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Supplementary Information for

Near Instantaneous Gelation of Crude Oil using Naphthalene Diimide based Powder Gelator

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1. Materials and Methods

All reagents were used as received from Sigma Aldrich Chemical Co., without further purification. Solvents were purchased from commercial sources and dried following reported protocol.[1]

Spectroscopic grade solvents were used for physical studies.

NMR spectra were recorded on AVANCE III 500 BRUKER spectrometer and the data were calibrated against TMS.

Differential scanning calorimetric (DSC) studies were performed on a Mettler Toledo DSC1 STAR e system in N_2 atmosphere. The gel was initially cooled down to 15 °C, and heated at the rate of 10 °C/min. Cooling run was performed at the rate of 1 °C/min.

FESEM was performed using JEOL-6700F microscope. Dried xerogel was dispersed in n-hexane and coated over a glass slide, dried for 3 hours under dynamic vacuum, and coated with Pt for SEM imaging.

Rheological data were recorded in an Anton Paar Modular Compact Rheometer (MCR 102).

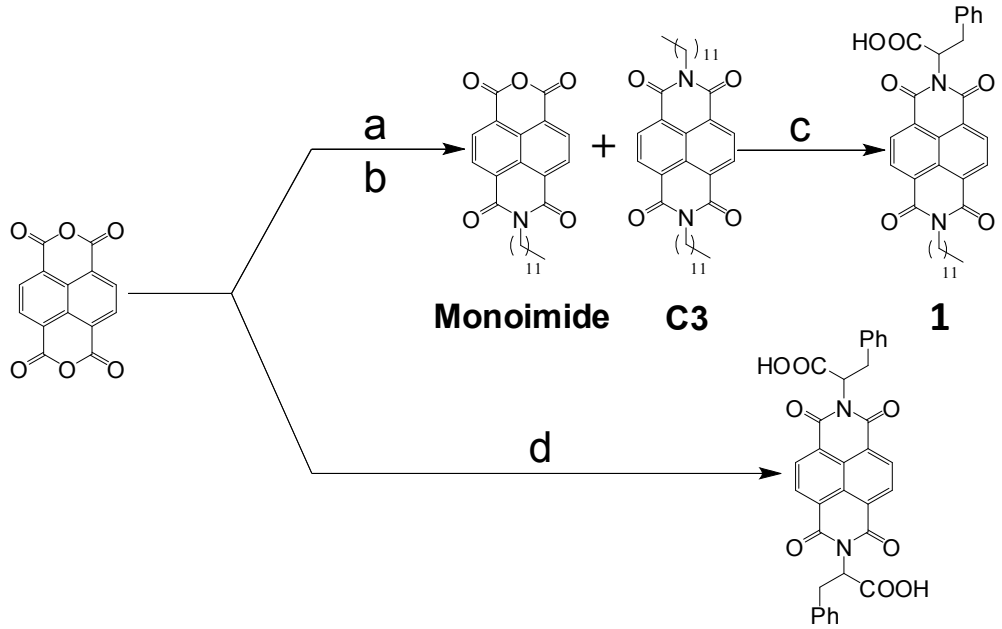
FT-IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

UV/visible absorption spectroscopy was performed on a Perkin-Elmer Lambda 35 spectrometer.

The pXRD patterns of the as prepared compound and dried MCH xerogel (2 wt%) were collected on a Rigaku SmartLab with a Cu Kα radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each sample was scanned over $1^{o} < 2\theta < 35^{o}$ region with a step size of 0.02^{o}. The instrument was pre-calibrated using a silicon standard.

Mass spectrometric data were acquired using an electron spray ionization (ESI) technique on a MASSLYNX 4.0 (WATER Micromass Q-Tof-micro TM (+ve) mode mass spectrometer.

2. Syntheses and Characterization



a) Dodecylamine ($C_{12}H_{25}NH_2$), 1:1 ^{i}PrOH/H_2O, 343 K, Ar, 24 hr. b) Glacial AcOH reflux c) Phenylalanine ($C_9H_{11}NO_2$), NEt_3 , MeOH, 353 K, 8 hr. d) Phenylalanine ($C_9H_{11}NO_2$), dry DMF, NEt_3, microwave (300 W), 2 min.

M

onoimide and Control C3

The synthesis is based on the reported procedure[2] after certain modifications. n-dodecylamine (12 mmol, 2.224 g) was added to a suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (3.73 mmol, 1 g) in a mixture of water (10 ml) and n-propanol (10 ml) at RT, under Ar flow. The suspension was heated to 70 °C for 24 hr. to obtain a brown precipitate. The reaction mixture was cooled down to 25 °C, acidified to pH 1 with 5 ml c.HCl, and stirred for 1 hr. The solid was filtered off and stirred in acetic acid (50 ml) at reflux condition for 1 hr. to a form deep brown solution. The mixture was then refrigerated overnight to ensure complete precipitation. The crude product was extracted in CH_2Cl_2 (200 ml) and washed with water (200 ml). The organic layer was collected, dried over anhydrous Na_2SO_4 and reduced in volume under low pressure. Addition of ethanol (50 ml) and evaporation of CH_2Cl_2 gave a suspension of the desired products in ethanol, which was filtered off, washed with ethanol, hexane and ether. The product was obtained as a 1:12 molar ratio of di- and mono-imide. The raw product obtained at this stage was purified using column chromatography using silica gel (100-200 mesh) as a stationary phase and hexane/dichloromethane (1:3) mixture as eluent. **C3** was isolated first, followed by the Monoimide. **C3** is a brownish white powder and monoimide is a pale yellow powder.

C3: ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ (ppm) = 8.75 (4H, m), 4.18 (4H, t, *J* = 8 Hz), 1.73 (4H, m), 1.62 (2H, m), 1.69 (2H, m), 1.41-1.22 (36H, m), 0.87 (6H, t, *J* = 7.0 Hz)

^{13}C NMR ($CDCl_3$, 500 MHz, 298 K), δ (ppm) = 162.83, 130.91, 126.63, 40.99, 31.90, 29.65, 29.50, 29.30, 28.07, 72.06, 22.67, 14.05.

