).

The excellent gelation ability of gelator **2** and **3** in fuel oils made us curious to know whether they are good candidates for efficient phase-selective gelation of oil from oil–water mixtures 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.

At first, we investigated the PSG process using a conventional heating–cooling method. In a typical experiment, compound **2** (6 mg) was added to 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

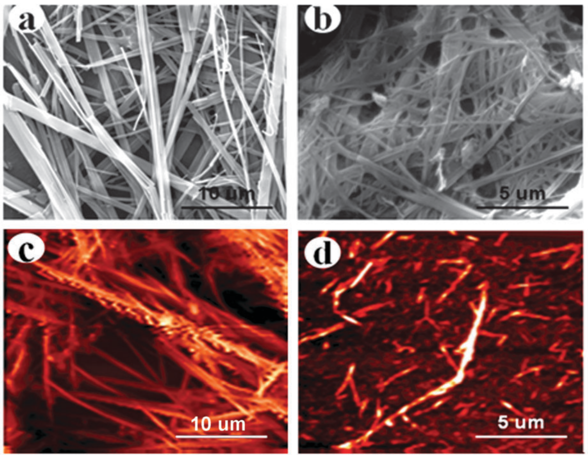


Fig. 2 SEM images of **2** (a) and **3** (b), and AFM images of **2** (c) and **3** (d) in toluene at their CGCs.

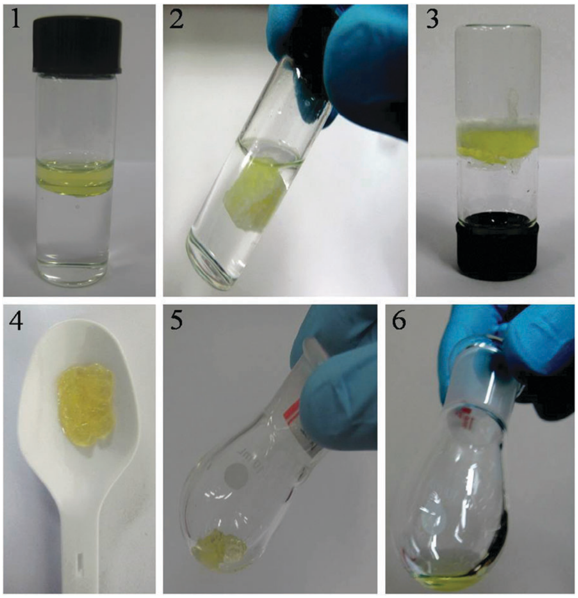


Fig. 3 Selective gelation of the diesel layer in a biphasic mixture of diesel and water at room temperature: (1) mixture of 2 mL water and 0.8 mL diesel, (2) instantaneous selective gelation of the diesel layer after addition of a solution of the gelator **2** (16 mg in 0.1 mL THF) and the diesel gel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

of oil spill recovery from sea. Therefore, the PSG at room temperature using the solution of gelator in a 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 a solution of the gelator in a co-solvent is quite practicable in real life applications to clean up an oil spill. A concentrated solution of compound **2** (16 mg in 0.1 mL THF) was added by syringe at 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 the water phase unaffected and within 45 s, the diesel gel was stiff enough to hold up its own weight plus the weight of the water upon inversion of vial. Finally, the gel was scooped out using a spatula and placed in a round bottom flask and vacuum distilled to recover the diesel. The isolated diesel gel melted upon heating to 91 °C (above the T_{gel}) and the diesel was subsequently distilled off into a round bottom flask (Fig. 3). The residue in the round bottom flask was characterized by mass spectrometry and thin layer chromatography, and the 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. The PSG of **3** in petrol at room temperature was also carried out using a similar process to that stated above, and in this case the biphasic CGC (BCGC), gel melting temperature and selective gelation time in the inverted vial condition were 1.5% w/v, 56 °C and 50 s respectively (Fig. S7, ESI†).

Furthermore, to examine the robustness of the PSG phenomenon, we performed it under several conditions such as in different oil–water ratios, and different types of aqueous solution (saturated NaCl, saturated $CaCl_2$, $KMnO_4$, $CuSO_4$) but for all these cases the selective gelation was unaltered. In addition, we also examined this selective gelation at low temperatures (0–5 °C using an ice bath) and importantly selective gelation time, efficiency and stability of the solidified oils were found the same as the room temperature method, increasing the robustness of our model system for 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 resulting gel was sufficiently strong enough that it could be scooped out by spatula (Fig. S9, ESI†). Subsequently, oil and gelator both could be recovered *via* distillation and the gelator could be reused for further batch of experiments.

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 to date. 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 a 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 the oil and gelator can be recovered easily and the gelator can be reused, and (5) the selective gelation efficiency and time were found to be unchanged at low temperature, allowing them a wide range of applications to clean up an oil spill. Thus, all these advantages strongly point out their bright future in oil spill recovery.

We thank the Natural Science Foundation of China (21273141), the Program for Changjiang Scholars and Innovative Research Team in University (IRT1070), and the 111 Project for financial support. Mr Gang Wang is acknowledged for his help in the fluorescence measurements.

