Probing DNA nucleobases with diamond (111) surfaces

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Abstract

DNA units, the nucleobases, are probed with diamond (111) surfaces. The nucleobases are placed on top of a diamond surface interacting in a very specific way with the surface atoms. Different elements, such as hydrogen, nitrogen, and fluorine are chosen for the termination of the diamond. The energetic features and electronic properties of the combined system ‘nucleobase/diamond surface’ are thoroughly studied using quantum-mechanical calculations. These point to nucleobase- and termination-specific characteristics linking to the potential of using diamond surfaces for identifying the DNA nucleobases. Focus is further given on mixed surfaces with a varying nitrogen and hydrogen coverage. For these, we provide pathways for tuning the electronic band gap of the surface/nucleobase complex with the nitrogen content of the surface. The results could unravel a clear crossover in the surface electron affinity and its relation to a reversal in the positions of the electronic band extrema from the material to the molecule and vice versa. These features link to a further selective modulation of the electronic transport and the excitation properties of the complexes with a strong biosensing potential.

1. Introduction

A vast number of applications require the use of biosensors [1–4]. Such applications in medical diagnostics, drug discovery, food industry, environmental control, etc require tools for analyzing and detecting biomolecular substances, their identity and possible modifications [5]. Biosensors are analytical instruments with a high biological specificity and sensitivity, which are typically combined with physicochemical transducers. Such transducers, together with a receptor and a processor are the basic components of a sensor. The bio-target to be sensed forms a recognition layer, which is integrated with a transducer via immobilization. The immobilization is possible through either covalent binding, cross-linking, or non-covalent binding, such as hydrogen bonding or van der Waals interactions. The type of a transducer in a biosensor is based on the type of measurements carried on for processing the signals. Accordingly, a vast number of biosensors are being employed, such as optical [6, 7], electrical [8], either amperometric [9, 10] or voltammetric [11], electrochemical [12, 13], colorimetric [14, 15], plasmonic [16, 17], etc. The vast number of biosensors that have been proposed, also differ in the material used to promote the sensing. In that respect, biomolecular systems have been proposed, such as microbes [18, 19], enzymes [20–22], phage [23, 24]. On the solid-state material side, polymers like polystyrene [25–28], gold [14, 29], zinc oxide [30, 31], silicon [32–34], graphene [35–37], carbon nanotubes [38, 39], and many more have been shown to possess a high bioselectivity.

Another very important issue towards medical applications is the biocompatibility of the receptor and often also the transducer in a biosensor. In view of this biocompatibility and non-toxicity, a very promising material is diamond [40–42]. It is known that diamond is indeed more biocompatible than other carbon forms [43], as well as highly stable and chemically inert. Although, other carbon materials have been proposed in the past for biosensing purposes, such as carbon nanotubes for the determination of paracetamol [44] or graphene for the detection of glucose or cholesterol [35], it seems that diamond surfaces exhibit a superior chemical stability [45]. The latter can be functionalized or hybridized with biomolecules, such as DNA or proteins, and become biologically active [46–49]. Typically, DNA and other molecules can be covalently bonded to diamond surfaces
resulting in a micropatterning [51] giving rise to a number of bioapplications [52, 53]. Depending on its form, diamond as a nanoparticle could be used for deliver in biological systems [54], while as a surface it could be chosen as the electrode material [55].

In view of medical diagnostics and epigenetics analysis, a biosensor should be able to detect and analyse DNA, its structure and sequence. DNA includes all the genetic information in the form of four nucleobases, adenine (A), guanine (G), cytosine (C), and thymine (T) [56]. Accordingly, sensing DNA would mean identifying the different nucleobases along its sugar–phosphate backbone, as well as possible modifications in these nucleobases (e.g. methylation [57]). In that respect, a DNA sensor is an electronic device highly sensitive to the type of DNA nucleobases. In such a device, though, the DNA nucleobases are supposed to be the target and not the probe. For this reason, these are not immobilized on the surface, but are expected to come close to the surface in order to be probed and sensed. According to the above points, diamond has the potential to be used for these purposes. Nevertheless, in order to evaluate this, a bottom-up approach needs to be followed. For this, the very basic details on the interaction of the probe (diamond) and the target (DNA) should be unraveled and well understood. Along these lines, here, we begin at a very fine level investigating the specific interactions of single DNA nucleobases with diamond surfaces. The aim is to provide a proof-of-principles on possible nucleobase- and/or material-specific features in the properties of the combined surface/nucleobase system that can be further explored for DNA detection applications. This article is structured as follows: the methodology followed in this work is outlined in section 2, the results are presented and discussed in section 3, and the conclusions and an outlook in section 4.

