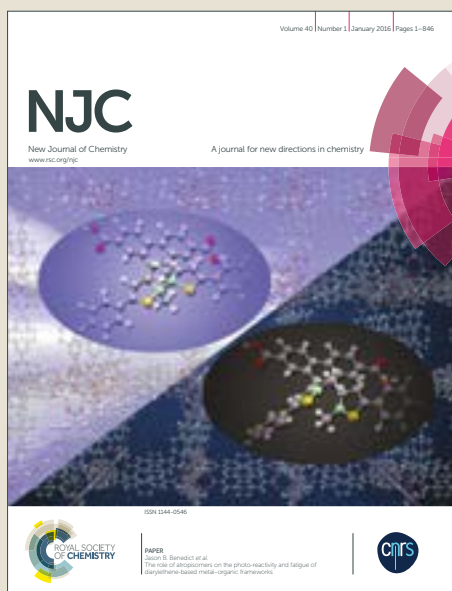


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A versatile carbohydrate based gelator for the oil water separation, nanoparticles synthesis and dye removal

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A versatile green gelator suitable for multiple applications is reported. Gelation of organic solvents in a significantly low gelation time (<5 sec) is achieved. The effect of the cooling and sonication on the gelation time is investigated. Apart from organic solvents, gelator is capable of forming gel with the fuel oils such as diesel and petrol also, therefore, it has been utilized for the separation of the oil from oil/water mixture through selective gelation of the oil. Gelator was also found to be capable of forming hydrogel through rational control of the reaction conditions. Hydrogel prepared using gelator was further explored as reaction medium for the growth of the gold nanoparticles. In the case of nanoparticles synthesis, gelator served not only as capping agent but also as a reducing agent. By taking advantage of the dual functionality of the gelator (capping and reducing agent), nanoparticles of both gold and silver were prepared in fluid medium also. The organogel, prepared using toluene and gelator, was utilized for the removal of the waterborne synthetic dye rhodamine B.

Introduction

Owing to the wide application spectrum, ranging from cosmetics to biomedical, a significant amount of research has been devoted to the low molecular weight gelators (LMWGs).¹⁻³ A wide variety of LMWGs have been designed in order to obtain gels suitable for different applications.^{2,4} Recently low molecular weight carbohydrates have garnered huge attention as gelators.⁵⁻⁹ Under favorable optimized conditions these carbohydrate based gelators (CBGs) form supramolecular structure which can be useful for variety of applications such as drug delivery, oil water separation, enzyme immobilization and nanomaterials preparation.^{6, 10, 11} CBGs exhibit several unique features such as ease of availability, environment friendly and cost effectiveness etc, which makes these preferred candidates of choice as gelator over other conventional organic gelators.^{12, 13} A plethora of reports mentioning use of various CBGs such as monosaccharide derived carbamates, *N*-acetylglucosamine derivatives and galactose derivatives have been documented.¹² Wang et al. reported *N*-linked carbamates gelators capable of forming gels in both nonpolar (*n*-hexane) as well as polar (aqueous DMSO and ethanol solution) solvents.^{5,6}

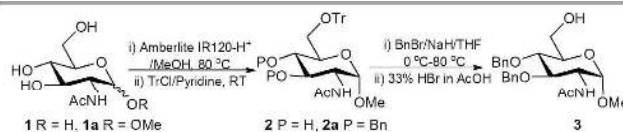
Recently several reports exploring CBGs for the removal of oil from water through selective gelation of oil have been surfaced.¹⁴⁻¹⁸ Selective gelation mediated oil removal process involves solidification of the oil in form of gel by gelator

followed by removal of the oil swollen gel through physical means such as filtration or using a scoop. Mukherjee and coworkers have recently reported instant phase selective gelation of oil from an oil/water mixture at room temperature using two sugar-derived phase selective gelators (PSG).¹¹

Carbohydrates are known to be excellent surface passivating agents for the nanoparticles synthesis. A variety of carbohydrates such as glucose, fructose, sucrose, starch and chitosan have served as capping agents for the restricted growth of the nanoparticles.^{19, 20} In few cases, apart from capping molecules, carbohydrates have also acted as reducing agents especially in metal nanoparticles synthesis.^{20, 21} Engelbrekt and coworkers reported green synthesis of gold nanoparticles using buffered glucose and starch solution.²² It was found that phosphate or MES buffers play a crucial role in the synthesis of nanoparticles. Gels have served very efficiently as reaction medium for the confined growth of the nanoparticles.²³ In the case of gels, the chances of agglomeration among synthesized nanoparticles are very less since the nanoparticles, embedded in the gel matrix, are deprived of free motion. Nanoparticles entrapped in semisolid gel matrix have acquired considerable interest for various biological and medical applications. These gel/nanoparticles hybrids are highly useful systems for various applications in biosensors, chiral catalysis, nonlinear optics and material science.²⁴⁻²⁶

In present report, successful use of a new *N*-acetyl

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Scheme-1 Synthesis of the gelator (compound-3)

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glucosamine based gelator for multiple applications such as oil/water separation, metals (Au and Ag) nanoparticles synthesis and removal of waterborne dye, has been demonstrated. Organogel formation capability of the *N*-acetyl glucosamine based gelator in different organic solvents is monitored. Apart from organogels, hydrogels are also prepared using the same gelator. Previously, carbohydrates based gelators are mainly explored for the oil/water separation whereas, in current report besides from oil/water separation, application of the carbohydrate based gelator for the synthesis of metals nanoparticles is also described. Additionally, *N*-acetyl glucosamine (GlcNAc) based organogel is also explored for the removal of rhodamine B dye from water.

