

Supplementary Materials for **Sacrificial amphiphiles: Eco-friendly chemical herders as oil spill mitigation chemicals**

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Other Supplementary Material for this manuscript includes the following:
(available at www.advances.sciencemag.org/cgi/content/full/1/5/e1400265/DC1)

Movie S1 (.mp4 format)

S1. Synthesis of saturated analog.

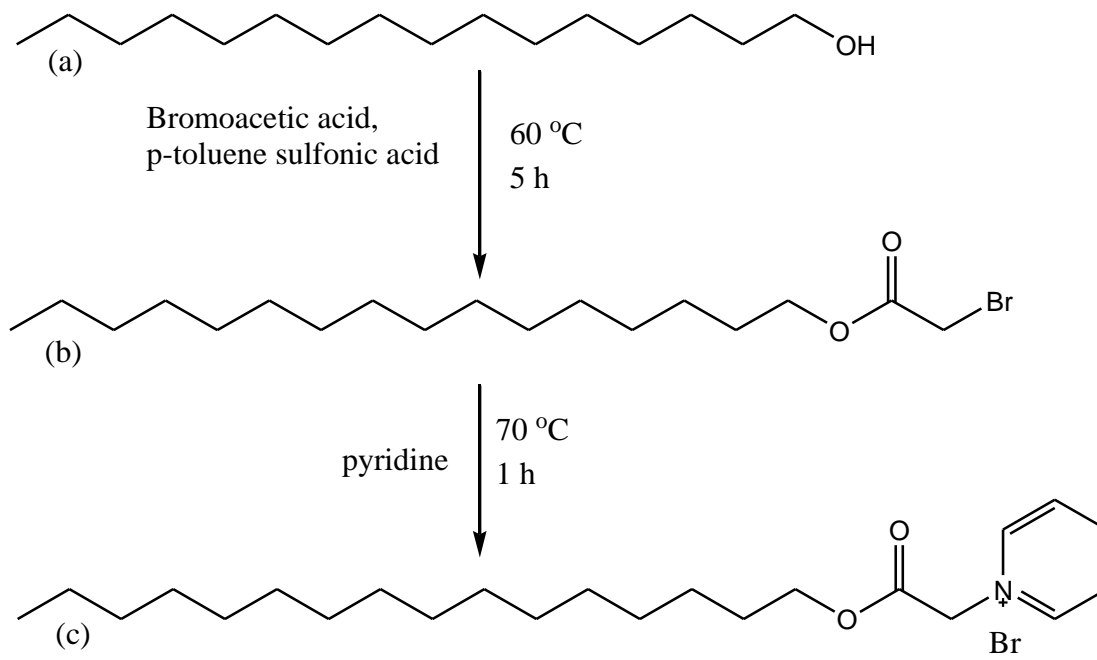


Fig. S1. Reaction scheme of the synthesis hexadecylpyridinium bromide.

In a typical procedure 1-hexadecanol (2 mmol) (a) was reacted with bromoacetic acid (2 mmol) in presence of catalytic amount of *p*-toluene sulfonic acid in solvent free conditions with stirring for 5 hours at 60°C. The reaction mixture was extracted with 100 ml of chloroform and washed twice with 100 ml of water, dried using anhydrous Na₂SO₄ to get hexadecyl-2-bromoacetate (b). The second step involves the quaternization of pyridine with hexadecyl-2-bromoacetate (b) resulting into hexadecylpyridinium bromide (c). In an oven dried single neck round bottom flask equipped with a magnetic stir bar, hexadecyl-2-bromoacetate (1 mmol) (a) synthesized in step 1 was dissolved in 1 ml of dry chloroform followed by addition of pyridine (1 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 70°C for 1 hour. The chloroform was removed from crude reaction mixture under reduced pressure at 50°C and was subsequently

washed with minimum amount of diethyl ether and dried under high vacuum. White powder was afforded and was characterized by ¹H-NMR, ESI-HRMS.