PSOG 1

Phenylalanine (4.2 mmol, 0.7 g) was taken in a 100 ml round-bottom flask with dry $CHCl_3$ (30 ml), 1 ml NEt_3 was added to it, and stirred under Ar atmosphere at 60 °C for 30 min. Monoimide (2.80 mmol, 1.22 g) was added to it, and the reaction mixture was refluxed under Argon at 80 °C for 8 hours. The progress of the reaction was monitored using TLC. Then the reaction mixture was cooled down to room temperature and the crude product was extracted in CH_2Cl_2 (200 ml) and washed with water (200 ml). The organic layer was collected, dried over anhydrous Na_2SO_4 and reduced in volume under reduced pressure. Resulting mixture was purified using column chromatography with silica gel (100-200 mesh) as a stationary phase and dichloromethane/methanol (20:1) mixture as eluent. The product was isolated as brown sticky solid. Yield = 83 %.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) = 8.66 (4H, m), 7.00-7.11 (5H, m), 6.06 (1H, dd, *J* = 4.5 Hz), 4.14 (2H, t, *J* = 8 Hz), 3.64 (1H, m), 3.46 (1H, m), 1.69 (2H, m), 1.41-1.22 (18 H, m), 0.86 (3 H, t, *J* = 7.0 Hz);

^{13}CNMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) =174.12, 162.54, 136.33, 131.28, 130.81, 128.99, 128.30, 126.60, 125.68, 54.56, 40.93, 34.49, 31.79, 29.35, 28.01, 26.97, 26.97, 22.53, 14.05

MS (ESI-MS) for $[M]^+$, 582.6860 (calc.), 582.7012 (found); for $[M+Na]^+$ 605.6758 (calc.), 605.6607 (found); for $[M+K]^+$ 621.7843 [calc.], 621.2382 (found).

One-step Synthesis

We were also able to synthesize **1** in single step procedure with considerably good yield. Phenylalanine (1.4 mmol, 0.25 g) was taken in dry DMF (50 ml), 1 ml NEt_3 was added and stirred under Ar atmosphere at 70 °C for 1 hr. 1, 4, 5, 8-Naphthalenetetracarboxylic dianhydride (2.8 mmol, 1.22 g) was added and the reaction mixture was stirred at 110 °C for 1 h. To this, n-dodecylamine (1.4 mmol, 0.27 ml) was added and refluxed for 24 hours. The progress of the reaction was monitored using TLC. The reaction mixture was concentrated under reduced pressure and the solid residue thus obtained was extracted in CH_2Cl_2, washed with brine solution, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product mixture was purified by silica gel column chromatography (60-120 mesh) using 20:1 CH_2Cl_2/MeOH mixture (20:1).

Control C2

The synthesis is based on a reported procedure.[3] 1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.22 g, 2.8 mmol) and phenylalanine (1.2 g, 7 mmol) were suspended in 20 ml of DMF in a 150-ml Erlenmeyer flask. To this suspension was added 1 ml of dry Et_3N. The suspension was sonicated until the mixture became homogeneous. The reaction mixture was heated under microwave irradiation at 300 W power for a total of 110 s, over multiple shorter (<10 s) exposures refluxing could be avoided (reaction temperature 120-140°C). The solvent was removed under reduced pressure. The crude product was extracted in CH_2Cl_2 (200 ml) and washed with water (200 ml). The organic layer was collected, dried over anhydrous Na_2SO_4 and reduced in volume under reduced pressure. No further purification was needed. Yield = 95 %.

^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm): 8.61 (4H, m), 7.2-6.95 (10H, m), 5.86 (2H, dd, *J* = 4.5 Hz), 3.57 (2H, m), 3.31 (2H, m)

^{13}C NMR (d^6 DMSO, 500 MHz, 298 K) δ(ppm): 170.93, 162.47, 138.80, 131.95, 129.43, 129.91, 126.91, 55.17, 35.40