Experimental

The gelator (compound-3) was synthesized by exploring selective protection and de-protection chemistry on the commercially available *N*-acetyl-D-glucosamine (Scheme 1),

Synthesis of Methyl 2-acetamido-2-deoxy- D-glucopyranoside (1a)

Amberlite IR 120-H⁺ resin (20 g) was added to a pre-stirred solution of *N*-acetyl glucosamine **1** (20 g, 90.41 mmol) in methanol (200 mL). The resulting mixture was stirred at 80 °C for 24 h. After completion of the reaction, reaction mixture was cooled down to room temperature, and filtered to remove the resin. The filtrate was evaporated under reduced pressure to obtain compound **1a** (Scheme S1) as white solid (19 g) in 89% isolated yield anomeric mixture (α : β , 9:1). ¹HNMR (400 MHz, CD₃OD): δ 4.65 (d, *J* = 3.5 Hz, 1H, H-1 α), 4.30 (d, *J* = 2.1 Hz, 0.1H, H-1 β), 3.91 (dd, *J* = 3.6 Hz 10.8 Hz, 1H, H-2), 3.82 (dd, *J* = 2.0 Hz, 11.6 Hz, 1H, H-6), 3.69 (dd, *J* = 5.6 Hz, 11.6 Hz, 1H, H-6), 3.63 (dd, *J* = 8.8 Hz, 10.0 Hz, 1H, H-3), 3.57 (ddd, *J* = 2 Hz, 5.6 Hz, 10Hz, 1H, H-5), 3.46 (s, 0.2H, OCH₃- β), 3.37 (s, 3H, OCH₃- α), 3.32 (dd, *J* = 3.8 Hz, 9.6 Hz, 1H, H-4), 3.26 (ddd, *J* = 2.2 Hz, 5.4 Hz, 9.6 Hz, 0.1H), 1.98 (s, NHAc- α , 3H), 1.97 (s, NHAc- β , 0.3H). ¹³C NMR (100 MHz, CD₃OD): δ 173.6 (C=O), 103.5 (C-1 β), 99.8 (C-1 α), 78.0, 76.2, 73.6, 72.9, 72.3, (C-3, C-4, C-5), 62.7 (C-6), 55.4 (OCH₃) 55.3 (C-2), 22.5 (COCH₃); HRESI-MS (m/z): Calcd for C₉H₁₇NO₆H⁺, [M+H]⁺: 236.1129, found 236.1128.

Synthesis of Methyl 6-O-triphenylmethyl-2-acetamido-2-deoxy- α -D-glucopyranoside (2)

To a stirred solution of compound **1a** (15.2 g, 64.68 mmol) in anhydrous pyridine, trityl chloride (21.63 g, 77.61 mmol) and DMAP (0.7 g, 6.46 mmol) were added and resulting mixture was stirred at room temperature for 72 h. After completion of reaction, reaction mixture was diluted with water (150 mL) and extracted with ethyl acetate (2 x 250 mL), combined organic layer was washed with copper sulfate solution (1 x 250 mL) followed by saturated brine solution (1 x 200 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to get the residue. The residue was purified by column chromatography (ethyl acetate/methanol: 95:5) to furnish compound **2** (Scheme S2) as amorphous solid (24.5 g) in 79% isolated yield. $[\alpha]_D^{20}$ 28.3° (c = 0.6, CHCl₃); ¹HNMR (400 MHz, CDCl₃): δ 7.47-7.21 (m, 15H, ArH), 5.91 (d, *J* = 8.4 Hz, 1H, NH), 4.70

(d, *J* = 4.0 Hz, 1H, H-1), 4.08 (ddd, *J* = 3.6 Hz, 8.8 Hz, 10.0 Hz, 1H, H-2), 3.68-3.59 (m, 2H, H-5, H-3), 3.54 (t, *J* = 8Hz, 1H, H-4), 3.43 (dd, *J* = 2.8 Hz, 6.4 Hz, H-6a), 3.40 (s, 3H, OCH₃), 3.34 (dd, *J* = 5.6 Hz, 10.0 Hz, 1H, H-6b), 2.75 (d, *J* = 1.8 Hz, 1H, OH), 2.04 (s, 3H, COCH₃). ¹³CNMR (100 MHz, CDCl₃): δ 172.0 (C=O), 143.9 (ArqC), 128.8, 128.0, 127.2 (ArC), 98.2 (C-1), 87.0 (CPh₃), 74.3 (C-3), 72.8 (C-4), 70.2 (C-5), 63.8 (C-6), 55.1 (OCH₃), 53.8 (C-2), 23.4 (COCH₃). HRESI-MS (m/z): Calcd for C₂₈H₃₁NO₆Na⁺, [M+Na]⁺: 500.2044, found 500.2063.

