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

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A R T I C L E   I N F O

Article history:
Received 14 January 2016
Received in revised form 16 April 2016
Accepted 20 April 2016
Available online 23 April 2016

Keywords:
Diamondoids
Carbene
Imidazolylidene
Electronic properties
Band-gap

A B S T R A C T

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 (C10H16) up to (121)-tetramantane ((121)C22H28). Specifically, we investigate a chemical modification based on a member of the carbene family, the imidazolylidene molecule (C3N2H6). 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 (C10H16). 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) 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. (R2N)2C, where the ‘R’s are typically
alkyl and aryl groups) are typically used as ligands for transition metals, upon coordination to p-block elements and as organocatalysts 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. Imidazolylidene (C₅N₂H₆), 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 imidazolylidene-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-derivative-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⁻¹. 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 (C₀H₁₆) up to (121)-tetratetramantane ((121)C₂₂H₂₈) are considered. These smaller diamond cages are attached to one end of the imidazolylidene (C₅N₂H₆) molecule, which we refer to as ‘carbene’ in the following. The imidazolylidene molecule was chosen among the members of the N-heterocyclic carbene (NHC) family, as it forms a simple structure with two nitrogen atoms and can be easily manipulated in both the simulation and experimental aspects. The term ‘carbene’ is defined as having the carbon and nitrogen atoms in the carbene ring, while the term ‘unmodified’ will be used for all structures that are not functionalized. For example, adamantane (C₁₀H₁₆) and (121)-tetratetramantane ((121)C₂₂H₂₈) are defined as ‘unmodified’ in the following. The complexes, such as NHC-adamantane (C₅N₂H₆-C₁₀H₁₆) 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 of the functionalized diamondoids with respect to unmodified diamondoids (see the variation of the band-gaps which should be obtained also within DFT). The electronic band-gaps of the functionalized diamondoids are considerably reduced with respect to the values of the unmodified diamondoids (see the variation ΔEg 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 functionalized diamondoid molecule is 3.87 eV. The total electronic density of states (eDOS) is 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 (imidazolylidene-C₅N₂H₆) which is similar in all the three cases (close to 1.46 Å) except (121)-tetratetramantane ((121)C₂₂H₂₈), 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)-tetratetramantane as compared to other diamondoid. Note, that the C–C bond-length in unmodified diamondoids is 1.52 Å for adamantane (C₁₀H₁₆) and 1.50 Å for diamantane (C₁₄H₂₀), triamantane (C₁₈H₂₄), and (121)-tetramantane ((121)C₂₂H₂₈). 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 ΔEg 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 (C₅N₂H₆-C₁₀H₁₆), (b) the carbene functionalized adamantane bonded to a metal atom M (C₅N₂H₆-C₁₀H₁₆-M). The labels correspond to the structural data discussed in the Results Section.
involved in each panel is shown on the right. The energy axis has been shifted with shaded areas mark the electronic band-gaps of the functionalized diamondoids. The colors correspond to the legends on the top of the figure. (Fig. 3 depicts the frontier orbitals of unmodified carbene ring induces very small changes in the band-gaps of the functionalized diamondoids (see also Table 1). This observation differs compared to previous work [35,36], in which a decrease of the band-gap with increasing diamondoid size was found. Here, the presence of the carbene ring induces very small changes in the band-gaps of the functionalized diamondoids and suppresses the effect of diamondoid size.

In order to provide a better qualitative understanding of the differences in the electronic structure of carbene-functionalized diamondoids, Fig. 3 depicts the frontier orbitals of unmodified carbene, unmodified and functionalized diamondoids. In unmodified carbene, both the HOMO and the LUMO are spread around the whole molecule. In the unmodified diamondoid cases, the HOMO (occupied states) are localized on the C–C bonds whereas the LUMO (unoccupied states) are mainly associated with the carbon atoms of the molecules. In the functionalized diamondoids, both HOMO and LUMO orbitals become localized on the carbene molecule and have similar shapes as in unmodified carbene. These observations indicate, that the properties, most importantly the metal-binding affinity, of the carbene molecule have been preserved in the functionalized diamondoids. This important finding denotes that carbene-functionalized diamondoids would be excellent candidates for the formation of self-assembled layers on noble metal substrates potentially realizing excellent electron emitters.

