



Complexes of carbene-functionalized diamondoids and metal atoms: Electronic properties



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ABSTRACT

Tiny carbon cages known as diamondoids have recently attracted attention and can be selectively chemically modified. In this work, we focus on lower diamondoids, from adamantane ($C_{10}H_{16}$) up to (121)-tetramantane ($(121)C_{22}H_{28}$). Specifically, we investigate a chemical modification based on a member of the carbene family, the imidazolylidene molecule ($C_3N_2H_6$). One carbon site of the lower diamondoids has been replaced with imidazolylidene. The electronic properties and the thermal stability of these modified diamondoids are analyzed. In view of practical applications involving self-assembled diamondoid metallic surfaces, the interaction of the modified diamondoids with a metal atom (Au, Ag, Cu or Pt) is evaluated. Our results are based on quantum-mechanical calculations within the density-functional-theory approach. The structural characteristics, the energetics, and the electronic properties of the carbene-functionalized diamondoids and their complexes with metal atoms are investigated. We find that the carbene-functionalized diamondoids form thermally stable structures, show a considerable reduction in their electronic band-gap with respect to the unmodified diamondoids, and retain the metal-bonding characteristics of carbene. For their metal complexes, a higher affinity and a stronger bond, for binding to platinum was evident. The platinum complex is also the only carbene-functionalized metal complex, which retains a non-metallic character. The high stability of these complexes and the strong bonding therein underlines the strong potential of carbene-functionalized diamondoids as building blocks in novel applications.

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1. Introduction

Nano-sized hydrogen terminated diamondoids can assume various sizes and chemical modifications and can be found in petroleum [1,2]. The diamondoids can also be selectively synthesized in the laboratory [3] or nucleated from energetic species [4]. These nanostructures have shown a high potential to be used in nanotechnology, from drugs to field emitting devices [5–8]. The first and smallest member of the diamondoid family is known as adamantane ($C_{10}H_{16}$). These nano-diamond cages can attach on metallic surfaces through a thiol group [9,10] and form self-assembled monolayers (SAMs) with a negative electron affinity [5,11] and a strong monochromatic emission [5,12]. Such properties make diamondoids very promising candidates for electronics applications especially electron emitting devices. In the past, thiol based SAMs on metal surfaces have led to significant applications in

the field of surface emission, sensing, electrochemistry, drug delivery, and microelectronics [13–17]. Nevertheless, the thermal instability of these thiol-based diamondoid SAMs on gold is questionable. There have been indications, that changes in the environmental conditions have a strong effect on these materials and their use for industrial purposes could be problematic [18–22]. Thiol-based SAMs are found to be stable only when stored in an ultra high vacuum in the absence of light, but tend to degrade after few weeks at room temperature [23–25].

As an alternative to thiol, carbene molecules have recently been used to promote binding of diamondoids on metal surfaces [26]. These molecules belong to the family of N-heterocyclic carbenes to which we refer to in the following. Carbene molecules ($R-(C:)-R'$ or $R = C:$) are usually defined as neutral compounds having a divalent carbon atom with a six-electron valence shell and are powerful tools in organic chemistry having numerous applications in chemical processes [27]. Various classes of carbene molecules can be synthesized using different methods [28] and most commonly contain at least one nitrogen atom within the ring structure [29]. N-heterocyclic carbenes (e.g. $(R_2N)2C:$, where the 'R's are typically

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alkyl and aryl groups) are typically used as ligands for transition metals, upon coordination to p-block elements and as organo-catalysts and are used in relevant applications in important catalytic transformations in the chemical industry and as organocatalysts. The reactivity of carbene molecules upon coordination to main group elements is an additional important property in view of applications. Imidazolyliene ($C_3N_2H_6$), a simple ring structure with two nitrogen atoms is one member of the carbene family. This molecule can form metal and transition metal complexes [30,31] to be used in catalysis and other chemical reactions.

In this work, we study the structural and electronic properties of imidazolyliene-functionalized diamondoids and their bonding and interaction to metal atoms. In the following sections, we present the methodology of our investigation and move on to the analysis of the results on the structural and electronic properties of carbene-functionalized diamondoids, their thermal stability, and the characteristics on their interactions with metals.

2. Methodology

This work is carried out within the density-functional-theory (DFT) based approach implemented in the code SIESTA [32], in which the Kohn-Sham eigenstates are expanded using a linear combination of atomic orbitals. The Perdew-Berke-Ernzerhof (PBE) general-gradient-approximation and a double-zeta-polarized basis set are used [33]. A mesh cutoff parameter of 220 Ry has been used for the calculations along with a very large box to avoid interaction of the images. The geometry optimization was performed using the conjugate gradient algorithm and the structure was relaxed until the forces on the atoms were below 0.04 eV/Å. In addition to the static DFT calculations we have also performed *ab initio* Molecular Dynamics (MD) to assess the thermal stability of the carbene functionalized diamondoids. For these simulations, a time step of 1.0 fs was used and the total simulation time of 6 ps. The temperature was varied from 500 K to 2000 K using Nosé dynamics [34]. No pressure was applied in the *ab initio* MD simulations and the volume of the computational cell was kept constant.