Synthesis of Methyl 3,4-di-O-benzyl-6-O-triphenylmethyl-2-acetamido-2-deoxy- α -D-glucopyranoside (2a)

To a stirred solution of compound **2** (14 g, 29.32 mmol) in dry THF, sodium hydride (3.5 g, 87.96 mmol) was added at 0 °C. After 20 min benzyl bromide (10.4 mL, 87.96 mmol) was added drop wise and the resulting mixture was allowed to heat at 80 °C with stirring for 1.5 h. After completion of reaction, the reaction mixture was allowed to cool down at room temperature then it was quenched by adding methanol (50 mL) and concentrated under reduced pressure. The residue was dissolved in ethylacetate (500 mL) washed with water (2 x 250 mL) and saturated brine solution (1 x 500 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to get the yellow colour residue. The residue was washed with pentane to furnish the compound **2a** (Scheme S3) as brown sticky solid (15 g 78%). The compound **2a** was used in next step without further purification. A purified compound **2a** was obtained through column chromatography (ethyl acetate) for analytical purpose. $[\alpha]_D^{20}$ 75.8° (c = 0.6, CHCl₃). ¹HNMR (400 MHz, CDCl₃): δ 7.51-7.49 (m, 6H, ArH), 7.37-7.18 (m, 17H, ArH), 6.89 (dd, *J* = 1.2 Hz, 6.4 Hz, 2H, ArH), 5.32 (d, *J* = 9.6 Hz, 1H, NH), 4.85 (d, *J* = 11.6 Hz, 1H, CH₂Ph), 4.77 (d, *J* = 3.6 Hz, 1H, C-1), 4.67- 4.57 (m, 2H, CH₂Ph), 4.32 (ddd, *J* = 3.6Hz, *J* = 6.4 Hz, 14.0 Hz, 2H, H-2, CH₂Ph), 3.82 (dd, *J* = 10.0 Hz, 1H, H-4), 3.75 (dd, *J* = 2.8 Hz, 10.0 Hz, 1H, H-5), 3.63 (t, *J* = 8.8 Hz, 1H, H-3), 3.52 (dd, *J* = 1.6 Hz, 12.0 Hz, 1H, H-6a), 3.37 (s, 3H, OCH₃), 3.24 (dd, *J* = 4.4 Hz, 10.0 Hz, 1H, H-6b), 1.86 (s, 3H, COCH₃). ¹³CNMR (100MHz,CDCl₃): δ 169.9 (C=O), 144.0 (ArqC), 138.6, 137.9 (ArqC), 128.9, 128.6, 128.5, 128.3, 128.3, 127.9, 127.8, 127.0 (ArC), 98.6 (C-1), 86.5 (CPh₃), 80.4 (C-3), 78.9 (C-4), 75.1 (CH₂Ph), 70.8 (C-5), 62.5 (C-6), 54.8 (OCH₃), 52.8 (C-2), 23.6 (COCH₃). HRESI-MS(m/z): Calcd. for C₄₂H₄₃NO₆Na⁺ [M+Na]⁺:680.2983; found 680.2959.

Synthesis of Methyl 3,4 -di-O-benzyl-2-acetamido-2-deoxy- α -D-glucopyranoside (3)

To a solution of compound **2a** (10 g, 15.28 mmol) in dry CH₂Cl₂, a 33% solution of HBr in acetic acid (6.6 mL) was added at 0 °C drop wise. The reaction mixture was stirred for 10 min at 0 °C. Completion of the reaction confirmed by TLC, after which the reaction mixture was quenched with ice cold water (50 mL) diluted with CH₂Cl₂ (1 x 400 mL) and washed with water (1 x 100 mL), saturated sodium bicarbonate solution (2 x 250 mL) and saturated brine solution (1 x 100 mL). The combined organic layer was dried over anhydrous sodium sulfate and filtered, evaporated under reduced pressure which gave a residue. The residue was purified by flash column chromatography (ethylacetate/hexane 80:20) which