3.1.1. Thermal stability

An important aspect in using functionalized diamondoids in potential applications is their stability under various environmental conditions. To this end, we study the thermal stability of the carbene-functionalized adamantane (C3N2H6−C0H15). The thermal stability is probed through ab initio MD. We have found that all functionalized cases are thermally stable at least up to a temperature of 2000 K. The structural properties with respect to the temperature for the unmodified and functionalized adamantane are shown in Table 2. In this Table, the ‘0 K’ data correspond to the initial structures obtained from the static DFT. The average bond-lengths and bond-angles and their fluctuations have been determined by taking into account all time steps after the system has relaxed. In the table, the C−C and C−C−C bonds refer to the diamondoid part, while N−C and N−C−N refer to bonding in the carbene ring. For all temperatures considered, the bond-length and bond-angle variations are small. Even for 2000 K, these fluctuations are within 0.1 Å and 6°, respectively. The average bond-lengths and bond-angles do not differ significantly from the initially relaxed structures (at 0 K).

The thermal stability of functionalized adamantane (C3N2H6−C0H15) is also revealed by inspection of the frontier orbitals, the HOMO and the LUMO, as a variation of the temperature. Fig. 4 shows snapshots of the distribution of the frontier orbitals at the last time step. Although, these are not averaged, they are indicative of the influence of the temperature. In all cases, both HOMO and LUMO distributions show only minor deviations from the static DFT calculations. For example, the HOMO in unmodified adamantane remains localized around the C−C bonds, while the HOMO in functionalized adamantane remains localized on the carbene ring up to 2000 K. The LUMO in unmodified adamantane is associated again with the carbon atoms, while in the functionalized case the LUMO is localized on the carbene ring, with a small contribution also seen in the adamantane part.

3.2. Carbene-functionalized diamondoids and metal complexes

We next turn to complexes of carbene-functionalized diamondoids and metal atoms. In these, the lower carbon atom of the carbene molecule in the functionalized diamondoids forms a bond to a metal atom. The resulting nanostructure is similar to that shown in Fig. 1(b). The structural details of these complexes are summarized in Table 3, where M is one of Au, Ag, Cu, and Pt. The results are compared to the functionalized diamondoids without the metal, discussed in the previous sections. ‘func.’ in the Table refers to these ‘non-metal’ structures from the previous sections, as the carbon atom which is bonded to a metal atom in the complex is saturated with two hydrogen atoms in the non-metal functionalized cases. For example, C3N2H6−C0H15 is the ‘func.’ molecule, while (C3N2H4−C0H5−M) is the respective metal ‘complex’ for adamantane. The labels Au, Ag, Cu, Pt in the Table denote the metal atom M bonded to the specific functionalized diamondoid. Again, the bond-length of the N−C bond in the carbene molecule and the angle between the N−C−N atoms are monitored, as well as the bond-length of the carbene carbon atom to the metal atom M (C−M) (see Fig. 1(b)). In almost all complexes the nitrogen-carbon (N−C) bond in the carbene ring decreases about 0.1 Å, while the decrease in the relevant bond-angle is about 1°. Shorter bond-lengths indicate that the structure becomes more stable when coordinating to a metal and that this conformation is favored. This is an important finding in view of the preparation of self-assembled monolayers of diamondoids on metal surfaces.

