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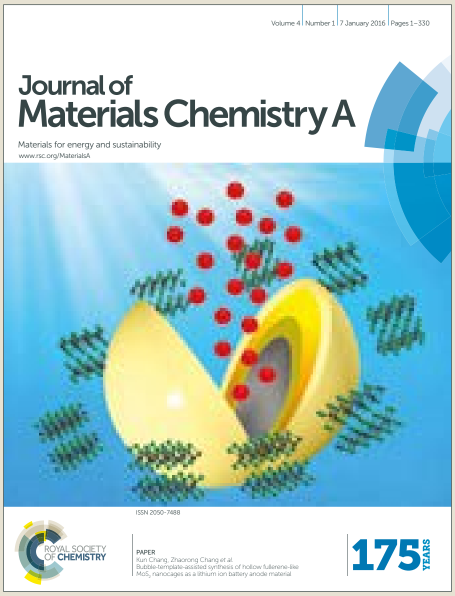

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PAPER
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COMMUNICATION

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

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Phase-selective organogelators (PSOGs) that congeal oil from water have emerged as a promising alternative to the existing methods of containing marine oil-spill. However, all PSOGs reported till date, suffer from one prohibitive limitation: a poor dispersibility in the oil phase. Consequently when used as dry powder, these PSOGs take long hours to congeal oil, and instead have to be applied after dissolving in, or wetting with toxic and inflammable solvents. We report a naphthalene diimide based gelator that when applied in the powder form can solidify heavy crude oil from water, in seconds. Exceptional mechanical strength of the resultant gel, easy recoverability of oil, ability to congeal oil at 0 °C, and a negligible aqueous solubility makes our compound by far the best reported PSOG for oil-spill remediation.

Introduction

Marine oil spill resulting from human activity and/or natural causes poses serious threat, both immediate and long-term,[1,2] to ocean and coastal ecosystem and human lives dependent on it, not to mention the economic loss associated with the wastage of a precious, non-renewable resource. Current measures of oil spill remediation focus primarily on containment,[3–7] but not so much on the recovery of the spilled oil. Additionally there are severe limitations with most of these containment methods. For instance, a controlled on-site burning of oil contributes to significant air pollution.[5] Using absorbent booms is not only too cumbersome to contain large-area ocean spills, but also necessitates safe disposal measures in order to avoid any secondary pollution.[6] Use of chemical dispersants leaves all toxic residues back in the ocean,[7] and increases its bioavailability.

Among the emerging strategies for oil-spill recovery, one that has gained considerable attention is the use of small molecule based phase-selective organogelators (PSOGs) that can selectively congeal oil from a biphasic oil-water mixture.[8–25] Despite significant development in recent times, one outstanding issue that severely limits the applicability of PSOGs lies with the slow diffusion of gelator molecules in the oil phase, particularly in the case of highly dense and viscous heavy crude oil. As a result of this limitation, most reported PSOGs either require considerable amounts of hazardous or inflammable carrier solvent,[8–20] or heating-cooling routines[21–24] to assist an effective dispersion of the gelator in oil, making these approaches non-viable. More recently, groups of Sureshan and Zeng developed PSOGs that can be applied directly as dry powder.[19,25] Despite the obvious advantage, these gelators suffer from impractically long gelation times (45 min. to 48 h), once again highlighting the problem of slow PSOG dissolution in the oil-phase. In a very recent communication,[26] Zeng and co-workers even argued that developing a powder gelator for rapid gelation of crude oil, though desirable, is "*almost insurmountable, if not impossible, task*". As an alternative, they offered a wetting strategy to improve the dissolution of powder gelator in oil, and reduce the gelation time considerably. Despite its success, even this method has limitations: it uses a significant amount of CH_3CN as wetting agent (1:1 w/w gelator-to-CH_3CN ratio), a solvent that is both toxic and inflammable. Moreover, a reasonably fast gelation (~10 min) of crude oils could only be achieved at a high gelator loading of 10-20 wt%, and under constant shaking. Here, we report a NDI based organogelator that almost instantaneously immobilizes heavy crude oil from water, when applied in the powder form, at a low loading of <2.5 wt.%.

