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# Supporting information

## Phase Selective Organogel from an Imine Based Gelator to Use in Oil Spill Recovery

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**Experimental Details:**

**Materials:** Methyl 3,4,5-trihydroxybenzoate, 9-anthracenecarboxaldehyde, 1-pyrenecarboxaldehyde and cyclohexane carboxaldehyde were purchased from Sigma Aldrich Chemical Co. 1-Bromododecane was bought from Spectrochem Pvt Ltd (Mumbai, India). Potassium carbonate ($K_2CO_3$), potassium iodide (KI), hydrazine hydrate ($NH_2NH_2.H_2O$) and N, N-dimethylformamide (DMF) were purchased from Merck, India. Petrol, diesel, mobile, kerosene and all other solvents were purchased from local commercial sources. Water was purified by double distillation and DMF was purified by distillation before use.

**Synthesis of Methyl 3,4,5-tris(dodecyloxy)benzoate (P1):** Methyl 3,4,5-trihydroxybenzoate or Methyl gallate (1000 mg, 5.43 mmol), anhydrous potassium carbonate (3450 mg, 25 mmol), potassium iodide (50 mg, 0.30 mmol) and dry DMF were taken together in a 100 ml round bottom flask and stirred at 80 $^oC$ for 2 hours under inert atmosphere. Thereafter 1-bromododecane (4362 mg, 17.5 mmol) was added to the reaction mixture and the resultant reaction mixture was vigorously stirred for 48 hours under inert atmosphere. The reaction mixture was then cooled to the room temperature and poured into the 250 ml beaker contained 100 ml ice-cold water and was extracted thrice with 30 ml diethyl ether. The organic layers were combined together and washed twice with 20 ml brine and dried over anhydrous $MgSO_4$. The crude product as light brown color solid was obtained after evaporation of the organic solvent under reduced pressure. The pure compound **P1** was obtained as colorless solid by column chromatography using basic alumina as stationary phase and petroleum ether as eluent (yield=3482 mg 93%).**$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm):** 7.25 (s, 2H), 3.99 - 4.03 (m, 6H), 3.88 (s, 3H), 1.72 - 1.82 (m, 6H), 1.43 - 1.47 (m, 6H), 1.26 - 1.33 (m, 48H), 0.86 - 0.89 (t, J = 6.8 Hz, 9H) (Figure SA).

**Synthesis of 3,4,5-tris(dodecyloxy)benzohydrazide (P2):** Compound **P1** (2000 mg, 2.90 mmol), hydrazine monohydrate (7.2 mL, 145.14 mmol) and MeOH:THF (2:1, 30 ml) were taken in a round bottom flask and vigorously stirred at 75°C for 24 hours. The reaction mixture was then allowed to cool to room temperature, and the volatiles were removed under reduced pressure. The solvent $CH_2Cl_2$ was added to the resultant residue and washed with $H_2O$ (50 ml) for several times to remove hydrazine. The organic layer was then dried over anhydrous $MgSO_4$, and the solvent was then evaporated under reduced pressure to get crude product as colorless waxy type solid. The pure product as a white solid was obtained by column chromatography using silica gel as the stationary phase and 5% MeOH in $CH_2Cl_2$ as the eluent. (Yield = 870 mg, 87 %); $^1$H NMR (500 MHz, $CDCl_3$): **δ (ppm):** 6.92 (s, 2H), 3.97 - 4.00 (m, 6H), 1.71 - 1.81 (m, 6H), 1.43-1.49 (m, 6H), 1.26 – 1.34 (m, 48H), 0.86-0.89 (t, J=7 Hz, 9H) (Figure SB); IR (KBr) ν = 3422, 3245, 2921, 2850, 1627, 1582, 1500, 1468, 1426, 1389, 1344, 1239, 1119, 844 and 720 $cm^{-1}$.

**Synthesis of compound OG-1:**

Compound **P2** (500 mg, 0.72 mmol) and 10 ml THF were taken in a round bottom flask, a solution of 9-anthracene carboxaldehyde (149.5 mg, 0.72 mmol) in 5 ml $CHCl_3$ was then added drop wise to the **P2** solution. The solution mixture was vigorously stirred for 3 hour. Thereafter the solvents were evaporated under reduced pressure and the resulting product was then washed with hot methanol to get pure product as a yellow powder (592 mg, 93 %); **$^1$H NMR (500 MHz , $CDCl_3$): δ (ppm):** 9.71 (s, CH=N, 1H), 9.61 (s, NHCO, 1H), 8.61 (broad, AnH, 2H), 8.49 (s, AnH, 1H), 8.00-8.01 (d, J= 5 Hz, AnH, 2H), 7.46 - 7.53 (m, AnH, 4H), 7.18 (broad, ArH, 2H), 4.00 - 4.03 (m, $ArCH_2O$, 6H), 1.73 - 1.77 (m, 6H), 1.46 - 1.47 (m, 6H), 1.25 (m, 48H), 0.83 (t, J=7 Hz, 9H) (Figure SC); **IR (KBr) ν =** 3433, 3184, 3057, 2920, 2850, 1644, 1582, 1543, 1501, 1467, 1426, 1368, 1334, 1227, 1118, 1074, 1015, 840, 783 and 728 cm$^{-1}$; **MS (MALDI-TOF):** ***m/z*** Calcd for $C_{58}H_{88}N_2O_4$: 876.67, found: 877.655 $[M+H]^+$, 899.640 $[M+Na]^+$ (Figure SD).

**Synthesis of compound OG-2:**

A solution of 1-Pyrenecarboxaldehyde (133.6 mg, 0.58 mmol) in $CHCl_3$ was added dropwise to a round bottom flask containing a pre-prepared solution of **P2** (400 mg, 0.58 mmol) in $CHCl_3$. The solution mixture was then stirred vigorously for 4 hour at room temperature. The formation of product was confirmed by TLC check-up, and thereafter, the volatile was evaporated by reduced pressure, the solid mass was then washed with methanol for several times and finally a light yellow powder was obtained. **$^1$H NMR (400 MHz , $CDCl_3$): δ (ppm):** 9.65 (s, CH=N, 1H), 9.43 (s, NHCO, 1H), 8.67 (broad, PyH, 2H), 8.08-8.21(m, pyH, 5H), 8.01-8.04 (t, J=7.2 Hz, PyH, 2H), 7.16 (s, ArH, 2H), 4.01-4.05 (m, $ArCH_2O$, 6H), 1.76-1.82 (m, 6H), 1.44 (broad, 6H), 1.25-1.26 (m, 48H), 0.85-0.89 (m, 9H) (Figure SE) ; **MS (MALDI-TOF):** ***m/z*** Calcd for $C_{50}H_{90}N_2O_4$: 782.69, found: 784.219 $[M+H]^+$, 806.208 $[M+Na]^+$ (Figure SF).