![Fig. 2. The total electronic density of states (eDOS) of the unmodified diamondoids (‘unmod.’), unmodified carbene (‘carbene’), and functionalized diamondoids (‘func.’). The colors correspond to the legends on the top of the figure. The type of diamondoid involved in each panel is shown on the right. The energy axis has been shifted with respect to the LUMO of the unmodified diamondoid (LUMO_{unmod}) in each panel. The shaded areas mark the electronic band-gaps of the functionalized diamondoids.](image)

<table>
<thead>
<tr>
<th>Functionalized</th>
<th>( E_g )</th>
<th>( \Delta E_g )</th>
<th>( r_b(N−C) )</th>
<th>( \theta_b(N−C−N) )</th>
<th>( r_b(C=C) )</th>
</tr>
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<td>ada-carbene</td>
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<td>47%</td>
<td>1.476</td>
<td>102.67</td>
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</table>

Table 1 Structural properties and electronic band-gaps of the carbene functionalized diamondoids (C3N2H6−C10H15). \( \Delta E_g \) denotes the % difference of the band-gaps compared to the unmodified diamondoids (C3N2H6−). Bond-lengths \( r_b \) are in Å, bond-angles \( \theta_b \) in degrees, and band-gaps \( E_g \) in eV.
In order to reach a quantitative understanding on the stability of the functionalized-diamondoid complexes we calculate the substitution energy, $E_s$, also given in Table 3. The substitution energy indicates the bonding efficiency of the carbene-functionalized diamondoid to the metal atom. It could also be seen as the degree of preferability in replacing a metal atom in the complex with another metal atom and links to the most preferred metal type for this binding. As a reference for the comparison of the metal substitution for all metals we use Au as the reference. Accordingly, the substitution energy is defined as:

$$E_s = E_{\text{tot}} - E_{\text{ref complx}} - E_{\text{isol. metal}} + E_{\text{isol. ref}}$$

where $E_{\text{tot}}, E_{\text{ref complx}}, E_{\text{isol. metal}}, E_{\text{isol. ref}}$ are the total energy of the specific complex, the total energy of the complex with the reference metal, the total energy of the isolated metal in the complex, and the total energy of the isolated reference metal, respectively. According to the definition from Eq. (1) low substitution energy means that the metal substitution is favored, while a negative substitution energy denotes a substitution that can occur almost naturally. Our results show that copper yields the shortest carbon-metal bond-length, which is close to 1.97 Å for all diamondoids. Platinum leads to the lowest substitution energy, which ranges from $-1.37$ eV to $-1.24$ eV. Note, that in Table 3, $E_s = 0$ for the Au complexes as these were taken as the reference.

For the same metal, the diamondoid size variation does not...
Structural properties and substitution energies of the complexes made up from carbene-functionalized diamondoids and metal atoms as compared to the complexes without the metal (func.). Each set of parameters corresponds to a specific diamondoid-metal complex as denoted through the diamondoid label and the labels for the metals. (For the notations, see text). Bond-lengths (\(r_b\)) are given in Å, bond-angles (\(\theta_b\)) in degrees, and substitution energies (\(E_s\)) in eV. The Au complexes have been taken as the reference. No relativistic effects have been considered when obtaining the results. Note, again that for the metal complexes two of the H atoms of the carbene ring are removed in order for the lower C atom to bond to the metal atom. Accordingly, the chemical formula for the carbene molecule in the metal complex is \(\text{C}_3\text{N}_2\text{H}_6\).

<table>
<thead>
<tr>
<th></th>
<th>func. ada</th>
<th>HOMO</th>
<th>LUMO</th>
<th>unmod. ada</th>
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<th>LUMO</th>
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<td>1.354</td>
<td>1.355</td>
<td>1.354</td>
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<tr>
<td>(r_b(\text{N–C}))</td>
<td>1.46</td>
<td>1.354</td>
<td>1.355</td>
<td>1.354</td>
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<td>1.360</td>
<td>1.364</td>
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<tr>
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<td>1.46</td>
<td>1.360</td>
<td>1.360</td>
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<tr>
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<td>1.362</td>
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<td>(E_s)</td>
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<td>–0.714</td>
<td>–1.369</td>
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Fig. 4. Snapshots of the HOMO and the LUMO of unmodified (‘unmod. ada’) and functionalized (‘func. ada’) adamantane, \(\text{C}_9\text{H}_{10}\) and \(\text{C}_7\text{N}_2\text{H}_8\–\text{C}_9\text{H}_{15}\), respectively at different temperatures.

