Electronic Supplementary Information (ESI†)

Mannitol based phase selective supergelator offers a simple, viable and greener method to combat marine oil spills

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Materials and methods:

All the chemicals, solvents and oils were purchased from commercial suppliers. Gelators **1** and **2** were synthesized as reported[13]. All Solvents (LR grade) were distilled before using. Pump oil, paraffin oil and other oils were directly used as purchased. Commercial petrol, diesel and kerosene were purchased from gas outlets and were used without further purification. Petrol was fractionated into different fractions by simple distillation under atmospheric pressure. Sea water was collected from Kovalam, Kerala (Arabian Sea). Rheological studies were carried out using MCR 150 modular compact rheometer using parallel plate sensor. The cylindrical shaped gels of 5 wt% concentration were prepared and allowed to set for 2-3 hours. The set sample (0.5 mL) was placed on the plain sample surface of the Rheometer. The experiment was done in frequency sweep as well as strain sweep modes. In the case of frequency sweep, the experiment was done with 1% strain. Differential scanning calorimetry experiments were done using a DSC Q20 (TA instruments) instrument.

Determination of Critical Gelation Concentration (CGC):

20 mg of the gelator was dissolved in 1 mL of the solvent under study by heating in a test tube and gelation test was done. If it passes gelation test (CGC = 2 wt%), further small measured volume of solvent was added and gelation test was conducted. This was repeated until the gel failed inversion of test tube test. The maximum amount of solvent that can be

gelated by 20 mg of the gelator was noted. From this, CGC was calculated as wt% (= weight of the gelator in g x 100/Volume of the solvent in mL).

Determination of Biphasic Critical Gelation Concentration (BCGC):

A biphasic mixture of water and appropriate non-polar liquid (oil or solvent) was made by mixing the two. Then a warm, concentrated gelator solution in the same non-polar liquid was introduced to the surface of the biphasic mixture so that the overall concentration of the gelator is same as the CGC. If it was not congealing the oil phase, further aliquots of the gelator solution was added till the oil phase was congealed completely. From this, the amount of gelator required to congeal the whole oil phase was calculated as wt%.

The effect of temperature on the gel formed over the aqueous phase:

The gels of all the organic solvents mentioned in the table 1 were made over a fixed volume of sea water in a test tube. For the sake of uniformity and easy comparison, 2 wt% gel was made in all the cases. The volume of sea water was kept uniform in all the cases. Once the gel was formed on the surface of the sea water, the test tube was immersed in an oil bath such that the upper meniscus of the gel is below the oil in the oil-bath. The test tube was then heated gradually (2°C per minute) and the gel melting temperature (the temperature at which the gel loses its rigidity and fall on inversion of the test tube) was measured using a thermometer. The Biphasic-T_{Gel} (B-T_{Gel}) of these gels are tabulated in Table S1. It is clear that the gel formed above the sea water is stable at normal marine surface temperatures. We have also checked the melting point of the gel (pump oil gel) at its BCGC (0.55 wt%) and found that this gel is stable up to 73°C.

Table S1. Biphasic-T_{Gel} (B-T_{Gel}) of gels formed by **2** with various non-polar solvents over sea water

S.No	Solvent	B-T_{gel} in °C

1.	Hexane	58
2.	Heptane	60
3.	Cyclohexane	54
4.	Pet ether	59
5.	Dodecane	68
6.	Undecane	67
7.	Petrol	--
8.	Kerosene	59
9.	Diesel	61
10.	Pump oil	82
11.	Silicon oil	74
12.	Paraffin oil	83

Explanation for the behavior of gel with a drop of water, MeOH and acetic acid:

Fig S1a. shows the schematic diagram for the self-assembly of the gelator molecules in oil medium forming the fibres. As water is immiscible with the oil medium, they form an emulsion as in Fig S1b. Since they are not miscible they don’t compete for hydrogen bonding with the gelator molecules. Hence a drop of water can not disrupt the gel structure. But methanol and acetic acid are soluble in oil phase forming a homogeneous solution (Fig S1c). Hence they compete for hydrogen bonding with the gelator molecules and thus disrupts or inhibits their self-assembly.