**Synthesis of compound OG-3:**

Cyclohexanecarboxaldehyde (65 mg, 0.58 mmol) was dissolved in 5 ml THF and added drop wise to the THF solution of **P2** (400 mg, 0.58 mmol) in a round bottom flask. The reaction mixture was stirred for 6 hour at room temperature. The product formation was confirmed by monitoring TLC test continuously. The solvent was then evaporated under reduced pressure to get crude product as colorless solid, which was purified by column chromatography using silica gel as the stationary phase and 5% ethyl acetate in hexane as the eluent to get the pure product as a white solid (yield =383 mg, 84%). . **$^1$H NMR (400 MHz , $CDCl_3$): δ (ppm):** 8.69 (s, CH=N, 1H), 7.40 (s, NHCO, 1H), 6.96 (s, ArH, 2H), 3.98-4.01 (m, -$CH_2O$, 6H), 2.4 (broad, CyH, 1H), 1.71-1.81 (m, 10H), 1.45 (broad, 6H), 1.26-1.29 (m, 54H), 0.86-0.89 (m, 9H) (Figure SG); **MS (MALDI-TOF):** ***m/z*** Calcd for $C_{60}H_{88}N_2O_4$: 900.67, found: 901.995 $[M+H]^+$, 923.978 $[M+Na]^+$ (Figure SH).