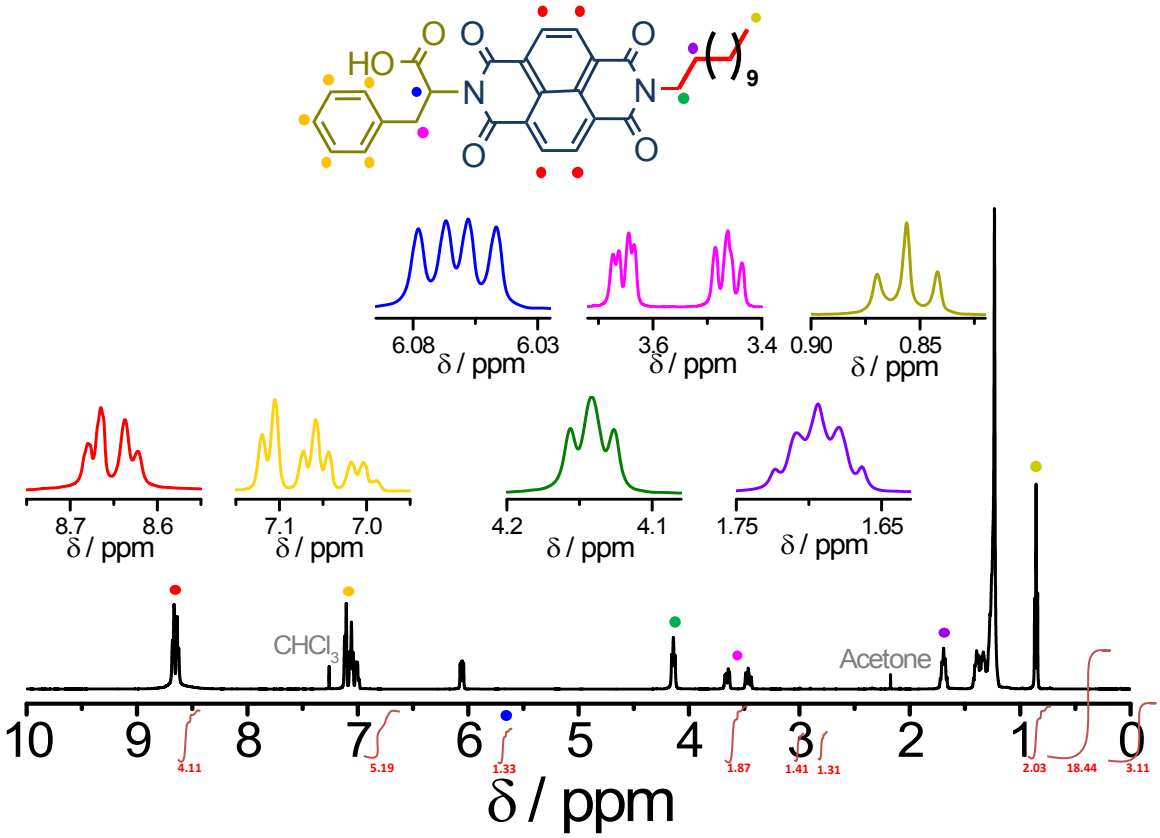


Figure S1: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **1**. The insets show certain regions magnified, and the colors used may be correlated with the colored dots placed to identify different kind of protons.

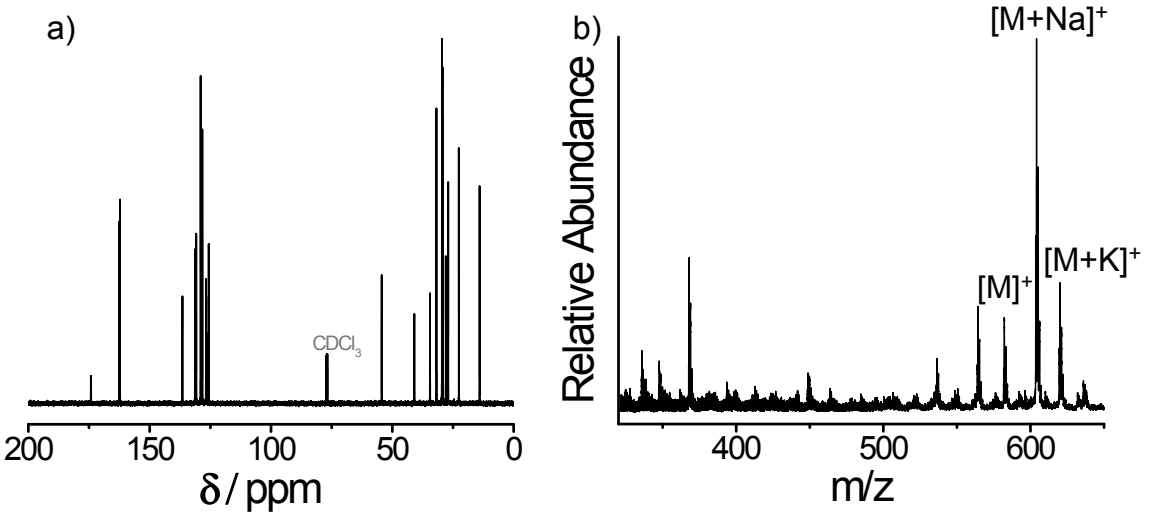


Figure S2. a) ^{13}C NMR (500 MHz, $CDCl_3$, 298 K) and b) ESI-MS spectra of **1.**