gave compound **3** (Scheme S4) as a white gelatinous solid, Further re-crystallization with CH_2Cl_2 furnished the title compound **3** as a white solid (5 g) in 80% isolated yield. $[\alpha]_D^{20}$ 108.3° (c = 0.6, CHCl_3); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.08 (d, J = 8.0 Hz, 1H, NH) 7.36 – 7.24 (m, 10H, ArH), 4.77 (t, J = 6.4 Hz, 1H, OH), 4.73- 4.60 (m, 4H, 2 x CH_2Ph), 4.54 (d, J = 3.6 Hz, 1H, H-1), 3.96 (ddd, J = 3.2 Hz, 10.4 Hz, 12.8 Hz, 1H, H-2), 3.71 (dd, J = 4 Hz, 8.4 Hz, 1H, H-3), 3.66 (dd, J = 4 Hz, 11.6 Hz, 1H, H-6a), 3.59-3.56 (m, 1H, H-6b), 3.51-3.47 (m, 2H, H-4, H-5), 3.30 (s, 3H, OCH_3), 1.85 (s, 3H, COCH_3). ^{13}C NMR (100MHz, CDCl_3): δ 169.2 (C=O), 138.7, 138.4 (ArqC), 128.2, 128.1, 127.5, 127.4, 127.3 (ArC), 98.2 (C-1), 79.9, 78.0 (C-3, C-4), 73.9, 73.9 (CH_2Ph), 71.6 (C-5), 60.1 (C-6), 54.3 (OCH_3), 52.6 (C-2), 22.5 (COCH_3). HRESI-MS (m/z) Calcd. for $\text{C}_{23}\text{H}_{29}\text{NO}_6\text{Na}^+$ [M+Na] $^+$: 438.1887; found 438.1910.

Gelation of both polar and non polar organic solvents was carried out by employing compound-**3** as gelator.

Organogel preparation

5 mg gelator and measured amount of organic solvent (according to critical gel concentration) were taken in a glass vial and sonicated, gently heated to dissolve the gelator completely. As obtained solution of the gelator was left at room temperature till it transforms into the gel (Fig. 1). A system was considered as gel if it doesn't fell down on keeping vial upside down. Table S1 lists all the organic solvents which were gelled using the gelator along with the gel formation time in different conditions and appearance of the gels.

In order to determine critical gel concentration (CGS) first 5 mg of the compound was dissolved in 0.9-1 mL of the test liquid (solvent/oil) in a vial. If gel forms, then the gelator solution was diluted by small fixed volume of same liquid and gelation test was re-executed. This cycle of dilution and gelation was repeated until the gel fell down on holding the vial upside down. Thus, the maximum amount of the fluid that can be contained by 5 mg of the gelator was measured which was further used to calculate CGC as wt%.

Ultrasonication gel

A fixed amount of gelator was taken in a glass vial containing organic solvent and heated slowly to dissolve the gelator completely. Then vial was kept under probe sonicator till gel formed.

Gelation test at cooling

5 mg gelator was taken in 5 mL vial containing 0.9 mL of measured solvent, as prepared reaction mixture was sonicated and heated slowly to dissolve the gelator completely, then the vial was kept on an Ice bath (0°C to 5°C) which leads to gel formation.

Oil water separation using gelator

In the case of organic solvents such as toluene and benzene, the gelator was easily getting dissolved however for the dissolution of gelator in diesel, petrol and crude oil an additional solvent tetrahydrofuran (THF) was required. First 5 mg of compound-**3** was dissolved in THF and as obtained solution of the compound-**3** in THF was added to a glass vial

containing oil/water mixture which results in gelation of oil layer.

Preparation of pristine hydrogel and Au nanoparticles containing hydrogel

For the preparation of the hydrogel, 10 mg gelator was dissolved in 1 mL of ethanol. Thereafter 3 mL of phosphate buffer solution (pH = 7.4) was added to the above prepared gelator solution. The resulting mixture was kept at room temperature for 10 min which led to the formation of a gel.

In order to prepare Au nanoparticles containing hydrogel 10 mg gelator was dissolved in 1 mL of ethanol. As obtained gelator solution was mixed with 3 mL phosphate buffer (pH = 7.4) and 0.2 mL 0.005M AuCl_3 solution; the resulting reaction mixture was left at room temperature for 10 min which produced a violet color hydrogel. The violet color of the hydrogel indicates the formation of Au nanoparticles. As obtained Au nanoparticles containing hydrogel was dissolved in water to prepare the Au nanoparticles suspension which was further characterized.

Preparation of metals (Au and Ag) nanoparticles in solution

For the preparation of the Au nanoparticles, 5 mg gelator was dissolved in 1 mL of ethanol. The resulting gelator solution was mixed with 0.2 mL of 0.005M AuCl_3 solution and 2mL of 20 mM phosphate buffer solution (pH =7.4) which changed the color of the solution from colorless to violet within few minutes. The appearance of the violet color indicates the formation of the Au nanoparticles. Since the amount of the gelator used is half of the amount used in case of the hydrogel so formation of hydrogel didn't take place.

Similar to the Au nanoparticles for the preparation of the Ag nanoparticles 5 mg gelator was dissolved in 1 mL of ethanol and resulting solution was mixed with 2 mL of 0.005M AgNO_3 solution. Thereafter few drops of 0.1M NaOH was added to the above prepared reaction mixture which instantly changed the appearance of the solution from colorless to yellow confirming formation of the Ag nanoparticles.