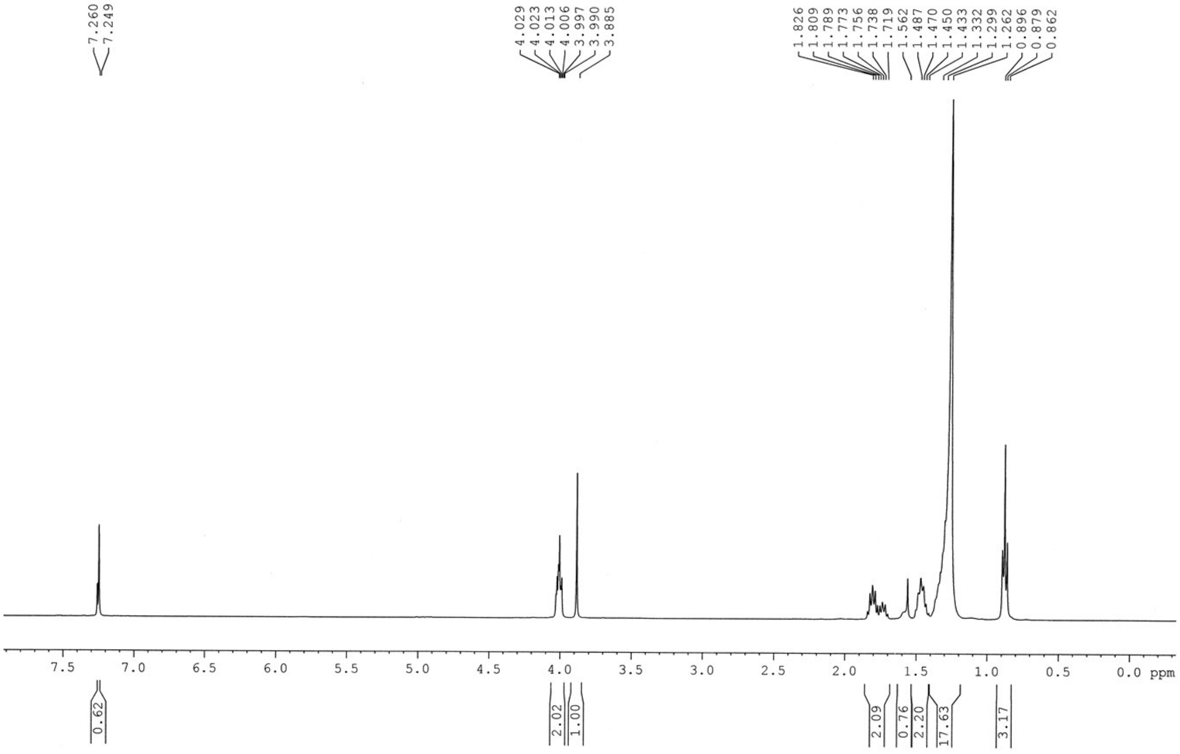

**Figure SA** $^1$H NMR (400MHz) spectrum of compound $P_1$ in CDCl3

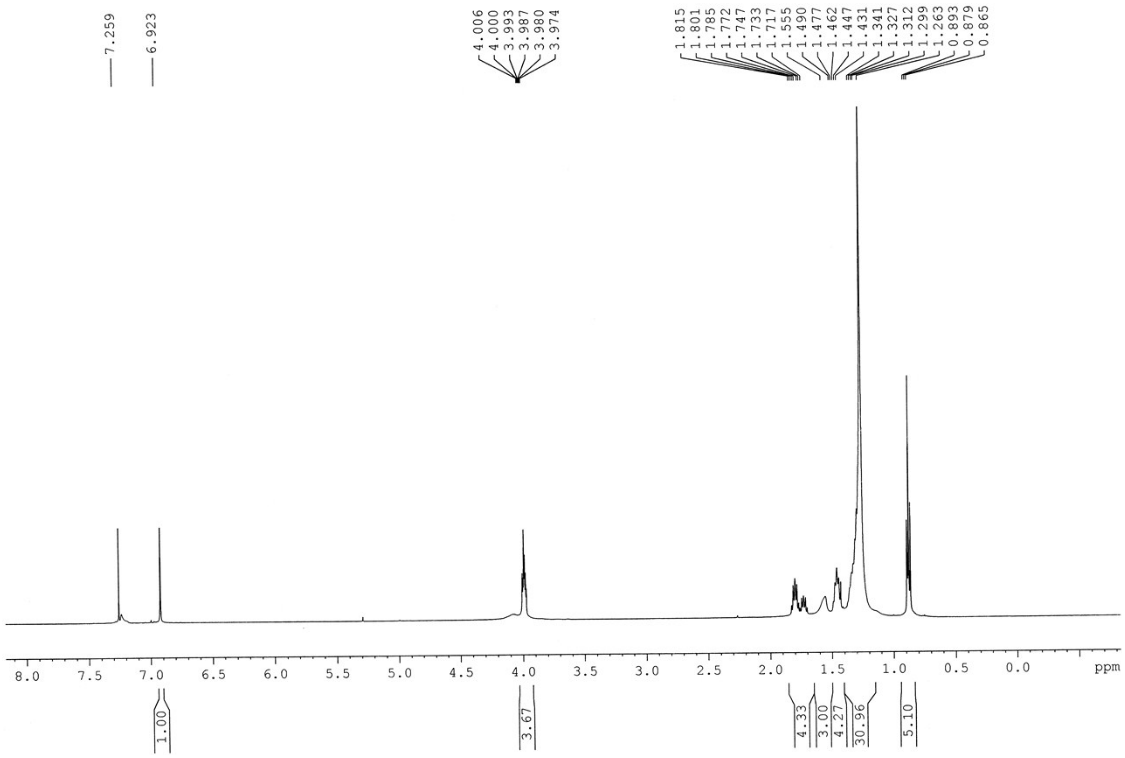

**Figure SB** $^1$H NMR (500MHz) spectrum of compound $P_2$ in $CDCl_3$.

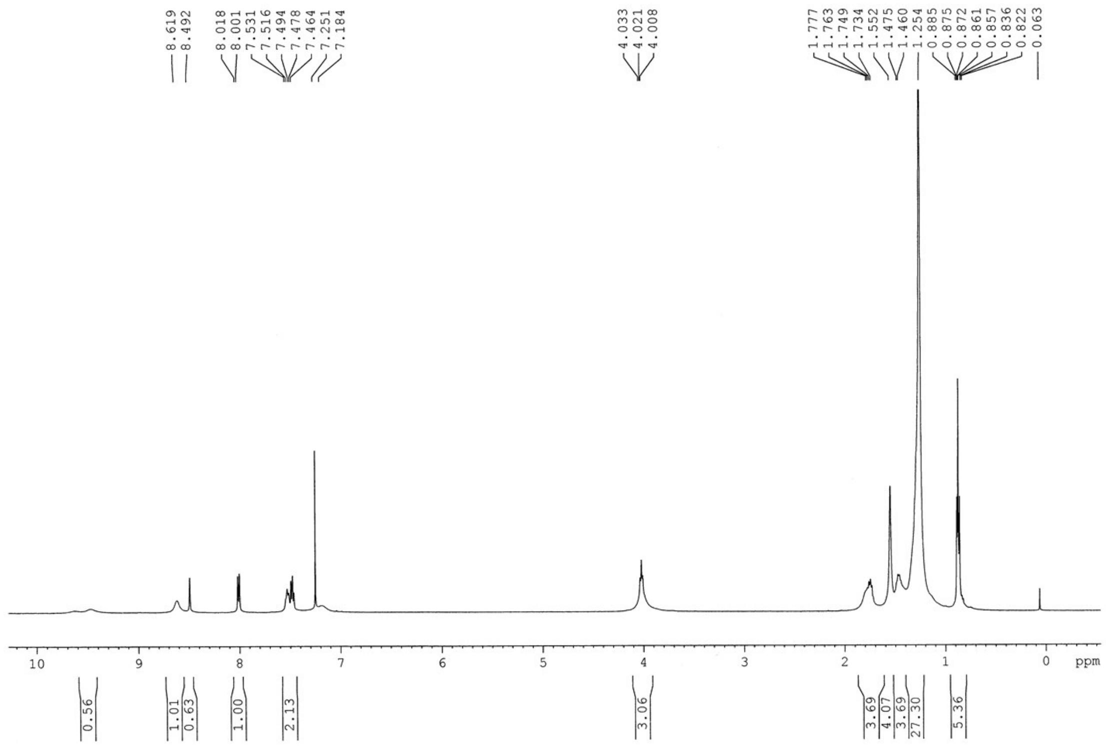

**Figure SC** $^1$H NMR (500MHz) spectrum of compound OG-1 in $CDCl_3$.

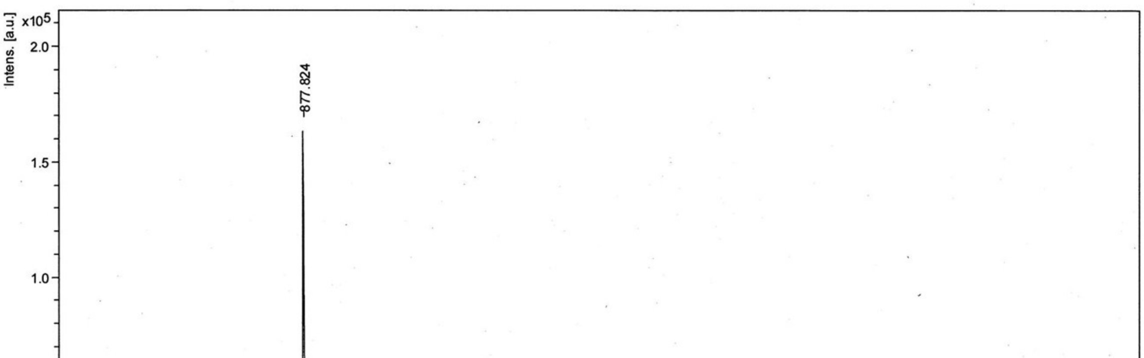
Intens. [a.u.]
x10^5
2.0
1.5
1.0
0.5
0.0
877.824
899.785
915.789
645.318
674.738
701.125
849.790
1069.781
1776.584
1811.510
1946.583
600
800
1000
1200
1400
1600
1800
2000
m/z

