

Sacrificial amphiphiles: Eco-friendly chemical herders as oil spill mitigation chemicals

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Crude oil spills are a major threat to marine biota and the environment. When light crude oil spills on water, it forms a thin layer that is difficult to clean by any methods of oil spill response. Under these circumstances, a special type of amphiphile termed as “chemical herder” is sprayed onto the water surrounding the spilled oil. The amphiphile forms a monomolecular layer on the water surface, reducing the air–sea surface tension and causing the oil slick to retract into a thick mass that can be burnt in situ. The current best-known chemical herders are chemically stable and nonbiodegradable, and hence remain in the marine ecosystem for years. We architect an eco-friendly, sacrificial, and effective green herder derived from the plant-based small-molecule phytol, which is abundant in the marine environment, as an alternative to the current chemical herders. Phytol consists of a regularly branched chain of isoprene units that form the hydrophobe of the amphiphile; the chain is esterified to cationic groups to form the polar group. The ester linkage is proximal to an allyl bond in phytol, which facilitates the hydrolysis of the amphiphile after adsorption to the sea surface into the phytol hydrophobic tail, which along with the unhydrolyzed herder, remains on the surface to maintain herding action, and the cationic group, which dissolves into the water column. Eventual degradation of the phytol tail and dilution of the cation make these sacrificial amphiphiles eco-friendly. The herding behavior of phytol-based amphiphiles is evaluated as a function of time, temperature, and water salinity to examine their versatility under different conditions, ranging from ice-cold water to hot water. The green chemical herder retracted oil slicks by up to ~500, 700, and 2500% at 5°, 20°, and 35°C, respectively, during the first 10 min of the experiment, which is on a par with the current best chemical herders in practice.

INTRODUCTION

Chemical herders are defined as oil-collecting agents that herd oil spilled on a sea surface into thickened slicks, which can then be removed by in situ burning (ISB) (1). The use of chemical herders was initiated in 1970 to facilitate the mechanical recovery of crude oil by thickening the oil slick (2). Recently, their potential role in ISB, which has significant advantages as an oil remediation tool, has sparked the need for further research and development in this relatively unexplored area. ISB minimizes the long-term risks of persistent toxicity to the marine ecosystem. It is the only method that works in remote ice-covered water and loose drift ice conditions where booms cannot be deployed (3, 4). The essential requirement for ISB is the availability of an oil slick ~3 mm thick to initiate and maintain the burning process. When crude oil spills on the sea surface, it spreads quickly over the surface because interfacial tension forces are not balanced at the three-phase contact line at the edge of the oil slick. Air-seawater tensions ($\gamma_{A/W}$) are typically ~73.5 mN/m (~60 to 65 mN/m if a natural biofilm is present), and this is larger than the sum of the oil-water $\gamma_{O/W}$ and oil-air $\gamma_{O/A}$ tensions, which is about 25 mN/m (5, 6). As a result, the air-seawater interface pulls on the contact line, causing the oil to spread quickly because the spreading coefficient $S = \gamma_{A/W} - (\gamma_{O/W} + \gamma_{O/A})$ is positive. In a typical herding process, the herder is sprayed onto

the water surrounding the spilled oil. The herder is an amphiphile and forms a monomolecular layer on the water surface. Upon reaching the edge of the oil layer, the herder lowers the air–sea surface tension so that the spreading coefficient becomes negative, and the slick retracts as the air–oil and oil–water tensions pull back at the contact line (4) (Fig. 1, A to C). To keep the slick contracted, the herder should also be relatively insoluble in the water column to maintain the tension reduction. Currently, the best-known commercial herders are silicone polyethers, namely, Silsurf A108 and Silsurf A004-D (7, 8).

