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Dendritic polymers as biocompatible oil spill dispersants

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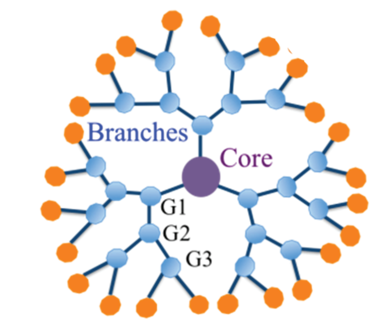
Abstract

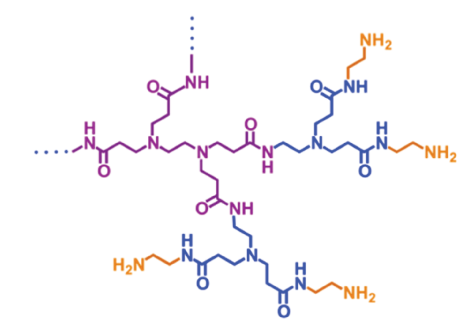
Dendritic polymers have recently been shown to encapsulate polycyclic aromatic hydrocarbons (PAHs) and other hydrophobic materials. We thus hypothesize that crude oil can be dispersed using dendritic polymers. Our objective is to gain a fundamental understanding of the interactions of the polymers with crude oil, taking toxicity and biodegradability into consideration. First-phase laboratory results show that poly(amidoamine) dendrimers and hyperbranched poly(ethyleneimine) polymers form complexes with linear (hexadecane) and polyaromatic (phenanthrene) hydrocarbons, increasing the dispersion of these model crude oil components. Ongoing efforts are examining the effects of hydrocarbon-polymer complexes on algal species to determine their biocompatibility. As a part of this project, community outreach workshops will carry the research knowledge to the public and allow community groups to participate directly in laboratory studies.

Materials

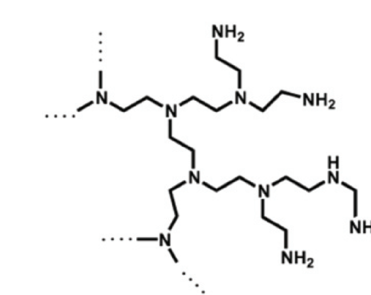
- Generation 4 PAMAM dendrimer (G4); $[NH_2(CH_2)_2NH_2]$:(G=4); dendri PAMAM $(NH_2)_{64}$; MW: 14,214; cationic.
- Hyperbranched polyethylenimine polymer, (HY or HY-PEI); $(-NHCH_2CH_2-)x[-N(CH_2CH_2NH_2)CH_2CH_2-]y$, MW: 10,000); cationic.
- Corexit 9500
- Hexadecane and phenanthrene
- Louisiana light sweet crude (LLS) oil
- *Synechocystis* sp.
- *Dunalliela* sp.



General dendrimer structure



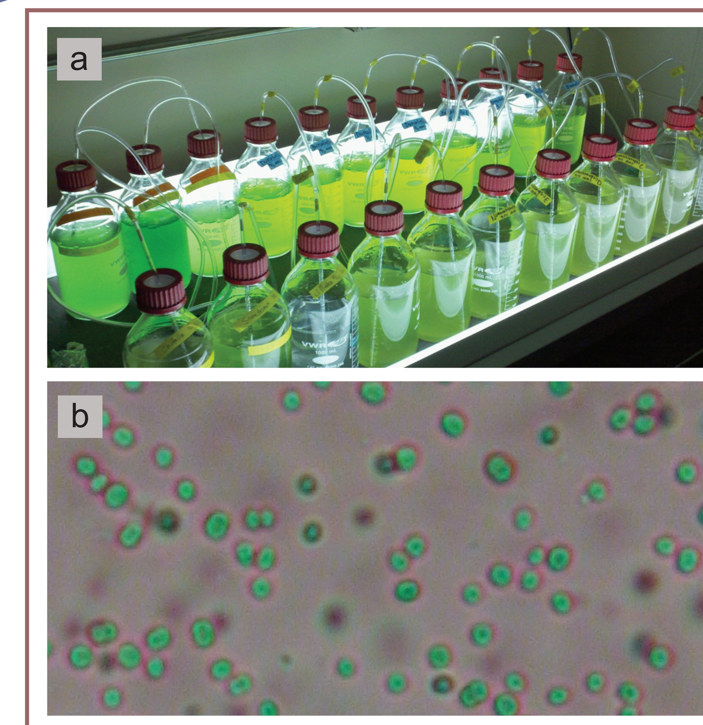
Amine-terminated PAMAM dendrimer branches