**Figure SD** The MALDI-TOF of compound OG-1.

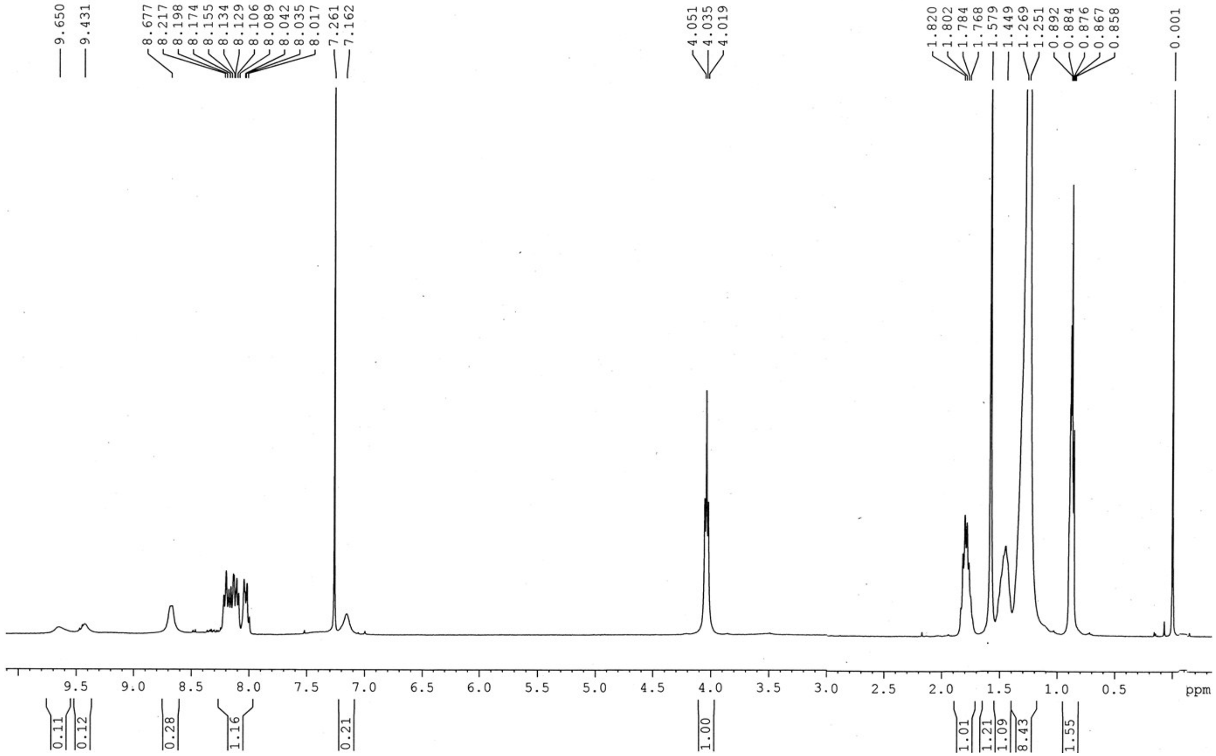

**Figure SE** $^1$H NMR (400MHz) spectrum of compound OG-2 in $CDCl_3$.

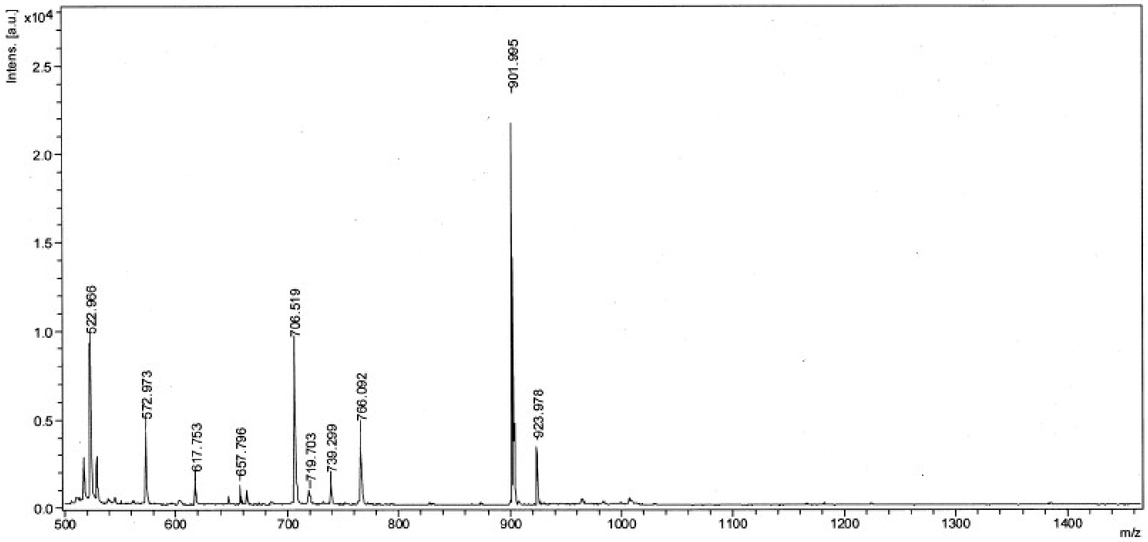

**Figure SF** The MALDI-TOF of compound OG-2.

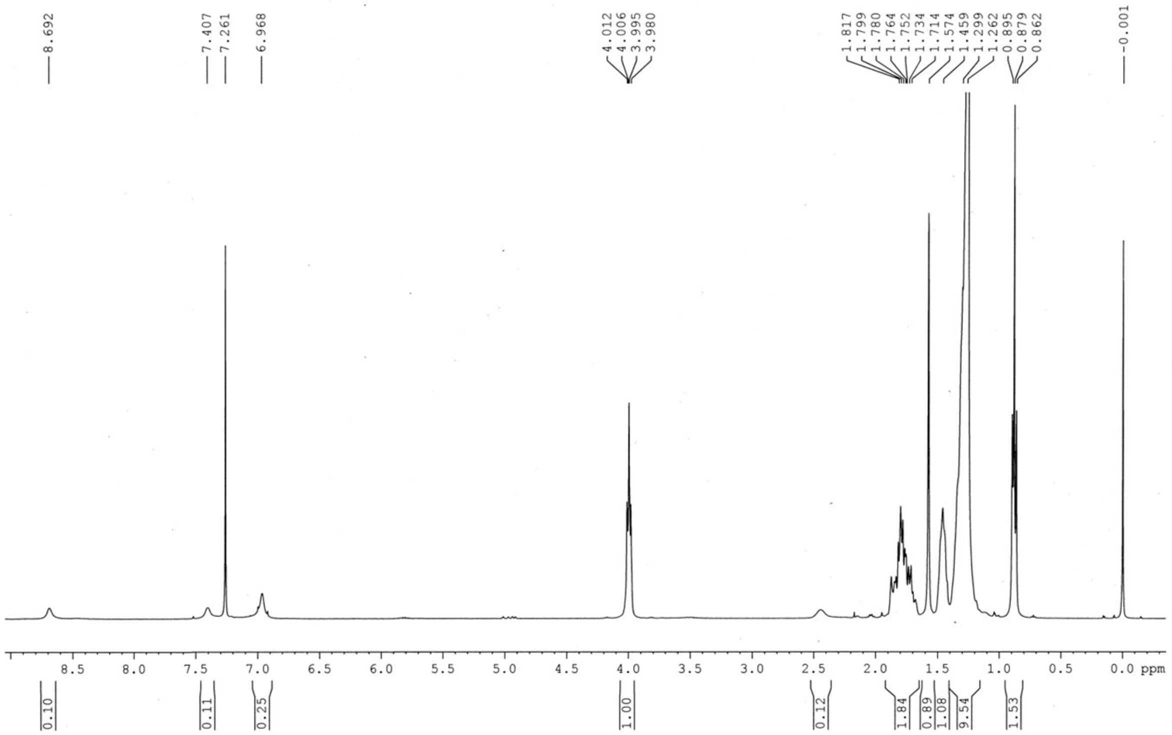

**Figure SG** $^1$H NMR (400MHz) spectrum of compound OG-3 in CDCl$_3$.

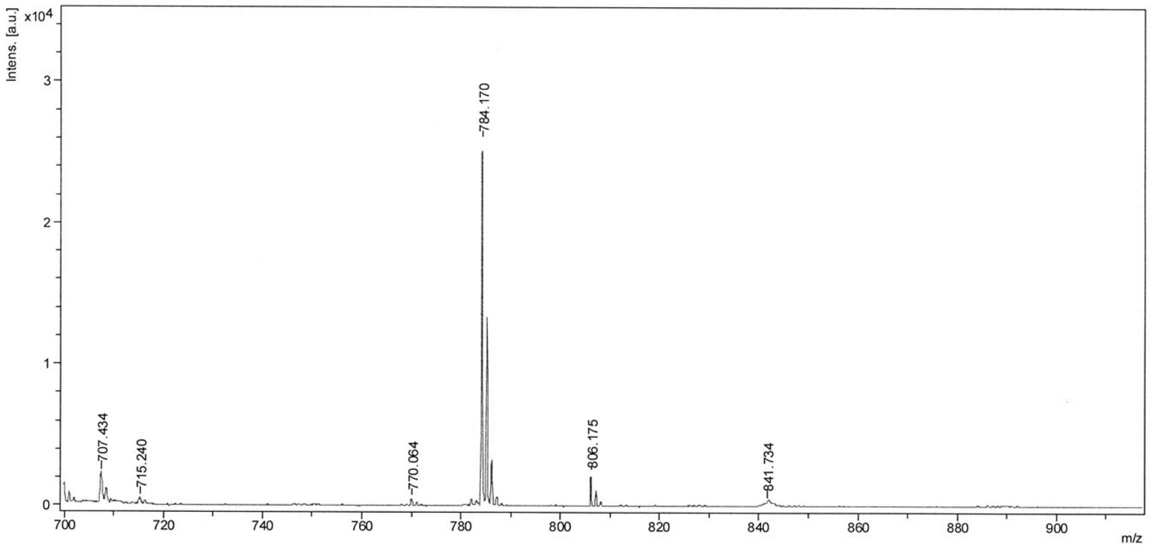

**Figure SH** The MALDI-TOF of compound OG-3.

**Table S1:** The gelation test of OG-1, OG-2 and OG-3 in different solvents and solvent mixtures. I= insoluble; PG=partial gel; G=gel; S=soluble

| Gelator → Solvent ↓ | OG-1 | | OG-2 | | OG-3 | |
|---|---|---|---|---|---|---|
| | MGC (w/v %) | Observation | MGC (w/v %) | Observation | MGC (w/v %) | Observation |
| Methanol | I | - | I | - | I | - |
| Ethanol | I | - | I | - | G(3) | Opaque |
| 1-Propanol | PG | Opaque | PG | Opaque | S | - |
| 1-Butanol | PG | Opaque | G(1) | Opaque | S | - |
| 1-Pentanol | PG | Opaque | G(1) | Opaque | S | - |