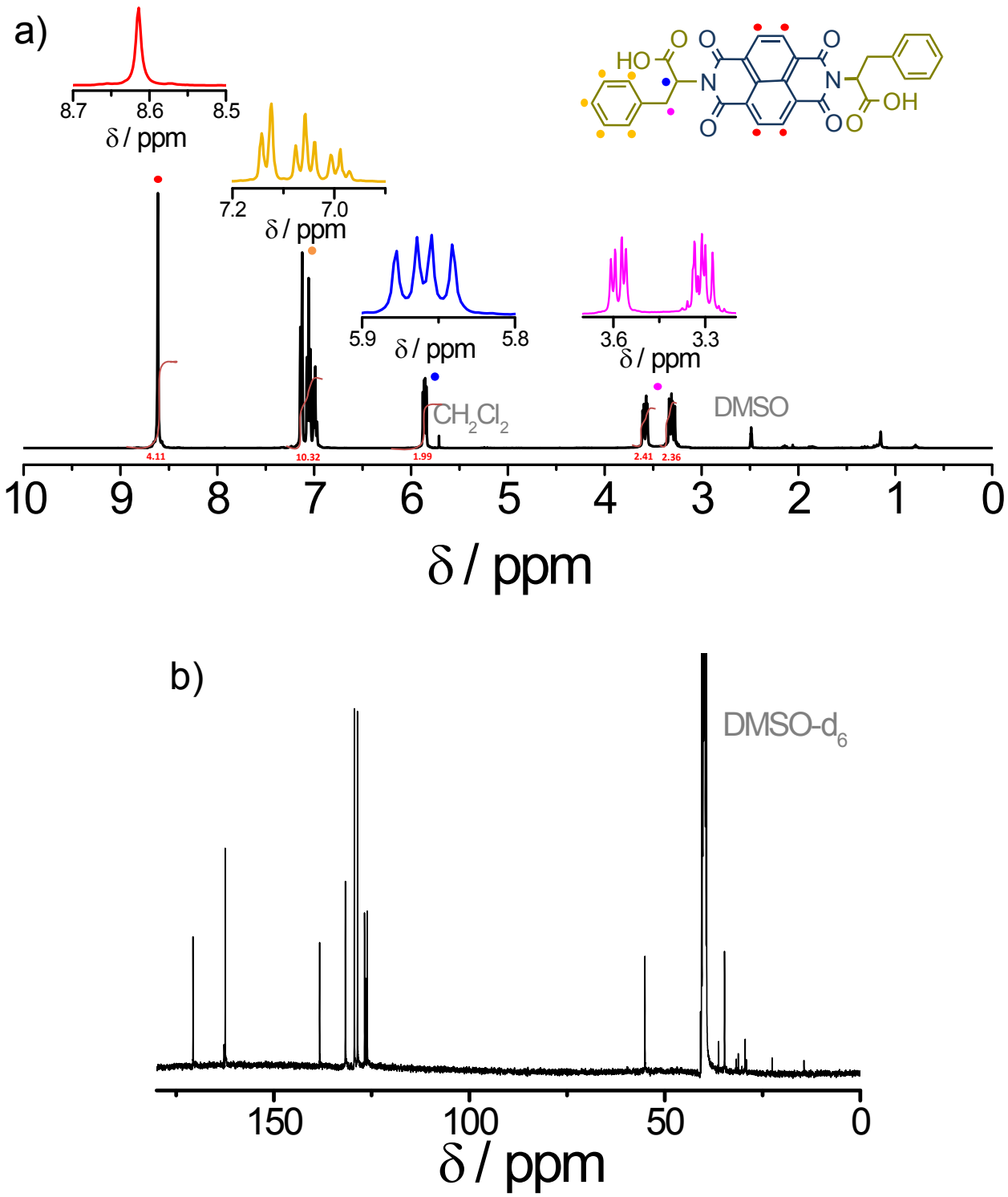


Figure S3: a) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **C2**. The insets show certain regions magnified, and the colors used may be correlated with the colored dots placed to identify different kind of protons. b) ^{13}C NMR (500 MHz, $CDCl_3$, 298 K) of **C2**.

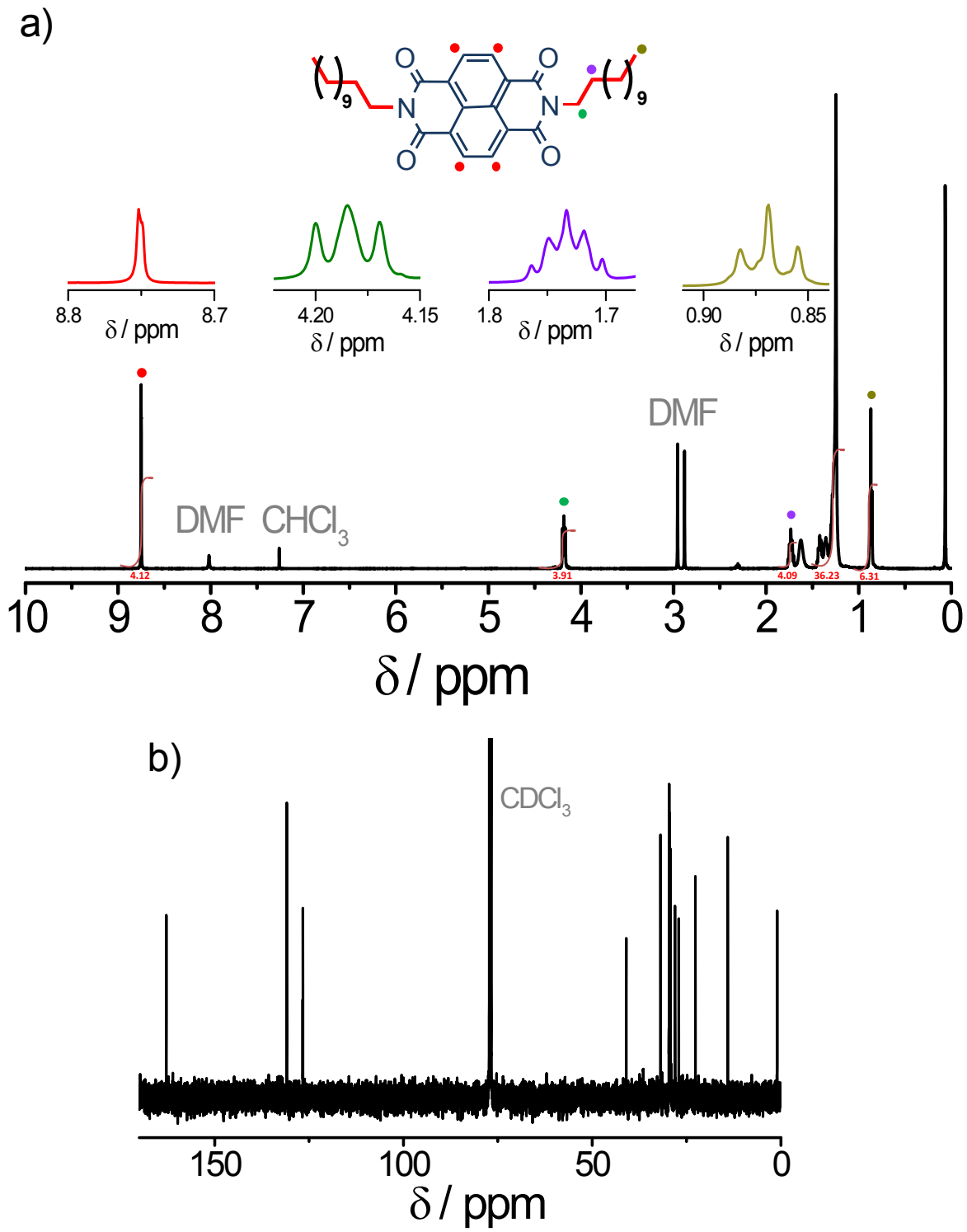


Figure S4: a) ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **C3**. The insets show certain regions magnified, and the colors used can be correlated with the colored dots placed to identify different kind of protons. B) ^{13}C NMR (500 MHz, $CDCl_3$, 298 K) of **C3**.

3. Aqueous Solubility and Acute Toxicology

Several napthalene diimides based compounds have been developed as potential anti-cancer agents with low hematotoxicity.[4] While evaluating any possible risk of aquatic toxicity associated with the use of PSOG **1**, one has to bear in mind that only the dissolved fraction of a compound is bio-available, and is therefore responsible for toxicity.

In a typical experiment, 15.4 mg (26.4 µmol, c.a. BCGC of diesel) PSOG **1** was added to 2 ml water (or 1:2 v/v diesel/water mixture), the mixture was stirred to ensure maximum solubility (or gelation), after which the aqueous layer was collected and analysed using absorption spectroscopy. Solubility of **1** in pure water at 25 °C was determined to be ~40 nM (molar extinction coefficient of **1** in $CHCl_3$ is 22000 L mol^{-1} cm^{-1}). In presence of a top diesel layer, retention of PSOG 1 in water is 30% lesser. This translates to nearly 99.999% retention of **1** in the congealed diesel layer. Clearly the fraction of **1** in water is too low to cause any concern.

