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Chintam Narayana,[a] Priti Kumari,[a] Ghanshyam Tiwari [b] and Ram Sagar[a,b]*

[a]Department of Chemistry, School of Natural Sciences, Shiv Nadar University (SNU), NH91, Tehsil-Dadri, Gautam Buddha Nagar, Uttar Pradesh, 201314, India.

[b]Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, Uttar Pradesh, 221005, India.

*E-mail (Corresponding author): ram.sagar@bhu.ac.in

ABSTRACT:

Marine oil-spills have along-lasting impact on environment, therefore is a major concern in scientific community to find solution for its remediation. Recently, phase selective organo-gelators emerged as potential materials for removal of oil from water through selective gelation. Herein, we report synthesis of a series of C-6 triazole linked *N*-acetylglucosamine derivatives, among which three of the derivatives have shown excellent selective gelation of organic solvents, diesel, petrol and crude-oils in water and sea water. We have studied phase selective gelation against different API grade crude oils (from light to heavy) and the gelation was achieved using non-toxic carrier solvent at room temperature in less than 15 minutes, and gelators were found useful for recovering crude oils. Critical gel concentration (C.G.C.) of crude oil gelators was found to be 2.3-12% (w/v). The variable temperature NMR and FTIR experiments reveal that, intermolecular hydrogen bonding was responsible for the gel formation. Furthermore, a gelator was utilized for selective dye removal from water.

INTRODUCTION

Marine oil spillages have been one of the major environmental concerns because it damages the environment by releasing toxic substances.[1,2] Generally, oil spillages occur due to leakage of oil from drilling the oil in the sea and transporting the oil from one place to another place. In 2010, Gulf Mexico oil spillage was one of the biggest spillage in petroleum industry and it released four million barrels of crude oil into sea water. The spillage caused extensive damage to the marine, wild life habitats, fishing and tourism industries.[3] These oil spills damages to environment and forced researchers to design efficient remediation strategies for removal and recovery of crude oil from sea water. Apart from these there are other pollutants which damage the water bodies like dyes, heavy metals and industrial organic wastes.[4-7] The mitigation of the consequences of these pollutants is the need of hour.

Conventional methods for oil spill recovery can be classified into three categories, physical, chemical and biological methods. Skimmers are mechanical devices used to remove oil from water surface.[8] Sorbents are insoluble chemical materials which can soak oil from water.[9-12] Another physical method known for spill oil recovery is using adsorption materials.[13-15] However, Dispersants are a group of chemical products sprayed onto an oil phase to remove crude oil.[16,17] *In situ* burning of oil is another popular process to remove oil from water but it requires ignition and controlled combustion of oil slicks.[18] Bioremediation involves use of microorganisms to detoxify the pollutants in order to accelerate the natural biodegradation.[19] However, all these methods have certain drawbacks like human hazard, high cost, long procedures storage and transport etc. Recently, phase selective organo-gelators (PSOG) have received great attention because of its numerous applications in oil scavenging, dye removal, nanoparticle synthesis etc.[20-22] They forms gels by self-assembly of organic molecules in defined three dimensional network fibers through non-covalent interactions such as hydrogen bonding, π-π stacking, van der Walls forces and dipole-dipole interactions.[23]

Several research groups have reported different structural motifs of PSOG, such as amino acids, carbohydrates, steroids, and peptides etc. Among all motifs, recently carbohydrate based low molecular weight gelators (LMWGs) have attracted attention of scientific community because of its benign nature and diverse properties.[18] Carbohydrates are readily available renewable

resources and having multiple chiral centers and hydroxyl groups. Most of the carbohydrates based LMWGs involves hydrogen bond mediated self-assembly process.[19]

After pioneer work by Bhattacharya and co-workers for oil water separation using amino acid based gelators,[24] several groups have been explored carbohydrate based gelators for crude oil gelation.[25-32] Somnath and co-workers reported phase selective gelation of crude oil using arabinose based LMWGs.[23] They further used C-1 triazole linked arabinose derivatives as gelators for the crude oil separation.[25] Sureshan and co-workers have reported benzilidine masked glycopyranoside derivatives, which showed phase selective gelation of crude oil in water.[26] Mukherjee and co-workers and ourselves disclosed *N*-acetylglucosamine derived gelators which shown instant gelation of oil in presence of water.[27,28] Other than carbohydrates, recently Zeng and co-workers revealed Fmoc protected amino acid derivatives[29,30] and Chaudhuri *et al*. discovered naphthalene based diimide derivatives, as potential gelators, have ability to form gel in light to heavy crude oils.[31]

We envisioned that C-6 triazole linked *N*-acetylglucosamine derivatives may serve as stable carbohydrate based PSGs for crude oil gelation in water. Previously reported carbohydrate based gelators, for crude oil gelation were having acid or base sensitive functional groups, therefore were not suited, if acidic or basic impurities are present in crude oil.[29] Further triazole motif is robustically accessible through "click-chemistry" and known for structural backbone of gelators. Its planar structure exhibits the ability of H-bonding due to the presence of both donor and acceptor groups with similar relative positions having π-π stacking.

Herein, we report design and synthesis of C-6 triazole linked *N*-acetylglucosamine based compounds **5a-5g**. Selective compounds were identified as potential phase selective gelators for gelation of organic solvents, mineral oils, and crude oils in water and sea water. Additionally, the PSOGs were found to be efficient for removal of waterborne pollutant (dye).

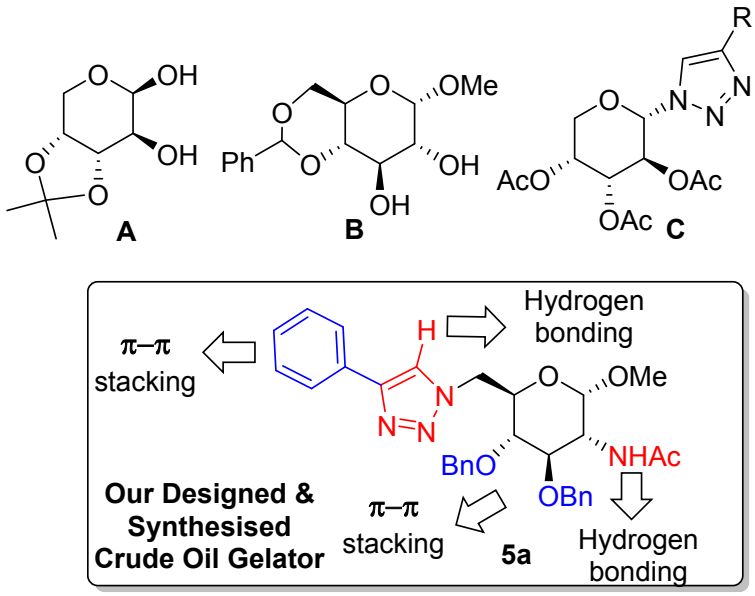
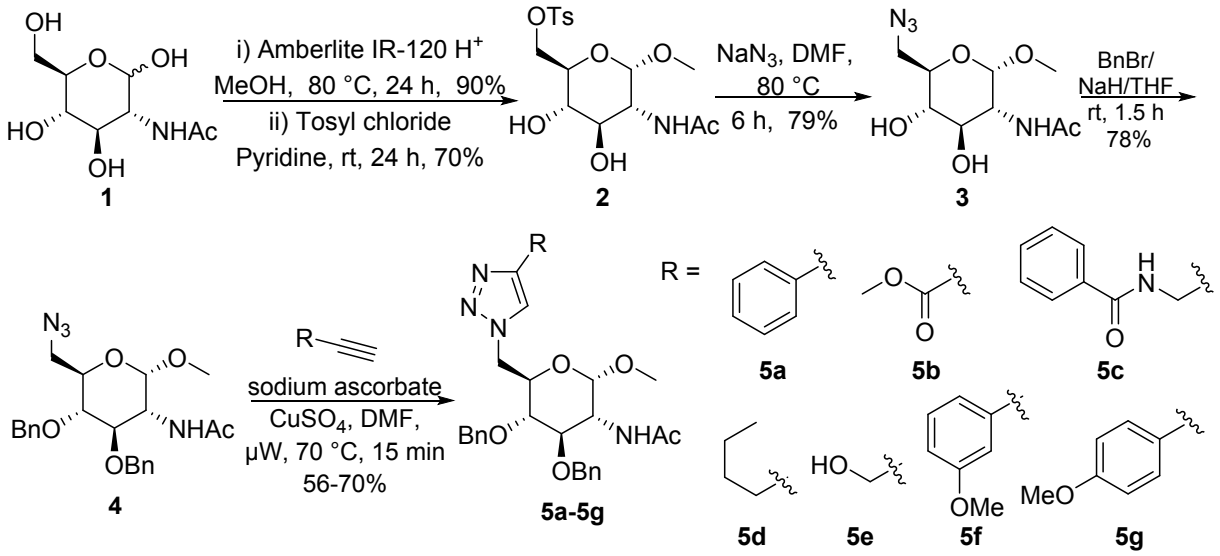


Figure 1. Carbohydrate based crude oil gelators **(A-C)** and our designed crude oil gelator **5a.**

RESULTS AND DISCUSSION

Synthesis

The synthesis commenced with the glycosidation reaction on commercially available *N*-acetyl glucosamine **1** with methanol in the presence of Amberlite IR-120 H^+ resin which afforded methyl glycoside as a mixture α: β (9:1) in quantitative yield. Subsequently, selective tosylation of C-6 OH using tosyl chloride in dry pyridine afforded the mixture of α- and β-tosyl derivatives. The major α-isomer compound **2** was separated through column chromatography and obtained in good isolated yield (70%).[32] Azidation reaction on compound **2** was carried out by sodium azide in DMF at elevated temperature which furnished azide derivative **3** in 79% isolated yield. Further, benzylation on azide derivative **3** led to di-*O*-benzylated compound **4** in 78% isolated yield (Scheme 1). Copper catalyzed click-chemistry was carried out on azido derivative **4** using different commercially available alkyne under microwave irradiation, which furnished C-6 triazole linked *N*-acetyl glucosamine derivatives in good to very good isolated yields. In order to understand the effect of substitution on triazole ring towards gelation, we have install different groups (aliphatic and aromatic) on traizole ring and synthesized amides, esters, phenyl substituted derivatives **5a-5g** in good yield (Scheme 1).