| 1-Hexanol | G(0.6) | Transparent | G(1) | Transparent | S | - |
| 1-Heptanol | G(0.75) | Transparent | G(1.1) | Transparent | S | - |
| 1-Octanol | G(0.8) | Transparent | G(1.2) | Transparent | S | - |
| Methanol:Ethanol (2:1) | I | - | I | I | G(1.5) | Opaque |
| Methanol: $CHCl_3$ (9:1) | G(0.4) | Opaque | G(0.6) | Opaque | G(2) | Opaque |
| Methanol:Acetone (1:1) | I | - | I | I | G(2) | Opaque |
| Methanol:$CH_3CN$ (1:1) | I | - | I | I | I | - |
| Methanol:THF (9:1) | G(0.5) | Transparent | G(0.5) | Transparent | G(2) | Opaque |
| Ethanol:$CHCl_3$ (9.5:0.5) | G(0.4) | Transparent | G(0.2) | Transparent | S | - |
| Kerosene | G(0.15) | Transparent | S | - | S | - |
| Diesel | G(0.2) | Transparent | S | - | S | - |
| Petrol | G(0.15) | Transparent | S | - | S | - |
| Mobil | G(0.4) | Transparent | S | - | S | - |
| Silicon oil | I | - | I | - | S | - |
| Mustard oil | G(0.4) | Transparent | S | - | S | - |
| Refine oil | G(0.4) | Transparent | S | - | S | - |
| Coconut oil | G(0.4) | Transparent | S | - | S | - |

