

SHAPE PERSISTENCE AND GAS PHYSISORPTION IN 3D POLYCONJUGATED DENDRIMERS: A MOLECULAR DYNAMICS STUDY

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Over the past years chemists have been able to synthesize new complex molecules, and to control their macromolecular and supramolecular architecture. These efforts have led to the transition in molecular scale from the picometer to the nanometer scale.

Among these new macromolecular structures, dendrimers have received increasing interest. Dendrimers are highly branched, three-dimensional macromolecules with branch points at every monomer, leading to a structure that has essentially as many end-groups as monomeric units. Among their most important properties are the molecular shape and size persistence along with their narrow molecular weight distribution. The synthesis of dendrimers starts by the addition of building units to a polyfunctional molecule which represents the core of the future dendrimer. The resulting molecule is the first generation (G1) of the dendrimer. Each newly generated branch is the starting point for several further sub-branches that will form second (G2) and higher generations of the dendrimer.

Mullen and coworkers have recently developed a divergent method to synthesize polyphenylene dendrimers up to the fourth generation and with different cores[1]. Due to their very dense intramolecular packing, these monodisperse polyaromatic dendrimers are of interest with respect to the design of nanostructures with invariant shape [2]. Besides their significantly enhanced thermal and chemical stability, their rigidity as compared to aliphatic dendrimer systems, coupled with the wide variety of possible functionalizations, provide the basis for a wide range of potential applications.

Due to their peculiar three dimensional structures, dendrimers exhibit physical properties generally not seen in other more traditional forms of highly branched polymers.

Although scattering and microscopic methods have been successfully applied to characterize the structure of dendrimers [3], only few computational studies on their intramolecular dynamics have appeared [4] while computational studies concerning the influence of intermolecular interactions in shaping the amorphous aggregates of these dendrimers as well as their interactions with other molecules have not been published, to the best of our knowledge.

In this work we present a computational study and we investigate both intramolecular and intermolecular properties of polyphenylene dendrimers. The first objective is to simulate and monitor the dynamical evolution of geometric characteristics of a single dendrimer (such as intramolecular distances, internal dihedral angles and gyration tensor). The second objective is to understand how these peculiar three dimensional structures interact reciprocally to form amorphous aggregates, to characterize their inter and intra molecular cavities and to provide estimates for gas transport properties and gas storage capacity. In this regard, we will concentrate on the hydrogen gas.

To this end we carried out classical molecular mechanics and molecular dynamics simulations using the TINKER software [5] and the MM3 empirical force field [6]. The extended calculations on the single dendrimer were carried out on a second-generation (G2) dendrimer based on a 1,3,5-tri-substituted benzene core (see Fig. 1) and information about the most probable conformations and the shape persistency of the polyphenylene dendrimer were obtained.

To study the intermolecular aggregation properties and gas storage and transport properties we restricted to the dendrimers of the first-generation (G1) [Fig. 2]. We included eight dendrimer molecules in the simulation box and studied bulk properties of the aggregate by applying periodic boundary conditions. To study the gas transport and storage properties, we included

an increasing number of (from fifty to six hundred) hydrogen molecules to the simulation box and followed the dynamics of the system.

References

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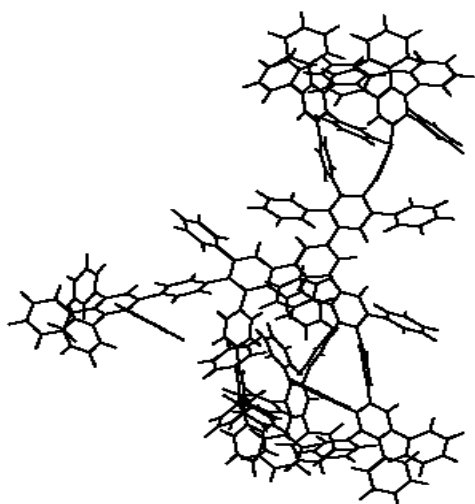


Figure 1. One of the lowest energy structures of the second generation polyphenylene dendrimer optimized with the MM3 force field

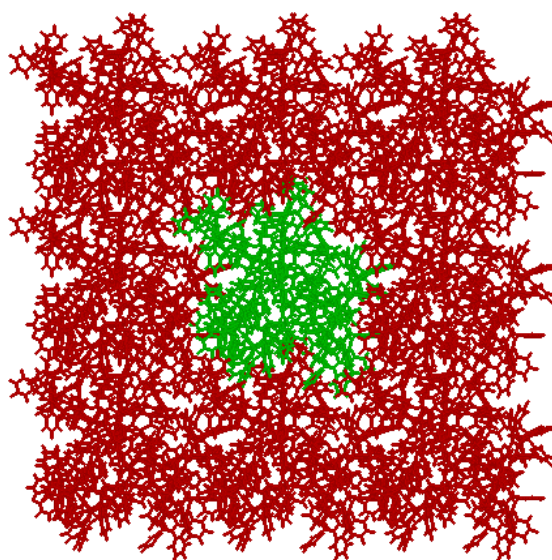


Figure 2. Simulation box of the dendrimer aggregate, surrounded by the first shell of image boxes, after the application of the periodic boundary conditions.