

Functionalized adamantane: fundamental building blocks for nanostructure self-assembly

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Abstract – We report first principles calculations on the electronic and structural properties of chemically functionalized adamantane molecules, either in isolated or crystalline forms. Boron and nitrogen functionalized molecules, aza-, tetra-aza-, bora-, and tetra-bora-adamantane, were found to be very stable, consistent with available experimental data. Additionally, a hypothetical molecular crystal in a zincblende structure, involving tetra-aza- and tetra-bora-adamantane, was investigated. This molecular crystal presented a direct and large electronic bandgap and a reasonably large bulk modulus. The viability of using those functionalized molecules as fundamental building blocks for nanostructure self-assembly is discussed.

Carbon is unique in nature because it carries several competing hybridization states for its valence electrons, leading to a number of stable, and sometimes exotic, organized structures. On the other hand, nanostructured forms of carbon, which have been discovered over the last two decades, could potentially lead to a much wider range of applications in a near future [1]. Those nanostructures, that included fullerenes, nanotubes, graphene, nanoribbons, and others, have been the focus of intensive investigation. [2, 3]. Striking developments have been recently attained in building, separating, manipulating, and functionalizing a different class of nanostructured carbon, called diamondoids [4]. They can be described as molecular diamond, with carbon atoms in a diamond-like structure saturated by hydrogen atoms in the surface. Due to the prevailing covalent nature of the interatomic interactions, those molecules carry outstanding stability and rigidity. Adamantane is the smallest diamondoid, with a $C_{10}H_{16}$ configuration, which consists of a single diamond-like carbon cage. They have also been considered as fundamental building blocks (FBBs) to build complex ordered nano-elements with sub-nanometric precision [5-7]. Using FBBs represents a potentially competitive building procedure for industrial applications within a bottom-up approach. FBBs can be thought as nanobricks, but manipulating them represents a major challenge. Current methods that allow positional control, such as atomic force microscopy, would be unrealistically too slow to build relevant systems in large scale. Therefore, new building procedures, such as those based on self-assembly, should be considered. Functionalization could solve several limitations, since it generates chemically active sites, leading to stronger intermolecular interactions and stiff nanostructures. Such functionalization could also help self-assembly, driving the system to pre-determined organized configurations. This investigation reports the physical properties of functionalized adamantane with boron and nitrogen to form bora-, tetra-bora-, aza-, and tetra-aza-adamantane, carrying out first principles calculations using the *Vienna ab initio simulation package* (VASP) [8]. We found that functionalization is strongly favorable and leads to at least two types of FBBs: tetra-bora- and tetra-aza-adamantane. In such context, we investigated a hypothetical crystalline structure, formed by a combination of those two functionalized adamantane molecules. [9]

References

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