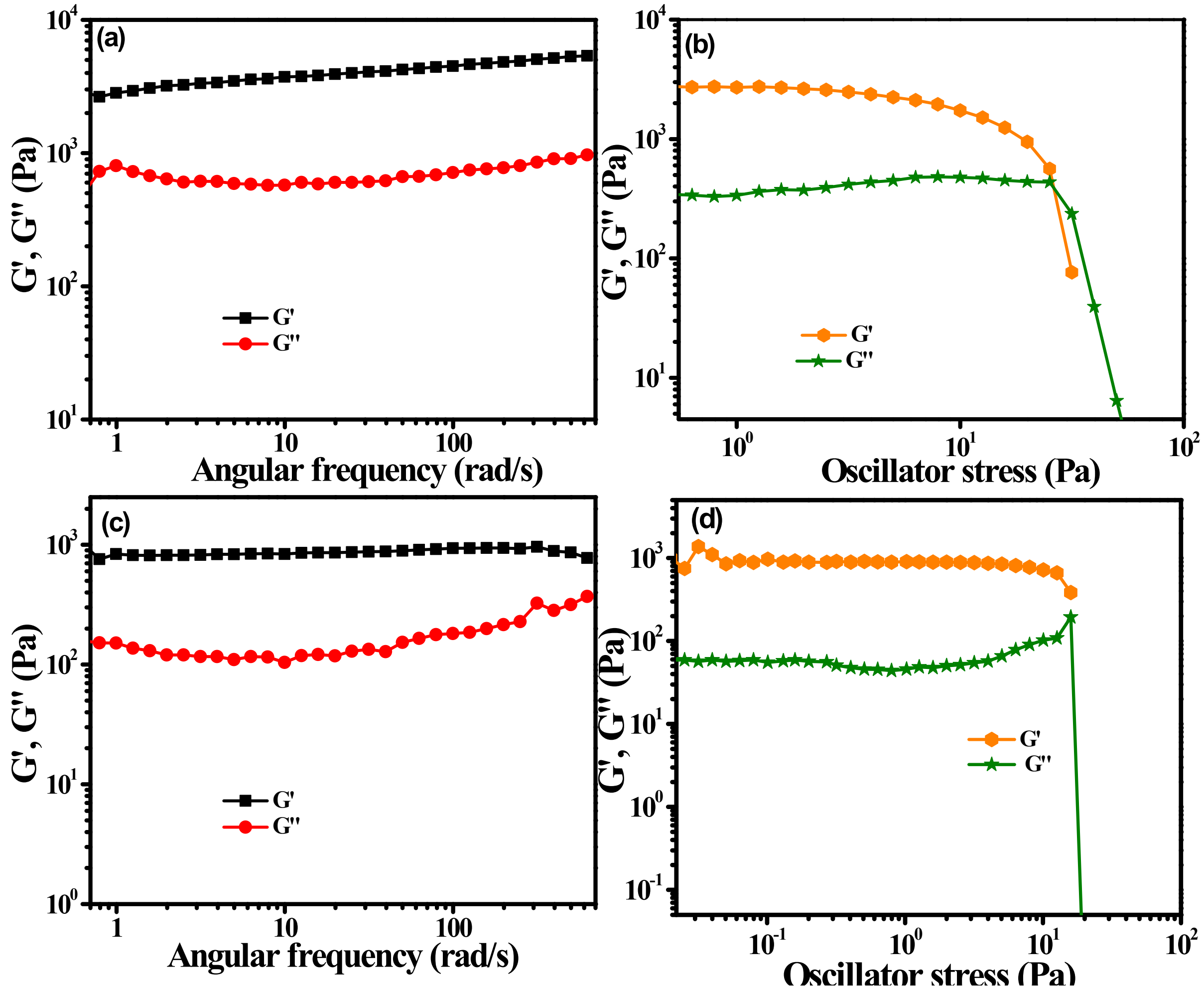
(a)
G', G'' (Pa)
Angular frequency (rad/s)
G'
G''
(b)
G', G'' (Pa)
Oscillator stress (Pa)
G'
G''
(c)
G', G'' (Pa)
Angular frequency (rad/s)
G'
G''
(d)
G', G'' (Pa)
Oscillator stress (Pa)
G'
G''

**Figure S1** Angular frequency of 1.5 % (w/v) of (a) OG-2 gel in EtOH:$CHCl_3$ (9.5:0.5) and (c) OG-3 gel in EtOH:MeOH (1:2). Stress sweep of 1.5 % (w/v) of (b) OG-2 gel in EtOH:$CHCl_3$ (9.5:0.5) and (d) OG-3 gel in EtOH:MeOH (1:2).

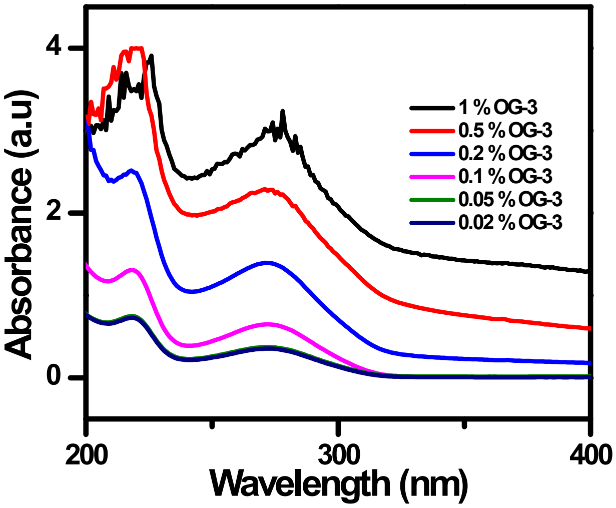

**Figure S2** UV-vis spectra of OG-3 in EtOH:MeOH (1:2).

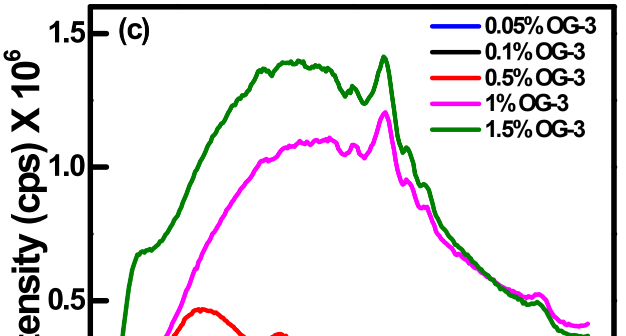

**Figure S3** Concentration dependent fluorescence spectra of OG-3 in EtOH:MeOH (1:2) mixture for excitation at 270 nm.

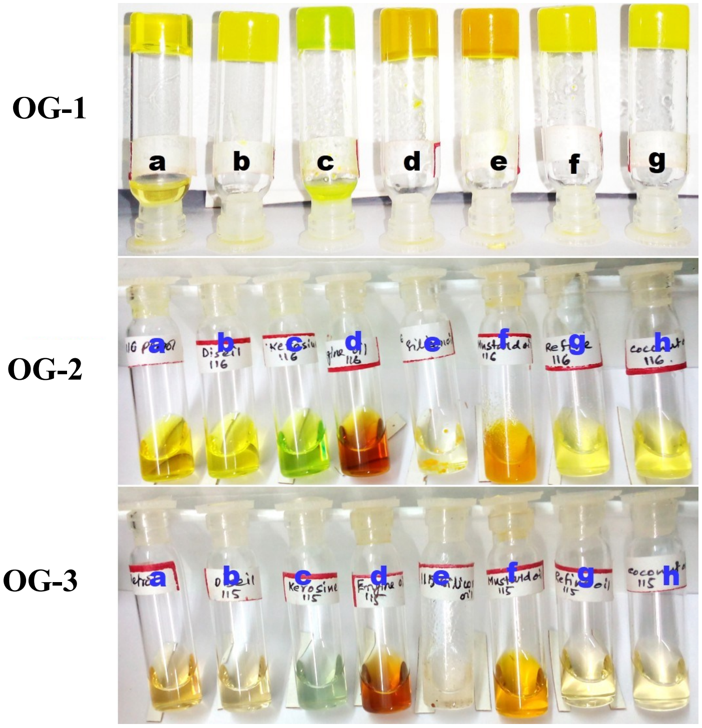

**Figure S4** The gelation test of OG-1 in (a) petrol, (b) diesel, (c) kerosene, (d) mobil, (e) mustard oil, (f) refined oil and (g) coconut oil. The gelation test of OG-2 in (a) petrol, (b) diesel, (c) kerosene, (d) mobil, (e) silicon oil, (f) mustard oil, (g) refined oil and (h) coconut oil. The gelation test of OG-3 in (a) petrol, (b) diesel, (c) kerosene, (d) mobil, (e) silicon oil, (f) mustard oil, (g) refined oil and (h) coconut oil.