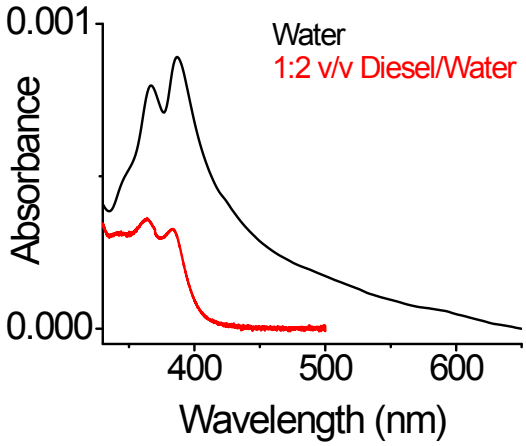


Figure S5. UV-Vis absorption spectra of a saturated solution of PSOG **1** in water (black line), and in the aqueous layer of 1:2 v/v diesel-water mixture (red line).

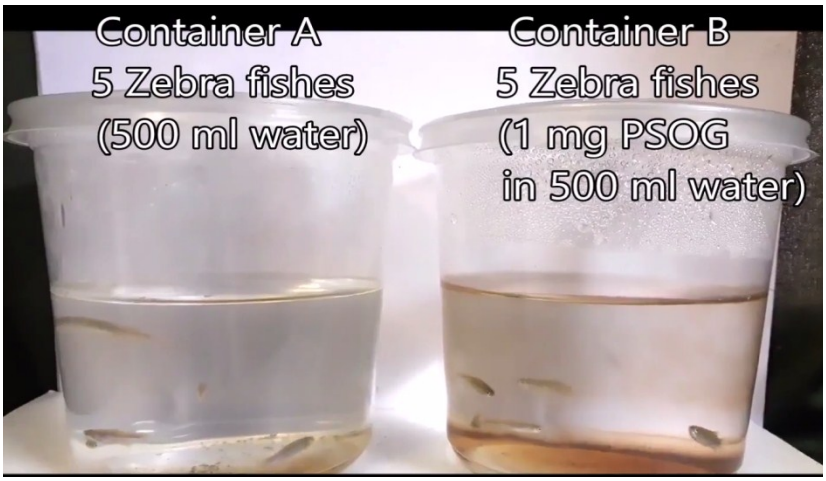


Figure S6. Exposure of a group (5 nos.) of adult zebrafish to a super-saturated aqueous solution of PSOG **1** (2 mg/L) for 23 days resulted in zero mortality. Also see video V1.

4. Gel Characterization

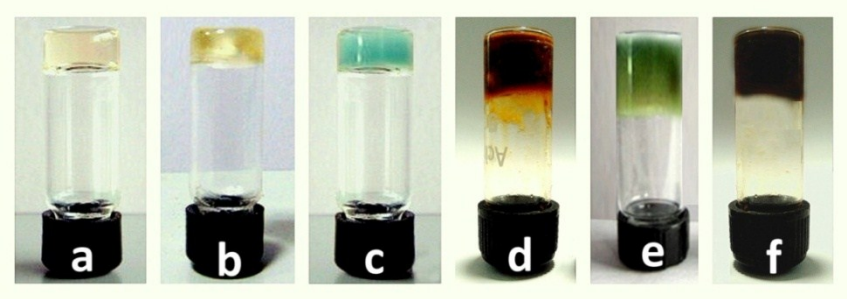


Figure S7. Inverted vial images of gels at CGC in a) Cyclohexane, b) Methylcyclohexane, c) Kerosene, d) Diesel, e) pump oil and f) heavy crude oil.

Figure S8. Image of crude oil (Haldia refinery) gelled from artificial seawater.[5] 10 ml gelled oil can withstand the weight of 70 ml water.

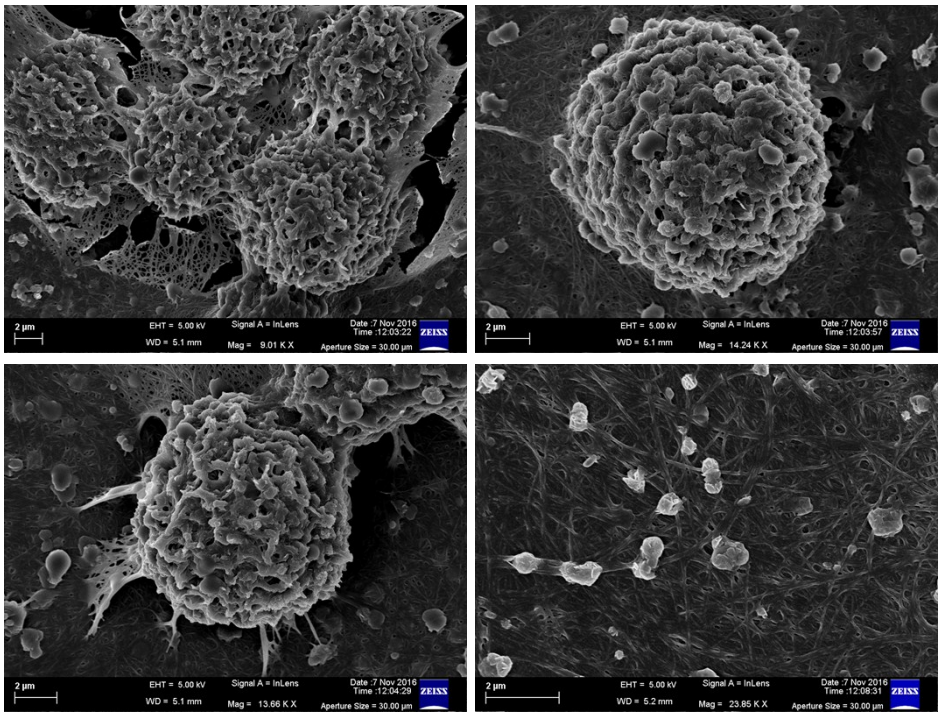


Figure S9. FESEM images of dried MCH xerogel.