Results and Discussion

Figure 1a presents the molecular structure of PSOG **1**, and control molecules **C2** and **C3**. PSOG **1** was synthesized in a two-step,[‡] sequential condensation of naphthalene dianhydride, with *n*-dodecylamine and phenylalanine (Phe) (see Supporting Information). There are two aspects of the molecular design of

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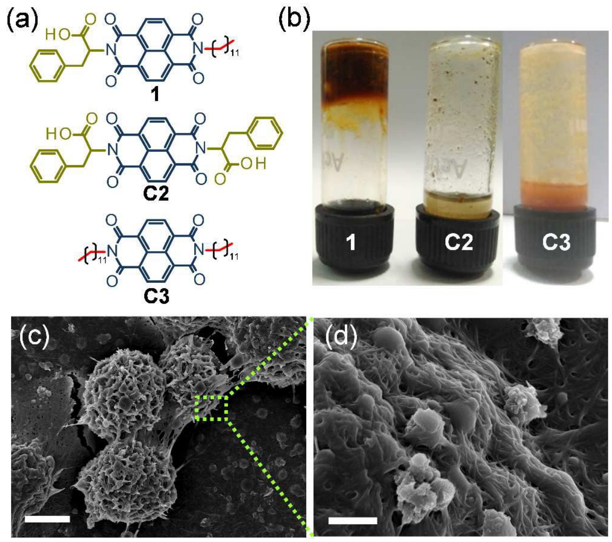

Fig. 1 (a) Molecular structures of PSOG **1** and the control molecules **C2** and **C3**, (b) **1** readily congeals diesel at 1.3 wt%, while **C2** and **C3** cannot, (c) SEM micrograph of 1.7 wt% MCH xerogel of **1** shows porous microglobular structure (scale bar: 5 μm) that (d) at a higher magnification reveals the underlying nanofibrillar morphology (scale bar: 1 μm).

Table 1. Gel characteristics of PSOG 1.

Gelling Medium	Density (g/ml), **API**	CGC (% w/v)	BCGC[a] (% w/v)	T_{gel} (°C) at CGC
Cyclohexane[b]	0.78, –	1.53	1.56	55
MCH[b]	0.77, –	1.66	1.59	56
Kerosene	0.8, –	1.72	1.91	60
Pump oil	–	1.63	1.83	57
Diesel	0.84, –	1.25	1.54	56
Crude, ONGC Mehsana	0.91, **24°**	2.15	2.25	58
Crude, Haldia refinery	0.98, **13.5°**	2.32	2.47	56

[a] in 1:1 biphasic mixture of oil/solvent and 3.5% aq. NaCl. [b] Gelation requires heating-cooling cycle.

PSOG **1** worth considering. In order to facilitate the formation of a robust supramolecular network leading to gelation, we incorporated two different non-covalent interactions: Phe as a H-bonding motif, and an NDI core for pi-stacking. While H-bonding interaction has been universally used in nearly all PSOGs designed till date,[8–25] we feel that incorporating too many polar, protic H-bonding functionalities can render a gelator partially hydrophilic, and adversely affect its solubility in the hydrophobic oil phase. As an alternative to using multiple H-bonding functionalities, we included an NDI moiety that owing to a high quadrupolar moment (or pi-acidity) is likely to support a strong pi-stacking interaction.[27] It is worth noting that the use of pi-stacking interaction in past PSOG designs were limited to weakly pi-stacking, electron-rich aromatic units.[9,13–15,19,23,25] Further, to ensure adequate dispersibility of **1** in a nonpolar medium such as oil, the other N-terminal of the NDI unit is functionalized with an *n*-dodecyl group. The resultant increase in the hydrophobicity of **1** offers an added advantage, in terms of a near negligible solubility in water, even in oil-water biphasic mixture (~0.001 % Figure S5, Supporting Information). This in turn drastically reduces the bioavailability of the gelator,[28,29] and significantly decrease any undesirable exposure to the marine life. This was confirmed by an acute toxicology study of **PSOG1** on a group of adult zebrafish[§] (Figure S6 and video V1). The control molecule **C2**, on the other hand, is designed to bear an additional Phe group, at the expense of the hydrocarbon side-chain. The detrimental effect of this trade-off is immediately clear from Figure 1b. While PSOG **1** forms a stable gel with diesel, heavy crude oil, and other organic solvents (Figure S7 and S8), compound **C2** shows no gelating ability. Likewise, sacrificing the H-bonding Phe group in favour of an additional *n*-dodecyl chain also adversely affects the ability of **C3** to gel oil (Figure 1b). It is therefore, clear that the performance of a PSOG is critically dependent on the balance between non-covalent interactions, and its dispersibility in the gelling medium. Field emission scanning electron microscopy (FESEM) images of dried xerogel of **1** from methylcyclohexane, MCH (Figure 1 c,d and S9, Supporting Information) reveals a nanofibrillar (~35 nm diameter) morphology that hierarchically assembles to form highly porous globular microstructures.

