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Dendrimers for Water Purification Applications: Molecular Dynamics Studies

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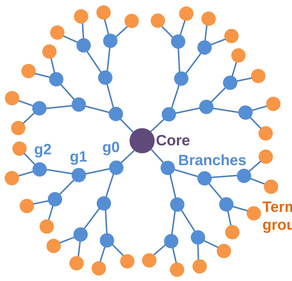
Abstract

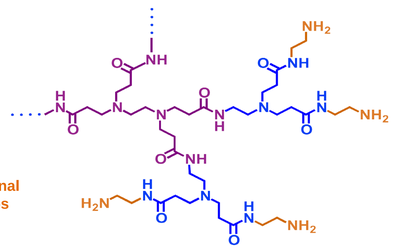
Solutions to many future challenges - including water purification, drug delivery, and energy storage - will require innovative new materials. Dendrimers are a class of materials with wide-ranging applications whose behavior is not fully understood. In many potential applications, dendrimers interact with small molecules. Our work focuses on describing the fundamental mechanisms governing the interactions between dendrimers and hydrocarbons using molecular simulations. Our results show that the association of a model aromatic hydrocarbon, naphthalene (NPH), involves interactions between the NPH molecules themselves and this effect increases as concentration of NPH in solution increases. We also investigate aggregation behavior of dendrimers in presence of linear hydrocarbons and find that dendrimer molecules aggregate to form larger complexes through hydrophobic interactions of linear hydrocarbons.

Overview of dendrimers

Dendrimers are three dimensional branched macromolecules comprising a central core, branches of repeating units that define their generation, and terminal groups.



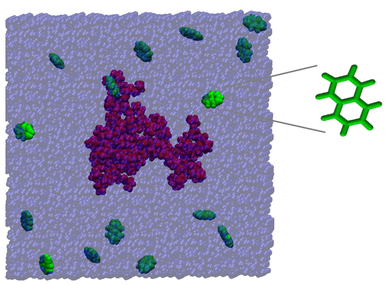
Schematic of dendrimer



Structure of PAMAM dendrimer

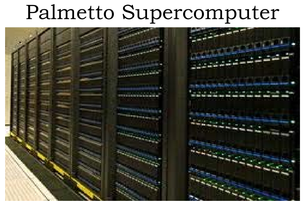
Molecular simulation of dendrimers

- Molecular dynamics simulations
- 3rd generation PAMAM dendrimer, 15 and 25 NPH, explicit water
- OPLS-AA force field
- TIP3P water model
- System size: 72,475 – 72,655 atoms
- Length of simulation: 50 ns
- Ensemble: NpT – 300 K, 1 bar
- Software: GROMACS



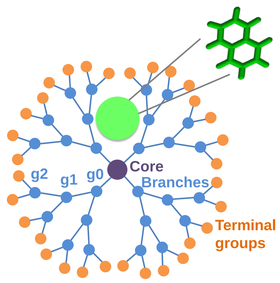
Starting configuration of the G3 PAMAM dendrimer-NPH-water simulations.

Palmetto Supercomputer

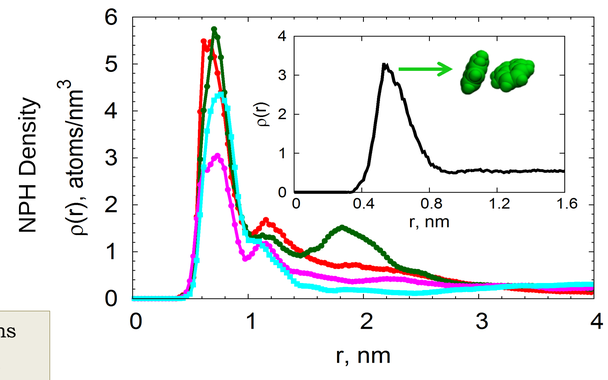


Acknowledgments: Palmetto Supercomputing @ Clemson, Dr. Pu Chun Ke, Dr. Ding, Dr. Nick Geitner and Dr. Priyanka Bhattacharya – our experimental collaborators.

How do small aromatic hydrocarbons associate with dendrimers?