Table 3

is not a crucial factor in determining the metal-bonding characteristics of the carbene unit. For the silver complexes (except the adamantane complex), our simulations led to unphysical values for the respective substitution energies and were not included in Table 3. In order to check whether this issue is based on computational parameters, we have repeated our calculations for the gold, silver, and platinum complexes using pseudopotentials which account for relativistic effects. (For copper no change in the results due to relativistic effects is expected). The results from the simulations including relativistic effects are given in Table 4. Overall, there are small increases in the bond-lengths within the carbene ring, and the respective bond-angles which is slightly more evident in the Pt complex. The carbene-metal bond-lengths (\(r_b(\text{C–M})\)) show a decrease of 0.1–0.2 Å with respect to the non-relativistic data in Table 3. These point to a stronger bonding to the metal, when accounting for relativistic corrections in Au, Ag, and Pt. For the substitution energies, our results denote that Au and Pt are more preferable in binding to carbene, than Ag and Cu. The platinum atom shows an even higher affinity to bind to the carbene-functionalized diamondoids. Again, no significant trends were found with the variation of the diamondoid size. Such a variation could be found in an investigation accounting for a larger variation in diamondoid size. Apparently, the inclusion of relativistic effects for Ag play an important role and need to be accounted for. However, for the electronic properties, no significant qualitative difference was observed when comparing the relativistic and the non-relativistic results. What differs is the value of the band-gap. Since, though, here we are interested in qualitative trends, we will proceed with the results from the non-relativistic simulations.

The electronic properties of all carbene-functionalized diamondoid metal complexes are probed through the electronic densities of states (\(\text{eDOS}\)). Qualitatively, all four diamondoids led to similar trends. Here, only one diamondoid case, that of carbene-
The distribution of the frontier orbitals of all tetramantane-metal cases are shown in Fig. 6. In the gold, silver, and copper complexes, the Fermi level coincides with an electron energy level, and a definition of HOMO and LUMO is not possible. Accordingly, three molecular orbitals are sketched: the one at the Fermi level, one below and one above the Fermi level, respectively. In the platinum complexes and the functionalized cases (no metal), the Fermi level falls between two energy levels, the HOMO and the LUMO. For the platinum complexes, an electronic band-gap exist and the HOMO and LUMO levels are well defined. This trend was observed for all diamondoid sizes considered in this work. Accordingly, in the figure we show results only for one of these, the tetramantane complex.

A further shift of the frontier orbitals towards the metal atom is evident in all complexes compared to the functionalized tetramantane (also shown). The lower orbitals, i.e. the ones below the Fermi level are associated with carbene and the metal atom. In the Cu case (C3N2H4−(121)C22H27−Cu), the respective molecular orbital is associated only with the Cu atom. The orbitals at the Fermi level and that of the LUMO in the Pt complex (C3N2H4−(121)C22H27−Pt) show a similar behavior. For these cases, the molecular orbitals are extended across the lower (N−C−N) chain of atoms of the carbene and the metal atom, showing a large distribution around the metal atom and its affinity to binding. The large electron energy distribution around the metal atom and the lower C atom of carbene denote the strong C-metal bond. The association of both the HOMO and the LUMO (or the state at the Fermi energy and one gap. The band-gaps for the different diamondoid complexes with platinum are 1.739, 1.636, 1.712, and 1.739 eV for adamantane, diamantane, triamantane, and (121)-tetramantane, respectively.

Table 4

<table>
<thead>
<tr>
<th>Complex</th>
<th>Au(rel)</th>
<th>Ag(rel)</th>
<th>Cu</th>
<th>Pt(rel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>adamantane-carbene</td>
<td>1.739</td>
<td>1.636</td>
<td>1.712</td>
<td>1.739</td>
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<td>diamantane-carbene</td>
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<td>triamantane-carbene</td>
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<td>1.361</td>
<td>1.360</td>
<td>1.371</td>
</tr>
<tr>
<td>tetramantane-carbene</td>
<td>1.46</td>
<td>1.361</td>
<td>1.360</td>
<td>1.371</td>
</tr>
</tbody>
</table>

Table 4 Structural properties and substitution energies of the complexes made up from carbene-functionalized diamondoids and metal atoms as compared to the case without the metal. All notations are similar to Table 3. Bond-lengths (r_b) in Å, bond-angles (θ_b) in degrees, and substitution energies (ΔE) in eV. The Au complexes have again been taken as the reference. Relativistic effects ('rel') have been assumed for Ag, Au, and Pt, respectively, but not for Co.