Scheme 1. Synthesis of triazole linked *N*-acetylglucosamine compounds **5a-5g.**

Gelation test: The gelation ability of C-6 triazole linked *N*-acetylglucosamine compounds **5a-5g** was tested in several different solvents and results are summarized in Table 1. Compounds **5a**, **5b** and **5f** displayed excellent ability to gelate different non polar organic solvents such as toluene, benzene, *o*-xylene, mesitylene etc. These gels were found to be transparent and stable at room temperature for more than 3 days. Furthermore, *m*-methoxy phenyltriazole derivative **5f** was found to forms stable gel selectively in aromatic solvents, whereas, *p*-methoxy phenyl triazole derivative **5g** forms unstable gel in all these solvents. These results are demonstrated that the changing the position of same functional group on phenyl ring influences the gel formation property. However, alkyl **5d**, hydroxyl alkyl **5e**, substituted C-6 triazole derivatives neither form gels in non-polar and nor in polar organic solvents. On the other hand, amide linked triazole derivative **5c** was insoluble in all the solvents (Table 1). Among all the identified gelators (**5a**, **5b** and **5f**), gelator **5a** was found best which exhibits minimum C.G.C. ranging between 0.14-0.8% (w/v) in all the tested solvents (Figure 2) and form stable gel (SI, Figure S1-S2). The lowest C.G.C. for **5a** was observed 0.14% (w/v) in mesitylene gel (Table 1). We observed that electron withdrawing group on triazole ring is essential for the gel formation, because it allows triazole ring proton to participate in intermolecular hydrogen bonding. In addition to that, π-π stacking interaction of phenyl ring and hydrogen bonding of the amide proton are also helpful for the gel formation. These gels display good thermal reversibility with a gel-sol transition temperature.

(a) (b) (c) (d) (e) (f)

Figure 2: Transparent gels formed by **5a** in different organic solvents: (a) Benzene (b) Toluene (c) *o*-Xylene (d)*m*-Xylene (e) *p*-Xylene (f) mesitylene

Gel formation time is very important and it contributes wide range functions and applications to gelator.[33] Thus we studied gelation property of compound **5a** in various solvents and noticed its gel formation time. We found that thermal induced gelation of **5a** took more than five minutes; whereas, ultrasonication induced gelation took less than one minute. It's worth to mention here that the ultrasonic energy can induce powerful stimulus to cause gelation.[34]

Table 1. Study of gel formation in different solvents at different concentration and conditions.

Solvents	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**	**Time**	
								Gelation of 5a in cold condition	**Gelation of 5a under Sonication**
Benzene	TG (0.80)	TG (0.92)	P	S	S	TG (0.80)	PG	10 min	35 sec
Toluene	TG (0.62)	TG (0.41)	P	S	S	TG (0.80)	PG	3 min 50 sec	28 sec
o-xylene	TG (0.45)	TG (0.31)	P	S	S	TG (0.80)	PG	4 min 50 sec	25 sec
m-Xylene	TG (0.27)	TG (0.22)	P	S	S	TG (0.38)	PG	3 min 20 sec	27 sec
p-xylene	TG (0.31)	TG (0.38)	P	S	S	TG (0.45)	PG	3 min 40 sec	35 sec
Mesitylene	TG (0.14)	TG (0.33)	P	S	S	TG (0.25)	PG	50 sec	20 sec
Chlorobenzene	S	S	P	S	S	S	S	S	S
Bromobenzene	S	S	P	S	S	S	S	S	S
Iodobenzene	S	S	P	S	S	S	S	S	S

Compounds were tested in 5 mg/mL concentration. S is soluble at room temperature, P is precipitated, () is C.G.C in mg/mL.TG is transparent gel, PG means partial gel. All C.G.C. were determined using heating and cooling method (thermal induced), which involves heating of gel mixture followed by quick cooling in ice cold water.

Morphological Properties of gels:

To gain insight into the aggregation mode, we recorded morphologies of xerogels formed by compounds **5a** and **5b** in mesitylene and toluene solvent using field emission scanning electron microscopy (FESEM). The images are shown in figure 3; a1, a2 are SEM images belongs to xerogel of **5a** and **5b** prepared in mesitylene solvent respectively. These images shows dense and entangled network of fibers with diameter less than 100 nm and length on a 5 micrometer scale which showed effective entrapment and immobilization of the solvent. On the other hand, xerogel images of **5a** and **5b** prepared in toluene displayed lamellar type texture (Figure 3; a3 and a4).The morphology of xerogels was clearly demonstrated the role of solvent influences in self-assembly of these gelators.

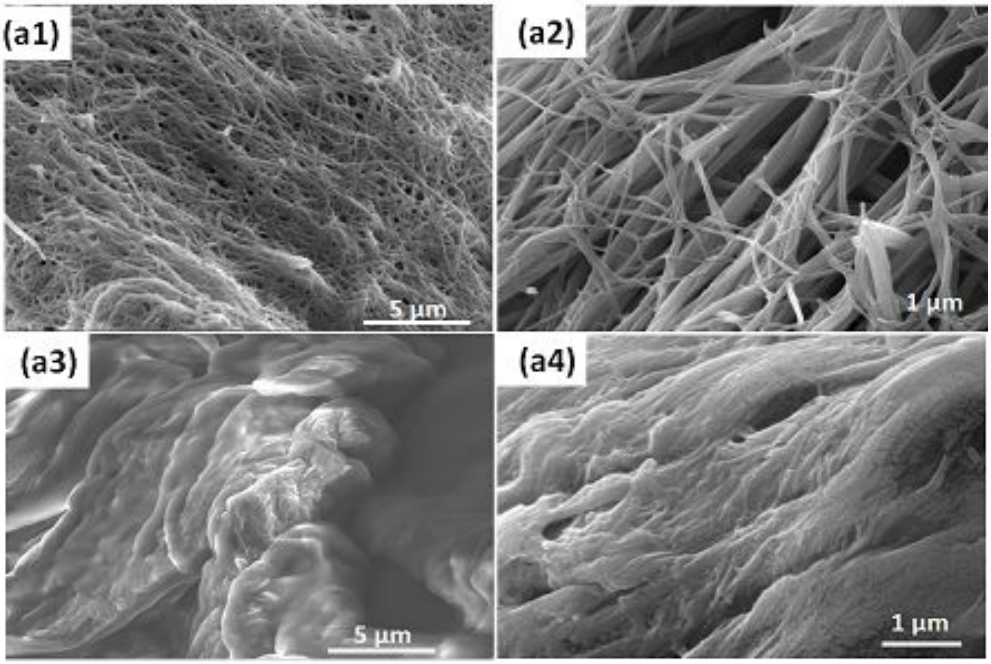


Figure 3. SEM images of mesitylene gel of compound **5a-**(a1) and **5b-**(a2) and toluene gel of compound **5a-**(a3) and **5b-**(a4).

For understanding mechanism of self-assembly resulting in to gel formation, we have performed variable temperature (VT) NMR experiment in DMSO-d_6 for compounds **5a** (Figure 4) and compound **5b** (SI, Figure S3). The triazole C-H proton in compound **5a** shifted from δ 8.605 ppm to 8.495 ppm, while increasing the temperature from 25 to 60 ºC. This upfield shift (Δδ =

0.117 ppm) clearly indicates that, triazole C-H proton was involved in intermolecular hydrogen bonding and it got weaken with increasing the temperature. Similarly, N-H proton of acetamido group was shifted to upfield ($\Delta\delta$ = 0.262 ppm) suggesting that N-H proton was involved in hydrogen bonding interactions as well (Figure 4). The protons of OCH_3 slightly shifted to downfield by $\Delta\delta$ 0.047 ppm upon increasing the temperature. This reflects that intramolecular hydrogen bond between NH and OCH_3 groups. These results support that, hydrogen bonding and π-π stacking interactions were responsible for gel formation in these compounds.

