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Diamondoid-based molecular junctions: a computational study

Bibek Adhikari, Ganesh Sivaraman and Maria Fyta

Institute for Computational Physics, Universität Stuttgart, Allmandring 3, D-70569 Stuttgart, Germany

E-mail: mfyta@icp.uni-stuttgart.de

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Abstract
In this work, we deal with the computational investigation of diamondoid-based molecular conductance junctions and their electronic transport properties. A small diamondoid is placed between the two gold electrodes of the nanogap and is covalently bonded to the gold electrodes through two different molecules, a thiol group and a N-heterocyclic carbene molecule. We have shown that the thiol linker is more efficient as it introduces additional electron paths for transport at lower energies. The influence of doping the diamondoid on the properties of the molecular junctions has been investigated. We find that using a nitrogen atom to dope the diamondoids leads to a considerable increase of the zero bias conductance. For the N-doped system we show an asymmetric feature of the $I$–$V$ curve of the junctions resulting in rectification within a very small range of bias voltages. The rectifying nature is the result of the characteristic shift in the bias-dependent highest occupied molecular orbital state. In all cases, the efficiency of the device is manifested and is discussed in view of novel nanotechnological applications.

Keywords: molecular electronics, DFT, doping, diamondoids, electronic transport

(Some figures may appear in colour only in the online journal)

Introduction

Diamondoids are a family of nanoscale diamond-like carbon nanoclusters, thermodynamically very stable, which are terminated by hydrogen atoms [1, 2] and are considered as novel nanoscale building blocks [3]. Diamondoids can occur in small amounts in earth petroleum as well as in rock crystals [4]. The electronic, optical, mechanical and thermal properties of these diamondoid surfaces exhibit properties of both single-crystal diamond and nanostructured diamond [5, 6]. They can self assemble [7], form self assembled layers on surfaces [8] and ordered phases in carbon nanotubes [9]. By modifying these molecules with synthetic techniques, these can be selectively functionalized on surfaces [10, 11]. It is also possible to tune the optical gap of these cages by sulfurization [12]. The electronic properties of diamondoids are influenced by the hydrogen terminations, a function with major consequences in the design of molecular-based diamondoids [13]. The influence of a single thiol functional group and other dopants on these properties has also been theoretically and experimentally determined [14, 15]. Diamondoids show a monochromatic photoemission peak when forming monolayers [16].

Diamondoids can be attached on metal surfaces through a thiol group [14, 17] to form self-assembled monolayers (SAMs) with a negative electron affinity [10, 18] and a strong monochromatic emission [8, 10]. These properties make diamondoids very promising for electronics applications. 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 [19–22]. A first theoretical study on thiol-functionalized diamantane molecules in a gold nano-junction has also pointed to the transport characteristics of chemical modifications of diamantane [23]. These thiol-based SAMs, though, are not very stable in different environmental conditions, which makes their use for industrial purposes problematic [24–27]. As an alternative to thiol binding we have proposed the use of N-hetero-cyclic carbene (NHC) molecules as linker groups of diamondoids on metal surfaces. Unlike typical carbene molecules, which are highly reactive and have very limited stability, NHCs usually have two hetero-atoms adjacent to the carbene carbon [28]. This feature...
increases the NHC stability. In addition, NHCs can be prepared on the industrial scale, can be crystallized, distilled, and stored for long periods of time in order to become commercially available reagents [29–31].

The fact that diamondoids are used as building blocks and can be efficiently attached on metal surfaces can naturally suggest their use in molecular conductance junctions [1, 23, 32, 33]. The field of molecular electronics was introduced four decades ago with the proposal of using a single organic molecule as a rectifier [34]. Since then, the idea that a molecule sandwiched between a metal junction could be used as a sub-nanometer electronic component has been vigorously pursued with the hope of replacing the existing silicon technology in electronics applications as they approach device scaling limits [35–40]. Doping and functionalization using boron and nitrogen has always been used in the past to tune the electronic properties of such devices [41–45]. The alteration and modification of transmission spectra is mainly due to the shift in the energy levels of the electrode which resulted in the rectifying behavior with respect to the applied source and drain voltage [46–52].

Along these lines, in this work, thiol- and NHC-diamondoids will be used to fill a gold nanogap and form diamondoid-based molecular devices. The transport properties across these devices and the influence on these of different functionalizations, dopants, and diamondoid sizes are our main focus. To our knowledge, such an extensive investigation has not been carried out before. This work is structured as follows: we first present the methodology used and then proceed to the results on the transport properties of the diamondoid-based molecular devices for different molecules. We perform a comparative study of various devices based on their electronic transport properties. We also present their structural and electronic characteristics. In the end, we discuss the implications of our results on novel nanotechnological applications of diamondoid-based molecular devices.