White powder, Yield 90%, (with respect to starting phytyl-2-bromoacete); 500 MHz ¹H NMR (CDCl₃) δ ppm: 9.40 (2H, pyridinium H), 8.48 (1H pyridinium H), 8.04 (2H pyridinium H), 6.28 (2H, -COO-CH₂-N⁺-), 4.18 (2H, -COO-CH₂-CH-), 0.84-2.14 alkyl protons of hexadecyl tail. ESI-HRMS positive ions m/z calculated 362.3059 (100%), 363.3093 (30%) and 364.3126 (4.3%) for (M⁺-Br⁻) or M⁺, found 362.3035, 363.3061 and 364.3126 respectively.

S2. Herding efficiency in terms of herding dynamics

Experimental data for the entire time scale of the herding process that is from the moment when the herder was placed on the water surface to the final moment of observation (final stage of the herding was assumed when there is no change in the area of oil slick) is plotted in Figure 5 using the following simplified equation

$$-\frac{dA}{dt} = kA$$

The first order dependence of surface area (or thickness for a given total volume of oil) reflects the fact that the mass of oil per unit surface area increases during the oil retraction step resulting in an increased difficulty of retraction. Thus:

$$\frac{A_t - A_0}{A_\infty - A_0} = 1 - \exp(-kt); A_0: \text{Initial area at } t = 0, A_t: \text{Area at time } t, A_\infty: \text{Final area at time } \infty.$$

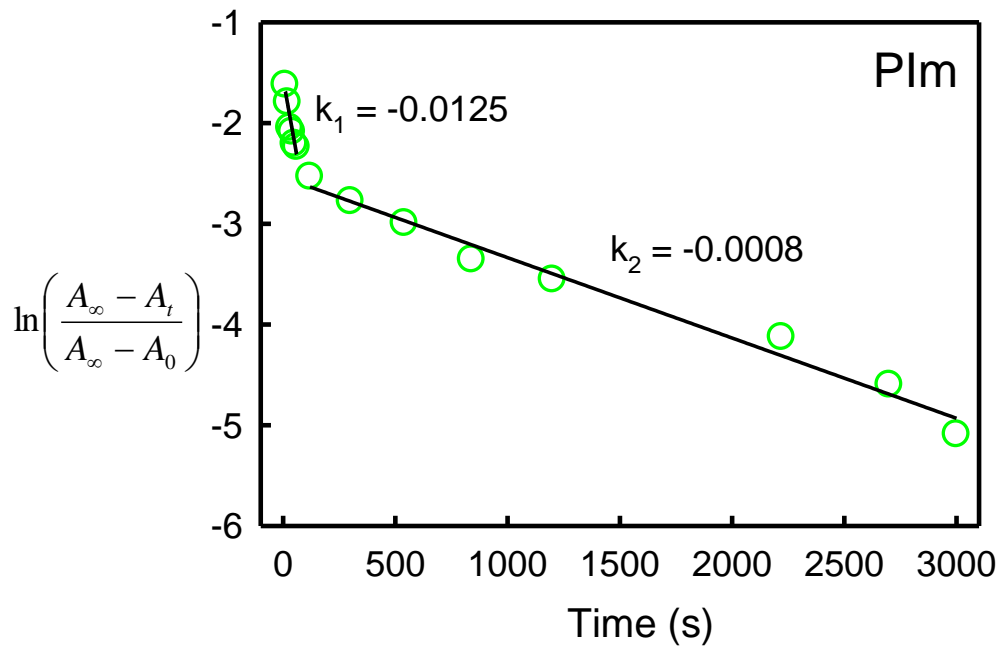
$$\ln\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) = -kt,$$

The data is fit by multiple rate constants to reflect early and late stages of oil slick retraction. It can be concluded from the graphs that both green herders show equivalent dynamics to Silsurf. These results suggest that green herders are as efficient as the state of the art silicone based herder. The first order dependence of surface area (or thickness for a given total volume of oil) reflects that the mass of oil per unit surface area increases during the oil retraction step resulting in an increased difficulty of retraction. Thus:

$$\frac{A_t - A_0}{A_\infty - A_0} = 1 - \exp(-kt); A_0: \text{Initial area at } t=0, A_t: \text{Area at time } t, A_\infty: \text{Final area at time } \infty.$$