Characterization details

TLC was visualized either by UV light or by treating with phosphomolybdic acid in EtOH followed by heating. ^1H NMR and ^{13}C NMR spectra were recorded by 400MHz spectrometer. ^1H and ^{13}C spectra were recorded by 400 MHz and 100MHz, respectively. Proton chemical shifts are given in ppm relative to the internal standard (tetramethylsilane) or referenced relative to the solvent residual peaks (CHCl_3 : δ 7.26; DMSO : δ 2.50; CD_3OD : δ 3.31). Multiplicity was stated as follows: s



Figure 1 Organogels of (a) benzene (b) toluene (c) o-Xylene (d) m-xylene (e) p-xylene (f) mesitylene (g) 1, 2 dichlorobenzene (h) chlorobenzene (i) bromobenzene (j) Iodo benzene (k) diesel.

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(Singlet); d (doublet); t (triplet); q (quartet); m (multiplet): dd (doublet of doublet); dt (doublet of triplet); td (triplet of doublet); ddd (doublet of doublet of doublet), etc. Coupling constants (J) were reported in Hz. Flash chromatography was performed by silica gel 100-200 and 230-400 mesh. Optical rotation was recorded using Polarimeter kruss P300. High resolution mass spectra determined from quadrupole/TOF mass spectrometer with an ESI source. FTIR measurements were performed using ATR FTIR spectroscopy (Thermo Scientific Nicolet™^{Is}™⁵ FTIR) with diamond ATR accessory. Gel samples were taken out from the closed vial and after subtle drying to remove physically absorbed solvents gels were mounted on the ATR crystal to record spectra. Rheological measurements were executed on Anton Paar MCR 302 rheometer equipped with steel coated parallel-plate geometry (50 mm diameter). The gap distance was fixed at 1 mm and a solvent-trapping device was placed above the plate to prevent solvent evaporation. All measurements were done at 25°C. Frequency sweep experiments were carried out from 0.1 to 600 rad s⁻¹ at a constant stress of 0.1%, fit within the linear visco-elastic region (LVER). UV-vis spectrum of the gelator was recorded by (Thermo Scientific Evolution-201). The Morphology of the gels was examined using scanning electron microscopic (SEM) Zeiss EVO40. A small amount of gel was placed on a carbon tape pasted to a copper grid and the gel was subjected to ambient drying, as prepared sample was coated with gold. The shape and size of the fibers present in hydrogel and metals nanoparticles was viewed using HR-TEM (Tecnai G2 20 twin, Tecnai 200 KV twin microscope). For the TEM viewing sample was prepared through drop casting method in which a drop of the metals nanoparticles suspension was drop dried on the copper grid.

Results and discussion

Gelator (compound-3) exhibited excellent gelation ability and was able to form gel with different organic solvents even at a very low concentration 0.38-0.7% (W/V). However, among α and β anomers of the compound-3 only α anomer exhibits gelation property while the β anomer forms precipitate in most of the organic solvents. Compound-3 formed highly strong gels with various organic solvents including benzene, toluene, o-xylene, m-xylene, p-xylene, mesitylene etc (fig. 1). It is well known fact that in the case of LMWGs, non-covalent forces, such as van der Waals attraction, π - π stacking and hydrogen bonding, among gelator molecules or gelator and solvent, underpin the formation of gels.¹² In the present case, the gelator molecule consists of several aromatic moieties and also readily forms gel with aromatic ring containing solvents, which suggests that π - π stacking is mainly responsible for the gel formation. Apart from aromatic rings, the hydroxyl group is also present in the gelator molecule which endows it with the capability of undergoing hydrogen bonding.

Owing to the low CGC, compound-3 can be considered as super-gelator. Apart from CGC, gel formation time is another

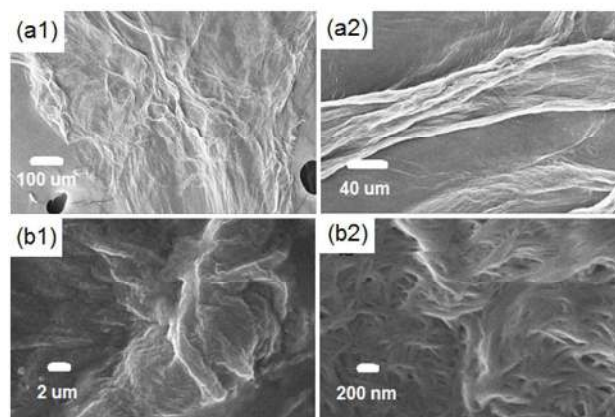


Figure 2 SEM images of (a1, a2) toluene gel (b1, b2) Hydrogel.