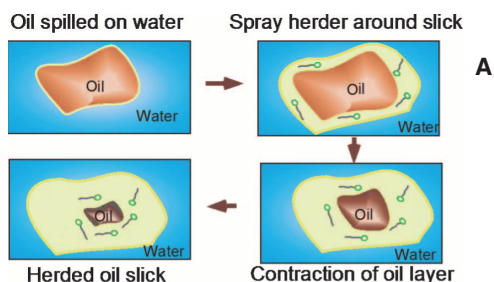
Although silicone herders are effective in thickening the spilled oil layer, their toxicological and environmental impacts are undocumented, and the lack of (bio)degradability indicates that they persist in the marine environment (9). This motivated us to create environment-friendly oil spill cleanup materials for a safe and sustainable future (10). The ultimate goal of this work is to develop safer and more broadly applicable herders from naturally occurring molecules that meet the hallmarks of a commercially available herder.

More specifically, our objective is to design and develop sacrificial and effective green herding amphiphiles based on phytol (11), a terpenoid (isoprenoid) with isoprene units as the hydrophobic tail and esterified with a cation (1-methylimidazolium/pyridinium) as the polar group, which offers a variety of chemical interactions, including electrostatic attraction, π - π stacking, and hydrogen bonding with water, to lock the herder at the air–seawater interface ensuring a large air–seawater tension reduction and a strong herding action (Fig. 2). We chose phytol as the starting material for several reasons: (i) It is a natural and abundant component of the marine biota as part of the chlorophyll molecule (12), and after release from chlorophyll (through

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Top view of herding process



Side view

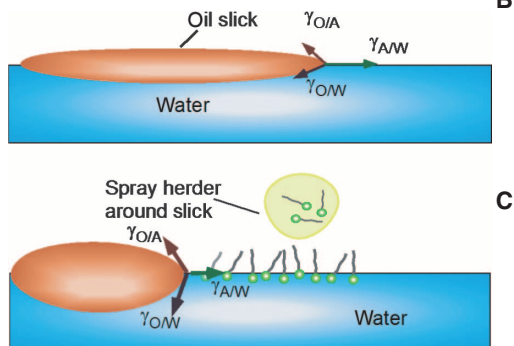


Fig. 1. Cartoon showing the herding process. (A) Top view shows the sequence of events starting from the spill of oil on water surface followed by the addition of 20 μl of herder delivering 2.34 mg of herder based on the standard dose of 150 mg/m^2 with a micropipette, altering the interfacial forces at the edge of oil slick and thus retracting the oil slick. (B and C) Side view of the herding process in terms of spreading coefficient and interfacial tension. (B) A positive value of spreading coefficient (S) refers to the spreading of crude oil onto seawater surface. (C) Application of herder at the edge of oil slick lowers the air-seawater interface causing a retraction of the oil slick with $S < 0$.

natural pathways), it is found as a major component of the sea surface microlayer—the layer of seawater immediately underneath the surface (13, 14). (ii) Phytol is biodegraded in the marine environment (11), and in particular, the isoprenoids found in marine and lacustrine sediments have been attributed to phytol biodegradation by marine bacteria (15, 16). (iii) Phytol is easily available and inexpensive and can be obtained directly from marine algae (17). (iv) The presence of the allylic bond of phytol next to the ester functional group facilitates rapid hydrolysis of the amphiphile, releasing the very water-soluble cationic group into the water column where it is readily diluted. The phytol hydrophobic terpenoid chain remains on the surface to maintain the tension reduction necessary for herding and is then further degraded along the usual phytol degradation pathways (15, 16).

To validate the design of the green herders, we tested a straight chain analog of (a) or (b), including cetyltrimethylammonium bromide (CTAB) and other surfactants (Supplementary information S1 and fig. S1) that proved less effective when compared to the proposed green herders; the results highlight the importance of phytol's novel, branched isoprene chain. We believe that the ester hydrolysis of the herder amphiphile to the phytol hydrophobe tail, which is degraded, and the release of the water-soluble cationic group into the water column where it is rapidly diluted make this design eco-friendly.