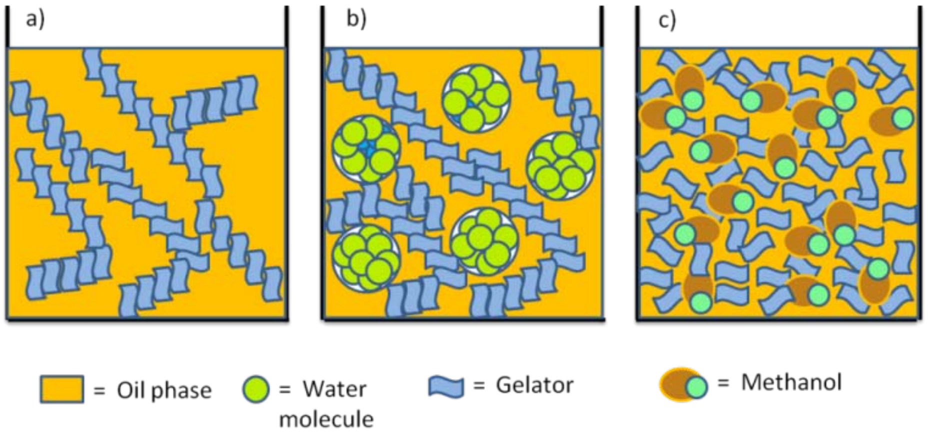

Fig. S1 a) Organogel showing the self-assembled fibrillar network (SAFIN) of gelator in oil phase. b) Emulsion formed by immiscible water droplets in an oil gel, wherein water molecules do not interact with SAFINs. c) Homogeneous solution of methanol and gelator in the oil; the hydrogen bonding interaction between methanol and gelator disrupts SAFINs, collapsing the gel.

Demonstration of the oil spill recovery in a model system:

A marine oil spill model was set up by pouring oil (diesel) in sea water taken in a flat glass vessel kept on a mechanical shaker. To this a warm (80 °C) concentrated solution (12 wt%) of the gelator **2** in the same oil (diesel) was sprayed/sprinkled uniformly over the oil layer. The concentration of the gelator was taken in such a way that the overall concentration of the system would be 0.75-1 wt%. The mixture was kept under mild mechanical agitation for 15-30 minutes, during which the oil phase got congealed. If the initial concentration of the gel is high, the recovered gel can be used as the gelator solution to recover additional amounts of diesel from a fresh diesel-water mixture (see video S1). This process could be repeated till the overall concentration of gelator in whole of diesel is approximately 1%. The gel formed could easily be scooped out from the aqueous layer using a sieve spatula. At slightly higher gelator concentrations, the gels formed are sufficiently strong that they can be separated as discs using a simple forceps. The recovery of the diesel gel was found to be 90-92% by volume. The isolated diesel gel was heated to melt and was distilled by a simple distillation set up to get the colorless diesel.

We also have demonstrated the recovery using pump oil as the oil phase (Fig. S2)

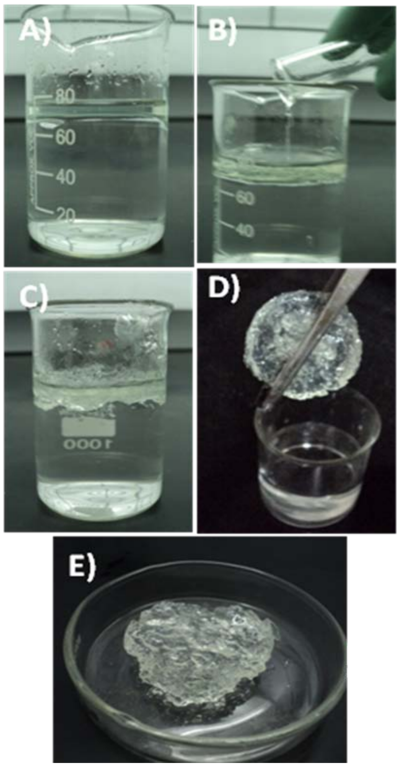

Fig. S2: Phase selective gelation of pump oil A) The biphasic system of pump oil and water B) Introduction of gelator **2** as a solution in pump oil (100 °C & 10 wt %) C) Congealed oil phase over the water layer D) Removal of the gel disc using a forceps E) The isolated pump oil gel from the mixture of pump oil and water (90 % recovery).

<u>Demonstration of the strength of the gel in presence of water:</u>

A 3 wt% gel of **2** was made above a liter of a dilute $KMnO_4$ solution in water (Fig S3a). When the gel was set, the flask was inverted (Fig S3 b). This did not break or deform the gel suggesting that the gel is strong enough to support not only its own weight but also several times its own weight.