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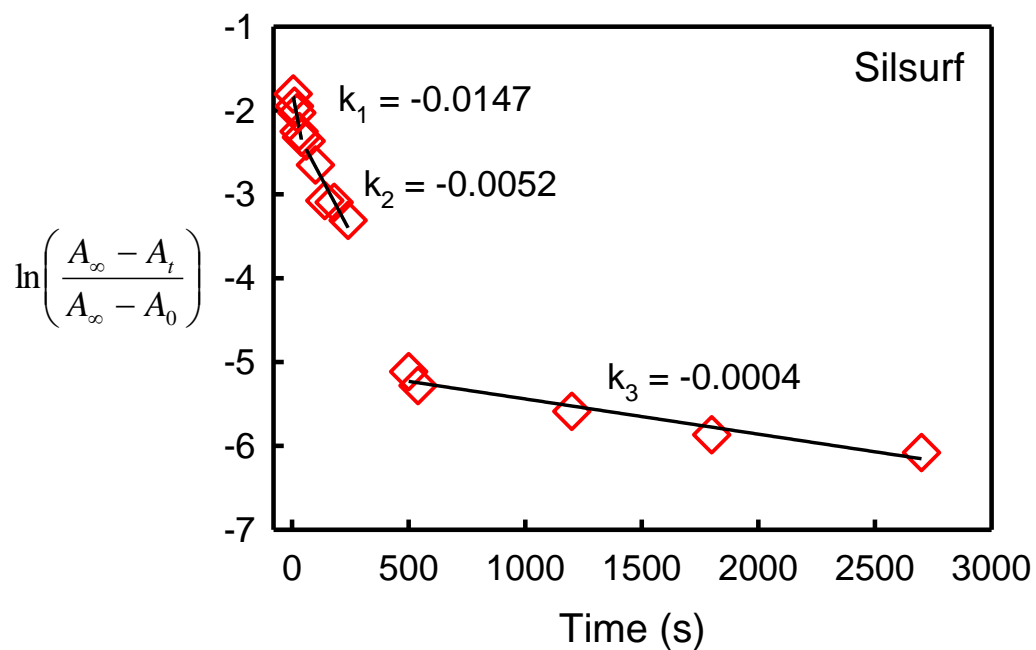
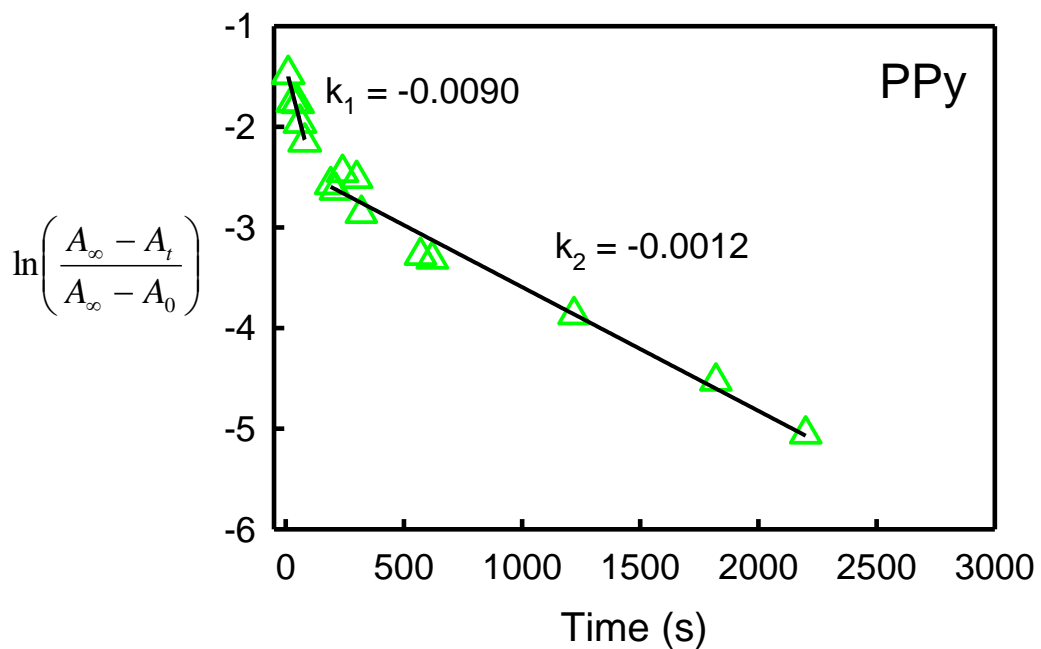


Fig. S2. Evaluation of the herding efficiency by fitting the area of oil slick obtained at 20°C and in freshwater as a function of time.