The gel-forming ability of **1** was evaluated in a variety of organic solvents, refined petrochemical products and heavy crude oils (ONGC Mehsana asset and Haldia refinery), the results of which are presented in Table 1. While gelation of pure organic solvents such as cyclohexane and MCH require mild heating (40-50 °C) followed by cooling, that of crude oils and refined petrochemicals can be carried out at room temperature by simply dispersing **1** in the powder form. Since, petrochemicals are mixtures of various saturated (linear, branched and cyclic), aromatic and olefinic hydrocarbons,[30] we believe their interaction with PSOG **1** is significantly more complex compared to a pure organic solvent. Nevertheless, a superior gel-forming ability of **1** with crude and refined petroleum at ambient temperature is evidently a desirable trait from a practical standpoint. The critical gelation concentrations (CGC) were estimated to be within 1.25–2.32 wt%. It is quite encouraging noting that gelation of highly viscous and dense (0.91 and 0.98 g/ml) heavy crude oils can be carried out at a marginally higher gelator loading of 2.15–2.32 wt%. Further, the CGC values do not change appreciably even in a biphasic mixture of organic medium with water, or 3.5 wt% aqueous NaCl. The gels displayed good thermal and temporal stability, with gel-to-sol transition temperature (T_{gel}, at CGC) in the range of 55-60 °C. Under ambient conditions, the gels remain stable for several months. Thermoreversibility is an important attribute from the standpoint of fuel recovery from the gel.[11] Differential scanning calorimetry (Figure S10, Supporting Information) of a representative MCH gel shows an endotherm (at 59.8 °C) upon heating, and an exotherm (at 39.5 °C) while cooling, consistent with a reversible first-order phase transition.

Practical applicability of a PSOG demands that the gel remains stable under the application of shear forces. In order

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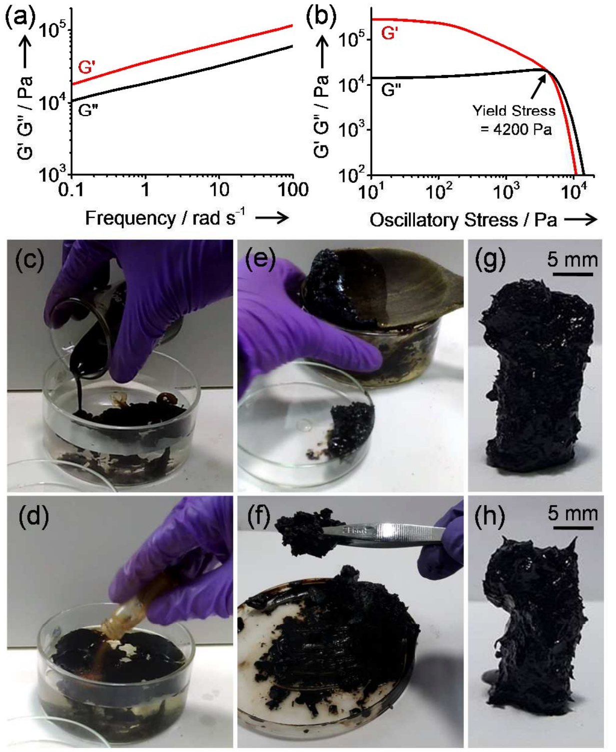