2. Methodology

In this study, we aim to numerically model the interactions between a diamond (111) surface and the four DNA nucleobases. For this, we take four types of surfaces, which differ in their surface termination in order to assess the influence of this on the interactions with the DNA nucleobases. As representative surface passivation, we use hydrogen, nitrogen, fluorine, and a mixture of hydrogen and nitrogen. We refer to these surfaces in the following as ‘H-terminated’, ‘N-terminated’, ‘F-terminated’, and ‘mixed HN-terminated’, respectively. These surfaces are used to probe the four nucleobases, adenine, guanine, cytosine, and thymine. To these nucleobases, we refer with the labels ‘A’, ‘G’, ‘C’, and ‘T’, respectively. The distinct systems used, surfaces and nucleobases, are depicted in figure 1 after being geometrically optimized. Note, that the termination atoms connect to carbon atoms on both top and bottom sides (left and right in the figure). The only exception is the mixed HN-terminated surface for which the N-coverage is varied only on the side interacting with the nucleobases. The other side is only H-terminated. The reason for this choice is to allow comparison with the literature [58]. After the optimization of the isolate structures, we bring one nucleobase close to one of the surfaces and perform a geometry optimization of the combined diamond/nucleobase system. Note, that here we only focus on non-covalent interactions of the two systems. As it is not practical and not the current purpose to do a full scan of the configuration space at this level of modeling, we place the nucleobase in a planar arrangement with respect to the surface. This arrangement models one of the highly probable configurations.

The geometry optimization and the calculation of the electronic properties of the combined surface/nucleobase system were performed using density functional theory (DFT) [59, 60] based calculations as implemented in SIESTA [61]. For the description of the exchange and correlation, we have used the LMKLL dispersion-including approach [62]. Initial tests with the the generalized-gradient approximation [63] under the Perdew–Burke–Ernzenhof (PBE) ansatz revealed the importance of van der Waals interactions. For the pseudopotentials, the norm-conserving Troullier–Martins scheme was taken [64]. For all elements, a double-ζ polarized basis-set (DZP) was applied. A real space sampling grid (mesh cutoff) of 300 Ry and 2 × 2 × 1 and 10 × 10 × 1 k-points using the Monkhorst–Pack scheme were set for the calculation of the energy and the density of states (DOS), respectively. The ionic relaxations were performed until the net atomic forces of each atomic component were smaller than 0.04 eV/Å.

In order to model the diamond (111) surface, we have created diamond (D) supercells with a size of 12.636 × 12.636 × 40.634 Å with a vacuum space of 20 Å along the z-direction. The latter ensures that spurious interactions with images due to the applied periodic boundary conditions (PBC) are avoided. 10 layers were used in total for the diamond surface. For the production simulations and the full geometry optimization of the surfaces interacting with the nucleobase, only the first five layers of the material were allowed to relax. In order to test our methodology, we have first carried out benchmark calculation for bulk diamond using both exchange-correlation functionals. The lattice constant for bulk diamond with the PBE and the LMKLL functional was calculated to be 3.573 Å and 3.588 Å in a relatively good agreement compared to the experimental result of 3.567 Å [65]. The LMKLL approach is also known to overestimate the bond length [66]. For the GGA and LMKLL calculations, the electronic energy band gap was found close 4.11 eV and 4.42 eV,
respectively. The band gap is underestimated to the experimental value of 5.48 eV $^{[65]}$, but is within the expected error. For the interaction energy ($E_{\text{int}}$) between the surface and the nucleobase, we use the following equation

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{surf}} + E_{\text{nuc}}),$$

with $E_{\text{complex}}$, $E_{\text{surf}}$, and $E_{\text{nuc}}$ being the total energy of the surface/nucleobase complex, the isolated surface, and the isolated nucleobase, respectively. In order to correct these energies for the basis set superposition error (BSSE) due to the use of atomic-like orbitals, we have followed the counterpoise correction $^{[67]}$.