The smaller diamondoids adamantane ($C_{10}H_{16}$) up to (121)-tetramantane ($(121)C_{22}H_{28}$) are considered. These smaller diamond cages are attached to one end of the imidazolyliene ($C_3N_2H_6$) molecule, which we refer to as ‘carbene’ in the following. The imidazolyliene molecule was chosen among the members of the N-heterocyclic carbene (NHC) family, as it forms a simple structure and can be easily manipulated in both the simulation and experiments. The abbreviations ‘ada’, ‘dia’, ‘tria’, ‘tetra’ will be used for the diamondoids adamantane ($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), triamantane ($C_{18}H_{24}$), and (121)-tetramantane ($(121)C_{22}H_{28}$), respectively. The term ‘unmodified’ will be used for all structures that are not functionalized. For example, adamantane ($C_{10}H_{16}$) and (121)-tetramantane ($(121)C_{22}H_{28}$) are defined as ‘unmodified’ in the following. The complexes, such as NHC-adamantane ($C_3N_2H_6-C_{10}H_{15}$) are the functionalized molecules. Note, that one of the H atoms of the diamondoid has been removed in order to functionalize it with the NHC molecule. We study the stability and structural details, as well as the alteration in the electronic properties imposed by the functionalization of the diamondoids with the carbene molecule. The dangling bonds of the carbene molecule are passivated with hydrogen atoms whenever necessary. The interaction of the imidazolyliene-functionalized diamondoids with metal atoms (Au, Ag, Cu, and Pt) is investigated at a next step. This interaction will link to the adsorption of the carbene-functionalized diamondoids on metal surfaces. The lower diamondoids are used for computational efficiency. The four diamondoids are chosen to assess the effect of the size variation on the physical properties of the functionalized molecules. The choice of the metals is based on

the fact, that these are typically used to form substrates in functional applications.

The investigation is carried out in two steps, mapped through the structures in Fig. 1. We begin with the functionalized diamondoids and move on to a complex including the functionalized diamondoids bonded through the tip of the carbene molecule to a metal atom. All systems have been structurally relaxed. The structural details of all structures are monitored through bond-lengths and bond-angles, while the electronic properties are probed through the total electronic density of states (eDOS), the frontier orbitals, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, as well as the electronic band-gap. Note, that the values of the electronic band-gaps obtained through the DFT methods are not accurate. However, in this work, we are not interested in the exact values, rather than in the trend shown in the band-gaps which should be obtained also within DFT.

3. Results and discussion

3.1. Carbene-functionalized diamondoids

We begin with the analysis of the structural modifications of carbene-functionalized diamondoids as the one shown in Fig. 1. We monitor the bond-length of the carbon and nitrogen atoms in the carbene unit (imidazolyliene- $C_3N_2H_6$) which is similar in all the three cases (close to 1.46 Å) except (121)-tetramantane ($(121)C_{22}H_{28}$), in which the bond shrinks to 1.36 Å. A similar behavior is observed in the bond-angle between N–C–N of the carbene ring, which shows a variation of 2° in case of (121)-tetramantane as compared to other diamondoid. Note, that the C–C bond-length in unmodified diamondoids is 1.52 Å for adamantane ($C_{10}H_{16}$) and 1.50 Å for diamantane ($C_{14}H_{20}$), triamantane ($C_{18}H_{24}$), and (121)-tetramantane ($(121)C_{22}H_{28}$). All structural details of the functionalized diamondoids are summarized in Table 1. In this Table, (N–C), (N–C–N), and (C=C) refer to bonding in the carbene ring (see Fig. 1 (a)).

The electronic band-gaps of the functionalized diamondoids are considerably reduced with respect to the values of the unmodified diamondoids (see the variation ΔE_g with respect to unmodified diamondoids in Table 1). These are 7.04, 6.69, 6.45, and 6.44 eV for unmodified adamantane, diamantane, triamantane, and tetramantane, respectively. The band-gap of the unmodified carbene molecule is 3.87 eV. The total electronic density of states (eDOS) is sketched in Fig. 2. The eDOS of the unmodified diamondoids is

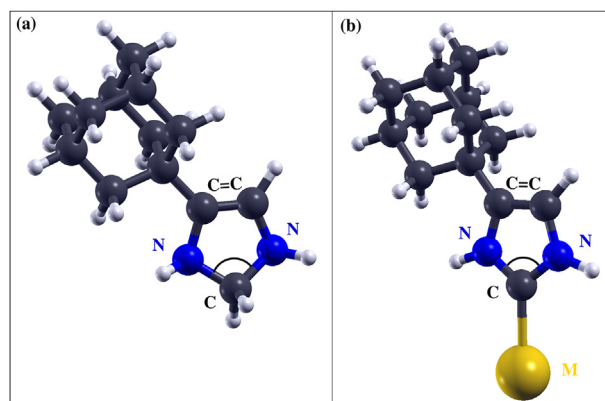


Fig. 1. The structures denote the two different steps followed in this investigation. The different panels show (a) the carbene functionalized adamantane ($C_3N_2H_6-C_{10}H_{15}$), (b) the carbene functionalized adamantane bonded to a metal atom M ($C_3N_2H_4-C_{10}H_{15}-M$). The labels correspond to the structural data discussed in the Results Section.

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