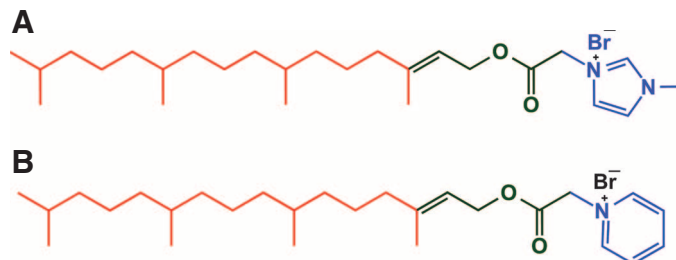


Fig. 2. Chemical design of proposed green herders. (A) 1-Methyl-3-(2-oxo-2-((phytyl)oxy)ethyl)-1H-imidazol-3-ium bromide (**PIIm**); (B) 1-(2-oxo-2-((phytyl)oxy)ethyl)pyridin-1-ium bromide (**PPy**). Red color indicates the phytol tail for optimum lipophilicity; green color indicates the ester bond next to allyl bond triggering quick hydrolysis to make it sacrificial; blue color shows the cationic head for a variety of interactions like electrostatic, π - π , and hydrogen bonding that help in locking the herder at the air-water interface.

RESULTS AND DISCUSSION

We prepared two types of cationic amphiphiles differing in their head group, that is, 1-methyl imidazolium and pyridinium, using experimental protocols reported elsewhere (18). The detailed procedure of synthesis and structural characterization of these molecules [^1H NMR (nuclear magnetic resonance) and ESI-HRMS (electrospray ionization high-resolution mass spectrometry)] is reported in Materials and Methods. Figure 2 shows the design of the phytol-based cationic amphiphiles, 1-methyl-3-(2-oxo-2-((phytyl)oxy)ethyl)-1H-imidazol-3-ium bromide and 1-(2-oxo-2-((phytyl)oxy)ethyl)pyridin-1-ium bromide, hereinafter abbreviated as **PIIm** and **PPy**, respectively, for convenience. We next studied the efficacy of the newly synthesized phytol-based amphiphiles as chemical herders. An amphiphilic molecule should fulfill the following requirements to act as a herder: (i) its physical state should be liquid at temperatures of potential use, that is, 5° to 35°C; (ii) it should spread spontaneously into a thin surface film on water; (iii) it should have a low evaporation rate; and (iv) it lowers the surface tension of water to ~ 25 mN/m (19).

Figure 3 schematically demonstrates the various steps involved in the herding process over a period of 30 min. The average slick thickness was calculated by dividing the volume of added crude oil by the area occupied by the oil slick in the image (7). The error in calculating the area of slick is negligible, being less than 2% with the parallax error at the wall of the plastic trays taken into account. Movie S1 shows a video of a herding experiment carried out in our laboratory using the green herder **PIIm**. The versatility of **PIIm** and **PPy** as green herders under different weather conditions was tested by varying the water salinity and temperatures. Two different water salinities, that is, fresh tap water and saline water (prepared by dissolving 41.8 g of sea salt per liter of deionized water), and three different temperature conditions, that is, cold ($\sim 5^\circ\text{C}$), ambient ($\sim 20^\circ\text{C}$), and warm ($\sim 35^\circ\text{C}$), were considered to mimic a range of salt concentration and water temperatures.

The herding efficiency of **PIIm** and **PPy** was measured by calculating the percent increase in thickness of the crude oil slick after herding. Figure 4 depicts the percent increase in thickness of the slick as a function of time at different temperatures and water salinities. The increase in thickness of the slick was more substantial during the first 10 min as discussed in the next section. As seen from Fig. 4 (A to C), the increase in thickness during the first 10 min was $\sim 500\%$ at 5°C, $\sim 700\%$ at 20°C, and $\sim 2500\%$ at 35°C. Thus, herding is enhanced at higher temperatures partly because the oil and water viscosities are inversely