Notes and references

1 (*a*) http://www.nytimes.com/2010/05/03/us/03spill.html; (*b*) L. Guterman, *Science*, 2009, **323**, 1558–1559; (*c*) A. M. Thayer, *Chem. Eng. News*, 2011, **89**, 12.
2 R. P. J. Swannell, K. Lee and M. Mcdonagh, *Microbiol. Rev.*, 1996, **60**, 342–365.
3 R. R. Lessard and G. Demarco, *Spill Sci. Technol. Bull.*, 2000, **6**, 59–68.
4 (*a*) Y. I. Matatov-Meytal and M. Sheintuch, *Ind. Eng. Chem. Res.*, 1997, **36**, 4374–4376; (*b*) M. O. Adebajo, R. L. Frost, J. T. Kloprogge, O. Carmody and S. Kokot, *J. Porous Mater.*, 2003, **10**, 159–170.
5 E. Pelletier and R. Siron, *Environ. Toxicol. Chem.*, 1999, **18**, 813–818.
6 (*a*) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821–836; (*b*) *Low Molecular Mass Gelators Design, Self-assembly, Function, Top. Curr. Chem.*, ed. F. Fages, 2005, vol. 256, p. 1; (*c*) in *Molecular Gels Materials with Self-Assembled Fibrillar Networks*, ed. R. G. Weiss and P. Terech, Springer, Dordrecht, 2006; (*d*) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133–3159; (*e*) O. Grownwald and S. Shinkai, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 148–156; (*f*) J. W. Steed, *Chem. Commun.*, 2011, **47**, 1379–1383.

7 (*a*) S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550–6551; (*b*) A. Ajayaghosh, V. K. Praveen and C. Vijayakumar, *Chem. Soc. Rev.*, 2008, **37**, 109–122; (*c*) F. Rodríguez-Llansola, J. F. Miravet and B. Escuder, *Chem. Commun.*, 2009, 7303–7305; (*d*) E. A. Wilder, K. S. Wilson, J. B. Quinn, D. Skrtic and J. M. Antonucci, *Chem. Mater.*, 2005, **17**, 2946–2952; (*e*) A. Vidyasagar, K. Handore and K. M. Sureshan, *Angew. Chem., Int. Ed.*, 2011, **50**, 8021–8024; (*f*) Y. Huang, Y. Lin, G. Zeng, Z. Liang, X. Liu, X. Hong, G. Zhang and S. C. Tsang, *J. Mater. Chem.*, 2008, **18**, 5445–5447; (*g*) Y. Li and M. Liu, *Chem. Commun.*, 2008, 5571–5573; (*h*) K. Liu, P. He and Y. Fang, *Sci. China: Chem.*, 2011, **54**, 575–586.

8 (*a*) K. Y. Lee and D. J. Mooney, *Chem. Rev.*, 2001, **101**, 1869–1879; (*b*) M. Ikeda, K. Fukuda, T. Tanida, T. Yoshiia and I. Hamachi, *Chem. Commun.*, 2012, **48**, 2716–2718; (*c*) G. Bastiat and J. C. Leroux, *J. Mater. Chem.*, 2009, **19**, 3867–3877; (*d*) P. N. Wambura, *Trop. Anim. Health Prod.*, 2009, **41**, 797–802; (*e*) P. K. Vemula and G. John, *Acc. Chem. Res.*, 2008, **41**, 769–782; (*f*) L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201–1217; (*g*) Y. Li and M. Liu, *Chem. Commun.*, 2008, 5571–5573.

9 (*a*) S. Bhattacharya and Y. Krishnan-Ghosh, *Chem. Commun.*, 2001, 185–186; (*b*) D. R. Trivedi and P. Dastidar, *Chem. Mater.*, 2006, **18**, 1470–1478; (*c*) T. Kar, S. Debnath, D. Das, A. Shome and P. K. Das, *Langmuir*, 2009, **25**, 8639–8648; (*d*) M. Xue, D. Gao, K. Liu, J. Peng and Y. Fang, *Tetrahedron*, 2009, **65**, 3369–3377; (*e*) J. Peng, K. Liu, X. Liu, H. Xia, J. Liu and Y. Fang, *New J. Chem.*, 2008, **32**, 2218–2224; (*f*) S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan and G. John, *Angew. Chem., Int. Ed.*, 2010, **49**, 7695–7698; (*g*) S. Mukherjee and B. Mukhopadhyay, *RSC Adv.*, 2012, **2**, 2270–2273; (*h*) S. Basak, J. Nanda and A. Banerjee, *J. Mater. Chem.*, 2012, **22**, 11658–11664; (*i*) A. Prathap and K. M. Sureshan, *Chem. Commun.*, 2012, **48**, 5250–5252; (*j*) C.-C. Tsai, Y.-T. Cheng, L.-C. Shen, K.-C. Chang, I.-T. Ho, J.-H. Chu and W.-S. Chung, *Org. Lett.*, 2013, **15**, 5830–5833; (*k*) H. Yu, B. Liu, Y. Wang, J. Wang and Q. Hao, *Soft Matter*, 2011, **7**, 5113–5115; (*l*) X. Yu, X. Cao, L. Chen, H. Lan, B. Liu and T. Yi, *Soft Matter*, 2012, **8**, 3329–3334; (*m*) X. Yu, L. Chen, M. Zhang and T. Yi, *Chem. Soc. Rev.*, 2014, **43**, 5346–5371; (*n*) P. Jing, J. Yan, X. Cai, J. Liu, B. Hu and Y. Fang, *Sci. China: Chem.*, 2013, **56**, 982–991.

10 S. Mandal, N. Sharma and B. Mukhopadhyay, *Synlett*, 2009, 3111–3114.