**Methodology**

Simulations based on the density functional theory (DFT) [53, 54] as implemented in the code SIESTA [55] were carried out. We have used the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE-GGA) [56], and the norm-conserving Troullier–Martins pseudopotentials [57]. For the basis set, we have considered a double-ζ with polarization basis-set (DZP) for the molecules, and a single-ζ with polarization (SZP) for the gold atoms (5d⁰, 6S¹) which has been proven efficient for similar setup [58]. An energy shift of 0.01 Ry with a real space sampling grid (mesh cutoff) of 200 Ry. A Monkhorst–Pack k-points mesh of 5 × 5 × 1 for the scattering region and 5 × 5 × 40 for the semi-infinite leads was used. The Au(111) unit cell was fully relaxed and we obtained the lattice constant of 4.186 Å which compares well with the data reported in the literature [59]. The geometry optimization of the length of the scattering region was performed using the conjugate gradient algorithm and the structure was relaxed until the net forces on each component were lower than 0.01 eV Å⁻¹.

The electronic transport calculations are performed using DFT combined with the non-equilibrium Green’s functions (NEGF) formalism, as implemented in the TranSIESTA [60] code. Bias dependent self consistent calculations were performed to obtain the current–voltage characteristics ranging from −0.9 to +0.9 V in steps of 0.1 V. The current (I) through the scattering region at a bias (V₈) is calculated by integration of the transmission spectrum using the Landauer–Büttiker formula [61]:

\[
I(V₈) = \frac{2e}{h} \int_{-\mu_R}^{\mu_L} T(E, V₈) \left[ f_L(E - \mu_L) - f_R(E - \mu_R) \right] dE,
\]

where \(T(E, V₈)\) is the bias dependent transmission probability of an electron with energy \(E\), and \(f_L(E - \mu_L)\), \(f_R(E - \mu_R)\) are the Fermi–Dirac distribution for the left and right electrode, respectively. The electro-chemical potential for the left electrode is given as \(\mu_L = E_L + V₈/2\) and \(\mu_R = E_R - V₈/2\) for the right electrode. The Fermi energy \(E_F\) is shifted to zero.

In our investigation, we study the influence of two different diamondoids (diamantane and tetramantane), the type of dopants, and the diamondoid functionalization on the properties of a metallic break-junction [62]. In such a device, a diamondoid is inserted and bonded through the functionalization groups on the metallic surfaces. For the electrodes, two Au(111) surfaces are taken. In order to evaluate the effects mentioned above, we pick two representative lower diamondoid cases, diamantane and tetramantane to vary the diamondoid size. For tetramantane, one of the isomers, the [121]-tetramantane molecule was chosen [63]. Boron (B), nitrogen (N) and boron with nitrogen (BN) are chosen to separately dope the diamondoids. Accordingly, in the doped cases, one of the carbon atoms of the diamondoid cages are replaced by one of the dopants. For the functionalization molecules we have used (a) a thiol group (commonly used to attach diamondoids on a metal surface) and (b) the N-hetero-cyclic carbene (NHC) molecule, a member of the carbene family [11].

Overall, we have considered a set of sixteen different diamondoid-based devices, which differ in the diamondoid size (two variations), the doping (four variations—three doped and one undoped case), and the functionalization molecules (two variations). These functionalized diamondoids chosen to be placed within the gold nanogap are shown in figures 1 and 2. In the following, we use the notation ‘diam’ and ‘tetra’ for diamantane and (121)-tetramantane, respectively. ‘X-doped’, with \(X = B, N, \text{and BN}\), denotes the doping of the diamondoid, while the term ‘undoped’ is used for the undoped diamondoids. Note, that the diamondoids are functionalized on both sides in order to bind to the Au(111) surfaces on each side of the nanogap. Accordingly, the notations ‘dithiol’, and ‘dNHC’ denote the double functionalization using a thiol or a carbene (NHC) group. The molecules are placed within the Au(111) nanogap and then relaxed. Five 5 × 5 Au(111) layers are used as the screening layer at each side of the surface between the electrode and the molecule as depicted in figure 3. These Au(111) surfaces together with the inserted molecule consist
the scattering region (device). The device is coupled on either side to three outer layers of Au(111) which form the semi-infinite leads. For the device relaxation, two inner atomic layers of the Au(111) surface on either side of the molecules were also allowed to relax to enable preferential binding. The other three outer layer of the device Au(111) were fixed at their bulk positions. Finally, for the fully relaxed devices, electronic transport calculations were performed by means of coupling to semi-infinite leads on either side, the results of which are discussed in the next section. There is no direct tunneling across the Au(111) nanogaps for a capacitor distance of 6 Å or more [58].