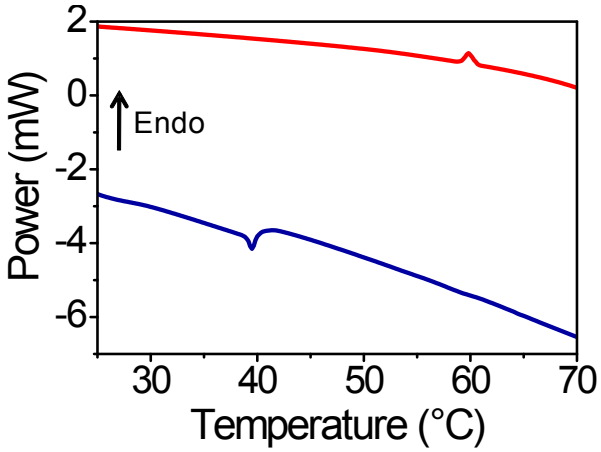


Figure S10. DSC of MCH gel shows a reversible first-order phase transition.

The gel-to-sol transition temperature (T_{gel}) was determined by gradually heating the organogel containing screw-capped glass vial in a thermostated oil bath. The temperature at which the gel melts into solution was recorded as T_{gel}. All of the above gels were found to be thermally reversible, such that the molten sol returns to the gel state upon cooling.

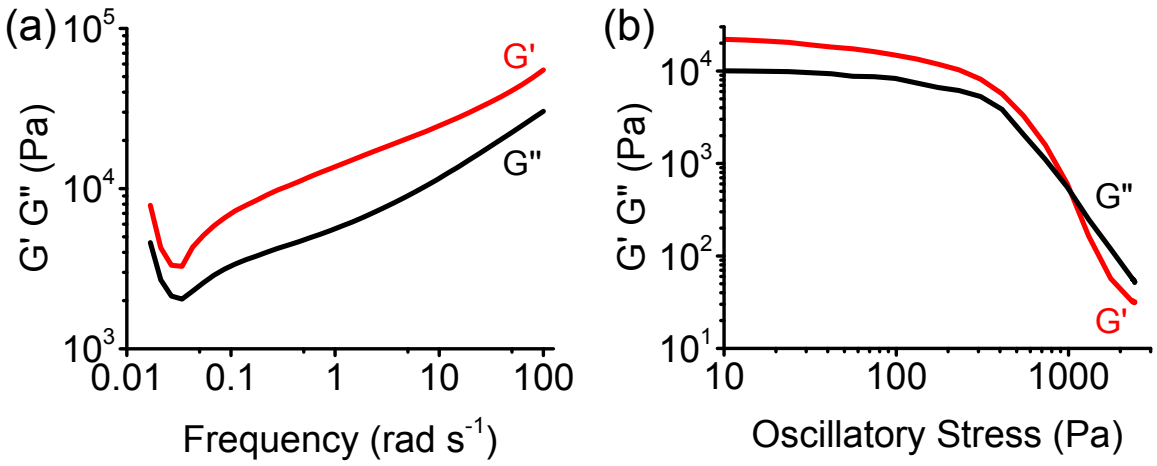


Figure S11. Dynamic rheology of 3 wt% gel of PSOG **1** in heavy crude oil (Haldia refinery) gelled from artificial seawater, (a) frequency sweep (b) oscillatory stress sweep.

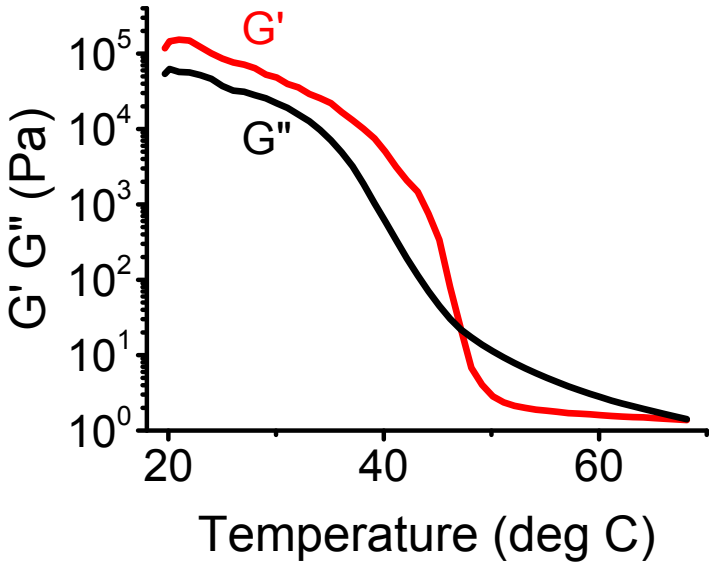


Figure S12. Temperature dependent rheology of 3 wt% gel of PSOG **1** in artificial seawater. The gel retains high mechanical strength upto temperatures as high as 40 °C, and remains viscoelastic (G' > G") upto 48 °C.

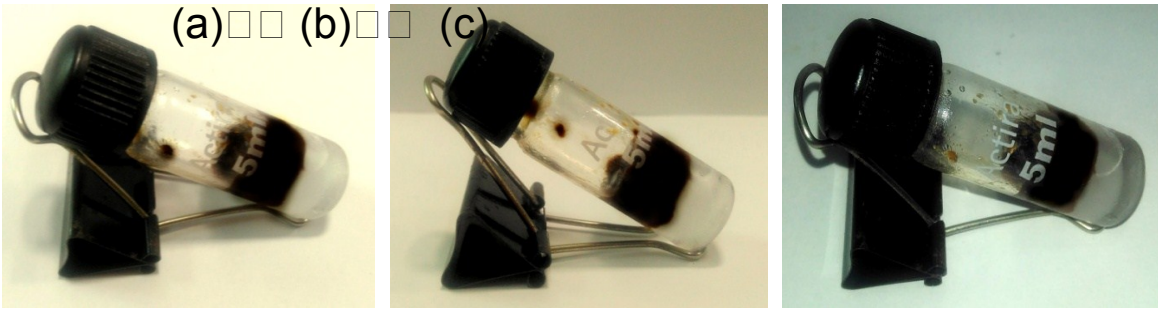


Figure S13. pH independent gelation. 2.5 wt% gel of **1** in heavy crude oil (Haldia refinery) at (a) pH = 6.5, using glacial acetic acid; (b) pH = 8.4, using NaOH; (c) pH = 9.0, using NaOH. Gelation times were in the order of 22 (± 3) s.