### 3. Results and discussion

#### 3.1. Isolated structures

We begin the analysis with the structural properties of the isolated diamond surfaces and summarize their structural properties after geometry optimization in table 1. Relevant data from the literature are also listed for comparison. Overall, our results are in a good agreement to the literature values within the expected methodological accuracy. For example, the LMKLL ansatz is known to overestimate the bond length $^{[66]}$. Regarding the electronic band gap, the H- and F-terminated surfaces show a similar value, which is higher than for the N-terminated surface. This can be assigned to the similar atomic configurations of the H- and F-terminated surfaces at which an electron is covalently bonded to the passivation and the carbon atoms. In the N-terminated surface, the nitrogen atom passes three electrons to the carbon atoms in order to sustain an octet.

### Table 1. The structural properties of the isolated diamond (111) surfaces with the various terminations: hydrogen, nitrogen, and fluorine.

| Parameter             | H-termination | N-termination | F-termination |
|-----------------------|---------------|---------------|---------------|
| Energy Gap (eV)       | 4.46          | 3.88          | 4.44          |
| Electron Affinity (eV)| $-1.46 (-1.27$ $^{[70]}$) | 3.70 ($-3.45$ $^{[58]}$) | 4.18 ($-3.60$ $^{[58]}$) |
| Bond Length           |               |               |               |
| C-C                   | 1.55 (1.54 $^{[72]}$) | 1.555 (1.54 $^{[72]}$) | 1.55 (1.54 $^{[72]}$) |
| C-X                   | 1.18 (1.09 $^{[72]}$) | 1.55 (1.48 $^{[72]}$) | 1.40 (1.37 $^{[72]}$) |

Figure 1. Left: the optimized geometries of the H-terminated, N-terminated, and F-terminated diamond (111) surfaces. Right: the optimized geometries of the four nucleobases as denoted by the legends. In gray, white, blue, green, and red are shown the carbon, hydrogen, nitrogen, fluorine, and oxygen, respectively. This color coding will be used throughout.
configuration. The electron affinity of the isolated surfaces was calculated [68] revealing a negative affinity of the H-terminated surface. Accordingly, the conduction band minimum (CBM) lies higher than the vacuum level and can be justified through the lower electronegativity of a hydrogen atom compared to that of a carbon atom [69]. The value from our work is in good agreement with experimental data [70] and more accurate than DFT calculations using a hybrid functional (−1.63 eV [58]). The N- and F-terminated surfaces show a positive electron affinity assigned to the higher electronegativity of nitrogen and fluorine compared to carbon. These results are in a good agreement with previous DFT calculations with a hybrid functional [58]. No relevant experimental result could be found in the literature. For the isolated nucleobases, the bond lengths are in good agreement to previous calculations with other exchange-correlation functionals [71]. The electronic band gap of the isolated nucleobases is compared to literature values in table 2. Compared to previous calculations [71] the LMKLL exchange-correlation functional has a tendency to yield larger energy gaps, except for cytosine.

### 3.2. Surface—nucleobase interactions

Using as a reference the properties of the isolated systems, we move on to the surface/nucleobase complexes. We take all combinations of the three (111) surfaces (H-, N-, and F-terminated) and the four nucleobases. At first, we seek the optimum distance between each surface and a nucleobase. For this, we step-wise vary the inter-complex distance between these two components and calculate at each distance the interaction energy according to equation (1). The variation of this interaction energy with the inter-complex distance for the H-terminated surface and the four nucleobases is given in figure 2. As a first note, the comparison between the DFT (uncorrected) and the BSSE corrected energies, reveals that the latter lead to a shallower minimum in the energy. However, the corresponding energy is still negative pointing to an attraction between the surface and the nucleobase. Overall, the form of all curves follows nicely that of an inter-molecular potential with a repulsion at very small distances and a negligible attraction at distances over 0.4 nm. For all surface/nucleobase complexes, we take the distance corresponding to the minima of the respective interaction energies and perform a full geometry optimization at these distances. The total energy obtained from this optimization is used in equation (1) in order to correct for the minimum interaction energies in figure 2 with respect to the optimized distance from these final calculations. The resulting configurations for the H-terminated surface and the four nucleobases are depicted in figure 3. In this figure, the given energies are the energies after the structural optimization of the complex performed at the distances corresponding to the minimum energies in figure 2. It is obvious, that the interaction energy between the diamond surface and guanine is the largest denoting a higher stability. The order of the interaction energies follows the mass of the nucleobases, that is D > G > D > A > D > T > D > C, where D represents the diamond surface. Further inspection of this figure, also reveals changes in the relative arrangement of the nucleobase with respect to the surface. Except for adenine, the other nucleobases perform a tilt with respect to the xy-plane. The change of the respective angle can be assigned to the presence of an oxygen atom in G, C, and T, which is attracted by the surface hydrogen atom. However, the inter-complex distances measured from the nucleobase plane are not affected.