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

The dynamic interfacial tension of **PIm** and **PPy**: The water-air interface containing PIm or PPy was investigated using the pendant drop technique (Attention Theta tensiometer, Biolin Scientific, Finland). The tensiometer is a real-time droplet analyzer that allows continuous droplet profile extraction. An inverted 16-gauge needle is submerged in the aqueous phase such that the tip is visible in the frame of capture. A gastight syringe [1 ml] (Hamilton Co., USA) is mounted in a microsyringe pump (Harvard Apparatus) to ensure instantaneous creation of a air bubble of preset volume. Before the bubble is formed, the image capture software is triggered, collecting images at 1 frame/s for the first 10 min and 1 frame/min thereafter, for a total aging time of 3,000 s. Edge detection is used to identify the droplet shape, with the interfacial tension determined using the Young–Laplace equation. Experimental runs of 1200s are chosen as surfactant solution attains equilibrium within the chosen time frame.

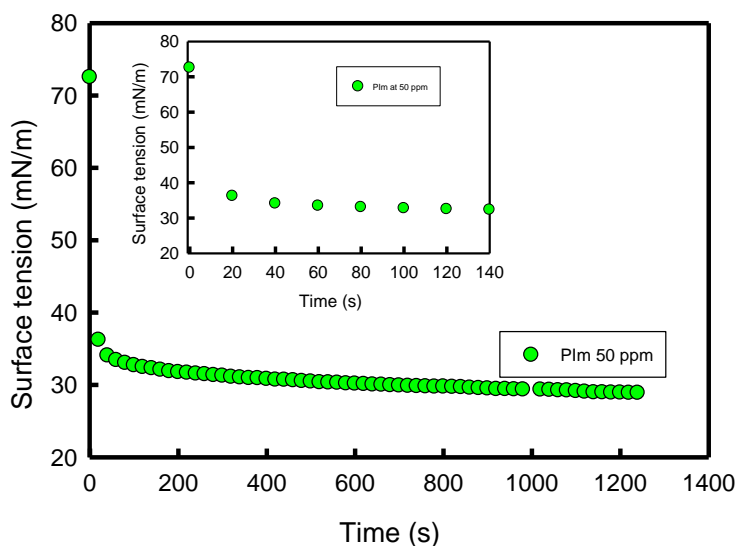


Fig. S3. Air-water surface tension for **PIm** using a pendant drop tensiometer.

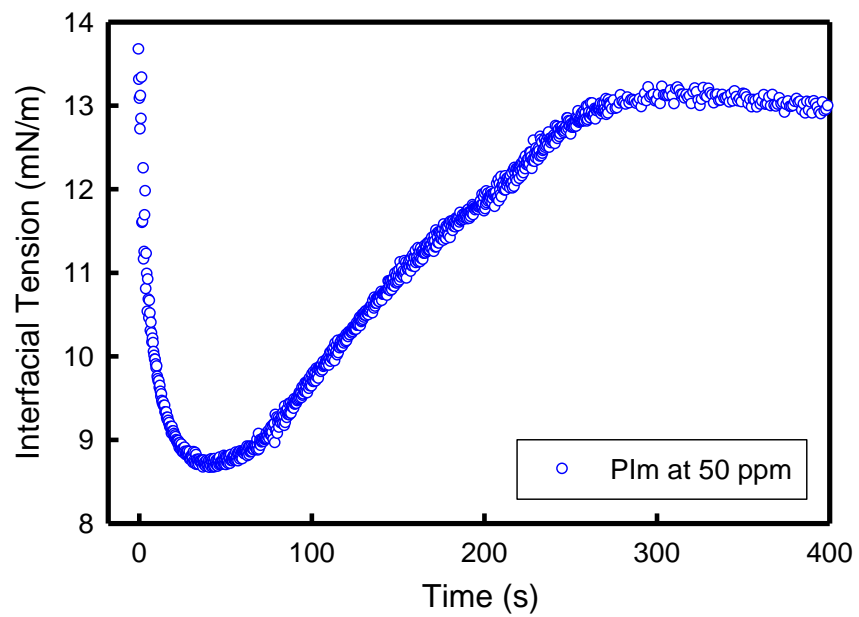


Fig. S4. Toluene-water interfacial tension for **PIm** using Pendant drop tensiometer.