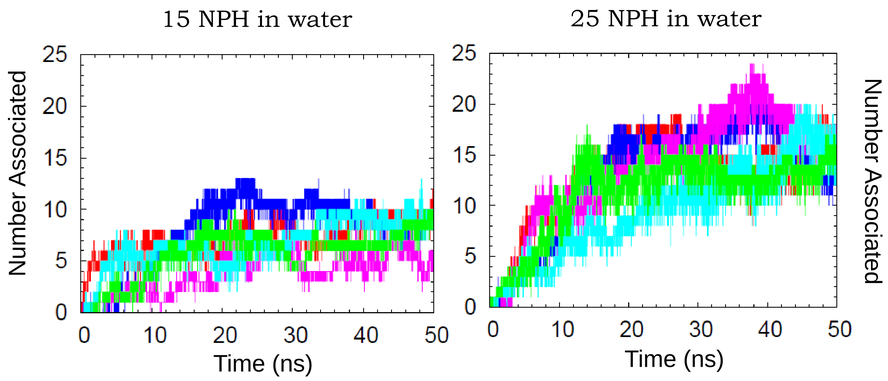


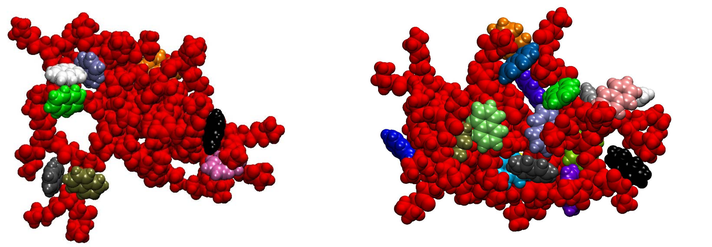
NPH – NPH interactions promote association



Distance from associated NPH

Effect of NPH concentration on dendrimer-NPH association

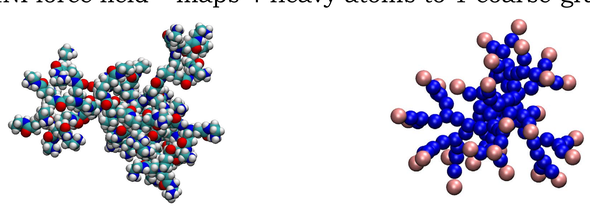




As NPH concentration is increased, association increases without an observed point of saturation

Coarse-grained simulations

MARTINI force field – maps 4 heavy atoms to 1 coarse-grained bead

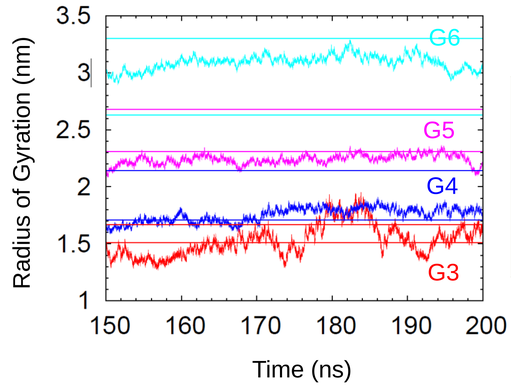


All-atom G3 dendrimer: 1124 atoms

Coarse-grained G3 dendrimer: 122 beads

Coarse-grained simulations allow us to simulate larger systems

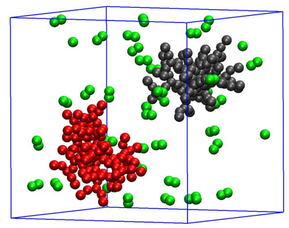
Coarse-grained simulations capture dendrimer behavior



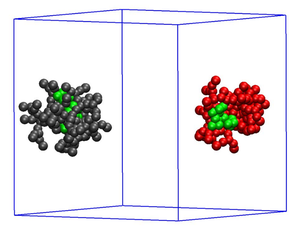
Radius of gyration predicted by coarse-grained models matches closely to values determined experimentally

How do systems with multiple dendrimers and linear hydrocarbons behave?

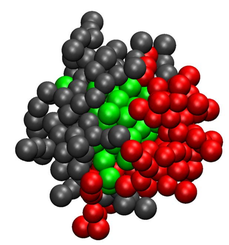
Simulation of two G3 dendrimers with octane in water



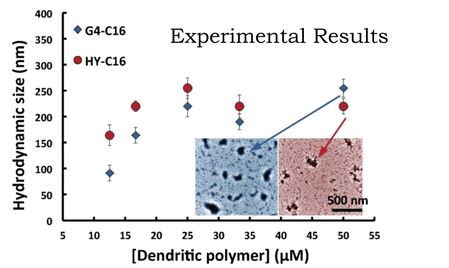
Initial configuration: Two G3 dendrimers with octane



150 ns: Octane molecules associate with the dendrimers



200 ns: Final configuration from simulations



Geitner et al, Understanding dendritic polymer–hydrocarbon interactions for oil dispersion, RSC Advances, 2012, 2, 9371–9375

Dendrimers aggregate via the octane molecules

Conclusions and future work

NPH association with dendrimers is assisted by favorable interactions between the naphthalene molecules themselves.

Dendrimers form larger complexes through hydrophobic interactions between linear hydrocarbons. The mechanism by which this occurs shares similar aspects as proposed by previous experimental studies.

- Concentration dependent studies to determine saturation behavior
- Coarse-grained studies of systems of PAMAM dendrimers with longer chains of linear hydrocarbons