Results and discussion

Structural characteristics

We begin our analysis with the structural details of the various diamondoids in the gold nano-gap. Representative devices are depicted in figure 4 for dithiol- and dicarbene-diamondoid devices. In all devices studied here, the diamondoids are bonded to both electrodes through the mediating molecules (thiol group or carbene). In figure 4 (bottom panel), the molecules are attached to the surface only through the lower carbon atom of the carbene ring. Two of the H atoms of the NHC molecule (on both electrodes) are very close (≈2.80 Å) to the gold surface and interact weakly with the surface. The bond-length of the molecule to the surfaces is in the range of (2.64–2.90) Å for the dithiol-diamantane and (2.61–2.92) Å for the dithiol-tetramantane cases, respectively and corresponds to the S–Au distance. In the diNHC-diamantane and tetramantane cases the C–Au distance for both electrodes are in the range of (2.19–2.20) Å and (2.19–2.21) Å, respectively. The dithiol-diamondoids are less flexible within the nanogap compared to the diNHC-diamondoids, hence the difference in the bonding behavior to the metal surface. This is also qualitatively observed through the orientation of the molecules with respect to the setups before structural relaxation.
In the dithiol cases, the preferred bonding site for S–Au is on the fcc center bonded with three gold atoms. In the NHC cases, the on-top site is preferred for the C–Au bond. We have observed that the gold atom bonded to the NHC moves closer (and out of the surface) to the lower carbon atom of the carbene ring as reported in previous studies [11, 64]. This is slightly visible in figure 4 (bottom panel). The flexibility of the C–O–C bond between NHC and diamondoid allows for additional conformational variability during relaxation. Here, though only a certain conformation will be examined for simplicity. Note, that a slight off-lattice movement of the Au atom bonded to the sulfur atom also in the dithiol cases was evident (see figure 4 top panel). Regarding the doped diamondoids, very small changes of about 2%–4% in the bond-lengths at the vicinity of the dopants were observed with respect to the undoped diamondoids. However, since B and N are typical dopants for carbon materials and have electronic configurations very close to C, no significant alterations in the structures have been observed. These small changes, though, have a higher impact in the electronic and transport properties as will be shown next. Note, that according to our simulations, the electronic band gaps for the isolated dithiol diamantane, dithiol tetramantane, diNHC diamantane and diNHC tetramantane molecules are 5.29, 5.36, 3.19 and 3.24 eV, respectively.

Electronic transport

Next, the electronic transport across the diamondoid junctions is analyzed. The quantum transport calculations lead to the calculated zero-bias transmission functions, \( T(E, V = 0) \) summarized in figure 5 for all cases studied here. The electronic transport across the molecule is strongly influenced by the choice of the functionalizing group through which the molecule is attached to the metal. We begin by investigating the effect of different functionalization groups: the dithiol (figure 5 top panel) and diNHC cases (figure 5 bottom panel) for undoped diamondoids on the transmission function. The first observation is that the transmission at the Fermi level for all dithiol diamondoids is at-least six orders of magnitude higher in comparison to their diNHC counterpart. The zero bias conductance \( G = \frac{2e^2}{h}T(E_F) \) where \( E_F \) is the Fermi
level for undoped dithiol diamondoids is summarized in table 1 and are comparable to the values reported for π-conjugated organic compounds [65]. Consequently with an applied bias voltage, a dithiolated diamondoid is expected to lead to a higher current flow in comparison to its diNHC counterpart. In all the undoped cases, the first transmission peak highest occupied molecular orbital (HOMO) is found to be further away the Fermi level. The HOMO levels are at $-2.53$ eV, $-2.10$ eV, $-3.21$ eV and $-2.87$ eV for dithiol-diamantane, dithiol-tetramantane, diNHC-diamantane and diNHC-tetramantane, respectively.