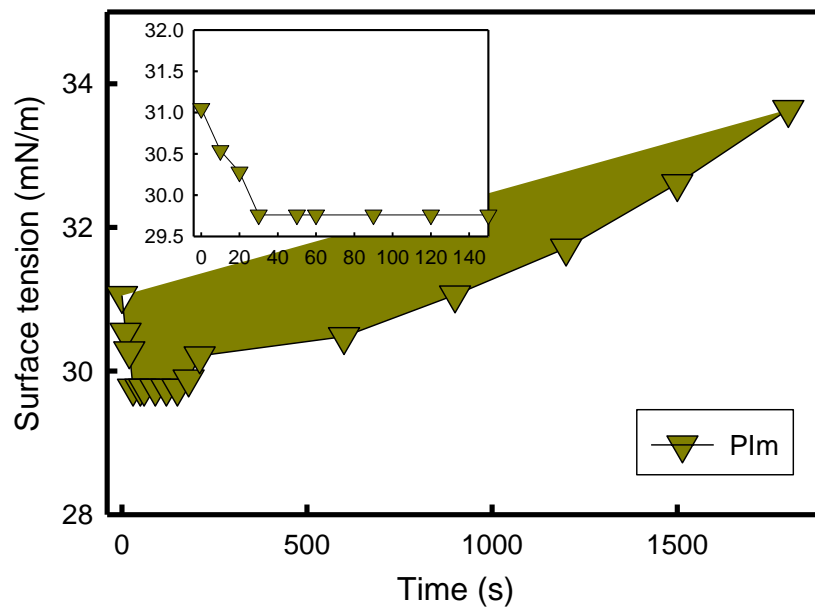
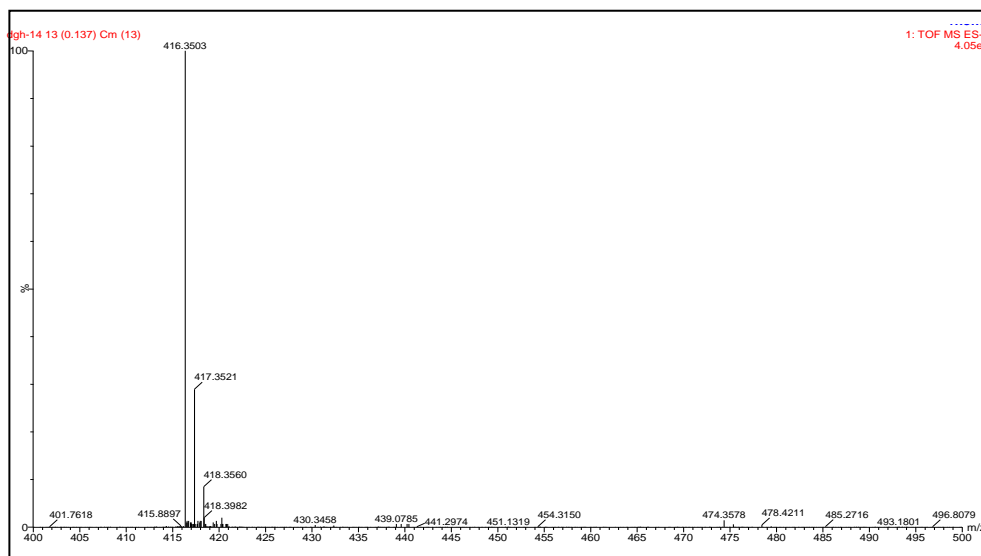


Fig. S5. In situ air-water surface tension of **PIm** using a Wilhelmy plate tensiometer.