important criterion which decides the usefulness of the gelator for practical large scale application;²⁷ gelators capable of forming gels in less time are highly desirable. In several previously documented reports carbohydrates based gelator are mentioned to be taking a very long time (several minutes)^{16, 17} for the gel formation which discourages their wide scale application. In order to shorten the gelation time different new carbohydrate based gelators have been designed and modifications in the gelation conditions have also been introduced.¹¹ In the current study, we have proposed two strategies, rapid cooling and ultrasonication, in order to expedite the gelation process. For the rapid cooling of solution, obtained after dissolution of the gelator in the solvent, it was transferred on an ice bath which drastically reduced the gel formation time and the gelation completed within few seconds. A significant lower gel formation time was recorded for gel prepared through cooling on ice bath compared to the gel obtained through cooling at ambient temperature (Table S1). For instance, in the case of toluene, at room temperature, the gel formation time was recorded to be 3 minutes 54 seconds while ice bath cooling accelerated the gel formation process and it completed within 52 seconds which clearly indicates that the cooling temperature dictates the rate of gel formation. A similar decrease in the gel formation time was observed for other solvents too. SEM images of the toluene containing gel confirmed the presence of interconnected network of fibers (Fig. 2).

In general practice sonication is usually considered for the re-dispersion of the aggregates, however, it has been found that in given right conditions sonication can also aggregate molecules in assemblies of minimum energy which can lead to the formation of gels; these gels are also referred as sonogels.^{28, 29} Sonication assisted gelation is not a general phenomenon; it is limited to only a few gelators. In the present case, a substantial decrease in the rate of gelation of the organic solvents by the compound-3 is observed when probe sonication was applied during gelation. For almost all the organic solvents the gel formation time for sonication assisted gelation was recorded to be lower than 5 seconds, which, according to the best of our knowledge, is the lowest gelation

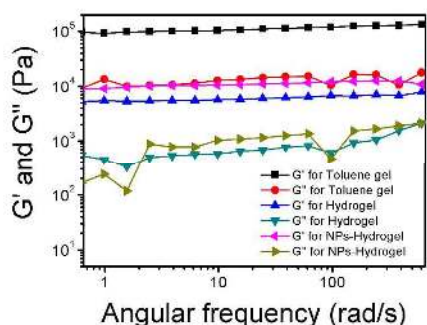


Figure 3 Frequency sweep measurements of the pristine and nanoparticles containing gels.

time among *N*-acetyl glucosamine based gelators (Table S1). Previously, it has been reported that sonication disrupts the intramolecular hydrogen bonding and promotes intermolecular hydrogen bonding,²⁸ in present case also we believe that the sonication driven quick alignment of the molecules into energy favorable orientations which promote intermolecular hydrogen bonding among gelator molecules, is the viable reason behind the quick formation of the gel. Besides aromatic nonpolar solvents, gelator was also able to form gel with polar organic solvents such as ethanol and DMSO (Fig. S5).

Mechanical strength is an extremely important property of the gels which decides their potential application. In order to probe the mechanical strength of the gels rheology analysis was carried out (Fig. 3). Frequency sweep measurement of the toluene gel (0.5% W/V) is shown in figure 3. It is well documented that for strong gels oscillatory frequency measurements exhibit a weak frequency dependent storage (G') and loss (G'') modulus throughout the frequency range while the value of G' always remains higher than the G'' .³⁰⁻³² In present case also we have made the same observation, both G' and G'' merely changed throughout the frequency range and $G' > G''$ through the entire frequency range (Fig.3).

Furthermore, apart from organic solvents, compound-3 is capable of forming gels with fuels such as diesel and petrol also; therefore, this gelator can be an interesting aspirant material for the separation of oil from water or vice versa through selective gelation of the oils (Fig. 4a-c). For the phase selective gelation of the diesel and petrol from water, the solution of gelator in the tetrahydrofuran (THF) (16mg/0.2 mL) was added to the both fuel oils (0.8 mL) which led to the formation of very thick gels. These gels can be separated out using a spatula and the fuel oils can be recovered through

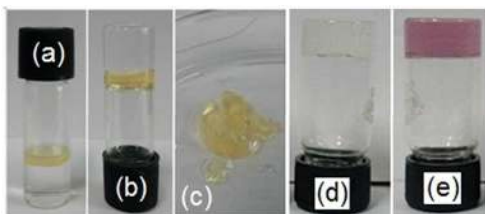


Figure 4 (a-c) Removal of petrol from petrol/water mixture using gelator (d) pristine hydrogel (e) Au nanoparticles containing hydrogel.