Table T1. Comparative study

Reference	**Gelling medium**	**Time / Condition**
Chem. Mater., 2016, **28**, 4001	Crude oil (Arab Heavy)	28−97 s; Carrier solvent (Ethanol and Ethyl acetate)
Langmuir, 2016, **32**, 13510	Crude oil (Arab Heavy)	50 s; Carrier solvent (Ethanol and Ethyl acetate)
RSC Adv., 2017, **7**, 37175	Crude oil	2 min; Carrier solvent (CH_2Cl_2)
RSC Adv., 2016, **6**, 107598	Crude oil	2 min; Warm carrier solvent (diesel)
RSC Adv., 2016, **6**, 76632	Crude oil	4-5 min; Carrier solvent (petrol)

RSC Adv., 2016, **6**, 53415	Crude oil	5 min; Heating–cooling in carrier solvent (toluene)
Chem. Commun., 2014, **50**, 12131	Crude oil	10 min; Carrier solvent (petrol)
RSC Adv., 2016, **6**, 92225	Crude oil	10 min; Warm solution in carrier solvent (m-xylene)
Angew. Chem. Int. Ed., 2017, **56**, 3847	Crude oil (Arab Heavy)	14 min; Wetting Solvent (CH_3CN)
Angew. Chem. Int. Ed., 2016, **55**, 7782	Crude oil	> 1 hour; Powder
Chem. Commun., 2014, **50**, 14839	Crude oil	Time unspecified; Warm solution in carrier solvent (petroleum ether)
ACS Appl. Mater. Interfaces, 2017, **9**, 33549	Pump oil	> 15 min; Carrier solvent (Ethanol)
Soft Matter, 2011, **7**, 5239	petrol	1 min; Sonication
Chem. Commun., 2001, 185–186	petrol	Time unspecified; Heating–cooling
Chem. Commun., 2014, **50**, 13940	diesel	50 s; Carrier solvent (THF)
J. Mater. Chem., 2012, **22**, 11658	diesel	90 s; Carrier solvent (ethanol)
New J. Chem., 2017, **41**, 2261.	diesel	180 s; Rapid cooling and ultrasonication after dissolution in carrier solvent (THF)
Chem. Commun., 2012, **48**, 5250	diesel	5 min; Warm carrier solvent (diesel)
RSC Adv., 2012, **2**, 2270–2273	diesel	10 min; Carrier solvent (THF)
ChemPlusChem 2014, **79**, 148	diesel	15 min; Heating –cooling
Int. J. Mol. Sci., 2015, **16**, 11766	diesel	“Within minutes”; ultrasound-aided concentrated solution (diesel)
Org. Lett., 2013, **15**, 5830	diesel	“a few minutes”; Carrier solvent (ethyl acetate)
Angew. Chem. Int. Ed., 2010, **49**, 7695	diesel	>one hour; Carrier solvent (ethanol)
Chem. Mater., 2003, **15**, 3971	diesel	“a few hours”; Heating-cooling
Chin. Chem. Lett., 2017, **28**, 782	diesel	5 hours; Powder
Soft Matter, 2017,**13**, 4066	diesel	>one day; Carrier solvent (pet. ether and ethanol 5%)
Sci. Rep., 2017, **7**, 13975	diesel	several days; shaken electrically