In order to get a more in depth information on the electronic distributions at the interface between the surface and the nucleobase, we compute the electron localization function (ELF) [76]. The ELF is a measure of the probability of finding an electron in the neighborhood of another electron with the same spin. As a result the ELF takes values in the range [0, 1] and allows the identification of regions where the electrons are localized. These regions could be atomic shells, bonding pairs, or lone-electron pairs [77]. For the H-terminated surface/
nucleobase complexes, a cross-sectional view of the ELF on the \(yz\)-plane at a \(x\)-position close to the center of the nucleobase is mapped in figure 3(right). Inspection of this figure reveals that localization of electrons with the same spin is found at the interface and mainly on the surface terminating atoms. As expected the shape of the ELF close to these surface atoms is modified depending on their interaction with the atoms of the nucleobase. In
that respect, the ELF on the surface H atoms further away from the nucleobase has a more circular shape, while exactly below the nucleobase the ELF circular shape is deformed and is smaller. This trend can be interpreted through a higher probability of finding neighboring electrons of the same spin further away from the interaction region of the surface and the nucleobase. This shifting of the ELF can be related to the existence of the dispersion forces between the two components, surface and nucleobase. Within the nucleobases, the ELF is on average lower than 0.5 with very small regions where it reaches 1. Turning to the diamond surface, a clear separation of the crystallographic planes is evident through the negligible ELF between the planes. A high ELF is found only on the in-plane C–C bond.

The electronic features of the surface/nucleobase system are further discussed through their projected electronic density of states (PDOS). For the H-terminated surfaces these are depicted in figure 4 together with the respective electronic energy band gap. Inspection of the PDOS reveals that the valence band maximum (VBM) in all complexes is set by the surface and the conduction band minimum (CBM) is defined by the nucleobases. This feature indicates that at the VBM level, the electrons are mainly accumulated on the surface. Furthermore, the band gaps between the complexes differ significantly between 4%–77%. Note, that DFT at this level of accuracy does not capture quantitatively the band gaps, but can nicely represent the trends. These large differences show highly nucleobase-specific features in the electronic characteristics of the complex. Comparison to the band gaps of the isolated nucleobases in table 2 reveals that the differences in the electronic features of the nucleobases are significantly enhanced when these are probed with the diamond surfaces. Similar to what was observed for the interaction energy in figure 2, the order in the electronic band gaps of the complexes follows that of the mass of the nucleobases.

3.3. Probing guanine

As a first summary here, we have observed from figures 2, 3 that the strongest interaction with the H-terminated surface resulting in the highest energy gap was found in the case of guanine. In the following, we focus on the different surfaces probing only the guanine molecule. We expect that for the rest, nucleobase-specific features will still hold for the other surface terminations. For the N- and F-terminated diamond (111) surfaces, we follow the same procedure as for the H-terminated one: we first vary the distance between G and these surfaces and find the minimum energy distance. At this distance, we perform a geometry optimization of the complex. The corresponding features from this optimization for the three surfaces interacting with guanine are summarized in table 3. It is obvious that terminating the diamond surface with nitrogen atoms yields the largest inter-complex

![Figure 4. The PDOS of the H-terminated diamond surface interacting with the four nucleobases, as denoted by the legends. All energies are shifted, so that the Fermi level ($E_F$) of the surface lies at 0 eV. The arrows and respective numbers correspond to the electronic energy band gap for each complex. The legends, A, G, C, and T, denote the complexes of the H-terminated surfaces with the respective nucleobases.](image-url)
distance, compared with the H- and F-terminated diamond surfaces for which these distances are very close. Apparently, a higher repulsion occurs between the surface nitrogen and guanine, moving the nucleobase further away in order to lower the interaction energy. The H-terminated diamond surface yields the largest interaction energy with guanine, followed by the N- and F-terminated surfaces. In the former case, the s-orbital of the hydrogen is attracted by the $\pi$-rings on the guanine creating an attractive force. On the other hand, the more electronegative and electron rich nitrogen and fluorine atoms create on the surface a larger electron cloud increasing the repulsion to the $\pi$-rings of the guanine, thus lowering the interaction energy. The energy band gap is surface-dependent and follows the trend in the inter-complex distance. This can be interpreted based on the fact that more energy is needed to excite the electron from the VBM to the CBM for larger inter-complex distance.