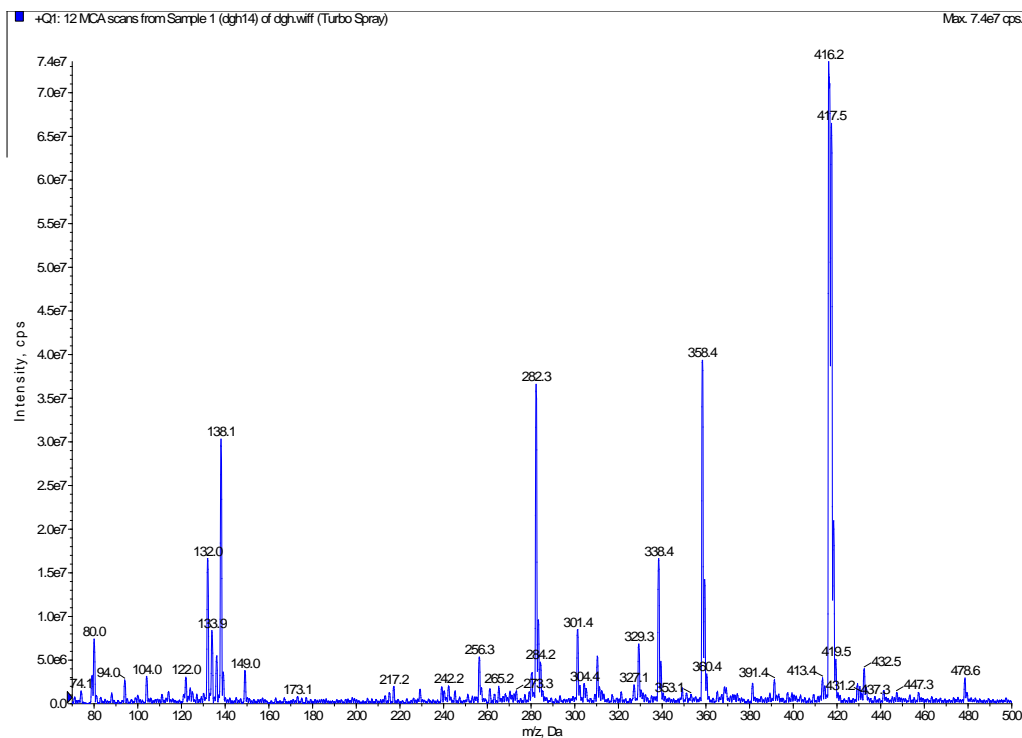
S6. Hydrolysis proof from mass spectroscopy.

Mass spectrum after eight days shows the presence of many peaks corresponds to the presence of hydrolysis products and the mass spectrum after one month shows the complete disappearance of peak of parent compound at 416.3503. It gives the clear indication that phytol based amphiphiles does not stay in marine biota for long time and degrade soon as they finish their job of herding. The presence of ester functionality next to allyl double bond in phytol-based herder molecules makes them sacrificial. Our previous study show that the presence of an allyl double bond next to ester functionality activates the ester group for early hydrolysis. The presence of particular head group i.e. N-methyl imidazolium or pyridinium affects the extent of hydrolysis. The detailed analysis on the kinetics of hydrolysis is under investigation and would be submitted soon for review as next part of this research work.