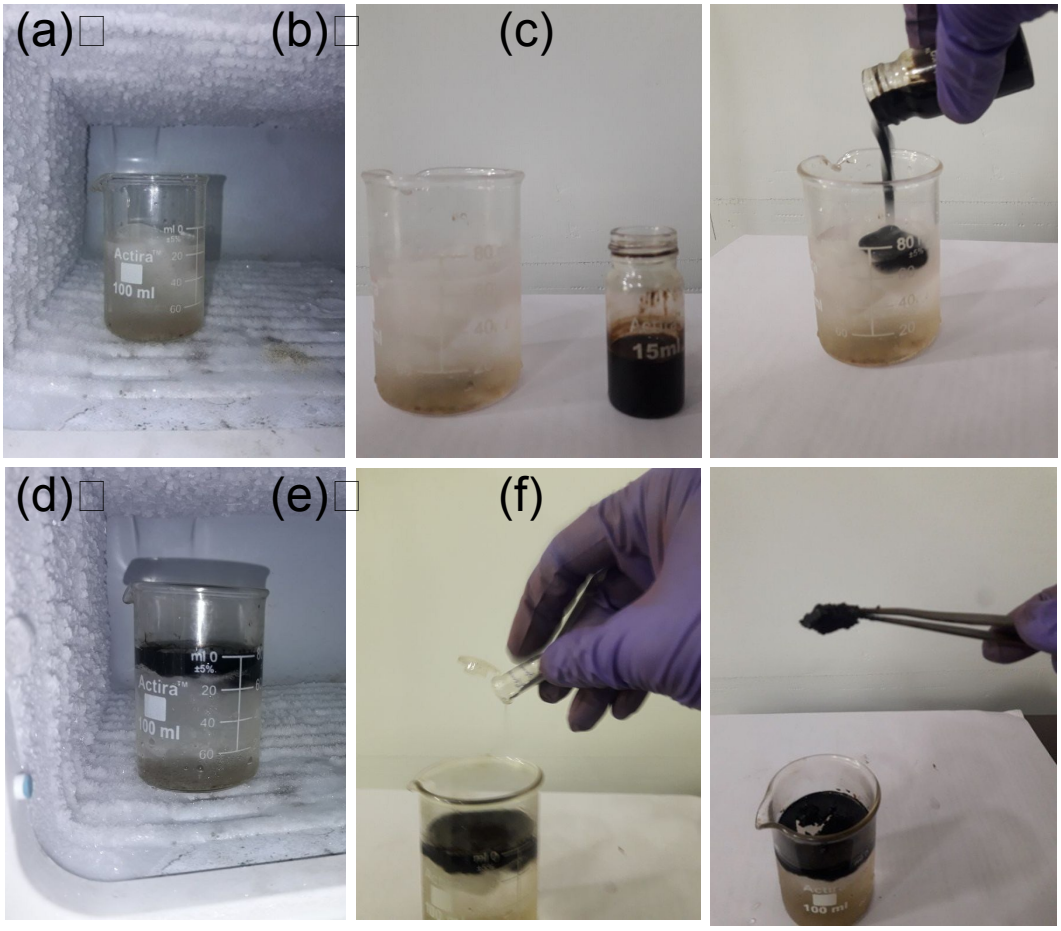


Figure S14. Gelation under freezing conditions. (a, b) Frozen artificial seawater (b) 10 ml heavy crude oil (Haldia refinery) was added to 70 ml frozen seawater. (c) Oil-water biphasic mixture was further cooled at –4 °C for 15 minutes. (e) powder gelator **1** (3 wt% w.r.t crude-oil) was sprinkled over the oil-water biphasic mixture. (f) After 10 minutes, the gelled crude oil can be scooped out.

5. Demonstration Videos

a) Acute toxicology studies of PSOG 1

Two batches of adult zebrafish (5 each) were placed in two separate containers, one containing 2 mg/litre of PSOG 1 in water, and other in pure water (negative control) for a duration of 23 days. No mortality was recorded.

Video V1: Acute toxicology study of PSOG 1 on adult zebrafish.

b) Instant gelation of heavy crude oil

3.5% aq. NaCl solution (150 ml) was taken in a glass bowl. 25 ml heavy crude oil was spilled over it. Then 630 mg of the powdered gelator was sprinkled over it. We observed an instant gelation of the crude oil, which could be conveniently scooped out. The gel is quite stiff that it can be held by a forceps.

Video V2: Instant gelation of the crude oil from biphasic oil-water mixture.

c) Solvent recovery and gelator reuse

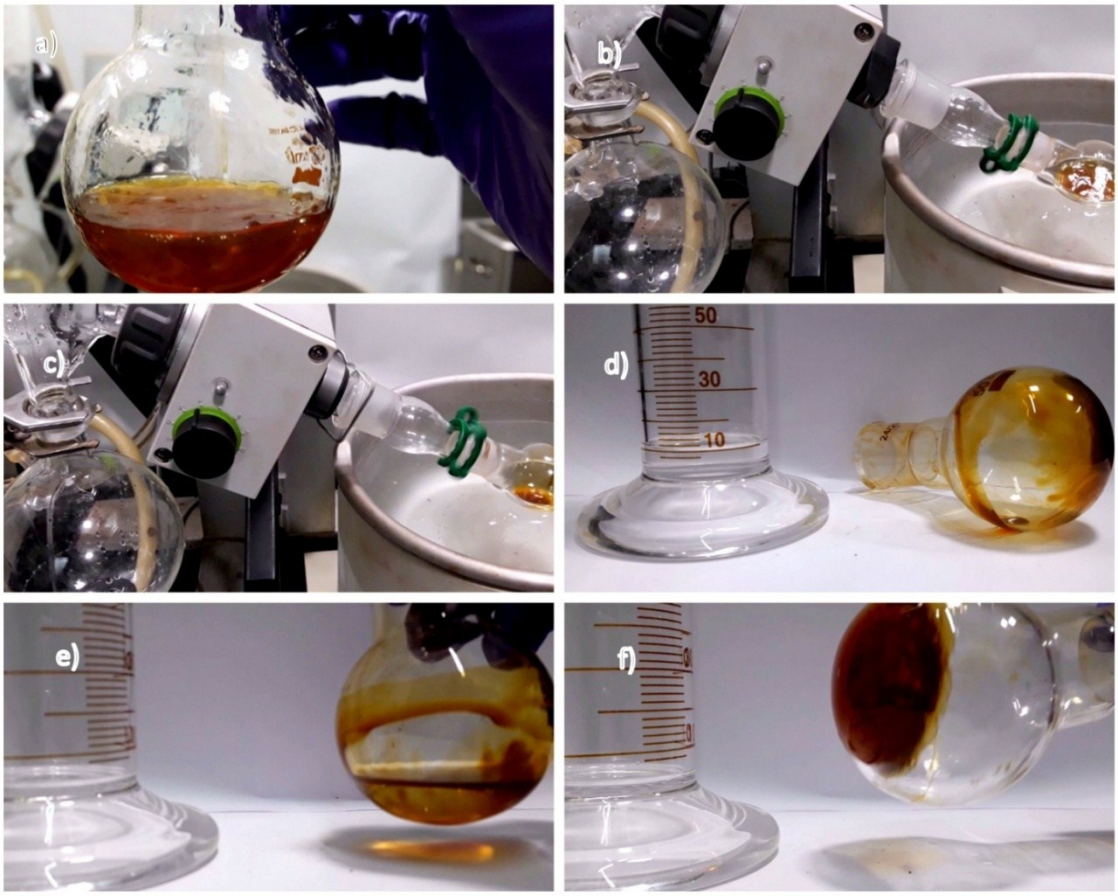


Figure S15: a) 2.0 wt% gel in MCH b) Vacuum distillation in a rotary evaporator c) Solvent evaporation and collection d) Recovered gelator and MCH e) Solvent added to recovered gelator f) Heating-cooling leads to gelation.

Video V3: Vacuum distillation of the gel in methylcyclohexane and reuse of the gelator

d) Gel disruption using methanol

1 ml of 2.0 wt % diesel gel was taken in a glass vial. 2-3 drops of methanol was added to it followed by a gentle shaking. The gel state is completely disrupted, establishing the role H-bonding.

Video V4: Disrupting diesel gel by adding methanol

6. References

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[2] S. Sao; B. R. Samanta; D. Chaudhuri; *RSC Adv.*, 2016, **6**, 34350.

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