Portion of amine-terminated HY-PEI

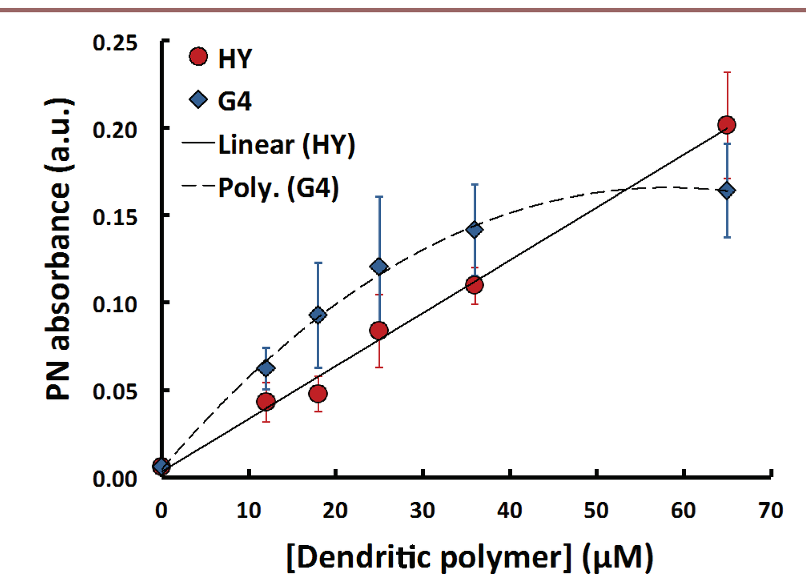
Methods

- Model compound experiments measured absorbance of phenanthrene and hexadecane interacting with polymers.
- Dispersant effectiveness tests used dichloromethane extractions to quantify dispersion. Dispersant to oil ratio (DOR) was varied.
- Photosynthesis inhibition experiments used a cyanobacterial strain, *Synechocystis* sp., grown in BG11 media and a seawater algal strain, *Dunaliella* sp., grown in DY-V media. pH indicater was added to a vial with algae, oil, and dispersants, and absorbance was measured to track pH changes caused by CO_2 utilization.

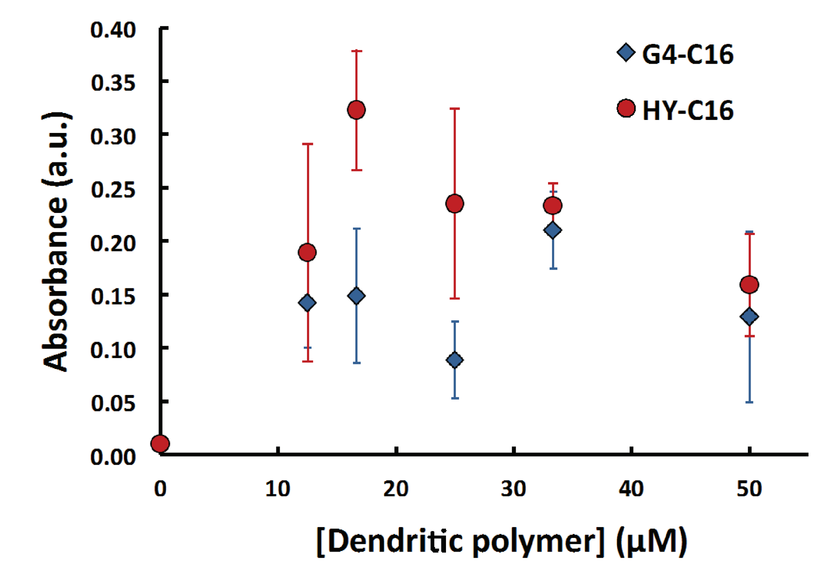


(a) *Synechocystis* sp.culture setup. (b) Microphotograph of Synechocystis sp. Cells are 1 to 2 µm in diameter.