The effect of dopants on the zero-bias transmission function can also be seen in figure 5. The diNHC-based doped diamondoid junctions has resonance peaks (figure 5 bottom panel) far below the Fermi level (beyond the range of a practical bias voltage window) similar to the undoped case. This is not the case with the dithiol-based doped junctions. In all dithiol cases, the transmission is higher for the N-doped diamondoids, which is not the case in the diNHC cases. In order to understand this further, we turn to the nitrogen doping on dithiol-based tetramantane junctions (figure 5 top right panel). The first transmission peak below the Fermi level (HOMO) in this case is found at around $-0.45$ eV. The calculations revealed that the resonance peak (at $-0.4578$ eV) in the projected density of states (not shown) corresponds to a density of states contribution from nitrogen doping. The lowest unoccupied molecular orbital (LUMO) is far from the Fermi level in all the cases. We only observe prominent peaks of the LUMO beyond 2.5 eV for the dithiol cases and beyond 2.0 eV for the diNHC cases respectively. In this respect, the LUMO level is not of high importance to the conduction within a bias window practically accessible in experiments. BN and B doping does not lead to any improvement in the zero bias conductance of dithiol junctions as also easily observed in table 1. Interestingly, the B-doped diNHC-tetra junctions shows the highest zero bias conductance compared to all the diNHC-tetra cases. However, all zero bias conductance values for all diNHC-diamondoid electrodes are at

![Figure 3](image-url)  
**Figure 3.** The setup for the transport calculations: the dithiol-diamantane and the inner ten layers of the Au(111) (five on each side of the molecule along the z-direction) form the scattering region. This is in turn coupled to semi-infinite leads (made of three layers of gold) on both sides. Electronic transport occurs along the z-direction.

![Figure 4](image-url)  
**Figure 4.** Final relaxed structure for: (top panel) a dithiol-tetramantane and (bottom panel) a diNHC-tetramantane in between Au(111) layers.

![Figure 5](image-url)  
**Figure 5.** The zero-bias transmission function is plotted on a semi-log scale for all diamondoid-based devices studied in this work. In the top panel, data for the dithiol diamantane (left) and dithiol tetramantane (right) based devices are depicted. In the bottom panel, data for the diNHC diamantane (left) and diNHC (right) tetramantane devices are shown. The color in the legends denote whether the diamondoids are doped or undoped.
least five orders of magnitude lower than the respective dithiol-diamondoid cases.

The size of the diamondoid also seems to affect the transmission. This is evident in the dithiol cases, in which the larger diamondoid (tetramantane) shows sharper transmission peaks (below the Fermi level) for the N- and BN-doped cases compared to the smaller diamantane, as seen in the top panel of figure 5. Nevertheless, in the diNHC cases, the transmission peaks are similarly sharp for both diamondoid sizes (lower panel of the same figure). In the latter cases, the transmission peaks of the N- and BN-doped diamantane are much broader, though almost at the same energies as in the respective tetramantane cases. The different features for the diamondoid sizes indicate that the increment in the size of diamondoids has an effect on the localization of the HOMO resonance peak close to the Fermi level. Overall, though the thiol-diamondoid devices show a larger transmission closer to the Fermi level, there are energy ranges in which the diNHC devices can better accommodate the flow of current. This happens, for example lower than $-1.5$ eV in the diNHC B-doped tetramantane devices, as compared to the respective dithiol case. The zero bias conductance values presented in table 1 imply that the conductance across the two dithiol-diamondoid junctions is of the same order of magnitude, but slightly larger for the smaller diamantane. Both the N-doped dithiol diamantane and N-doped dithiol tetramantane cases show the zero bias conductance of $1.67 \times 10^{-2} G_0$ and $2.49 \times 10^{-3} G_0$, which is comparatively higher with respect to the previously investigated systems [36]. The respective value for the N-doped tetramantane case, though, is still higher than the values of the other tetramantane cases. This suggests that diamondoids could be used as a molecular conductance junction in the design of highly functional devices.

Table 1. Conductance in units of $2e^2/h$, at zero bias for the modified diamondoid junction at the Fermi level. The higher transmission for each junction is given in boldface text.