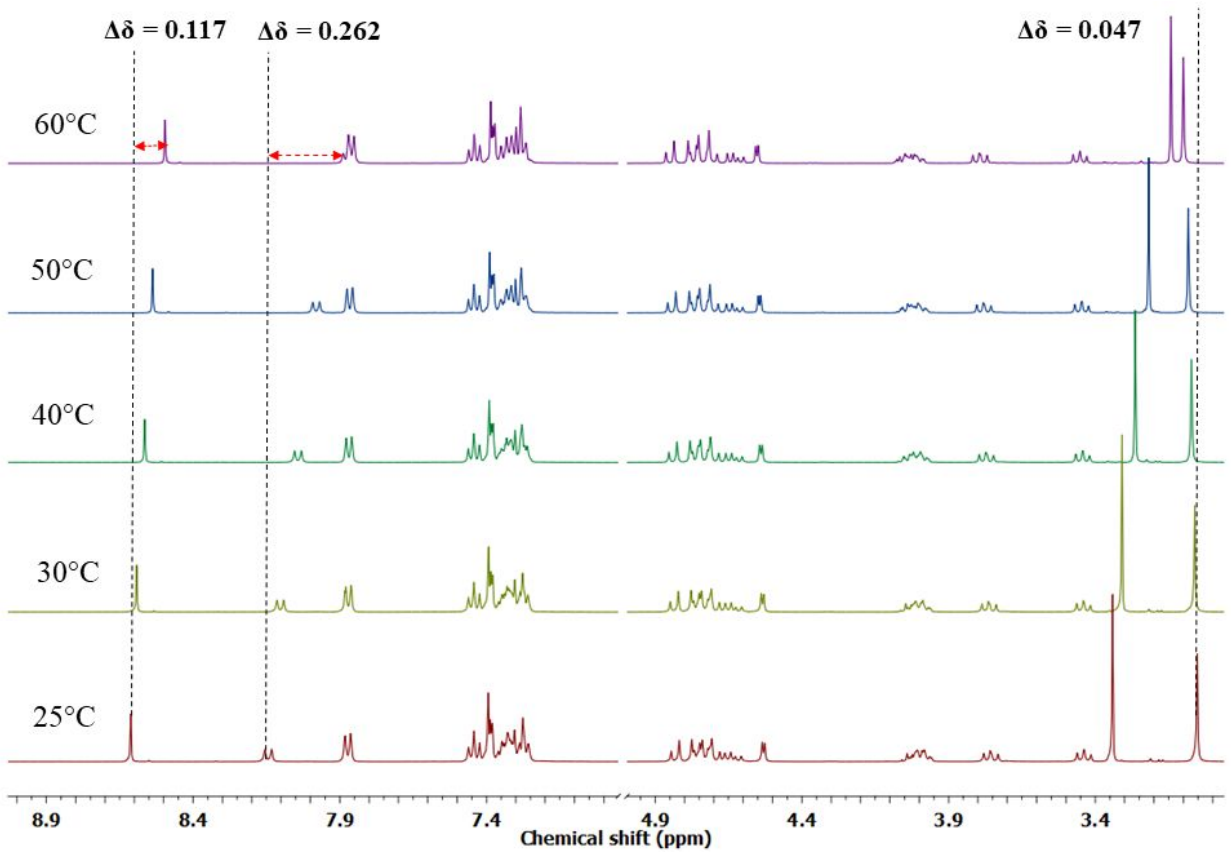


Figure 4. ^{1}H NMR spectra of compound **5a** at different temperature in DMSO-d_6

Phase selective organo-gelators are capable of congeal the oil in presence of water. The main advantage with this is that, gelled oil float on water, which can easily be separated from water. There are different methods reported for phase selective gelation of oil in presence of water,[35-37] i) dissolution of the gelator in a suitable environment friendly solvent followed by drop wise addition it to the oil phase or ii) applying xerogels directly to the oil phase. In our study, we have investigated phase selective gelation ability of compounds **5a**, **5b** and **5f** in petroleum products such as diesel, petrol, pump oil and silicon oil. The gelation ability of gelators was found in

decreasing order of **5a** > **5f** > **5b** (Table 2). All oil gels are scoopable, thermo reversible and stable for several months (SI, Figure S4). In case of diesel and petrol C.G.C. for compound **5a** was 2.8% (w/v) and 2.0% (w/v) respectively.

Table 2. Phase selective gelation different oils in water.

Solvents (1:2 v/v)	**5a**	**5b**	**5f**
Diesel-water	G (2.8)	G (5.7)	G (3.2)
Petrol-water	G (2.0)	G (3.9)	G (2.3)
Silicon Oil-water	G (3.0)	G (5.5)	G (3.2)
Pump Oil-water	G (3.6)	G (6.4)	G (4.0)

G = Gel, () C.G.C. = critical gelation concentration, 0.2 mL of EtOAc was used as co-solvent in each case.

X-ray Diffraction study:

To understand the molecular packing, we have performed powder XRD for 1% (w/v) toluene gel of **5a.** The XRD pattern of the xerogel showed three reflection peaks 2θ = 14.8°, 19.4°, 24.4°. Their corresponding d spacing is 5.9 Å, 4.5 Å and 3.6 Å. Strong peak at 2θ value 24.4° can be attributed to π-π stacking interactions and corresponding d-spacing 3.6 Å. And another peak at 2θ = 19.4° corresponding to H-bonding interactions with an average distance of d = 4.5 Å (Figure 5).[23]

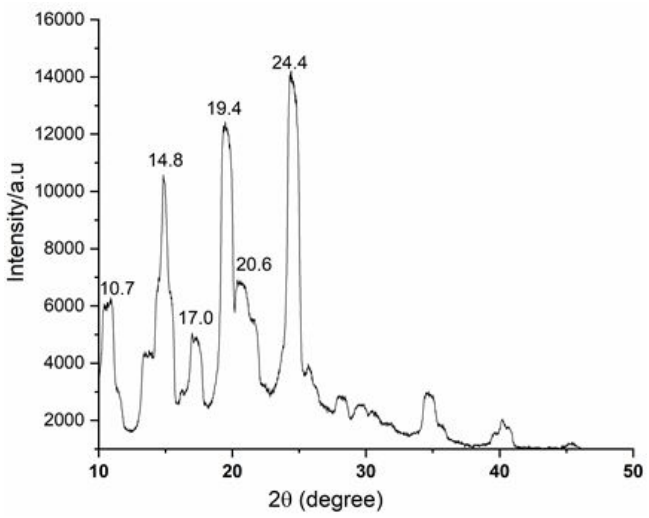


Figure 5. Powder XRD pattern of xerogel of **5a**

In order to understand the non-covalent interactions, we have acquired and studied the IR spectra of solid compound **5a** and its gel formed in diesel. We observed N-H stretch vibration 3295 cm^{-1} in powder form shifted to 3290 cm^{-1} in gel state, which further indicates intermolecular hydrogen bonding taking place for gel formation. In solid state Ar C-H and triazole C-H stretch vibration for compound **5a** appears at 2911 and 2832 cm^{-1} respectively. Slightly red shift was observed for these C-H stretches in gel state from 2911 to 2922 cm^{-1} and 2832 to 2853 cm^{-1}. The shift is due to strong hydrophobic interactions in the gel state of **5a**. Moreover, these signals got enhanced in the gel state. The amide C=O bond stretch band in powder form at 1645cm^{-1} shifted to gel state 1648 cm^{-1} and amide N-H bending frequency shifted from 1548 cm^{-1} to 1549 cm^{-1}. These findings indicate hydrogen bonding and hydrophobic interactions were responsible for gel formation in this compound (Figure 6).

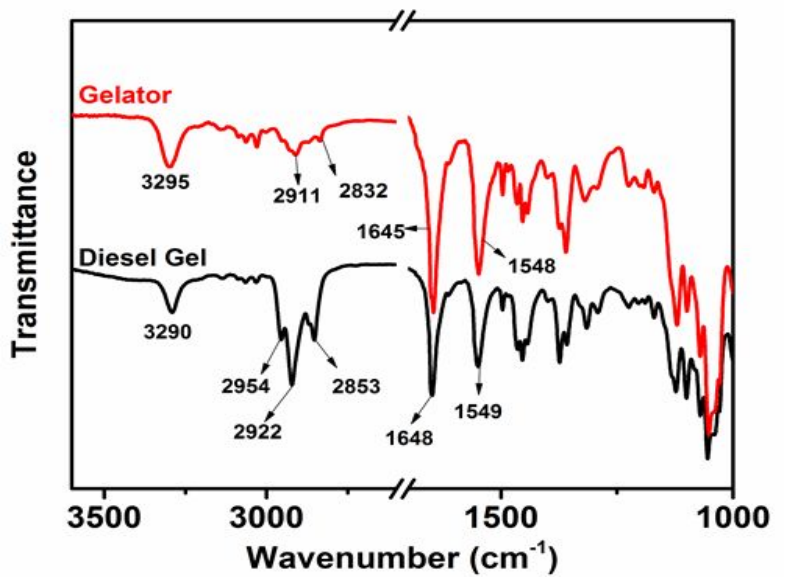


Figure 6. FT-IR spectra of gelator **5a** in powder form and in diesel gel form.

Oil spill recovery:

Crude oils have different ratio of composition of hydrocarbons and non-hydrocarbons. The hydrocarbon contains alkenes, aromatic compounds and non-hydrocarbons are mostly Sulphur and transition metals (Hg, V, Pb and Ni) containing compounds. We have studied three different crude oils for phase selective gelation using our gelators **5a**, **5b** and **5f** (SI, Figure S5-S7). We have applied different methods for phase selective gelation with Erha crude oil in water and sea water. The powder form gelator **5a** did not exhibit gelation property with Erha crude oils. Whereas, selective crude oil gelation was achieved by dissolving gelator in non-toxic carrier solvent at room temperature. We found ethyl acetate as a suitable carrier solvent, which is less toxic than crude oil and better carrier solvent for gelation.

When compound **5a** was applied to crude oil in carrier solvent, the crude oil layer became gel within 15 min it holds the water layer. The C.G.C..of gelator was 2.39% (w/v), (Figure 7) which is higher compare to aromatic solvents. The high C.G.C. value in crude oil is due to long chain hydrocarbons and contaminated with elemental sulfur (Table 3).