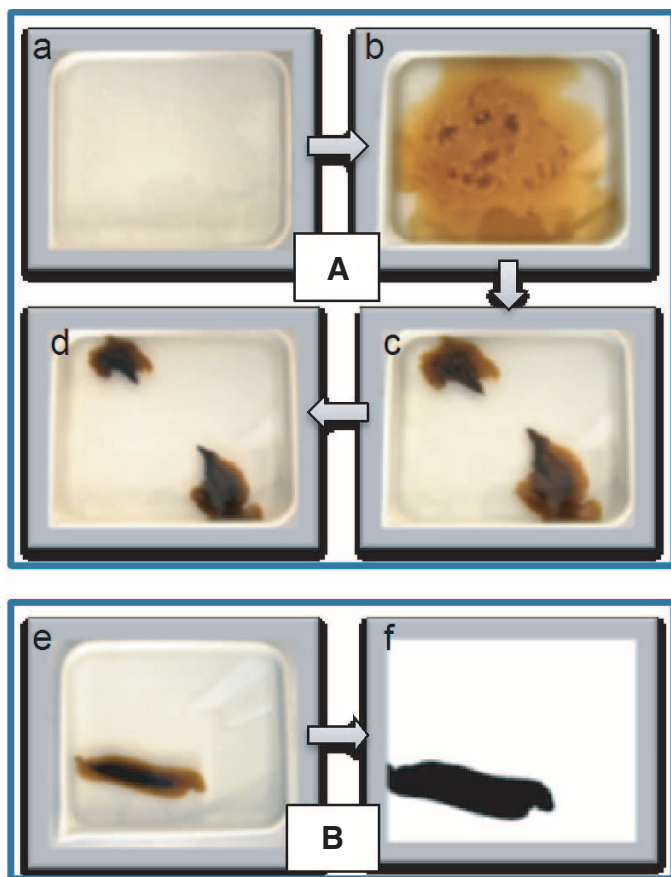


Fig. 3. Pictorial presentation of the herding process of crude oil in the laboratory to mimic real oil spill conditions. (A) Real photographs of the herding process. (a) Water filled in a tray up to 2 cm deep representing oil-free water surface. (b) Macondo crude oil (2 ml) was added on the water surface to create an oil spill scene. (c) Instantaneous shrinking of oil slick after herder injection. (d) Further shrinking of oil slick until 10 min of herder injection. **(B)** Conversion of a digital photograph to a binary picture to determine the area of oil slick (total number of black pixels divided the by the number of pixels per unit area in the original image, using ImageJ).

proportional to temperature and fluid motion is easier (20, 21). However, here, the relevance of such results is to propose the suitability of these herders for use in water at higher temperatures. **PI_m** performed slightly better than **PPy** at all three temperatures and in both freshwater and saline water. This might be due to the difference in the cationic head group responsible for a variety of secondary interactions. However, water salinity did not significantly affect the herder's effectiveness in all cases as shown in Fig. 4 (A and B), in agreement with the observations made by Buist and co-workers (3). In all three conditions, **PI_m** performed better than **PPy**; that is, at 5° and 20°C, the increase in thickness was ~1000%, and at 35°C, it was ~2500%. Further, **PI_m** demonstrated similar performance to the commercial silicone-based herder Silsurf in cold water by increasing the thickness of oil slick by ~1000% for the initial 30 min, as shown in Fig. 4D.

Herding efficiency

The herding efficiency is defined in terms of herding dynamics, that is, how fast or slow herding occurs. As shown in Fig. 4 (A

to C), the increase in thickness of the crude oil slick is more substantial during the first 10 min. As the herder solution touches the water surface, a surface tension gradient is generated because of non-uniformities in the surfactant's interfacial concentration resulting in Marangoni stresses (22), hence leading to a surface tension-driven retraction of the oil slick.

Marangoni forces direct the herder solution to move from higher to lower concentration; this concentration gradient causes the retraction of thin oil layer (23, 24). Experimental data for the herding process starting from the moment when herder was placed onto the water surface to the final moment of retraction (final stage of the herding was assumed when there is no change in the area of oil slick) are shown in Supplementary information S2 and fig. S2.