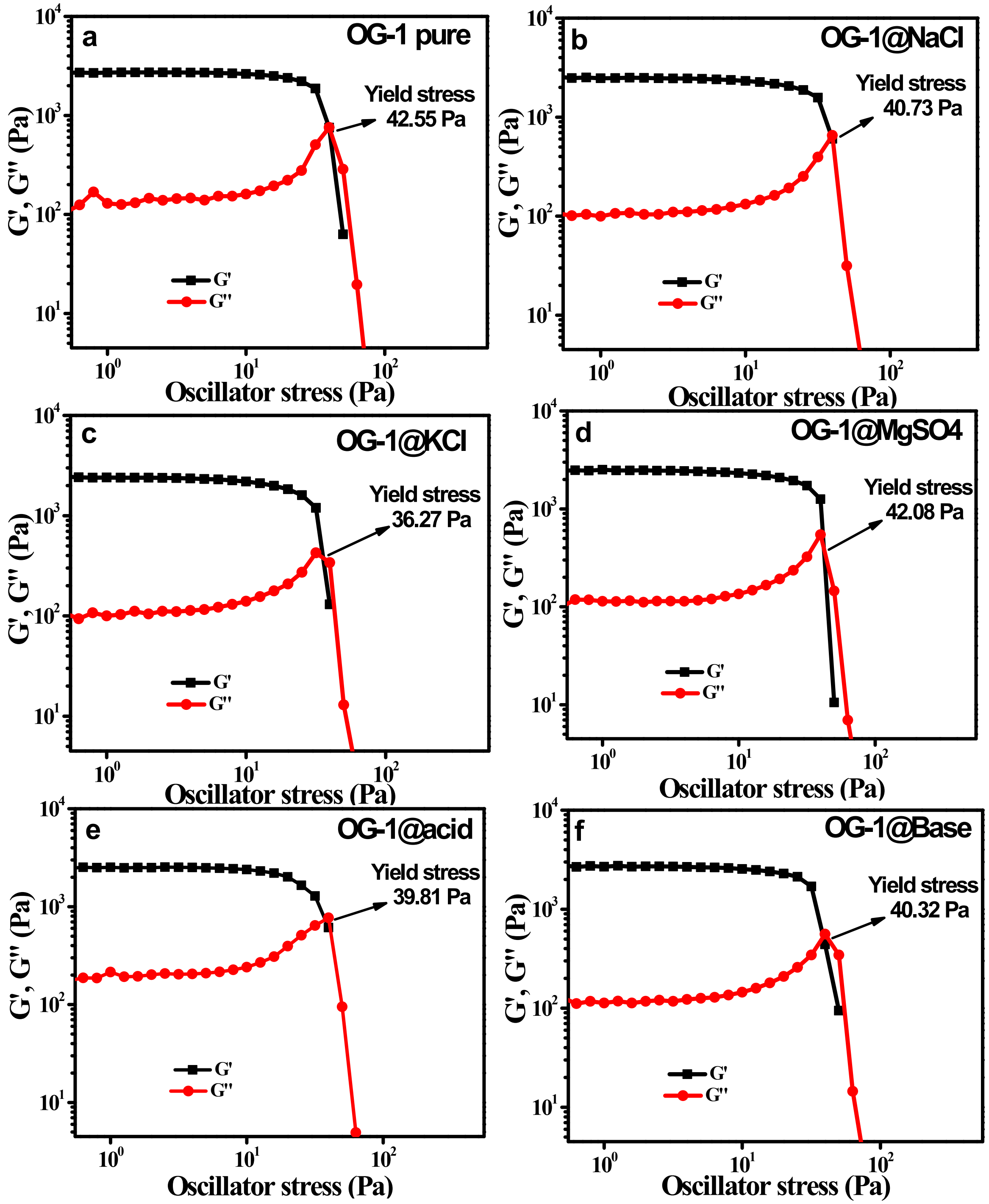

**Figure S5** Stress sweep experiments of OG-1 gel 1.2 % (w/v) in kerosene in water medium (a) pure and in presence of (b) NaCl (3.5%), (c) KCl (3.5%), (d) $MgSO_4$ (3.5%), (e) 0.01 N HCl and (f) 0.01N NaOH.

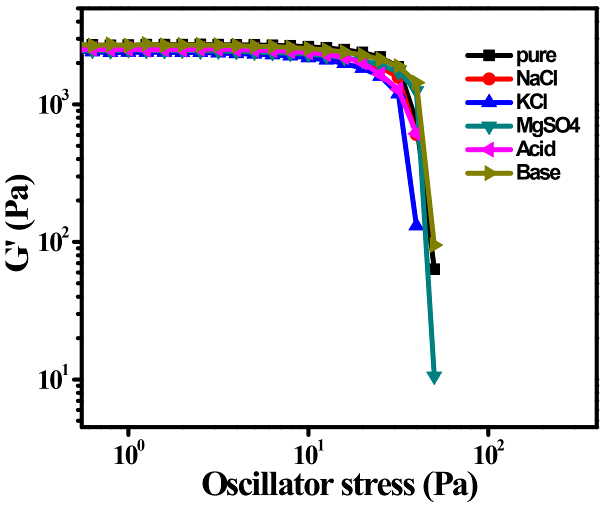

**Figure S6** Comparison of G' vs oscillatory stress plots OG-1 gel 1.2 % (w/v) in kerosene-water mixture in absence and presence of different salts, acid and base at concentrations same as Fig.5.

