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 underexplored 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 $\gamma_{OW}$ and oil-air $\gamma_{OA}$ 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 $S = \gamma_{A/W} - (\gamma_{OW} + \gamma_{OA})$ 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 environmentally 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...
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 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.

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 […] and pyridinium-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.
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) Mavondo 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 by the number of pixels per unit area in the original image, using ImageJ).

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 PIm 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...
completely hydrolyze in a month. We suggest exploiting the applicability of PIm and PPy green herders as safe and effective oil spill mitigation chemicals for a sustainable future.

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 Na₂SO₄ 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 (CDCl₃) δ ppm: 0.84 to 0.86 (12H 4×-CH₃ proton), 1.06 to 1.53 (19H alkyl proton from phytol tail), 1.69 to 1.74 [3H -(CH₃)C=CH-], 2.0 to 2.06 [2H -(CH₃)C-CH₂-CH₂-], 3.81 (2H from -COO-CH₂-Br), 4.66 to 4.69 (2H from -COO-CH₂=CH-), 5.33 [1H from -CH=C(CH₃)CH₂-].

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 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 Na₂SO₄ 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 (CDCl₃) δ ppm: 0.84 to 0.86 (12H 4×-CH₃ proton), 1.06 to 1.53 (19H alkyl proton from phytol tail), 1.69 to 1.74 [3H -(CH₃)C=CH-], 2.0 to 2.06 [2H -(CH₃)C-CH₂-CH₂-], 3.81 (2H from -COO-CH₂-Br), 4.66 to 4.69 (2H from -COO-CH₂=CH-), 5.33 [1H from -CH=C(CH₃)CH₂-].

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.
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-d6) δ ppm: 0.84 to 2.0 (alkyl protons of phytol tail), 3.92 (3H, N-CH3), 4.67 to 4.68 (2H, -COO-CH2-), 5.26 (2H, -COO-CH2-N-), 5.33 (1H, -COO-CH2-CH2-), 7.76 (2H, NCH=CHNH), 9.14 (1H, -N=CH-); 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-d6) δ ppm: 0.81 to 2.5 (alkyl protons of phytol tail), 4.60 to 4.72 (2H, -COO-CH2-CH2-), 5.31 to 5.33 (1H, -COO-CH2-CH2-), 5.70 (2H, -COO-CH2-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/m2) 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).

REFERENCES AND NOTES


Author contributions: D.G. and G.J. conceived and designed the experiments. D.G. carried out the synthesis, characterization, and evaluation of herders. B.S. and K.T. helped in herding experiments. D.G., V.J., C.M., and G.J. discussed and analyzed the results. D.G. prepared the manuscript. G.J. supervised the project. Competing interests: The authors declare that they have no competing interests. Data and materials availability: Reprint and permission information is available online at http://advances.sciencemag.org/reprints. Requests for materials can be addressed to G.J. (john@sci.ccny.cuny.edu), C.M. (charles@che.ccny.cuny.edu), and V.J. (vij@tulane.edu).

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