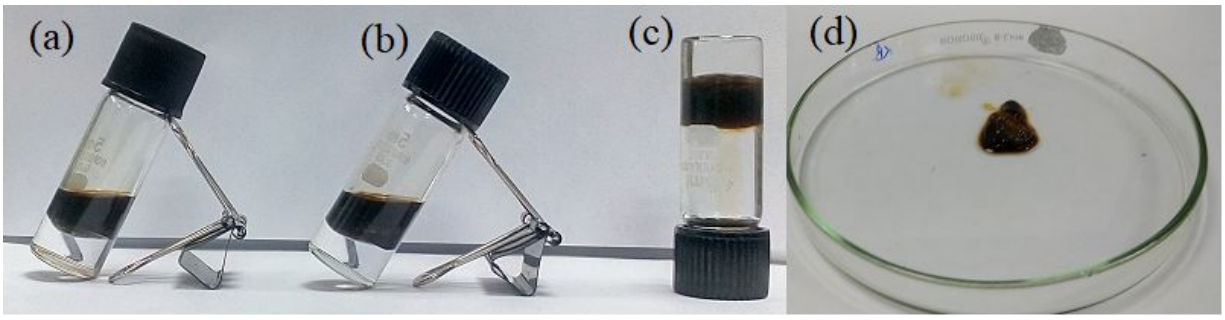


Figure 7. C.G.C. of crude oil gelation of compound **5a** for (a) 8 mg of **5a** in ethyl acetate 0.5 mL crude oil: 1.0 mL water (b) 9 mg of **5a** in ethyl acetate 0.5 mL crude oil: 1.0 mL water (c) 10 mg of **5a** in ethyl acetate (d) scooped crude oil gel from water.

Further, we have studied gelation of compound **5a** with three different crude oils which are Erha, Kuwait export, and WCS crude oils (Figure 8). American petroleum institute (API) is divided Erha, Kuwait export and WCS crude oils on the basis of API gravity. The API gravity of Erha, Kuwait export and WCS crude oils 32.8°, 31.4° and 21° respectively, which are classified as light, medium and heavy crude oils respectively (SI, Table S1). Heavy crude oil contains higher resins and asphaltenes in larger quantities compare to lighter crude oil.[38] The gelation property of C-6 triazole linked *N*-acetylglucosamine derivatives **5a**, **5b** and **5f** was studied with these three crude oils and resulted gel formation are shown in figure 8.

Figure 8. C.G.C. of different crude oils gelation of compound **5a** (a) Erha crude oil (b) kuwait export (c) WCS crude oil.

The C.G.C. for compound **5a** in these different crude oils were calculated and results are summarized in Table 3. Compounds **5a**, **5b** and **5f** showed gelation in three different crude oils. The critical gelation concentration of compound **5a** was having higher C.G.C. value in heavy crude oil and lower C.G.C. value in light crude oil. The C.G.C. of compound **5a** in light API grade oil was 4.6% (w/v) and 8.4% (w/v) in medium crude oil (Table 3 entry 2 and 3). Whereas,

Compound **5f** C.G.C. was 4.9% (w/v) in medium crude oil. These results indicate C.G.C. of gelation by different gelators was dependent on composition of crude oil (Table 3).

Table 3. Phase selective gelation of different crude oils in presence of water.

Entry	**Crude oils-water** (1:2 v/v)	**5a**	**5b**	**5f**
1	Erha-water	G (2.3)	G (3.6)	G (2.7)
2	Kuwait export-water	G (8.4)	G (12)	G (4.9)
3	WCS crude oil-water	G (4.6)	G (9.3)	G (4.6)

G = Gel, () C.G.C. = critical gelation concentration

We have performed a glass bath experiment, where Erha crude oil (2.5 mL) was poured over a 100 mL of tap water and gelator **5a** (60 mg) was dissolved in ethyl acetate (1.2 mL) and added drop wise on top of crude oil layer, the entire crude oil layer was completely congealed within less than 15 minutes, which was scooped off leaving behind clear water.

Crude oil gelation with gelator **5a** was also carried out with natural seawater, collected from Bay of Bengal, to realise its real application for crude oil spillage recovery. As shown in figure 9 the gelator **5a** at C.G.C. selective gelated crude oil from the surface of sea water (Crude oil:Sea water 1:10 v/v) within 15 minutes. which was scooped off leaving behind clear sea water. Same experiment was performed using gelator **5a** at C.G.C. by adding 1 mL of Erha crude oil in different ratio of sea water (1:20, 1:50, 1:200, 1:500 and 1:1000 v/v) and indeed the gelation of crude oil was obsrved in all tested cases.

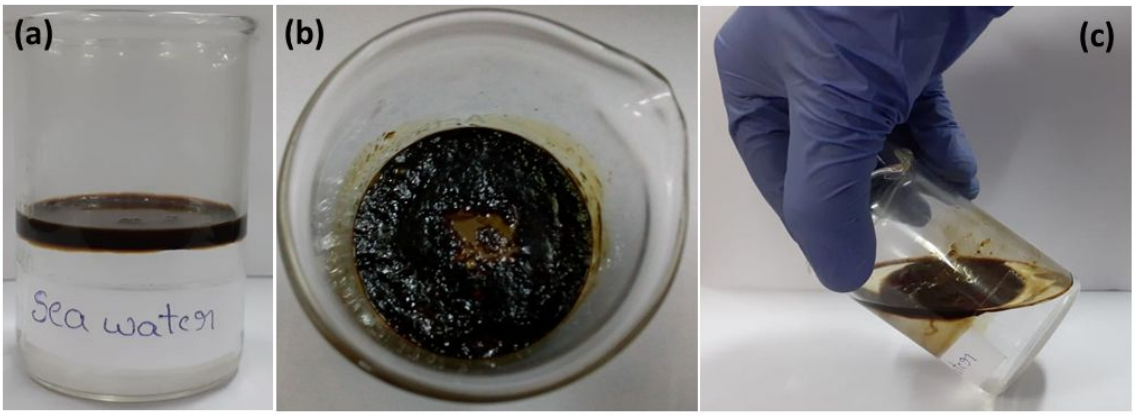


Figure 9. Erha crude oil gelation in natural sea water (a) 2.5 mL of Erha crude oil gel was placed in 25 mL of natural sea water (b) Addition of 57 mg of gelator **5a** dissolved in 1.2 mL of EtOAc (c) Crude oil gelation within 15 min.

The crude oil gel strength was studied by rheological experiments with 2.3% (w/v) erha crude oil gel from gelator **5a**. Frequency sweep and stress sweep experiments presented in figure 10. Storage modulus (G') and loss modulus (G") were important parameters for these experiments, where G' measures elasticity of the material and G" measures viscosity of the material. It's documented that, stable gelator showed storage modulus is always higher than the lose modulus.[39]

In frequency sweep experiment G' and G" was measured as a function of frequency at constant strain 0.01%. The crude oil gelator from **5a** showed G' is higher than the G" over the frequency range 0.1-600 Hz and they did not cross each other. These results indicate that the crude oil gel was elastic in nature.

The stress sweep experiments were also conducted for crude oil gels obtained from **5b** and **5f** (SI, Figure S8). In stress sweep experiment of where G' and G" measured as a function of stress amplitude at constant frequency 0.1 Hz. Storage modulus (G') and loss modulus (G") with respect to constant frequency at particular pressure cross each other and the cross section point called yield stress. Gelator **5a** yield stress was found 97.4 Pa. The high value of yield stress indicates crude oil stiffness and good tolerance to external pressure (Figure 10).

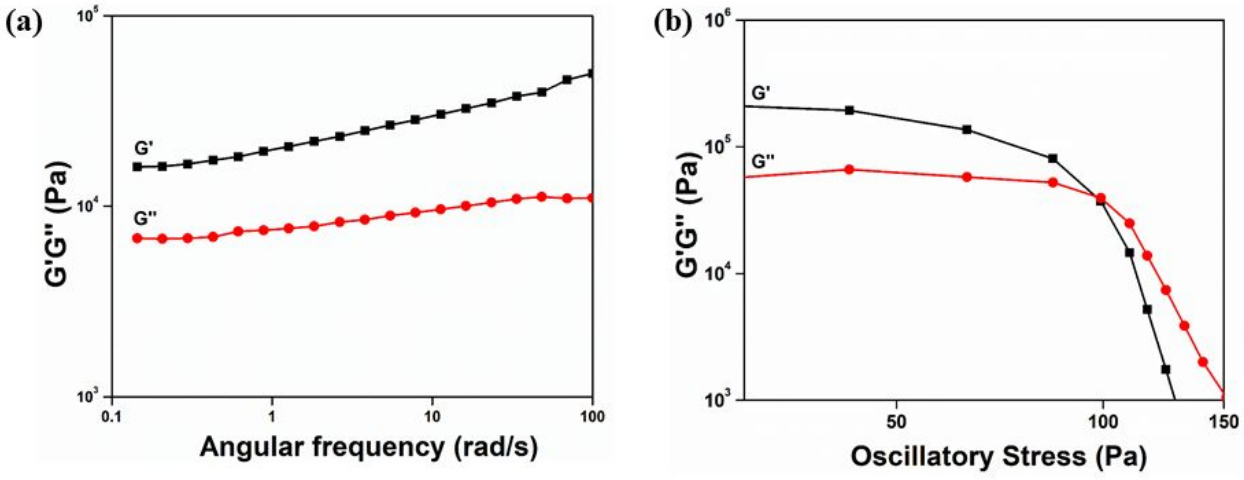


Figure 10. Rheology of Erha crude oil gels: **(a)** frequency sweep of **5a** gel **(b)** stress sweep of **5a** gel

Selective dye Removal:

Highly toxic dyes are non-biodegradable, when it releases into environment and it causes deleterious effects on environment as well as human health. LMWGs are playing an important role for dye removal because of their larger nano surface area which effectively adsorbs the dye molecules.[40] We have studied removal of three types of toxic dyes from artificially polluted water. We have taken 10 mL of Rhodamine B dye or crystalline violet or methylene blue (0.05M) solution in a vial, 5 w/v % mesitylene gel of compound **5a** was added to this and removal of dye was observed. The dye removal was monitored by UV-Visible spectroscopy and the adsorption was recorded at different time intervals (Figure 11). UV-Visible spectra reveals complete absorption of Rhodamine B dye molecules on gel surface in 15 h (Figure 11 (a)), whereas, crystalline violet adsorption takes 10 h 30 min (Figure 11 (b)). But in case of methylene blue, it could not able to entrap on gel surface (SI, Figure S9).These results suggest that the gelator **5a** can be utilized for the dye removal of waterborne organic pollutants such as dyes from the pollutant water.