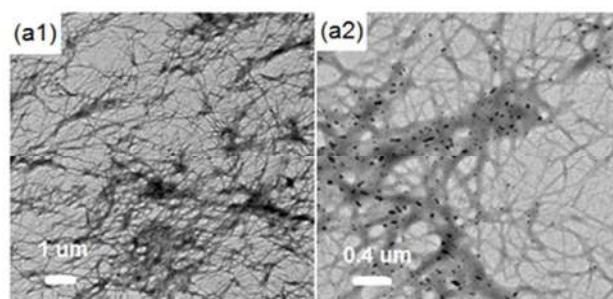


Figure 5 TEM images of the Au nanoparticles containing hydrogel.

distillation. Akin to organic solvents in case of diesel and petrol also cooling reduced the gelation time substantially. Room temperature gelation of the diesel took ~ 3 minutes while in the case of cooling assisted gelation, gel formation completed within a minute, similar observation was made in case of petrol also which makes gelator highly suitable for the recovery of the fuel oil spills from the sea water in geographic regions with low atmospheric temperature. Gelator formed a very strong gel with both diesel and petrol so the chances of re-dissolution of the gel during mechanical agitation are very less. In addition to the strength and stability these gels are also thermo-reversible in nature and can be converted back to fluid form by simple heating and further gel stage could be restored through cooling. Fluid-gel cycles were repeated multiple times and no significant change in the gelation ability of the gelator was observed insinuating high stability and thermo-reversible nature of the gels. All gels were found to be stable at room temperature and didn't experience any significant physical change during storage for long duration.

The gelation ability of the gelator is not restricted to the organic solvents and oils but it is also capable of forming hydrogels under specified conditions which further expands its application domain. Hydrogels were prepared through rational control of the buffer solution/gelator/ethanol ratio. For the preparation of hydrogel, 10 mg gelator was dissolved in 1 mL ethanol, as prepared gelator solution was mixed with phosphate buffer (3 mL) and left at room temperature until gel formation completed (Fig. 4d). Formation of the hydrogels requires buffer and ethanol in a very specific quantity so the formation of hydrogel in oil/water separation experiments is not feasible. SEM images of the hydrogel revealed that similar to the toluene gel it is also composed of interconnected fibers (Fig. 2b1, b2). Further efforts were also made to exploit hydrogel as reaction medium for the growth of Au nanoparticles. For the preparation of Au nanoparticles containing hydrogel, 0.2 mL of Auric chloride (0.005M) was added to the reaction mixture during hydrogel formation. It was found that compound-3 not only served as gelator but also acted as a reducing agent which eliminated the need of external reducing agent for the reduction of gold salt into the Au nanoparticles. The dual functionality of the compound-3 makes it an enticing material for the preparation of the nanoparticles. Figure 5 shows the TEM images of Au nanoparticles containing hydrogel, it can be clearly seen from the figure that the hydrogel exhibits fibrous structure with an

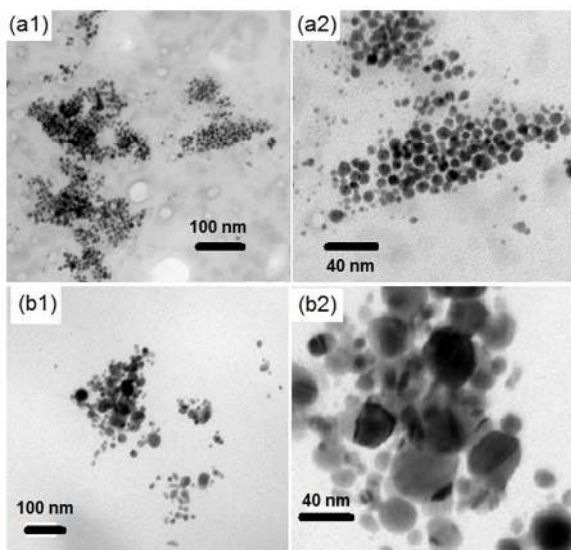


Figure 6 TEM images of the (a1, a2) Au nanoparticles (b1, b2) Ag nanoparticles.

individual fiber having length in micrometers and diameter in the range of 40-60 nm (Fig. 5). Au nanoparticles, imbedded in the fibers of hydrogel, can be easily noticed, the size of the Au nanoparticles is in the range of 5-10 nm. TEM images confirm that the Au nanoparticles are distributed uniformly throughout the fibers in form of agglomerates.

Compound-3 was utilized as surface passivating agent as well as green reducing agent for the preparation of Au and Ag nanoparticles in the fluid medium also. Figure 6 (a1, a2 and b1, b2) show the TEM images of the Au and Ag nanoparticles prepared by taking advantage of the dual functionality of the compound-3. In case of Au nanoparticles spherical particles having particle size in the range of 10-20 nm were obtained (Fig. 6a2). Similar to Au, in case of Ag nanoparticles also spherical particles were obtained, however, in addition to spherical particles, few particles having elongated structure were also visible (Fig. 6b2). The particle size of Ag nanoparticles was estimated in the range of 20-50 nm which is higher compare to the Au nanoparticles. Apart from higher particle size, Ag nanoparticles are more agglomerated compare to the Au nanoparticles. These results suggest that

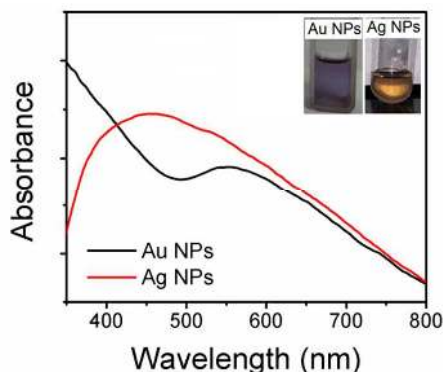


Figure 7 UV-Vis spectra of the Au and Ag nanoparticles.

