Dendrimer-Guest Interactions: Challenging Conventional Wisdom

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Dendrimer – Guest Interactions: Challenging Conventional Wisdom
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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 modeling and computer simulations. A common view of dendrimer-host-guest interactions is that the guest molecules are encapsulated in protected interior voids within the dendrimer structure. Our results present an alternative picture and show that the association of a model aromatic hydrocarbon, naphthalene (NPH), involves temporary pockets formed by the dendrimer branches and interactions between the NPH molecules themselves.

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

Molecular Simulation of Dendrimers
- Molecular dynamics simulations
- 3rd - 6th generation PAMAM dendrimer, 10-17 NPH, explicit water
- NPH:water ratio constant
- OPLS-AA force field
- TIP3P water model
- System size: 72,637 – 131,747 atoms
- Length of simulation: 50 ns
- Ensemble: NpT = 300 K, 1 bar
- Software: GROMACS

Starting configuration of the G5 PAMAM dendrimer-NPH-water simulations.

How do small aromatic hydrocarbons associate with dendrimers?
Conventional wisdom: Small molecules sit in protected voids of the PAMAM dendrimers

What do simulations reveal?
More than just static voids contribute to the association

Interactions between associating molecules
Association sites which reduce water in NPH hydration shell

NPH – NPH interactions promote association

NPH molecules associate in pockets created by dendrimer branches

Some dehydration rather than interior voids is required for association

Conclusions and Future Work
NPH association with dendrimers is assisted by favorable interactions between the naphthalene molecules themselves.

- Concentration dependent studies to determine saturation behavior
- Coarse-grained studies of PAMAM dendrimers to examine linear hydrocarbon-dendrimer interactions
- Simulations of hydrocarbon-hyperbranched poly(ethyleneimine) systems.

• G3 and G4 dendrimers show increased NPH-NPH interactions
• Open dendrimer structure facilitates NPH-NPH interactions

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The pockets are mostly formed by the outer generation branches of the dendrimer

NPH molecules close to the dendrimer center are no more dehydrated than those in the middle regions of the dendrimer

NPH molecules that have their hydration shell dehydrated by about 50% remain associated for more than 2 ns

NPH molecules in water in NPH hydration shell