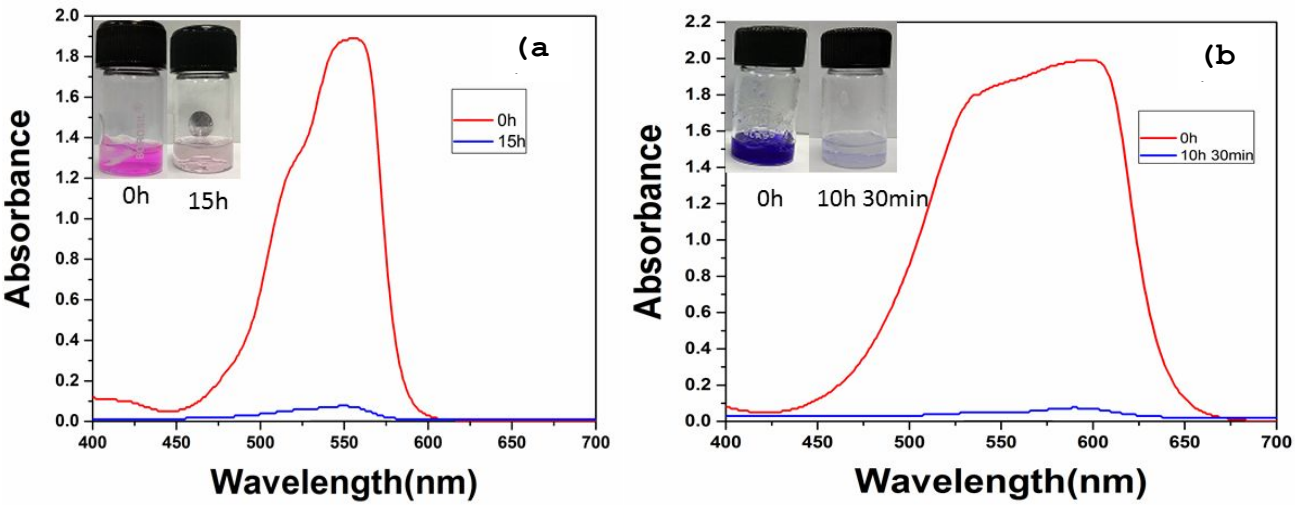


Figure 11. UV spectra for removal of dyes: (a) rhodamine B; (b) crystalline violet.

CONCLUSION

In a conclusion, C-6 triazole linked *N*-acetylglucosamine derivatives were designed and efficiently synthesized. Compound **5a** was identified as an excellent phase selective gelator for different hydrocarbon solvents, oils and crude oils in water as well as in natural sea water. The

gelator **5a** formed stable and strong gel in a lesser time, which qualifies it as a suitable gelator for the crude oil spill recovery application. FT-IR and ^{1}H NMR studies reveal that hydrogen bonding and π-π stacking interactions were responsible for gel formation. The gelator **5a** was successfully utilized for entrapment of the waterborne synthetic dyes which makes this gelator was suitable for water treatment. The gelator **5a** was successfully utilized for crude oil recovery application at experimental level using sea water which makes it a potential candidate for future development in larger applications.

EXPERIMENTAL SECTION

General experimental material and methods.

All reagents and solvents were purchased from commercial sources. TLC was visualized either by UV light or by treating with 10% H_2SO_4 in EtOH followed by heating.^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer at ambient temperature. ^{1}H recorded by 400 MHz and ^{13}C recorded by 100 MHz. Proton chemical shifts are given in ppm relative to the internal standard (tetramethylsilane) or referenced relative to the solvent residual peaks ($CDCl_3$:δ 7.26; DMSO-*d*$_6$:δ 2.50; CD_3OD: δ 3.31). Multiplicity was stated as follows: s (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. Column chromatography was performed by using silicagel 60-120 and 100-200 mesh. High resolution mass spectra obtained from quadrapole/Q-TOF mass spectrometer with an ESI source. FTIR measurements were recorded using ATR FTIR spectroscopy (Thermo Scientific Nicolet^{TM}Is^{TM}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 performed on Anton Paar MCR 302 rheometer equipped with steel coated parallel-plate geometry (25 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. UV-vis spectrum of dye removal was recorded by (Thermo Scientific Evolution-201). The Morphology of the gels was examined using scanning electron microscopic (SEM) FEI Nova Nano SEM-450. 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 sea water used in this study was collected from Bay of Bengal.

Gelation test:

8 mg compound **5a** was taken in 2.0 mL glass vial and added 1.0 mL of benzene was added into it. The compound was partially soluble at room temperature upon heating it was completely soluble. After that glass vial allowed to cool at room temperature, if inverted vial having no flow of the solution then it's confirmed as a gel.

Critical gel concentration (C.G.C.):

Initially 10 mg of gelator **5a** was dissolved in 1.0 mL of mesitylene solvent to make mesitylene gel. After that every cycle small amount of solvent was added and this process was repeated several times until gel became unstable. The maximum amount of solvent required for the stable gel formation used for the C.G.C. calculation.

Scanning electron microscopy (SEM) studies:

Gels using compounds **5a** and **5b** were prepared in toluene and mesitylene solvents at their respective C.G.C. These gels were coated on carbon plates, after 15 minutes gel gets dried. Morphology of gels examined by scanning electron microscopy FE Nova Nano SEM-450.

Rheology experiment:

Rheological experiment was conducted on MCR-102 Anton par (25 mm, stainless steel). The distance between the plates was 25 mm. The experiment carried out by Erha crude oil gels obtained from compounds **5a**, **5b** and **5f** at C.G.C. 2.3% (w/v), 3.6% (w/v) and 2.7% (w/v) respectively. The gels samples were kept in between parallel plates and it's covered complete plates. Frequency sweep and strain sweep experiments were performed to find the viscoelastic nature of the gels. Frequency sweep experiment was conducted 0.1 Hz to 600 Hz at constant strain 0.01%. Stress sweep experiment was conducted at constant frequency 1.0 Hz.

Phase selective gelation of different oils and crude oils:

Phase selective gelation experiments (Table 2) were performed using different oils (0.5 mL) and water (1.0 mL) in ratio of 1:2, using ethyl acetate as co-solvent (0.2 mL). The gelator **5a** (~ 14 mg) was dissolved in 0.2 mL of ethyl acetate and applied to oil water mixture at room temperature. The oil layer was completely congealed within 15 min. The experiments of gelators **5b** and **5f** with different oils were performed adopting similar protocol.

For crude oils gelation (Table 3), we have performed a glass bath experiment, where Erha crude oil (2.5 mL) was poured over a 100 mL of tap water and gelator **5a** (60 mg) was dissolved in ethyl acetate (1.2 mL) and added drop wise on top of crude oil layer, the entire crude oil layer was completely congealed in less than 15 minutes, which was scooped off leaving behind the clear water. The experiments of gelators **5b** and **5f** with different crude oils were performed using similar protocol.

Dye removal experiment:

10 mL 0.05 M Rhodamine B dye solution was taken in a vial and then added 0.5% (w/v) mesitylene gel of compound **5a**. After some time the dye absorbed on the gel surface which was measured by UV absorption experiment. Similar experiment was performed with methyl orange and methylene blue dyes (Figure 11 and S9).

Powder XRD experiment:

Powder XRD experiment carried out using Bruker D8 discover diffractometer using Cu-Kα radiation (λ=1.54Å) with a secondry graphite crystal monochromator. 1.0% (w/v) toluene gel of compound **5a** used in this experiment.

Synthesis and spectral data of compounds:

((2R,3S,4R,5R,6S)-5-acetamido-3,4-dihydroxy-6-methoxytetrahydro-2H-pyran-2-yl) methyl 4-methylbenzenesulfonate ***2.*** Amberlite IR 120-H^+ resin (20 g) was added to a pre-stirred solution of *N*-acetylglucosamine**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 methyl glycoside as white solid (19 g) in 89% isolated yield anomeric mixture (α:β, 9:1). Methyl glycoside was used for tosylation without further purification.