It can be deduced that both green herders show similar herding dynamics to Silsurf; therefore, green herders are as efficient as the state-of-the-art silicone-based herder. As mentioned earlier, a good herder has to lower the air-seawater interfacial tension to low values, should be insoluble in water, and should partition at the air-water interface to form monomolecular films onto the water surface, thus significantly reducing the surface tension of water. The details of the individual surface and interfacial tension values are given in Supplementary information S3 to S5 (figs. S3 to S5).

The sacrificial (degradation) tendency of phytol-based herders was investigated by analyzing the mass spectra of the aqueous solution of the green herder **PPy**. The mass spectra of the aqueous solution of **PPy** after certain time intervals were recorded (Supplementary information S6 and fig. S6). The data show the disappearance of peak 416.35 corresponding to the parent compound (the green herder) after a month, whereas various other peaks were generated showing the presence of fragmented products. A recent study by our group on farnesol-based cationic amphiphiles and their time-dependent hydrolysis in water (25) showed that a pyridinium analog of farnesol started hydrolyzing in 6 hours and completed the hydrolysis in 48 hours. We hypothesized that phytol (a diterpenoid) and farnesol (a sesquiterpenoid) have common structural features, which may undergo a similar hydrolytic pathway in water. Thus, green herders, upon rearrangement of the phytol tail, will release small molecules and other degradation products that will not be harmful to marine biota. On the other hand, Silsurf, a well-known superspreader, works very well in water and its aqueous solution is stable; therefore, it remains in water for a long time.

Thus, the design and function of phytol-based green herder make them appealing over silicone herders and present an excellent alternative because of their efficient and effective herding ability and environmental friendliness. Additionally, green herders are based on a plant-derived molecule, pose no threat to the marine environment, and are degraded by hydrolysis and therefore do not persist in the marine environment.

Conclusion

Effective, eco-friendly, and sacrificial phytol-based green herders were developed as an alternative to currently used silicone-based herders. Their herding efficiency was compared with a commercial silicone-based herder under different temperatures and water salinities to confirm their versatility. We observed that application of **PI_m** increased the thickness of crude oil by ~1000%, similar to its commercial counterpart. The added advantage of the newly synthesized green herder over the commercial silicone-based herder is its propensity to hydrolyze quickly after herding. We found that phytol-based green herders

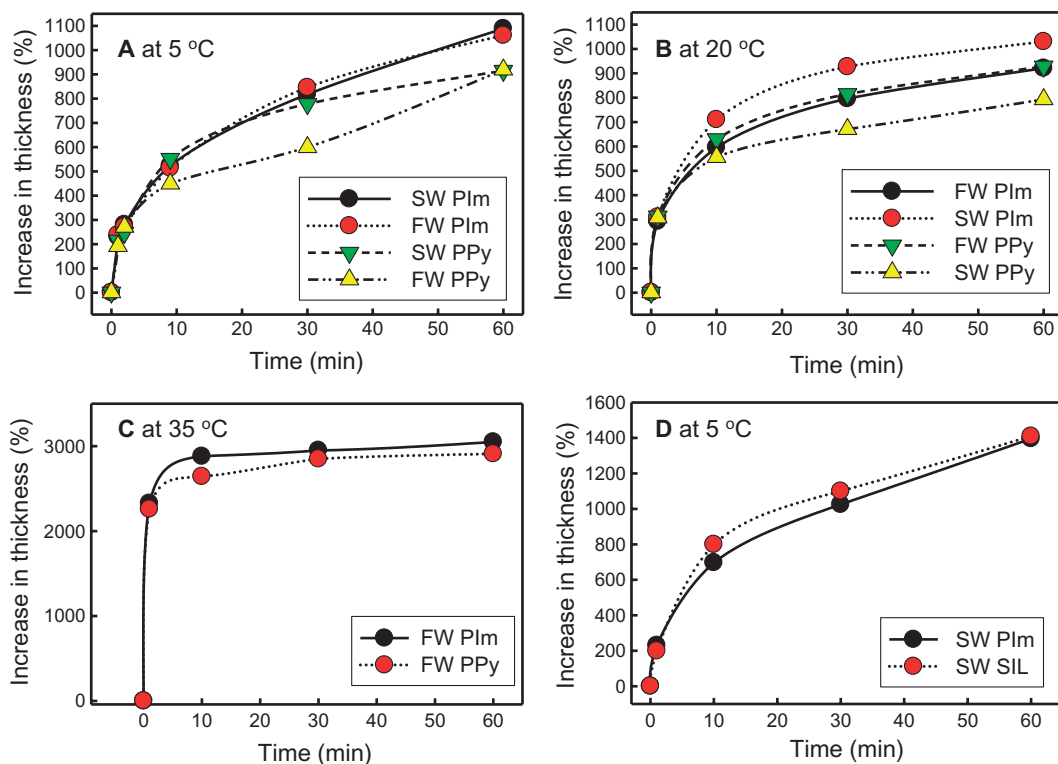
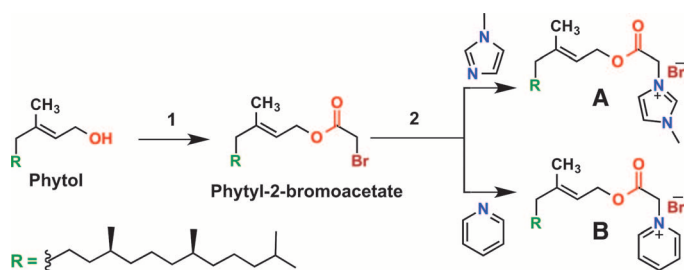