PPy in water at the beginning



After 8 days



After 1 month

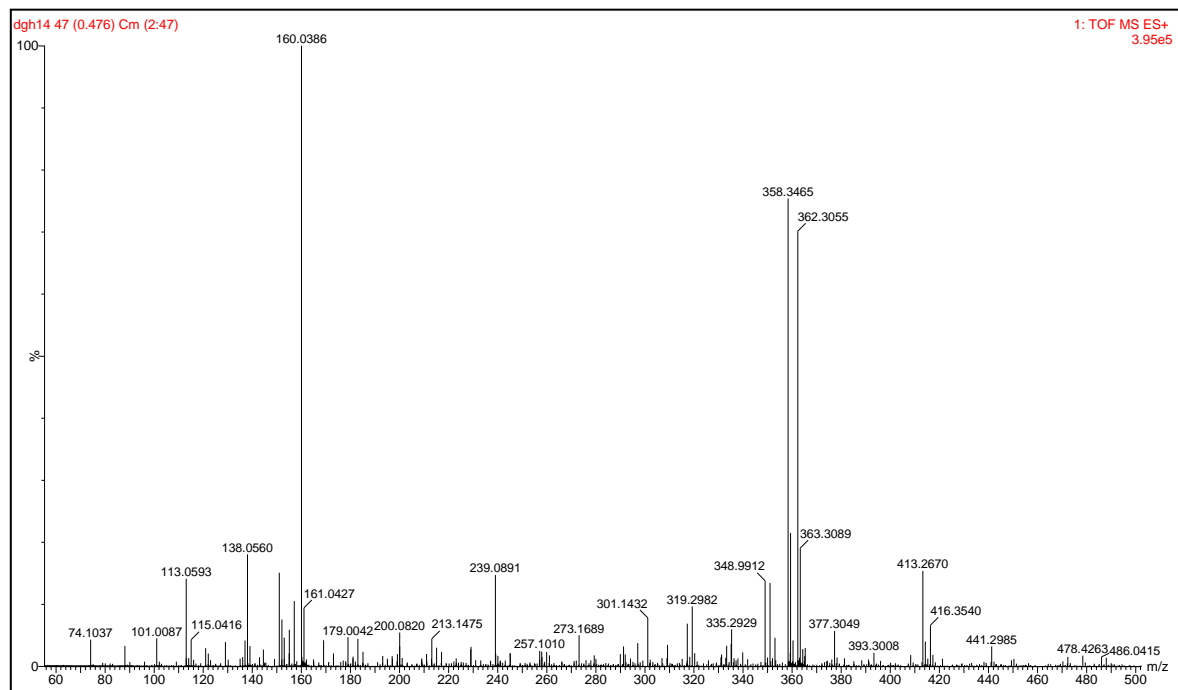


Fig. S6. ESI-HRMS of PPy at beginning, after 8 days, and after 1 month.

S7. Image J computer program.

(1) Convert colored image to black and white image and get the area occupied by oil slick in cm^2 using *Image J* computer program.

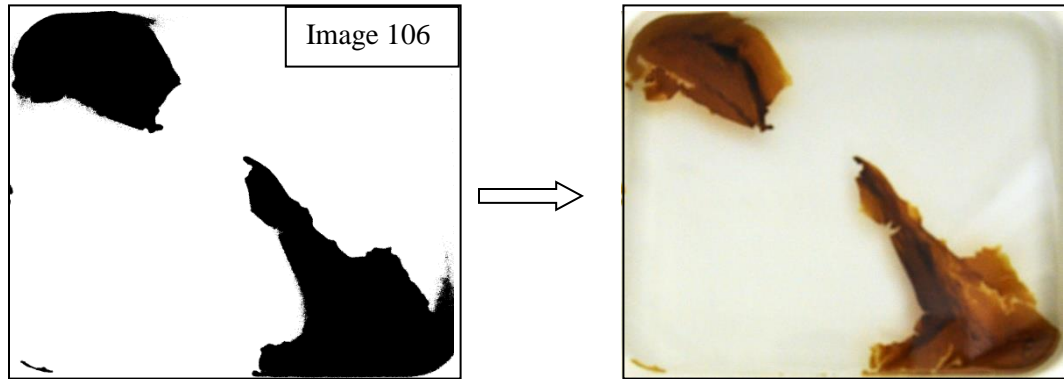


Fig. S7. Representative example of calculating the thickness of oil slick using ImageJ computer program.

(2) Then divide the volume of oil which is 2 cm^3 by the area occupied by oil slick for example in case of image 106 i.e. $2 \text{ cm}^3 / 179.2656 \text{ cm}^2 = 0.0112 \text{ cm}$.

(3) % change in thickness is calculated:

$$[(\text{thickness at time } t - \text{thickness at time } t=0) / \text{thickness at time } t=0] * 100$$

In case of image 106 it comes: $[(0.0112 - 0.00271) / 0.00271] * 100 = 313\%$

All the calculation was performed using above mentioned method.

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.

Image	Min	Total area (cm ²)	Area occupied by oil (%)	Area occupied by oil (cm ²)	Thickness (cm)	% Change in thickness
101	0	794.793	92.902	738.3786	0.00271	
106	1	794.146	22.573	179.2625	0.0112	313
115	2	785.458	19.080	149.8654	0.01334	394
121	4	762.936	15.19	115.8899	0.0173	540
125	5	752.992	14.30	110.9157	0.01803	568
129	6	770.472	15.135	116.6109	0.01715	535
135	11	780.750	12.286	95.9229	0.02085	672
143	21	786.069	10.994	86.02739	0.02325	761
149	31	792.111	10.175	80.59729	0.02481	819
153	37	798.604	9.642	77.00139	0.02597	862
164	62	789.865	9.088	71.7829	0.02786	932