To a stirred solution of Methyl glycoside (10 g, 42.55 mmol) in pyridine was added tosyl chloride (9.7 g, 51.06 mmol) portion wise. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, reaction mixture was evaporated to dryness. crude compound purified by column chromatography (ethyl acetate/ methanol 95:5) to afford pure α-isomer of compound **2** (11.7 g, 70%) as a sticky solid. ^{1}HNMR (400 MHz, CD_3OD): δ 7.81 (d, *J* = 8.4 Hz, 2H, ArH), 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 4.55 (d, *J* = 3.6 Hz, 1H, H-1), 4.35 (dd, *J* = 10.8 Hz, 1.6 Hz, 1H, H-6a), 4.21 (dd, *J* = 10.8 Hz and 6.0 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-6b), 3.84 (dd,*J* = 10.4 Hz, 3.6 Hz, 1H, H-2), 3.69-3.66 (m, 1H, H-5), 3.59 (dd, *J* = 10.8 Hz and *J* = 9.0 Hz, 1H, H-3), 3.30 (s, 3H, OCH_3), 3.27 (t, *J* = 9.2 Hz, 1H, H-4), 2.47 (s, 3H, $CH_3C_6H_4$), 1.98 (s, 3H, $COCH_3$) ^{13}C NMR (100 MHz, CD_3OD): δ 173.7, 146.5, 134.4, 131.0, 129.1, 99.7, 72.8, 71.8, 71.1, 71.0, 55.6, 55.0, 22.5, 21.6, HRESI-MS (m/z): $C_{16}H_{23}NO_8S$, $[M+H]^+$: 390.1217, found 390.1216.

*Synthesis of N-((2S,3R,4R,5S,6R)-6-(azidomethyl)-4,5-dihydroxy-2-methoxytetrahydro-2H-pyran-3-yl) acetamide**3*.** To a stirred solution of compound **2** (7.2 g, 18.5mmol) in DMF was added NaN_3 (0.7 g, 6.46 mmol) at room temperature. The reaction mixture was stirred at 100°C for 12h.TLC showed that the starting material was consumed completely. The reaction mixture was concentrated under vacuum to obtain a residue. The residue was purified by column chromatography (ethyl acetate/methanol: 95:5) to furnish compound **3**as a white solid (3.8 g) in 79% isolated yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 5.99 (d, *J* = 8.5 Hz, 1H), 4.70 (d, *J* = 3.8 Hz, 1H), 4.09 (ddd, *J* = 10.3, 8.6, 3.8 Hz, 1H), 3.83 (s, 1H), 3.76 – 3.70 (m, 1H), 3.62 (d, *J* = 10.1 Hz, 1H), 3.60 – 3.44 (m, 4H), 3.43 (s, 2H), 3.16 (s, 1H), 2.06 (s, 3H).^{13}CNMR (100 MHz, $CDCl_3$): δ 172.4, 98.4, 72.5, 70.8, 55.4, 51.6, 23.3 ($CO\mathit{CH_3}$). HRESI-MS (m/z): Calcd for $C_9H_{16}N_4O_5$ $[M+H]^+$: 261.1193, found 261.1194.

*Synthesis of N-((2S,3R,4R,5R,6R)-6-(azidomethyl)-4,5-bis(benzyloxy)-2-methoxytetrahydro-2H-pyran-3-yl) acetamide **4**.* To a stirred solution of compound **3 (**2.1 g, 8.07mmol) in dry THF, sodium hydride (0.8 g, 1.44mmol) was added at 0 °C. After 20 min benzyl bromide (2.3 mL, 20.17mmol) 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 ethyl acetate (500 mL) washed with water (2 x

250 mL) and saturated brine solution (1 × 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 purified by column chromatography (ethyl acetate: hexane 20:80) to furnish the compound **4** (2.5 g, 71%) as a white solid. ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.39-7.28 (m, 10H), 5.30 (d, *J* = 9.3 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.67-4.61 (m, 3H), 4.30-4.24 (m, 1H), 3.80-3.76 (m, 1H), 3.71-3.67 (m, 1H), 3.61-3.56 (m, 1H), 3.49 (dd, *J* = 13.1, 2.3 Hz, 1H), 3.37 (s, 3H), 3.36 – 3.32 (m, 1H), 1.87 (s, 3H).^{13}CNMR (100MHz,$CDCl_3$): δ 128.7, 128.3, 128.1, 128.0, 98.7 (C-1), 80.3, 79.2, 75.3, 75.0, 70.8, 55.3, 52.6, 23.5. HRESI-MS(m/z): Calcd. for $C_{23}H_{28}N_4O_5$ $[M+H]^+$: 441.2137; found 441.2132.

Synthesis of N-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-2-methoxy-6-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)tetrahydro-2H-pyran-3-yl)acetamide ***5a.***

Toa solution of compound **5** (0.4 g, 0.98 mmol) in DMF was added phenyl acetylene (0.11 g, 1.078 mmol), $CuSO_4$ (0.019 g, 0.098 mmol) and sodium ascorbate (0.007 g, 0.0294 mmol). The reaction mixture was stirred at70 °C for 3h. After completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate) to yield compound **5a** as a white solid, (0.35 g, 71%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (s, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.45-7.25 (m, 12H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.76 – 4.70 (m, 4H), 4.67 – 4.59 (m, 1H), 4.52 (d, *J* = 3.5 Hz, 1H), 4.03 – 3.95 (m, 2H), 3.74 (dd, *J*= 10.6, 8.9 Hz, 3H), 3.45-3.40 (m, 1H), 3.04 (s, 3H).^{13}CNMR (100MHz, DMSO-d_6): δ 169.8, 146.5, 138.6, 138.3, 132.9, 130.8, 129.1, 128.6, 128.4, 128.1, 128.0, 127.8, 125.3, 122.7, 98.3, 80.1, 79.2, 74.4, 69.4, 54.5, 52.7, 50.7, 22.7.HRESI-MS (m/z) Calcd. for $C_{31}H_{34}N_4O_5$ $[M+H]^+$:543.2628; found 543.2637.

Synthesis of Methyl 1-(((2R,3R,4R,5R,6S)-5-acetamido-3,4-bis(benzyloxy)-6-methoxy–tetrahydro-2H-pyran-2-yl) methyl)-1H-1,2,3-triazole-4-carboxylate ***5b.***

To a solution of compound **5** (0.5 g, 1.13 mmol) in DMF was added acetylene compound (0.113 g, 1.35 mmol), $CuSO_4$ (0.018 g, 0.113 mmol) and sodium ascorbate (0.006 g, 0.033 mmol). The reaction mixture was stirred at 70°C for 3h. After completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 500 mL), combined

organic layer was washed with brine solution (1 × 200 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: methanol, 9:1) to yield compound **5b** as a white solid (0.4g, 67 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75 (s, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.37 – 7.24 (m, 10H), 4.82-4.62 (m, 6H), 4.50 (d, J = 4.5 Hz, 1H), 4.01 – 3.94 (m, 2H), 3.82 (s, 3H), 3.73 (dd, J = 10.6, 8.8 Hz, 2H), 3.41 (d, J = 9.5 Hz, 3H), 3.01 (s, 6H), 1.83 (s, 3H).^{13}CNMR (100MHz, DMSO-d_6): δ 169.2, 160.6, 138.42, 130.41, 130.0, 128.2, 128.1, 127.8, 127.6, 127.5, 98.1, 79.8, 78.9, 74.0, 68.8, 54.2, 52.3, 51.6, 50.6, 22.4. HRESI-MS (m/z) Calcd. for $C_{27}H_{32}N_4O_7$ $[M+H]^+$: 525.2344; found 525.2345.

Synthesis of N-((1-(((2R,3R,4R,5R,6S)-5-acetamido-3,4-bis(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-1H-1,2,3-triazol-4-yl)methyl)benzamide ***5c.***

To a solution of compound **5** (0.2 g, 0.45 mmol) in DMF was added acetylene compound (0.078 g, 1.078 mmol), $CuSO_4$ (0.008 g, 0.045 mmol) and sodium ascorbate (0.003 g, 0.0135 mmol). The reaction mixture was stirred at 70°C for 3h. After completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: methanol 9:1) to yield compound **5b** as a white solid, (0.15 g, 56%). ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.4 Hz, 1H), 7.49 – 7.26 (m, 8H), 6.85 (bs, 1H), 5.23 (d, J = 9.6 Hz, 1H), 4.90 – 4.78 (m, 3H), 4.64 – 4.54 (m, 4H), 4.15 – 4.10 (m, 1H), 3.93 (m, 1H), 3.71-3.66 (m, 2H), 3.29 (dd, J = 19.6, 9.9 Hz, 1H), 3.12 (s, 3H), 1.82 (s, 3H).^{13}CNMR (100MHz, $CDCl_3$): δ 169.8, 167.4, 138.1, 137.8, 134.0, 131.8, 128.7, 128.4, 128.2, 128.1, 127.1, 98.7, 80.3, 78.5, 75.2, 75.1, 69.7, 55.3, 52.4, 50.6, 35.5, 23.5. HRESI-MS (m/z) Calcd. for $C_{33}H_{37}N_5O_6$ $[M+H]^+$: 600.2817; found 600.2816.