Fig. 4. Evaluation of green herder's effectiveness as a function of time, temperature, and water salinity. (A to C) Change in thickness for **PIm** and **PPy** in freshwater (FW) and saline water (SW) at 5°C (A) and 20°C (B) and only in freshwater under a warm condition (35°C) (C). **(D)** Change in thickness for Silsurf and **PIm** in saline water at 5°C mimicking cold water conditions.



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MATERIALS AND METHODS

Materials

The following materials were used: phytol, bromoacetic acid, 1-hexadecanol, *N*-methyl imidazole, pyridine, toluene, CTAB, SDS, Brij-35, Louisiana sweet

crude oil [obtained from the BP Macondo Prospect (SOB-20100617032)], toluene, sea salt, and deionized water.

Synthesis of green herders

The synthesis of green herders (**PIm** and **PPy**) was carried out in a two-step process as shown in Scheme 1. The first step comprises the synthesis of phytol-2-bromoacetate. In a typical procedure, phytol (2 mmol) was reacted with bromoacetic acid (2 mmol) under solvent-free conditions with stirring for 22 hours at 68°C. The reaction mixture was dissolved in 100 ml of hexane and washed twice with 100 ml of water; the combined organic portions were dried using Na_2SO_4 and removed under reduced pressure in a rotary evaporator at 40°C. Subsequent purification on a silica gel (200 to 400 mesh) column chromatography using hexane afforded pure phytol-2-bromoacetate in 50% isolated yield; 500-MHz ^1H NMR (CDCl_3) δ ppm: 0.84 to 0.86 (12H 4 \times - CH_3 proton), 1.06 to 1.53 (19H alkyl proton from phytol tail), 1.69 to 1.74 [3H -(CH_3)C=CH-], 2.0 to 2.06 [2H -(CH_3)C- CH_2 - CH_2 -], 3.81 (2H from - $\text{COO}-\text{CH}_2$ -Br), 4.66 to 4.69 (2H from - $\text{COO}-\text{CH}_2$ -CH=), 5.33 [1H from - $\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2$ -].

The second step involves the synthesis of cationic amphiphiles. In an oven-dried single-neck round-bottomed flask equipped with a magnetic stir bar, phytol-2-bromoacetate (1 mmol) synthesized was dissolved in 1 ml of dry chloroform followed by addition of *N*-methyl imidazole or pyridine (1 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 50°C for 2 hours. The chloroform was removed from the crude reaction mixture under reduced pressure at 50°C and was subsequently washed with a minimal amount of diethyl ether and dried under high

vacuum. A translucent highly viscous product was obtained, which was characterized by ^1H NMR and ESI-HRMS.