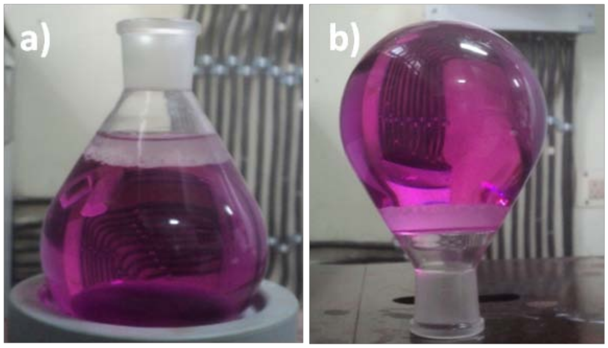

Fig. S3: a) A 3 wt % gel formed on the surface of a liter of a dilute $KMnO_4$ solution b) gel holding the weight of a liter of water

Lower boiling fraction of the Petrol as carrier solvent:

In order to make the aerial spray more effective (in less volume of carrier solvent), a concentrated solution of the gelator as spray solution is required. As the Lower Boiling Fraction of Petrol (LBFP) made a clear solution of **2** even at high concentrations (Table 2), it was chosen as the carrier solvent. Thus 80 wt% (80 g of gelator **2** in 100 mL of LBFP) solution of gelator **2** was made in LBFP. This solution was sprayed into a biphasic mixture of diesel and water kept on a mechanical shaker. The diesel layer got congealed completely at an overall concentration of 1.5 wt%. However, the gels were relatively weaker than the gel formed at this concentration by spraying the diesel solution. After 12 hours of shaking, the oil gel could be scooped out using a sieve spatula. We could recover 83% of the oil by this way.

Differential Scanning Calorimetry Experiments:

A warm gel solution (approximately 30-40 mg) was taken in an ampoule and allowed to congeal for an hour. This was placed in the DSC instrument and the T_{gel} was measured in heating mode. The Tgel obtained by this method was in agreement with the T_{gel} obtained by the inversion test tube method.