Synthesis of N-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((4-butyl-1H-1,2,3-triazol-1-yl)methyl)-2-methoxytetrahydro-2H-pyran-3-yl)acetamide ***5d.*** To a solution of compound **5** (0.3 g, 0.68 mmol) in DMF was added acetylene compound (0.066 g, 0.816 mmol), $CuSO_4$ (0.010 g, 0.068 mmol) and sodium ascorbate (0.004 g, 0.020 mmol). The reaction mixture was stirred at 70°C for 4h. After Completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate, filtered and evaporated under

reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: methanol 9:1) to yield compound **5d** as a brown colour solid, (0.2g, 57%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H), 5.22 (d, *J* = 9.3 Hz, 1H), 4.87 – 4.76 (m, 3H), 4.63-4.60 (m, 2H), 4.52-4.50 (m, 2H), 4.14 – 4.08 (m, 2H), 3.94 – 3.90 (m, 2H), 3.72 – 3.67 (m, 2H), 3.26 – 3.22 (m, 2H), 3.14 (s, 3H), 2.73 – 2.69 (m, 2H), 1.81 (s, 3H), 1.64 (dd, *J* = 15.0, 6.9 Hz, 2H), 1.37 (dt, *J* = 14.9, 7.5 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}CNMR (100MHz, $CDCl_3$): δ 137.9, 128.74, 128.71, 128.4, 128.1, 98.7, 80.3, 78.8, 75.1, 70.0, 55.1, 52.6, 50.4, 31.6, 25.4, 23.5, 22.4, 13.9. HRESI-MS (m/z) Calcd. for $C_{29}H_{38}N_4O_5$ $[M+H]^+$: 523.2915; found 523.2936.

Synthesis of N-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)methyl)-2-methoxytetrahydro-2H-pyran-3-yl)acetamide ***5e.***

To a solution of compound **5** (0.15 g, 0.34mmol) in DMF was added acetylene compound (0.030 g, 0.408 mmol), $CuSO_4$ (0.027 g, 0.489 mmol) and sodium ascorbate (0.002 g, 0.0122 mmol). The reaction mixture was stirred at 70 °C for 3h. After completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: methanol, 9:1) to yield compound **5e** as an off white solid (0.11g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.40 – 7.28 (m, 10H), 5.27 (d, *J* = 9.3 Hz, 1H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.84 – 4.76 (m, 4H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.55 (d, *J* = 4.4 Hz, 2H), 4.13 – 4.07 (m, 1H), 3.96 – 3.91 (m, 1H), 3.70 (dd, *J* = 10.8, 8.8 Hz, 1H), 3.23 (dd, *J* = 12.3, 6.4 Hz, 1H), 3.15 (s, 3H), 3.11 (dd, *J* = 14.8, 7.5 Hz, 2H), 2.32 (s, 1H), 1.82 (s, 3H).^{13}CNMR (100MHz, $CDCl_3$): δ 170.0 (C=O), 138.0, 137.8, 128.7, 128.4, 128.2, 128.1, 123.5, 98.7 (C-1), 80.2, 78.6, 75.2, 75.1, 69.8, 56.8, 55.3, 52.5 (C-2), 50.5, 46.0, 23.5. HRESI-MS (m/z) Calcd. for $C_{26}H_{32}N_4O_6$ $[M+Na]^+$: 519.2214; found 519.1377.

Synthesis of N-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-2-methoxy-6-((4-(3-methoxyphenyl)-1H-1,2,3-triazol-1-yl) methyl)tetrahydro-2H-pyran-3-yl)acetamide ***5f.***

To a solution of compound **5** (0.25 g, 0.56 mmol) in DMF was added acetylenecompound (0.078 g, 1.078 mmol), $CuSO_4$ (0.009 g, 0.056 mmol) and sodium ascorbate (0.003 g, 0.0168 mmol).

The reaction mixture was stirred at 70 °C for 3h. After Completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: hexane 8:2) to yield compound **5f** as a white solid (0.2 g, 62%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.49 – 7.27 (m, 14H), 6.89 (ddd, *J* = 7.7, 2.5, 1.5 Hz, 1H), 5.25 (d, *J* = 9.3 Hz, 1H), 4.89 (t, *J* = 11.9 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 2H), 4.68 – 4.53 (m, 4H), 4.18 – 4.10 (m, 1H), 3.99 (ddd, *J* = 9.3, 6.0, 2.9 Hz, 1H), 3.88 (s, 3H), 3.72 (dd, *J* = 10.5, 8.8 Hz, 1H), 3.35 – 3.25 (m, 1H), 3.15 (s, 3H), 1.81 (s, 3H).^{13}CNMR (100MHz, $CDCl_3$): δ 169.9 , 138.1, 137.8, 130.0, 128.7, 128.49, 128.44, 128.2, 128.1, 121.6, 118.3, 114.5, 110.8, 98.7, 80.3, 78.7, 76.8, 75.2, 75.1, 69.9, 55.5, 55.3, 52.5, 50.7, 23.5. HRESI-MS (m/z) Calcd. For $C_{32}H_{36}N_4O_6$ $[M+H]^+$: 572.2707; found 573.2725.

Synthesis of N-((2S,3R,4R,5R,6R)-4,5-bis(benzyloxy)-2-methoxy-6-((4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl) methyl)tetrahydro-2H-pyran-3-yl)acetamide ***5g.*** To a solution of compound **5** (0.2 g, 0.45 mmol) in DMF was added acetylene compound (0.133 g, 0.9mmol), $CuSO_4$ (0.007 g, 0.045 mmol) and sodium ascorbate (0.002 g, 0.0135 mmol). The reaction mixture was stirred at 70°C for 3h. After completion of the reaction, reaction mixture was quenched with ice cold water (50 mL) diluted with ethyl acetate (1 × 400 mL), combined organic layer was washed with brine solution (1 × 100 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to give a residue. The residue was purified by flash column chromatography (ethyl acetate: methanol 8:2) to yield compound **5g** as a white solid, (0.2 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.76 (dd,*J* = 2.4, 6.8 Hz, 2H), 7.43-7.27 (m, 10 H), 6.96 (dd,*J* = 2H), 5.24 (d, *J* = 9.3 Hz, 1H), 4.88 (t, *J* = 10.5 Hz, 2H), 4.81 (d, *J* = 11.3 Hz, 2H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.62 – 4.53 (m, 3H), 4.16 – 4.10 (m, 1H), 4.00 – 3.96 (m, 1H), 3.84 (s, 3H), 3.72 (dd, *J* = 10.5, 8.8 Hz, 1H), 3.30 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.16 (s, 3H), 1.81 (s, 3H).^{13}CNMR (100MHz, $CDCl_3$) δ 169.9, 159.7, 147.8, 138.1, 137.9, 128.7, 128.49, 128.44, 127.2, 120.6, 114.3, 98.7, 80.3, 78.7, 75.2, 75.1, 69.9, 55.4, 55.3, 52.5, 50.7, 23.5. HRESI-MS (m/z) Calcd. for $C_{32}H_{36}N_4O_6$$[M+H]^+$: 573.2707; found 573.2723.

ASSOCIATED CONTENT

The supporting information is available free of charge on the https//

Copies of ^{1}H NMR and ^{13}C NMR spectra of all compounds, Crude oil gelation and recovery of diesel from gelator, Rheology data of toluene and mesitylene gel, Rheology of Erha crude oil gels with compound **5b** and **5f**, Crude oil gel formation with gelator **5a** and sea water, VT NMR studies of compound **5b**

AUTHOR INFORMATION

Corresponding Author

Email: ram.sagar@bhu.ac.in

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Guterman, L. Exxon Valdez Turns 20. *Science* **2009**, *323*, 1558–1559.

(2) Adebajo, M. O.; Frost, R. L.; Kloprogge, J. T.; Carmody, O.; Kokot, S. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *J. Porous Mater*. **2003**, *10*, 159–170.

(3) Schrope, M. Oil spill: Deep wounds. *Nature* **2011**, *472*, 152−154.

(4) Shi, X.; Wang, C.; Ma, Y.; Liu, H.; Wu, S.; Shao, Q.; He, Z.; Guo, L.; Ding, T.; Guo, Z. Template-free microwave-assisted synthesis of FeTi coordination complex yolk-shell microspheres for superior catalytic removal of arsenic and chemical degradation of methylene blue from polluted water. *Powder Technol.* **2019**, *356*, 726-734.

(5) Pan, D.; Ge, S.; Zhao, J.; Tian, J.; Shao, Q.; Guo, L.; Mai, X.; Wu, T.; Murugadoss, V.; Liu, H.; Ding, T. Synthesis and characterization of ZnNiIn layered double hydroxides derived mixed metal oxides with highly efficient photoelectrocatalytic activities. *Indus. Eng. Chem. Res*. **2019**, *58*, 836-848.

(6) Qian, Y.; Yuan, Y.; Wang, H.; Liu, H.; Zhang, J.; Shi, S.; Guo, Z.; Wang, N. Highly efficient uranium adsorption by salicylaldoxime/polydopamine graphene oxide nanocomposites. *J. Mater. Chem. A* **2018**, *6*, 24676-24685.

(7) Li, S.; Yang, P.; Liu, X.; Zhang, J.X.; Liu, C.; Xie, W.; Wang, C.; Guo, Z. Graphene Oxide Based Dopamine Mussel-like

Cross-linked Polyethylene Imine Nanocomposite Coating with Enhanced Hexavalent Uranium Adsorption. *J. Mater. Chem. A* **2019**, 7, 16902-16911.

(8) Broje, V.; Keller, A. A. Improved mechanical oil spill recovery using an optimized geometry for the skimmer surface. *Environ. Sci. Technol.* **2006**, *40*, 7914-7918.