Characterization of PIm: Off white translucent viscous liquid, yield 80% (with respect to starting phytol-2-bromoacetate); 500-MHz ^1H NMR (DMSO- d_6) δ ppm: 0.84 to 2.0 (alkyl protons of phytol tail), 3.92 (3H, N-CH $_3$), 4.67 to 4.68 (2H, -COO-CH $_2$ -), 5.26 (2H, -COO-CH $_2$ -N $^+$ -), 5.33 (1H, -COO-CH $_2$ -CH-), 7.76 (2H, NCHCHN-), 9.14 (1H, -NCHN-); ESI-HRMS positive ions mass/charge ratio (m/z) calculated, 419.3638 (100%), 420.3671 (28.9%), and 421.3705 (4%) for (M^+ -Br $^-$) or M^+ ; found, 419.3644, 420.3696, and 421.3731, respectively.

Characterization of PPy: Light pale translucent viscous liquid, yield ~82% (with respect to starting phytol-2-bromoacetate); 500-MHz ^1H NMR (DMSO- d_6) δ ppm: 0.81 to 2.5 (alkyl protons of phytol tail), 4.60 to 4.72 (2H, -COO-CH $_2$ -CH-), 5.31 to 5.33 (1H, -COO-CH $_2$ -CH-), 5.70 (2H, -COO-CH $_2$ -N $^+$ -), 8.25 (2H pyridinium H), 8.73 (1H pyridinium H), 9.06 to 9.07 (2H, pyridinium H), ESI-HRMS positive ions m/z calculated, 416.3529 (100%), 417.3562 (30%), and 418.3596 (4.3%) for (M^+ -Br $^-$) or M^+ ; found, 416.3503, 417.3521, and 418.3560, respectively.

Herding experiments

A plastic tray was filled with water up to 2 cm deep, and then the calculated amount of oil was poured on the water surface and allowed to spread to equilibrium to create a thin film of oil. A digital photograph was taken from an automatic overhead camera for subsequent oil area analysis. Next, the recommended dose of green herder (20 μl of herder's stock solution in toluene delivering 2.34 mg of herder based on the standard dose of 150 mg/m 2) was supplied using a micropipette and, instantaneously, the thin oil layer contracted to a thick oil slick. Photographs were taken every minute for at least 60 min. The herding experiments were performed at two water salinities, that is, freshwater and saline water (the latter was prepared by dissolving at 41.8 g/liter), and under three different temperature conditions, that is, room temperature (~20°C), cold (~5°C), and warm (~35°C). The effects of water salinities and temperature on the thickness of herded oil slick were evaluated over time. The captured images were processed using ImageJ software to determine the area of oil slick that was used to calculate the change in thickness with time (Supplementary information S7, fig. S7, and table S1).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/1/5/e1400265/DC1>

S1. Synthesis of saturated analog.

S2. Herding efficiency in terms of herding dynamics.

S3 to S5. Determination of surface tension and interfacial tension using the pendant drop method.

S6. Hydrolysis proof from mass spectroscopy.

S7. ImageJ computer program.

Fig. S1. Reaction scheme of the synthesis of hexadecylpyridinium bromide.

Fig. S2. Evaluation of the herding efficiency by fitting the area of oil slick obtained at 20°C in freshwater as a function of time.

Fig. S3. Air-water surface tension for PIm using a pendant drop tensiometer.

Fig. S4. Toluene-water interfacial tension for PIm using Pendant drop tensiometer.

Fig. S5. In situ air-water surface tension of PIm using a Wilhelmy plate tensiometer.

Fig. S6. ESI-HRMS of PPy at the beginning, after 8 days, and after 1 month.

Fig. S7. Representative example of calculating the thickness of oil slick using ImageJ computer program.

Table S1. Data obtained for different images of an oil slick spread over freshwater at 20°C in a plastic tray; PPy was used as a chemical herder to retract the oil slick.

Movie S1. Oil herding experiment at the lab scale mimicking an oil spill scenario.

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