Fig. 2 Dynamic rheology of 3 wt% gel of **1** in diesel, (a) frequency sweep (b) oscillatory stress sweep. (c) 25 ml heavy crude oil (ONGC, Mehsana) added to 150 ml 3.5% aqueous NaCl solution. (d) 2.5 wt% PSOG **1** powder added. (e) Congealed oil scooped out after 20 sec. (f) Resultant gel shows remarkable stiffness. (g,h) Solidified gels of two different heavy oil crude oils placed vertically upright.

to characterize the mechanical properties, we performed rheological studies on diesel gel (crude-oil gel from artificial seawater, Figure S11) at twice the CGC (~3 wt%). Frequency sweep experiment carried out at a constant strain of 1% (Figure 2a, S11a) shows that the storage modulus (G′) remains significantly higher than the loss modulus (G″) over a wide range of frequencies, a clear signature of its elastic nature. Further, a very high value of G′ (10^4 – 10^5 Pa) indicates its outstanding stiffness. Dependence of G′ and G″ on the stress amplitude (Figure 2b, S11b) reveals an exceptionally high value of yield stress (4200 Pa), which is nearly *5 times higher* than the best reported value till date.[15] It is even higher than the recently reported oil-absorbed gelator-cellulose composite.[31] These results clearly demonstrate the remarkable ability of the PSOG **1** gel to withstand mechanical stress (Figure S10) associated with the process of recovery from the ocean surface and its eventual transportation.Further, temperature dependent rheology (Figure S12) confirms that the crude-oil gel retains its stiffness as well as elasticity at reasonably high temperatures (~ 48 °C), making it suitable for oil-spill remediation near tropics.

Having demonstrated the ability of **1** to gel oil at a significantly reduced concentration, we now evaluate its performance in a laboratory re-enactment of marine oil-spill (Figure 2c-f and video V2, Supporting Information). In a glass bath, heavy crude oil (ONGC Mehsana, 25 ml) was poured over a 3.5% aqueous solution of salt (150 ml) to simulate a real-life oil-spill scenario. PSOG **1** in dry powder form was sprinkled (2.5 wt%) over the oil layer. Quite remarkably, the entire crude oil layer fully congeals within *less than 20 seconds*, which can be subsequently scooped off leaving behind clear water with no gelator residue (see Supporting Information). Such an instantaneous gelation of heavy crude oil at such low gelator concentrations, without the aid of any dispersing or wetting solvent, has been hitherto unprecedented (Table T1, Supporting Information). The resultant gel displays exceptional stiffness and mechanical strength (Figure 2g-h) that allows one to handle it using tweezers.

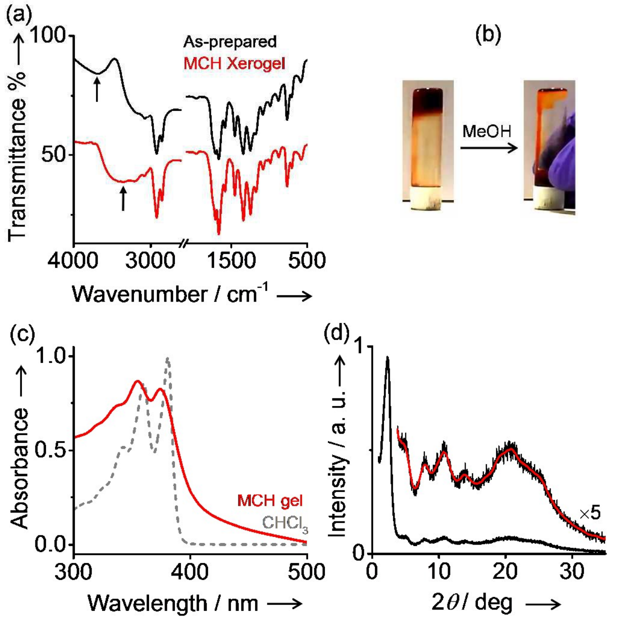

Fig. 3 (a) Comparison of O–H stretching frequency (black arrows) in the FTIR spectrum of as-prepared **1** vis-a-vis that of **1**/MCH xerogel. (b) Addition of a few drops of methanol completely disrupts the gel state of 2 wt% **1** in diesel (see video V4, Supporting Information). (c) Optical absorption spectrum of MCH gel (red) reveals H-type packing of NDI units, spectrum in $CHCl_3$ (grey, dashed line) is shown for comparison. (d) pXRD pattern of 2 wt% MCH xerogel (black line) shows partially crystalline structure. A magnified view of the $4 < 2\theta < 35$ region reveals several weak reflections; red curve is data after smoothing.