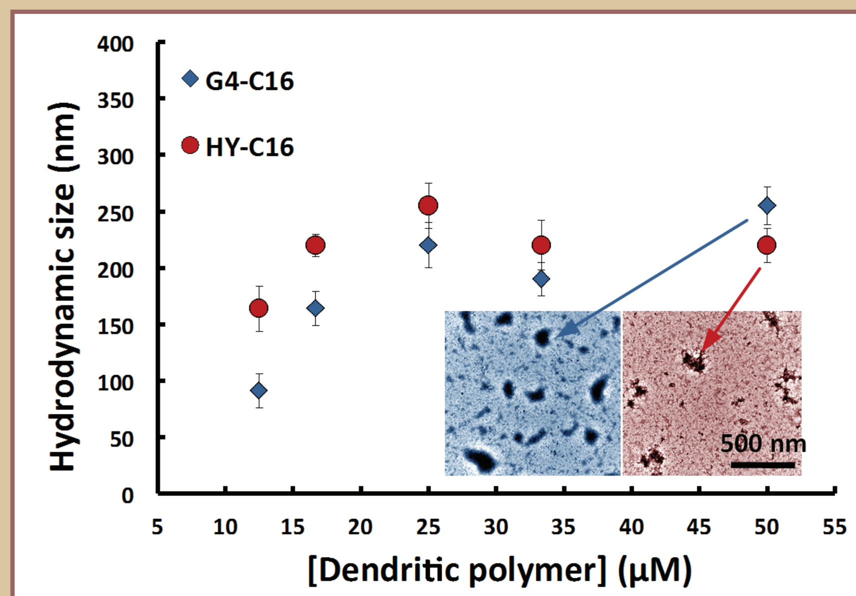
Dispersion Effectiveness Results



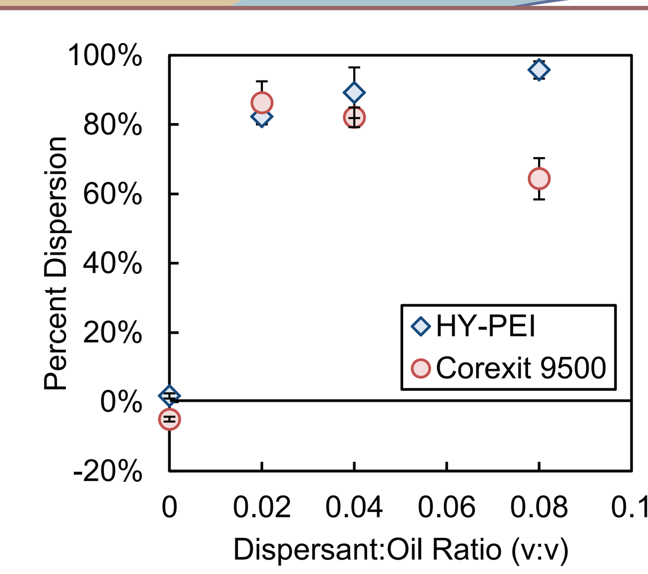
Absorbance for phenanthrene (PN) mixed with dendritic polymers at 292 nm. The G4 curve (blue diamonds) appears to exhibit saturation behaviour corresponding to a PN solubility of 35.3 mg/L, unlike the linear curve for HY (red circles) which reaches 43.3 mg/L solubility without saturation. Neat PN solubility is