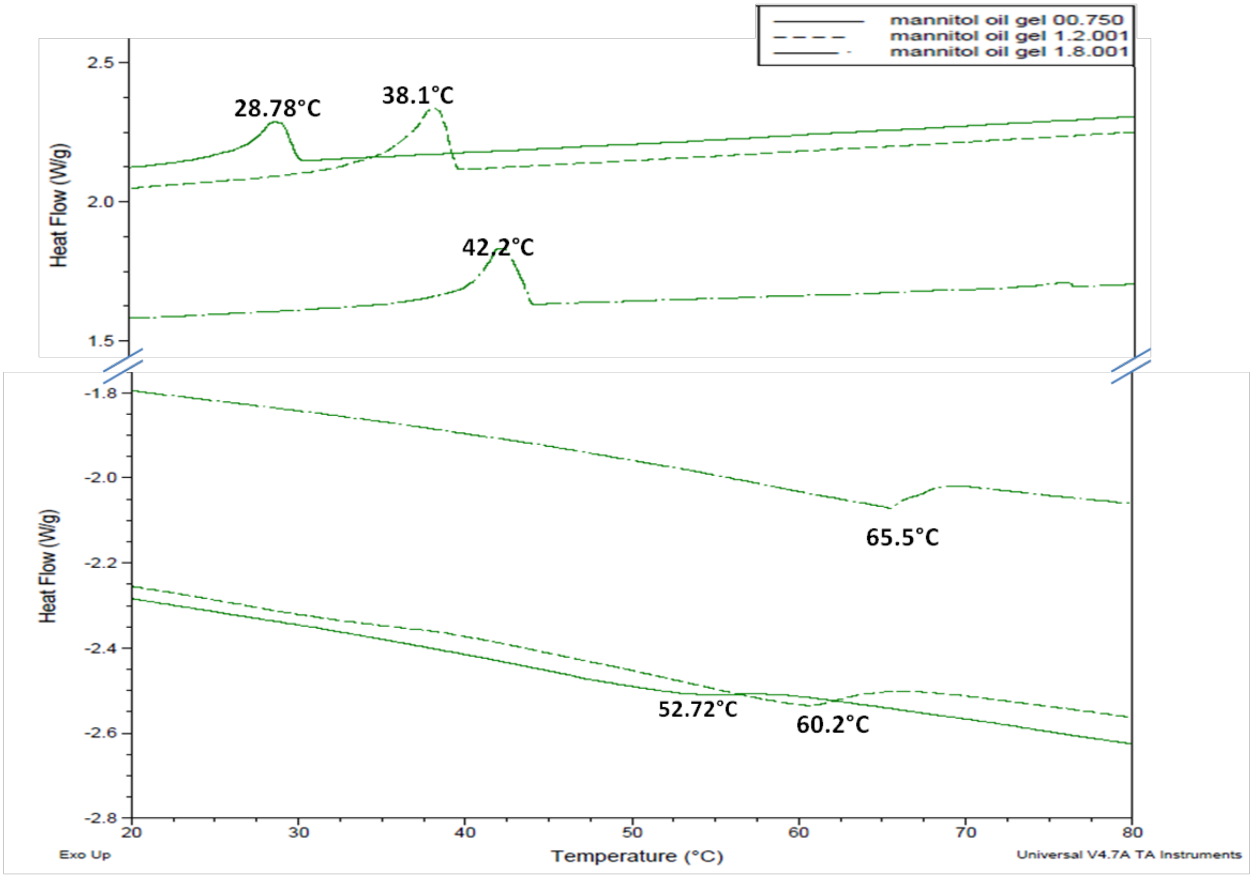

Fig. S4. DSC thermograms of pump oil gels of **2** at concentrations 0.75 wt% (——) , 1.2 (------) wt% and 1.8wt % (—— -). Top three curves are cooling curves and bottom three curves are heating curves. The heating and cooling rates are 5 °C /min

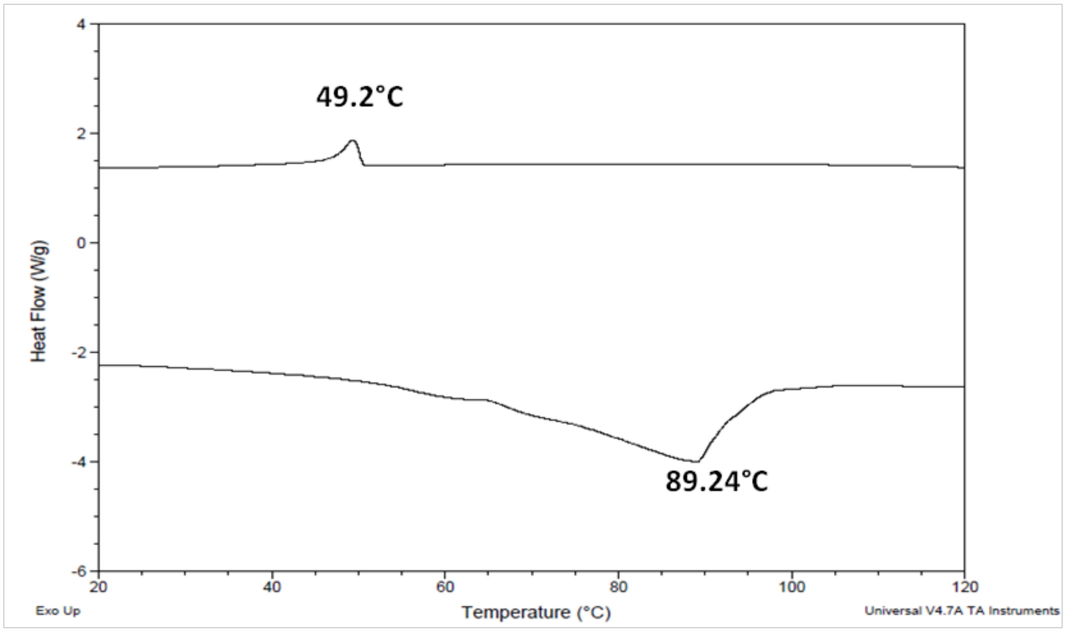

Fig. S5. DSC thermograms of dodecane gels of **2** at 2.65 wt%. Upper curve is cooling curve and bottom curve is the heating curve. The heating and cooling rates are 5°C/min. The melting point of 89 °C under heating mode is matching with the T_{gel} determined by the heating cooling method (88 °C).

Supporting reference:

13. A. Vidyasagar, K. Handore and K. M. Sureshan *Angew. Chem. Int. Ed.* 2011, **50**, 8021.