<table>
<thead>
<tr>
<th>Type</th>
<th>Dithiol-diam</th>
<th>Dithiol-tetra</th>
<th>diNHC-diam</th>
<th>diNHC-tetra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>$6.94 \times 10^{-3}$</td>
<td>$1.77 \times 10^{-3}$</td>
<td>$4.34 \times 10^{-9}$</td>
<td>$8.00 \times 10^{-10}$</td>
</tr>
<tr>
<td>B-doped</td>
<td>$5.11 \times 10^{-3}$</td>
<td>$1.50 \times 10^{-3}$</td>
<td>$2.29 \times 10^{-9}$</td>
<td>$2.29 \times 10^{-9}$</td>
</tr>
<tr>
<td>N-doped</td>
<td>$1.67 \times 10^{-2}$</td>
<td>$2.49 \times 10^{-3}$</td>
<td>$5.55 \times 10^{-9}$</td>
<td>$3.81 \times 10^{-10}$</td>
</tr>
<tr>
<td>BN-doped</td>
<td>$6.65 \times 10^{-3}$</td>
<td>$1.36 \times 10^{-3}$</td>
<td>$1.10 \times 10^{-8}$</td>
<td>$3.02 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

In order to further understand the undoped vs doping among the dithiol-tetramantane junctions, we have plotted the the eigenchannel wavefunctions (EWF) [66]. For the undoped, N-doped and BN-doped dithiol-tetramantane cases, these are plotted in figure 6, each at two different energies. The EWF plotted correspond to the Fermi level at $0$ eV and the first transmission peak below the Fermi level i.e. at $-2.10$, $-0.45$ and $-0.68$ eV for the undoped, N-, and BN-doped cases respectively. At the Fermi level, due to finite transmission (of the order of $10^{-3}$ according to figure 5), the EWF are localized towards the left of the device and then decay in the transport direction. The peaks in the transmission across the doped dithiol-tetramantane junctions in figure 5 (top panel) correspond to a strong electronic coupling of the two electrodes as depicted in figure 6. For both the doped dithiol-tetramantane junctions, the EWFs spread out across the whole device region. In the undoped case, the molecular orbital corresponding to strong electronic coupling is far below the Fermi level. Hence, doping shifts transmission peaks closer to the Fermi level, which might contribute to conductance in a practically accessible bias voltage region.

**Current–voltage characteristics**

As a further analysis to understand the effect of doping, we report on the $I–V$ eigenchannel wavefunction curve for undoped and N-doped dithiol-tetramantane junctions. We focus on the bias-dependent transport properties of the junctions. We will also report on the shift of the zero-bias ‘reference’ transmission peak at $-0.45$ eV seen in (figure 5 top right panel) with respect to applied voltage bias. The current voltage ($I–V$) curves for two different cases (a) dithiol tetramantane and (b) N-doped dithiol tetramantane are shown in figure 7. The asymmetric behavior of the current at positive and negative bias in the range $[-0.9, +0.9]$ V for both the junctions, investigated in our work is evident from the $I–V$ characteristic depicted in the upper panel of figure 7. The current in both the undoped and doped cases seems to increase with the application of higher bias. There is a clear distinction in the current for the undoped and doped cases. The distinction being that the current in doped case is even more pronounced, when we increase the bias in both positive and negative direction. For the undoped case the current increases and reaches up to a maximum of $\pm 0.087 \mu A$ for the applied bias voltages. However in the doped case, the current was found to be $-0.124 \mu A$ for $-0.9$ V and $0.128 \mu A$ for $+0.9$ V.

In order to compare the efficiency of doped devices we have defined the rectification ratio (RR) as: $RR(V) = |I(V)/I(-V)|$. Our aim was to use RR as a means to gain a qualitative understanding of the influence of doping and guide the experiment towards a direction which would certainly effect the rectification. Our work is not intended to fully evaluate in a quantitative way the rectification effect. For this, a more extended study including additional molecules would be needed. The rectification ratios for both the undoped and doped cases are shown in the lower panel of figure 7. Dithiol N-doped tetramantane-based junctions show a higher rectification ratio for the bias voltages applied in this work as compared to the undoped case. We observe a sharp increase in the rectification from 0.1 V upto 0.4 V. The highest
The efficiency of the junction is found to be at 0.6 V, at which the rectification ratio is found to be 1.07. There is a sudden drop at 0.7 V where the efficiency decreases up to 1.06. A similar drop is also observed for 0.9 V where the (RR) drops to 1.03.

In the undoped case there is a drop in the (RR) at 0.5 V, but interestingly a minor increase in the efficiency is seen at a higher bias unlike the doped case.