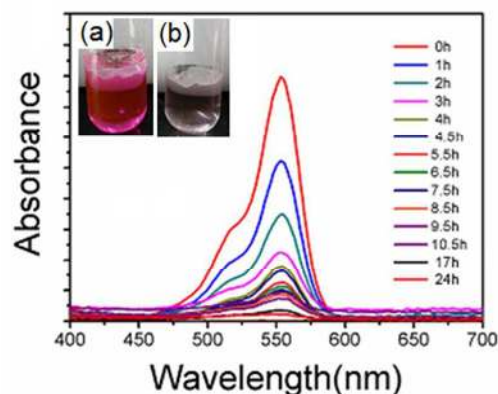


Figure 8 Removal of the waterborne dye using toluene gel (inset a-dye solution, b-after removal of dye from water).

compound-3 serves better as capping agent in case of Au nanoparticles compare to the Ag nanoparticles. UV-vis spectrum of the Au nanoparticles consists of a broad peak centered at 540 nm which is characteristic surface Plasmon peak for Au nanoparticles (Fig. 7). The absorption spectrum of the Ag nanoparticles also exhibits a broad surface Plasmon peak around 450 nm (Fig. 7). Compare to the Au nanoparticles, surface Plasmon resonance peak in case of Ag nanoparticles is wide suggesting higher agglomeration which is corroborated by the TEM images also. With time a monotonic increase in the absorbance is observed for both metal nanoparticles.

The removal of waterborne pollutants such as organic solvents, oils and toxic synthetic dyes from water is very crucial from the point of view of remediation of polluted water.³³ Organic synthetic dyes are found to be responsible for various health deteriorating effects on the mankind. It has been reported previously that carbohydrate based PSG can be utilized for the removal of the dyes from dyed water/oil mixture.^{17, 34} In PSG based dye removal process, first, transfer of dye from water to nonpolar solvent takes place thereafter oil can be solidified in form of gel using gelator and finally using simple filtration solid gel containing oil and dye can be recovered from the oil/dyed water mixture. We have also successfully utilized compound-3 for the dye removal from oil/dyed water mixture. However, in present case, the extraction of dye from water into organic solvent was allowed to precede post gelation unlike previously published report where first dye was extracted into the organic solvents and then gelation was carried out. For dye absorption experiments 5 mg of compound-3 was added to a 1 mL of toluene and heated until it dissolved completely, as obtained clear solution of compound-3 in toluene was left for ~5 minutes at room temperature which led to the formation of gel. Thereafter 10 mL of rhodamine B dye solution was added to a test tube containing above prepared toluene gel. UV-vis spectrum of the dye solution, taken out from the reaction mixture at a regular interval, was recorded in order to monitor the removal of the dye. Absorption spectra revealed that up to 96% of the dye can be removed using toluene gel (Fig. 8). Results suggest that the gelator can be utilized efficiently for the removal of not only oil

but also waterborne organic pollutants such as dyes from the oil/water mixture.

Conclusions

In conclusion, a multifunctional gelator, which is capable of forming both organogel and hydrogel, is reported. The gelator could produce highly strong gel in a very short gelation time. Through the rational implementation of the strategies such as ice bath assisted cooling and sonication, the gelation of different solvents was achieved in few seconds. Particularly, through sonication, gelation of different solvents was achieved within 5 seconds which is probably the shortest gelation time for *N*-acetyl glucosamine based gelators. In addition to organic solvents, the gelator was proven to be equally efficient for the gelation of the oils such as diesel and petrol which qualifies it as a suitable material for the oil spill recovery application. Organogel was also successfully utilized for the removal of waterborne synthetic dye which makes gelator useful for the environmental applications such as water treatment also. The hydrogel of the same gelator was explored as growth medium for the fabrication of Au nanoparticles, where besides acting as a structural unit, gelator also served as a reducing agent. Synthesis of Au and Ag nanoparticles was also carried out in fluid medium using gelator as stabilizing cum reducing agent.

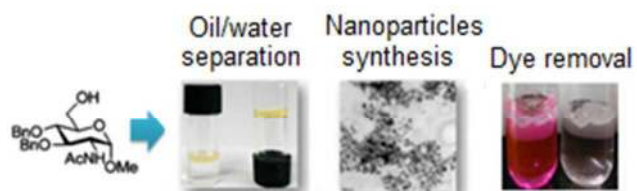
Overall, instead of developing separate molecules for different applications herein we have identified one single molecule with wide possible application spectrum.

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