The respective relaxed complexes are depicted in figure 5. As for the H-terminated surface, we again observe for the N- and F-terminated surfaces a similar re-orientation of the $\pi$-rings of guanine in order to accommodate to the presence of the surface. As opposed to the H-terminated surface, the interaction of the other two surfaces with guanine allows guanine to remain flat, while the hydrogen atoms of the amine group in G move slightly closer to the surface. This behavior can be assigned to the attraction of these two hydrogen atoms to the nitrogen or fluorine atoms of the surfaces. The PDOS of these complexes are shown in the same figure. Interestingly, the trends found for the H-terminated surface is reversed. For both the N- and F-terminated surfaces, the VBM is assigned to the nucleobase and the CBM to the surface. In terms of excitation that would mean that for the H-terminated surface an electron would be excited from the surface to the nucleobase, while for the N- and F-terminated surfaces, the excitation would be in a reversed order. These differences of the VBM and CBM

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**Table 3.** A comparison of the surface-guanine distance, the interaction energy, and the electronic band gap for the interaction of the three surfaces with guanine. The results are shown for the optimized configurations. The inter-complex distance is calculated by taking the distance between the centroid of the surface atoms and the plane of guanine.

| Surface     | Distance (Å) | $E_{\text{int}}$ (eV) | Energy gap (eV) |
|-------------|--------------|-----------------------|-----------------|
| H-terminated| 2.74         | -0.422                | 1.74            |
| N-terminated| 3.05         | -0.294                | 1.82            |
| F-terminated| 2.69         | -0.105                | 1.34            |
positions are possibly related to the different electron affinity of the surfaces: negative for the H-termination and positive for the N- and F-terminations.

3.4. Influence of nitrogen coverage
In this final part, we proceed with diamond (111) surfaces terminated by a mixture of N and H atoms. The aim is to unravel the influence of the N-coverage of the surface on its interaction with guanine. In order to have a reference for our investigation, we begin the analysis with the properties of isolated mixed HN-terminated diamond (111) surfaces for which we vary the nitrogen coverage ($X_N$). As mentioned at the very beginning, the coverage is changed only on the surface interacting with guanine. The other side of the slab is only H-terminated. Accordingly, one should have in mind, that the $X_N = 1.00$ results of the interaction energy and the band gap do not correspond to the results from the N-terminated surfaces above. For $X_N = 0.00$, though, we get back the results for the H-terminated surfaces above. Note, that the H sites for the substitution with N have been randomly chosen. Since our surfaces are periodic any site-specific features should be averaged out in the trends provided. The optimized geometries with different $X_N$ are depicted in figure 6. $X_N$ is defined as the number of N-surface atoms over the total number of surface atoms. We have also calculated the electron affinity (EA) of these isolated surfaces as seen in figure 7(a). It is clear that the EA of the surface increases from negative to positive values as the N coverage increases. The transition from a negative EA (NEA) to a positive EA (PEA) occurs slightly over $X_N = 0.6$. This is in a good agreement with previous calculations [58]. The differences in the crossover point from a NEA to a PEA can be assigned to the different exchange-correlation functional used. The energy band gap of the isolated surface (figure 7(b)) shows a reversed trend to the EA with a small decrease over the range of the N-coverage.

After the discussion of the properties of the isolated mixed HN-terminated surfaces, we move on to the interacting surfaces with a guanine. Representative optimized structures and the corresponding PDOS are given in figure 8. Evidently, varying the N-coverage ($X_N$) results in differences in the structural arrangement of the two components, the interaction energy, and the electronic features of the complexes. It is obvious from the figure, that guanine is always almost planar, but arranged differently with respect to the surface. We can always observe a small incline of the oxygen atom of G towards the surface due to its attraction to the surface H atoms. On the other hand, the two hydrogen atoms of the amine group in G are tilted away from the surface due to their repulsion to the surface H-atoms. These variations influence the respective interaction energies between the surface and G, which are summarized in table 4. The largest $E_{int}$ is found for $X_N = 0.36$ and is followed by
 Accordingly, for these compositions a more stable complex is formed. The lowest interaction was found for \(X_N = 1.00\) corresponding to a fully N-covered surface.