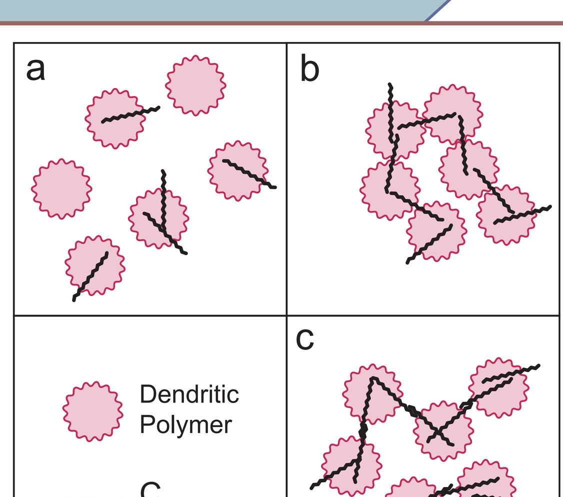
Absorbance for hexadecane (C16) mixed with dendritic polymers near 230 nm, corresponding to the new complex absorption peak.



Hydrodynamic size of dendritic polymers mixed with C16. Both G4 (blue diamonds) and HY (red circles) saturate in size growth near 200 nm. This growth indicates strong inter-complex interactions. Inset: transmission electron microscopy images of G4-C16 (blue) and HY-C16 complexes (red). Scale bar: 500 nm.

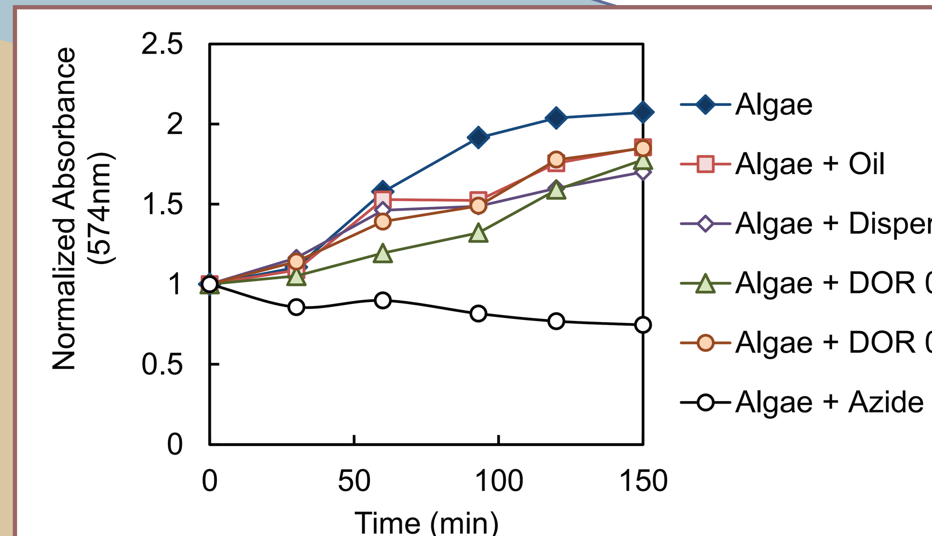


Dispersant effectiveness comparison between HY and Corexit. Oil-dispersed-in-water extractions were divided by total-oil extractions to calculate the percent dispersion. HY dispersed the oil as well or better than Corexit. The decreasing dispersion at high Corexit concentrations is likely due to formation of large, unstable dispersed particles.