In recent times, oil exploration in the environmentally fragile arctic region has been a subject of heightened interest. Due to extreme weather conditions, responding to oil-spills in frozen seas poses additional challenges,[32] as the oil becomes more viscous and dense at low temperatures. To our great satisfaction, we found that **1** can successfully and rapidly congeal oil at temperatures below freezing (Figure S14, Supporting Information). Finally, a quantitative recovery of oil from gel by vacuum distillation was demonstrated using representative MCH gel (Figure S15 and video V3, Supporting Information). The gelator residue thus obtained can be successfully reused for further gelation.[†,33]

In order to understand the nature of various non-covalent interactions that makes PSOG **1** such a better candidate over

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other reported gelators, we carried out a detailed spectroscopic and structural investigation into the xerogel. Figure 3a presents the FTIR spectra of as-prepared **1**, vis-a-vis that of the dried xerogel from MCH. The O-H stretching frequency that appears at 3690 cm^{-1} in the as-prepared sample shifts to 3420 cm^{-1} in the xerogel. This large hypsochromic shift along with an overall broadening of the O-H stretching band is indicative of the presence of intermolecular hydrogen bonding in the xerogel. The role of H-bonding is however, best demonstrated by the fact that addition of a few drops of a competing H-bonding agent, such as methanol or acetic acid, completely disrupts the diesel gel[§§] (Figure 3b, Video V4). Optical absorption spectroscopy offers a convenient way to characterize the nature of NDI pi-stacking in the gel state (Fig 3c). The absorption spectrum of molecularly dissolved **1** in $CHCl_3$ (10 μM) is characterized by well-defined vibronic progressions at 380, 360 and 340 nm, typical of an isolated NDI chromophore.[34] In comparison, the solid-state absorption spectrum of a thin dried film of the xerogel (from MCH) shows a distinct reversal in the relative absorbance of the 0-0 (A_{0-0}) and 0-1 (A_{0-1}) vibronic features. The corresponding increase in the A_{0-1}/A_{0-0} ratio from 0.86 (in $CHCl_3$) to 1.06 (in xerogel) is a clear sign of exciton-coupled H-aggregation, through pi-stacking.[35] Powder X-ray diffraction (pXRD) pattern of MCH xerogel (Figure 3c) is dominated by a sharp low-angle peak at $2\theta = 2.33°$. In addition, several weaker reflections appear in the wide-angle region, including a broad peak at $2\theta = 25.3°$ (d = 3.52 Å) that is consistent with the presence of pi-stacking in the xerogel. The broad nature of XRD peaks indicates the partially crystalline nature of xerogel, which is expected considering the rapid rate of supramolecular gelation.

Conclusions

To conclude, we report a small molecule based organogelator that shows superior performance as a phase selective gelator for a variety of crude and refined petroleum products from water. Its unprecedented ability to congeal heavy crude oil in tens of seconds, even when applied in the powder form, marks a big improvement over the best reported organogelators till date. Its ease of synthesis, low gelation concentration, negligible aqueous solubility and bioavailability, ability to gel oil at 0 °C, excellent mechanical, thermal and temporal stability of the resultant gel, the ease of fuel recovery from gel, and reusability are the attributes that makes PSOG **1** a very promising candidate for marine oil-spill remediation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ We also synthesized **1** by a single-step condensation of naphthalene dianhydride with n-dodecylamine and Phe, followed by purification to separate **1** from symmetrically substituted NDI side-products (Supporting Information).

§ Toxicology experiment using live zebrafish were performed in compliance with the CPCSEA rules and guidelines set by the Institutional Animal Ethics Committee of IISER-Kolkata.

† While distillation of congealed crude oil can be carried out at refineries, it is not possible to recover the gelator that remains in the residue, subsequently used as bitumen. However, presence of low molecular weight gelators in bitumen is known to improve its mechanical properties, see Ref. 33.

§§ Methanol does not have a similar effect on crude-oil gel, in which the gelator-oil interactions are presumably more robust.

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