When analyzing the electronic features in figure 8, we observe that for \(X_N = 0.20\) the positions of the VBM and CBM are similar to the case of the H-terminated surface above. On the other hand, for the surface with \(X_N = 0.92\), the position of the VBM and CBM are the same as for the N-terminated surface. For the intermediate N-coverage \(X_N\), the positions of the VBM and CBM are given in table 4. As expected, for a small N-coverage the positions of the VMB and CBM are the same as for the H-terminated case, while the opposite occurs for a high N-coverage resembling more the N-terminated case. An interesting feature is observed for \(X_N = 0.76\), which is close to the crossover from NEA to PEA and for which the positions of both the VBM and the CBM are located at guanine. As evident from this table, the different characteristics of the VBM and CBM positions are related to the EA of the surface. For a NEA, the VBM and CBM are located at the surface and guanine, respectively. The reversed occurs for a PEA, except for \(X_N = 0.76\). This exception indicates that the surface with \(X_N = 0.76\) marks the transition from the H-like terminated surface to the N-like terminated surface.

In order to assess the influence of the interaction, we compare in figure 7(b) the energy band gap for the isolated mixed HN-surface and the same surface interacting with guanine. Inspection of the results, clearly reveals that the interaction leads to overall smaller band-gaps for the complexes and a different trend at least until the crossover to a PEA surface. For an increasing N-coverage, the band gap for the complex increases, while after the crossover a clear decrease can be seen as in the isolated surface. The smaller band gaps can be assigned to the existence of the molecular states within the gap of the surface in the complex case. The trends in the energy gap with the N-coverage follow the respective trends of the distance between the surface atoms and the nucleobase. In order to reveal this, we present in figure 7(c) the inter-complex distance. An increase of this distance is clearly observed with an increasing N-coverage until the crossover at which a decrease begins. The only exception is found at \(X_N = 0.92\), for which though the deviation should be within the error of the distance calculation.

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4. Conclusions

As a summary, we have probed DNA nucleobases with terminated diamond (111) surfaces using quantum mechanical calculations. The investigation started with H-terminated surfaces interacting with the four nucleobases. Nucleobase-specific features were found in the electronic properties of the complexes. Based on the fact that the strongest interaction of the surface was found in the case of guanine, we continue the study focusing on this nucleobase. This was further probed with a N- and F-terminating surface. The interaction energy was found to decrease moving from a H- to a N- and then to a F-terminated surface, while the largest band gap was found for the N-terminated case. Interestingly, for the latter two surfaces the positions of the VBM and CBM are reversed with respect to the former surface. At a next step, we were interested in mixed surfaces with a varying H and N coverage. Their electron affinity has shown a clear increase with a crossover from a negative to a positive electron affinity close to a 60% N-coverage. No specific trends were found in the interaction energy of these surfaces when probing G, but the largest interaction was found for $X_N = 0.36$. However an increase in both the electronic band gap and the inter-complex distance was found up to the crossover N-coverage. Overall, smaller
band gaps were found for the complex as compared to the isolated surface, due the existence of guanine molecular states within the surface gap. We could further identify a crossover in the positions of the VBM and CBM in the complex and assign this to the crossover in the surface affinity.

The results presented here show clear nucleobase and surface-termination dependent trends. Our aim was to unravel the bioselectivity of diamond surfaces through its distinct interaction to the different DNA units. We have provided a proof-of-principles on the trends within complexes of various diamond surfaces with the DNA nucleobases. Although, other factors such as a fluidic environment, dynamic effects, longer DNA molecules, conformational variability such as rotation of the nucleobases with respect to specific surface atoms, etc. were on purpose omitted, we could identify very important features that can be further explored. As an example the surface-termination specific trends in the position of the VBM and CBM can be tuned in order to promote specific electron transport and excitation effects in view of electronic and optical sensing. The results from the mixed HN-surfaces have clearly shown additional possibilities of tuning the electronic features through the different interaction that occurs when varying the N-coverage. Such features should be transferable to the electronic transport properties of the surface, which could be further enhanced and be measured. Turning to the fluidic environment typically involved in the biosensing devices implicitly implied here, its presence would alter the trends shown in this work. However, by carefully choosing the type and concentration of ions in the solution, the DNA specificity provided through our work could also be enhanced. Overall, this work attempted to provide insights on tuning terminated diamond (111) surfaces for detecting DNA. Our results serve as the first step along a bottom-up approach and could give directions for additional investigations on the use of terminated diamond as a bio-probe. In the end, these results have paved a pathway along the identification of factors able to enhance the differences among nucleobases, natural and mutated DNA or other biomolecules in order to tune the detection measurements, thus the bioselectivity.

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