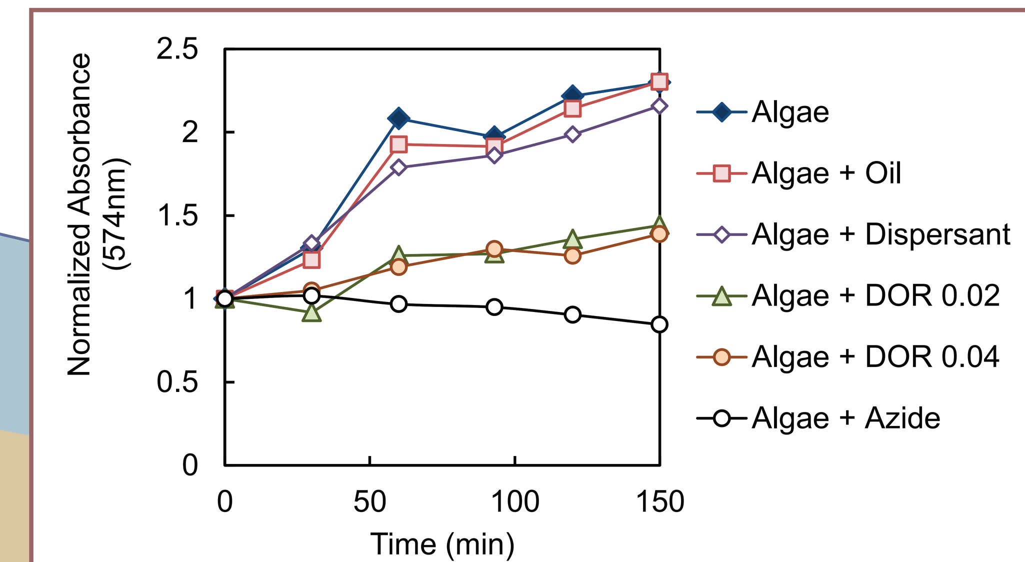


Proposed schemes of C16 complexation with dendritic polymers. (a) C16 molecules are partitioned into dendritic polymers. Potential interactions leading to super-complexes include (b) C16 capping by dendritic polymers and (c) C16 end-to-end complexation, both through hydrophobic interactions

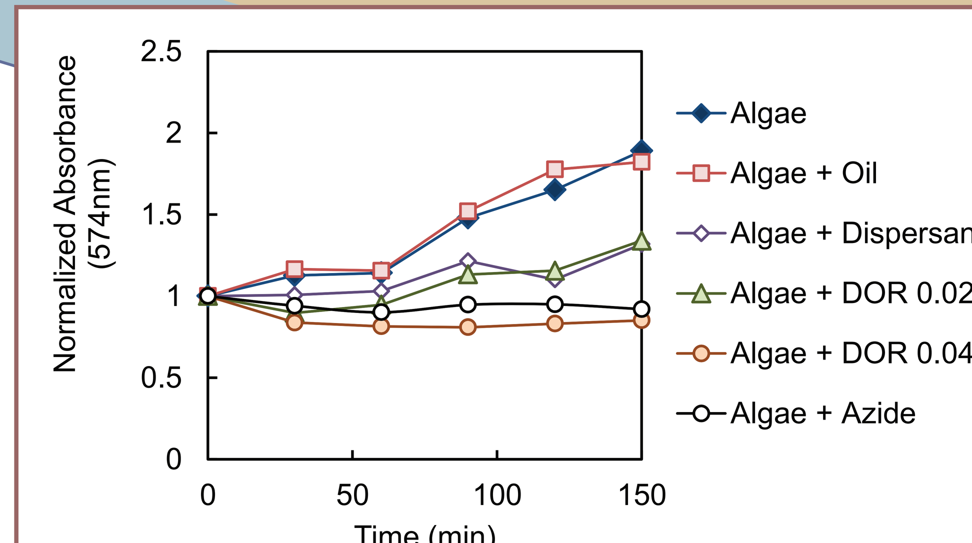
Toxicity Results



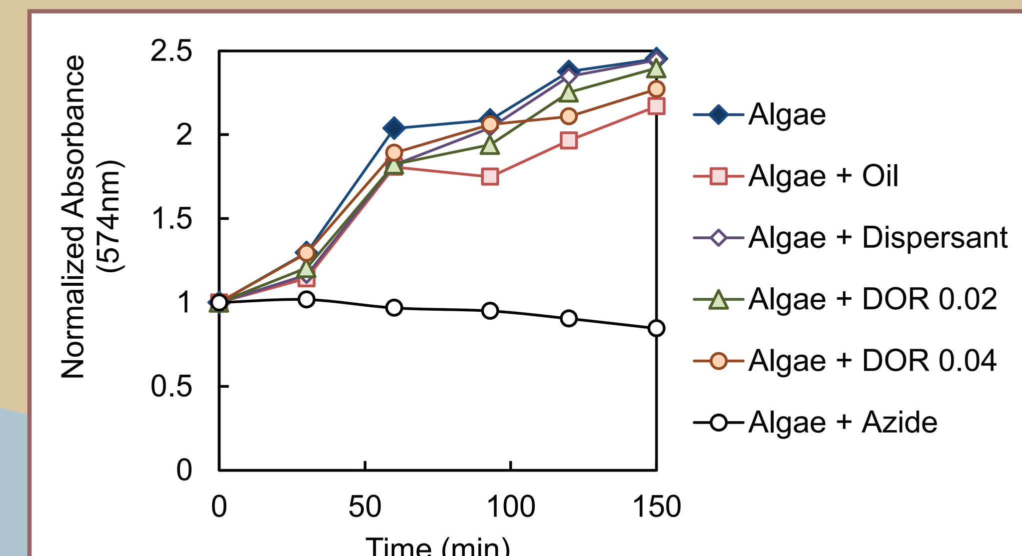
Photosynthesis inhibition results from G4 dendrimers with *Dunaliella*. An indicator caused absorbance to increase as pH was elevated during photosynthesis. Some photosynthesis inhibition may have occurred, but was similar for G4, oil, and combinations.