(9) Yuan, J.; Liu, X.; Akbulut, O.; Hu, J.; Suib, S. L.; Kong, J.; Stellacci, F. Superwetting nanowire membranes for selective absorption *Nat. Nanotechnol.* **2008**, *3*, 332-336.

(10) Bi, H.; Yin, Z.; Cao, X.; Xie, X.; Tan, C.; Huang, X.; Chen, B.; Chen, F.; Yang, Q.; Bu, X.; Lu, X.; Sun, L.; Zhang, H. Carbon Fiber Aerogel Made from Raw Cotton: A Novel, Efficient and Recyclable Sorbent for Oils and Organic Solvents. *Adv. Mater.* **2013**, *25*, 5916- 5921.

(11) Ruan, C.; Ai, K.; Li, X.; Lu, L. A Superhydrophobic sponge with excellent absorbency and flame retardancy. *Angew. Chem., Int. Ed.* **2014**, *53*, 5556-5560.

(12) Sabir, S. Approach of cost-effective adsorbents for oil removal from oily water. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45,* 1916-1945.

(13) Li, Z.; Wang, B.; Qin, X.; Wang, Y.; Liu, C.; Shao, Q.; Wang, N.; Zhang, J.; Wang, Z.; Shen, C.; Guo, Z. Superhydrophobic/superoleophilic polycarbonate/carbon nanotubes porous monolith for selective oil adsorption from water. *ACS Sustain. Chem. Eng.* 2018, *6*, 13747-13755.

(14) Zhang, X.; Wang, X.; Liu, X.; Lv, C.; Wang, Y.; Zheng, G.; Liu, H.; Liu, C.; Guo, Z.; Shen, C. Porous polyethylene bundles with enhanced hydrophobicity and pumping oil-recovery

ability via skin-peeling. *ACS Sustain. Chem. Eng.* **2018.** *6*, 12580-12585.

(15) Zhang, J.; Li, P.; Zhang, Z.; Wang, X.; Tang, J.; Liu, H.; Shao, Q.; Ding, T.; Umar, A.; Guo, Z. Solvent-free graphene liquids: promising candidates for lubricants without the base oil. *J. Colloid Interface Sci.*, **2019**, *542*, 159-167.

(16) Steen, A. Findlay, A. Frequency of dispersant use worldwide. Int. Oil Spill Conf. Proc. **2008**, *2008*, 645–649.

(17) Prince, R. C. Oil spill dispersants: Boon or bane? *Environ. Sci. Technol.* **2015**, *49*, 6376–6384.

(18) Fingas, M. An overview of *in-situ* burning In *Oil Spill Science and Technology;* Elsevier, Gulf Publishing Company: New York, NY, **2011**; pp 737-903.

(19) (16) Atlas, R. M. Petroleum biodegradation and oil spill bioremediation. *Mar. Pollut. Bull.* **1995**, *31*, 178–182.

(20) Sun, K.; Dong, J.; Wang, Z.; Wang, Z.; Fan, G.; Hou, Q.; An, L.; Dong, M.; Fan, R.; Guo, Z. Tunable negative permittivity in flexible graphene/PDMS metacomposites. *The Journal of Physical Chemistry C*, **2019**, *123*, 23635-23642.

(21) Guo, Y.; Ruan, K.; Yang, X.; Ma, T.; Kong, J.; Wu, N.; Zhang, J.X.; Gu, J.; Guo, Z. Constructing fully carbon-based fillers with hierarchical structure to fabricate highly thermally conductive polyimide nanocomposites. *J. Mater. Chem. C* **2019**, 7, 7035-7044.

(22) Gu, H.; Xu, X.; Cai, J.; Wei, S.; Wei, H.; Liu, H.; Young, D.P.; Shao, Q.; Wu, S.; Ding, T.; Guo, Z. Controllable organic magnetoresistance in polyaniline coated poly (p-phenylene-2, 6-benzobisoxazole) short fibers. *Chem. Comm.* **2019**, *55*, 10068-10071.

(23) Rajkamal, R.; Chatterjee, D.; Paul, A.; Banerjee, S.; Yadav, S. Enantiomeric organogelators from D-/L-arabinose for phase selective gelation of crude oil and their gel as a photochemical micro-reactor *Chem. Comm*. **2014**, *50*, 12131–12134.

(24) Bhattacharya, S.; Krishnan-Ghosh, First report of phase selective gelation of oil from oil/water mixtures. Possible implications toward containing oil spills Y. *Chem. Comm*. **2001**, 185–186.

(25) Rajkamal, R.; Pathak, N. P.; Chatterjee, D.; Paul, A.; Yadav, S. Arabinose based gelators: rheological characterization of the gels and phase selective organogelation of crude-oil. *RSC. Adv.* **2016**, *6*, 92225-92234.

(26) Vibhute, A. M.; Muvvala, V.; Sureshan, K. M. Sugar-Based Gelator for Marine Oil-Spill Recovery. *Angew. Chem., Int. Ed.* **2016**, *55*, 7782–7785.

(27) Mukherjee, S.; Shang, C.; Chen, X.; Chang, X.; Liu, K.; Yu, C.; Fang, Y. *N*-Acetylglucosamine-based efficient, phase-selective organogelators for oil spill remediation *Chem.Comm*. **2014**, *50*, 13940-13943.

(28) Narayana, C.; Upadhyay, R.K.; Chaturvedi, R.; Sagar, R. A versatile carbohydrate based gelator for oil water separation, nanoparticle synthesis and dye removal *New J. Chem.* **2017**, *41*, 2261-2267.

(29) Li, J.; Huo, Y.; Zeng, H. Polar Solvent-Induced Unprecedented Supergelation of (Un)Weathered Crude Oils at Room Temperature *Langmuir*, **2018**, *34*, 8058-8064.

(30) Ren, C.; Chen, F.; Zhou, F.; Shen, J.; Su, H.; Zeng, H. Low-Cost Phase-Selective Organogelators for Rapid Gelation of

Crude Oils at Room Temperature *Langmuir*, **2016**, *32*, 13510-13516.

(31) Datta, S.; Samanta, S.; Chaudhuri, D. Near instantaneous gelation of crude oil using naphthalene diimide based powder gelator *J. Mater. Chem. A*, **2018**, *6*, 2922-2926.

(32) Borowski, S.; Michalik, D.; Reinke, H.; Vogel, C.; Hanuszkiewicz, A.; Duda, K. A.; Holst,O. Synthesis of methyl 2-acetamido-2,6-dideoxy-α-and β-d-*xylo*-hexopyranosid-4-ulose, a keto sugar which misled the analytical chemists *Carbohydr. Res.* **2008**, *343*, 1004-1011.

(33) Poolman, J. M.; Boekhoven, J.; Besselink, A.; Olive, A. G. L.; van Esch, J. H.; Eelkema, R. Variable gelation time and stiffness of low-molecular-weight hydrogels through catalytic control over self-assembly. *Nat. Protoc*. **2014**, *9*, 977–988.

(34) Wang, Y. B.; Zhan, C. L.; Fu, H. B.; Li, X.; Sheng, X. H.; Zhao, Y. S. ; Xiao, D. B.; Ma, Y.; Ma, J. S.; Yao, J. N. Switch from Intra- to Intermolecular H-Bonds by Ultrasound: Induced Gelation and Distinct Nanoscale Morphologies. *Langmuir*, **2008**, *24*, 7635–7638.

(35) Debnath, S.; Shome, A.; Dutta S.; Das, P. K. Dipeptide-Based Low-Molecular-Weight Efficient Organogelators and Their Application in Water Purification. *Chem*. *Eur*. *J*. **2008**, *14*, 6870-6875.

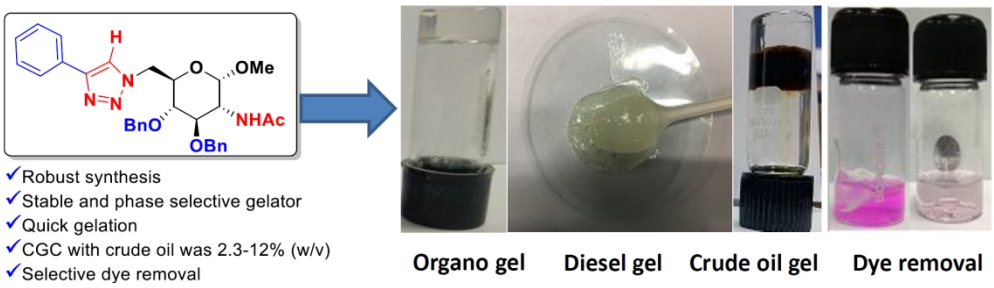
(36) Kar, T.; Mukherjee, S.; Das, P. K. Organogelation through self-assembly of low-molecular-mass amphiphilic peptide *New J. Chem*. **2014**, *38*, 1158-1167.

(37) Basak, S.; Nanda, J.; Banerjee, A. A new aromatic amino acid based organogel for oil spill recovery *J. Mater*. *Chem*. **2012**, *22*, 11658-11664.

(38) Hart, A. A review of technologies for transporting heavy crude oil and bitumen via pipelines. *J. Petrol Explore Prod. Technol.* **2014**, *4*, 327-336.

(39) Aldmal, K.; Dyre, J.; Hvidt, S.; Kramer, O. Towards a phenomenological definition of the term ‘gel’ *Polym. Gels Netw.***1993**, *1*, 5-17.

(40) Okesola, B.O.; Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting–self-assembled gels as smart materials for pollutant removal *Chem. Soc. Rev.* **2016**, *45*, 4226-4251.



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