Functionalized (121)-tetramantane metal complexes (C3N2H4−(121)C22H27−M) is presented in Fig. 5. The gold, silver, and copper complexes introduce an additional state at the Fermi energy, which is located inside the band-gap of the functionalized tetramantane (no metal). All notations are similar to Table 3. Bond-lengths (r_b) in Å, bond-angles (θ_b) in degrees, and substitution energies (ΔE) in eV. The Au complexes have again been taken as the reference. Relativistic effects ('rel') have been assumed for Ag, Au, and Pt, respectively, but not for Co.
below) to a specific site of the complexes is a characteristic of a chemical bond. The orbitals above the Fermi levels in the gold, silver, and copper cases, show a localization across the carbene unit. In all cases, the diamondoids are not associated with any of the frontier orbitals in the complexes. The carbene ring is the component in the functionalized diamondoid which promotes the molecule-metal binding.

4. Summary

In this work, within the framework of density functional theory we have modeled and investigated the functionalization possibilities of diamondoids (C\textsubscript{x}H\textsubscript{y}) with a carbene unit C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}, the imidazolylidene molecule. Diamondoids from adamantane up to two level study on carbene-functionalized diamondoids as assembled diamondoid monolayers on substrates for applications functional nanostructures and provide a physical understanding of molecule to express its excellent electron emitting properties on a substrate. The results denote that the carbene-functionalized diamondoids can strongly be adsorbed on a platinum surface and form self-assembled monolayers. A decrease in the band-gap for all functionalized diamondoids (C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}–C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}) as compared to the unmodified diamondoids (C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}–C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}) was observed. The band-gap variation is related to a localization of the frontier orbitals (both HOMO and LUMO) across the carbene unit. The functionalized structures show the expected characteristics, that is the carbene unit maintains its electronic properties. Accordingly, the affinity of carbene to attach to metal atoms would allow the diamondoid unit in the functionalized molecule to express its excellent electron emitting properties on a substrate. In this work, the main aim was to investigate novel functional nanostructures and provide a physical understanding of their properties and binding to metal atoms in view of building self-assembled diamondoid monolayers on substrates for applications in molecular electronics and electron emitting devices. Through the two level study on carbene-functionalized diamondoids (C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}–C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}) and their complexes with metal atoms (C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}–C\textsubscript{3}N\textsubscript{2}H\textsubscript{6}–M), we could provide a proof of principles on the interaction of functionalized diamondoids with metals. For this, it was not necessary to account for additional diamondoid sizes or shapes and distributions of their molecular orbitals have been discussed. The main aim of this study was to understand the physical properties of carbene-modified diamondoids and link to possibilities of the adsorption of the carbene-functionalized diamondoids on metal surfaces. The functionalized diamondoids were found stable up to a high temperature. In all complexes, the functionalized diamondoids form short bonds to the metal atoms indicating a strong binding. On the basis of the substitution energy analysis for the diamondoid-metal complexes, the Pt atom was found to most preferably bind to the complex. The Pt and the C\textsubscript{u} complexes show also the shortest carbon-metal bond. These results denote that the carbene-functionalized diamondoids can strongly be adsorbed on a platinum surface and form self-assembled monolayers.

Acknowledgments

A. N. is thankful to G. Sivaraman for critically discussing the results. The authors acknowledge support from the German Funding Agency (Deutsche Forschungsgemeinschaft–DFG) as a part of the collaborative network SFB 716 “Dynamic simulations of systems with large particle numbers”. This work was performed on the computational resource ForHLR Phase I funded by the Ministry of Science, Research and the Arts Baden-Württemberg and DFG.

References