Photosynthesis inhibition results from G4 dendrimers with *Synechocystis*. G4 alone caused minimal inhibition, but G4-oil dispersions caused significant inhibition.



Photosynthesis inhibition results from Corexit with *Dunaliella*. Corexit alone inhibited photosynthesis. Corexit with oil at a 0.04 DOR caused complete photosynthesis blockage, similar to totally killing the cells with sodium azide.



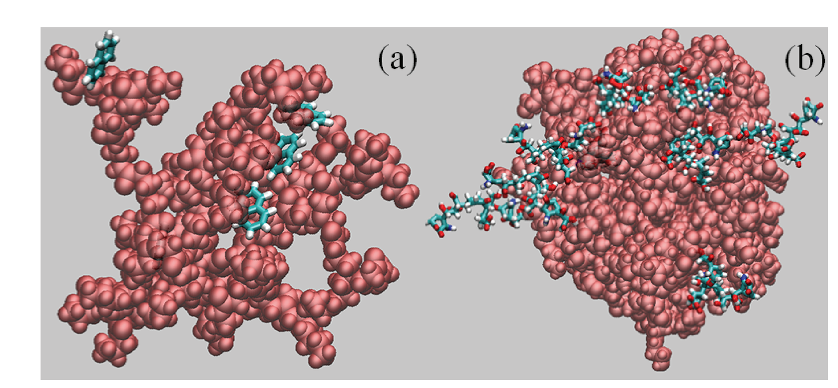
Photosynthesis inhibition results from Corexit with *Synechocystis*. Neither Corexit, oil, or combinations appeared to significantly inhibit photosynthesis.

Conclusions

- Dendritic polymers demonstrate oil-dispersing effectiveness due to their hosting capacity for hydrocarbons. The amphiphilic nature of the polymers allows them to remain soluble even after hydrocarbon capture.
- The oil-dispersing ability of HY-PEI is as good or better than Corexit 9500, particularly at higher DOR.
- G4 dendrimers were less toxic than Corexit in terms of photosynthesis inhibition for the saltwater algae *Dunaliella*. The result was different for the fresh-water cyanobacteria *Synechocystis*; G4-oil combinations were inhibitory, G4 alone was less harmful, and Corexit caused minimal inhibition. Thus, speceis and matrix are important for photosynthesis inhibition tests, and likely for other toxicity tests.

Ongoing and Future Work

- Evaluation of other dendritic polymers for dispersant effectiveness and toxicity.
- Toxicity tests with *Daphnia*.
- Microcosm experiments with various speceis.
- Molecular dynamics modeling to elucidate interaction mechanisms between oil and dispersants.
- Evaluation of interactions between dendritic polymers and natural organic matter when dispersing oil.
- Investigation of distribution and fate of dendritic polymers and hydrocarbons in algal cells.



Molecular dynamics simulations of (a) 10 naphthalene molecules complexing with a G2-PAMAM dendrimer after 15 ns; and (b) 10 humic acid monomers and one G5-PAMAM dendrimer after 2 ns. Water molecules are not shown for visual clarity.

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