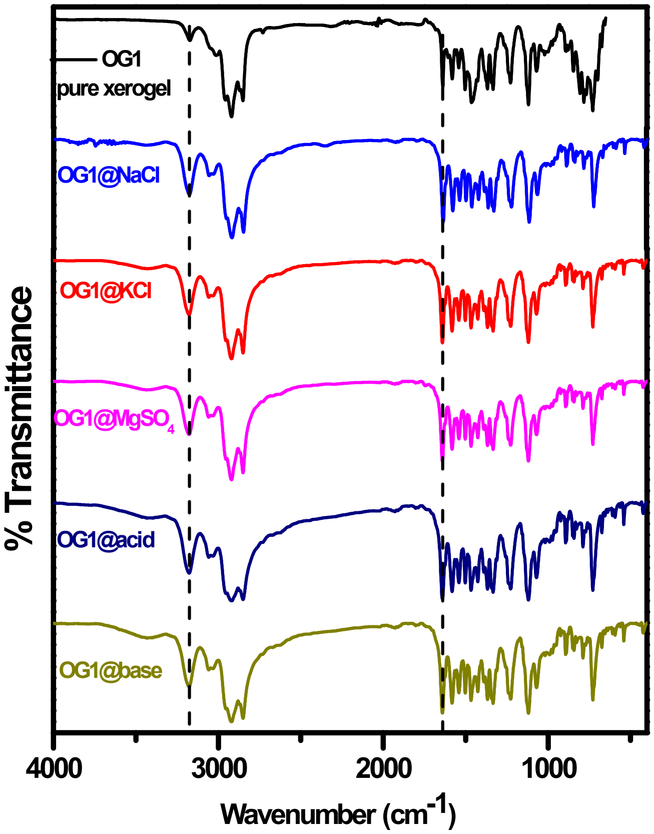

**Figure S7** FTIR Spectra of pure OG-1 xerogel obtained from pure OG-1 gel in kerosene. OG-1@NaCl, OG-1@KCl, OG-1@MgSO$_4$, OG-1@acid and OG-1@base xerogels obtained from the kerosene-water mixture in presence of NaCl (3.5 %), KCl (3.5%), MgSO$_4$ (3.5%), 0.01 N HCl and 0.01 N NaOH respectively.

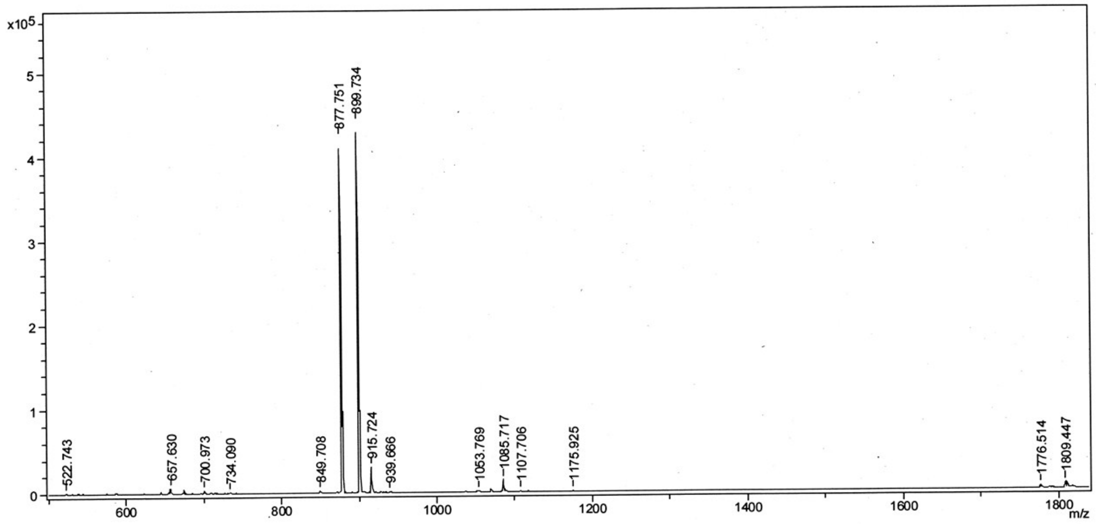

**Figure S8** The MALDI-TOF of compound OG-1 obtained after vacuum distillation of scooped gel in diesel oil.

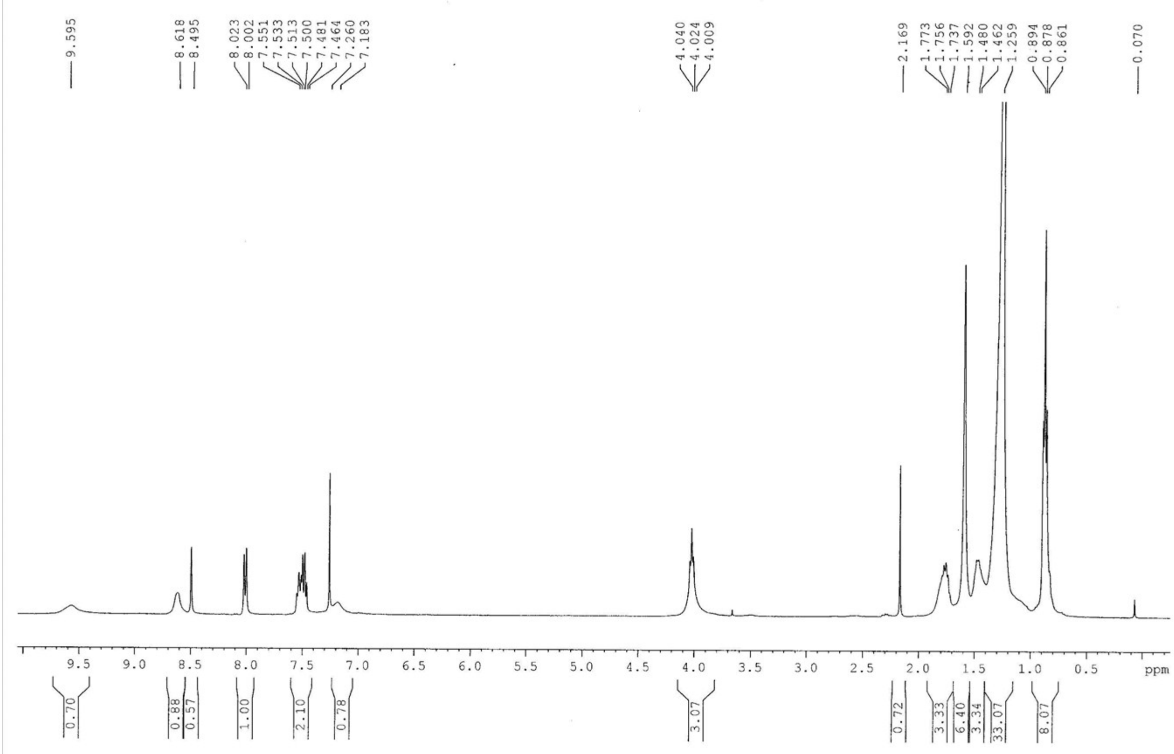

**Figure S9** $^1$H NMR (400MHz) spectrum of compound OG-1 in $CDCl_3$ obtained after vacuum distillation of scooped gel in disel oil.

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