A comparison of the transmission spectra under applied bias is depicted in figure 8. We present the plots for 0 V, ±0.6 V, and ±0.9 V respectively. For both the undoped and N-doped cases, we can observe an increase in the conductance at the Fermi level for ±0.9 V. We also observe notable peaks for the positive energy range in the transmission spectrum. However, these are not related to the LUMO levels, which are further away from the Fermi level and not in the practically accessible range, as also previously discussed for the zero-bias transmission spectra. At this point, there is no strong indication of the origin of these small peaks and a further investigation is needed. In case of the undoped case the molecular conductance was found to be 2.92 × 10⁻³G₀ for +0.9 V and 2.94 × 10⁻³G₀ for −0.9 V respectively. Similarly, for the doped case the molecular conductance (Fermi level) was found to be 3.15 × 10⁻³G₀ for +0.9 and 3.33 × 10⁻³G₀ for −0.9 V, respectively. As observed in the lower panel of figure 8, there is a characteristic shifting of the zero-bias ‘reference’ transmission peak with respect to the applied bias. The shift in the positive and negative bias for the N-doped dithiol tetramantane case results in rectification. After the comparison of the shift for the reference peaks among symmetric bias voltages (for example: −1, +1 V), we observe that the shift for the positive bias up to 0.6 V is only slightly perturbed with respect to the zero bias reference peak. Further increasing the positive voltage bias moves the reference peak away from the zero bias case towards left. One can

Figure 6. Eigenchannel wavefunctions for the dithiol-tetramantane devices: (a)–(b) undoped dithiol tetramantane, (c)–(d) N-doped dithiol tetramantane and (e)–(f) BN-doped dithiol tetramantane each shown at the energy given in the label. ’0.00’ eV corresponds to the Fermi level in each case. The plots in the right panels correspond to the first transmission peaks (HOMO) below the Fermi level for each setup. For clarity all wavefunctions are plotted for the same isovalues. Positive values of the wavefunctions are in red and negative in blue.
undoped dithiol tetramantane level for also observe that the bias dependent conductance at the Fermi level. Figure 8.

Figure 7. I–V characteristics (top panel) and rectification ratio (bottom panel) of undoped dithiol tetramantane (red) and N-doped dithiol tetramantane (blue) based junctions at different bias voltages close to the Fermi level.

also observe that the bias dependent conductance at the Fermi level for −0.9 is higher compared to its positive counterpart i.e. +0.9. Combinations of these factors could contribute to lowering of rectification ratios beyond an applied bias of 0.6 V.

Figure 8. Transmission spectra as a function of the applied bias for undoped dithiol tetramantane (top panel) and N-doped dithiol tetramantane (bottom panel).

electronic and transport properties of the diamondoid-based molecular junctions by doping the molecules with boron and nitrogen. The doping with nitrogen leads to an addition of a transmission peak very close to the Fermi level leading to higher molecular conductance. Increasing the diamondoid size leads to a slight decrease in the zero bias conductance. Such a decrease was also observed when using the carbene molecules as linkers of the diamondoid on the nanogap surfaces. Bias dependent transport calculations revealed that doping leads to a higher rectification ratio at very small applied bias voltages. This behavior is the result of the energy shift of the HOMO peaks with respect to the zero bias case. Overall, the rectifying effect in N-doped diamondoids is related to the asymmetry in the structure when introducing the dopant. Since a similar asymmetry is introduced by means of doping in the case of B and B–N co-doping, we can assume that a similar rectifying behavior is observed also for these latter cases. Nevertheless, a separate study needs to be carried out to further quantify these effects.

We have investigated certain conformations of the modified diamondoids within the gold nanogaps. Our aim was to provide a proof of functioning principles for such molecular junctions. For a more extensive analysis, a conformational scan of the molecules would be needed, which could be the subject of a separate study. The investigation carried out here has an impact on the design of novel molecular devices for electronics and sensing applications. A careful choice of the materials can lead to functional devices with desired properties. Our work indicates that the search for the molecule indented to fill a metallic nanogap should be made with care, as small modifications in its structure significantly influence the properties of the molecular device. The use of a simple thiol group for grafting the diamondoid on metal electrodes typically leads to high electronic transmission. Additional investigations should further quantify the effect of structural fluctuations of the molecule in the junction on the signal-to-noise ratio in the electronic measurements. This issue was not tackled here, but is expected to have a great impact on the efficiency and the rectification properties of diamondoid-based molecular devices. In the end, these investigations need to be supplemented by research at the experimental level in order to prove the optimal functionality of these junctions.

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Summary

We have studied the electronic transport across molecular junctions made up of functionalized and doped diamondoids. The comparison of the results were discussed based on the functionalization, the type of dopants, and the diamondoid size. Di-thiol linker groups were found to be efficient as compared to a carbene group attached to the Au(111) nanogap. The zero bias transmission function of the undoped diamondoid systems reveals that the HOMO peaks are away from the Fermi level, which is beyond any practical voltage bias window (−1 to +1 V). We have selectively tuned the
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