Abstract: The formation of flexible self-assembled monolayers (SAMs) in which an external trigger modifies the geometry of surface-anchored molecules is essential for the development of functional materials with tunable properties. In this work, it is demonstrated that NO$_2$-functionalized N-heterocyclic carbene molecules (NHCs), which were anchored on Au (111) surface, change their orientation from tilted into flat-lying position following trigger-induced reduction of their nitro groups. DFT calculations identified that the energetic driving force for reorientation was the lower steric hindrance and stronger interactions between the chemically reduced NHCs and the Au surface. The trigger-induced changes in the NHCs’ anchoring geometry and chemical functionality modified the work function and the hydrophobicity of the NHC-decorated Au surface, demonstrating the impact of a chemically tunable NHC-based SAM on the properties of the metal surface.

Introduction

N-Heterocyclic carbene molecules (NHCs) have emerged as a new molecular platform for the formation of highly stable self-assembled monolayers (SAMs).[1] The high affinity of NHCs towards metal,[2] metal-oxide[3] and semimetal[4] surfaces along with their wide chemical tunability[5] have made NHCs an attractive alternative to thiols for generation of SAMs. It has been widely demonstrated that the anchoring geometry of NHCs on surfaces is directed by the steric properties of their substituents (Scheme 1, top panel).[2a, 6] NHCs with small side groups, such as methyl (marked by yellow disks in Scheme 1), which do not lead to strong lateral interactions, form planar bis-carbene metal complexes on metal surfaces.[2a] NHCs with larger dimethyl substituents formed films with mixtures of flat and upright orientations, whereas surface-anchored NHCs with larger diisopropyl and disopropylphenyl groups (marked by blue spheres in Scheme 1) were detected only in an upright position.[6a, 7] Density functional theory (DFT) calculations also support the hypothesis that the orientation of surface-anchored NHCs is directed by the steric properties of their side groups.[8] Interestingly, NHCs functionalized with isopropyl groups were anchored in a tilted position on Au (111) surface when adsorbed

Scheme 1. Upper panel: Surface-anchored NHCs were previously observed either in standing or flat-lying position. The orientation of NHCs was correlated to the steric properties of their side groups: bulky side groups (marked by blue spheres) led to standing NHCs, whereas NHCs with small side groups (marked by yellow spheres) were mostly observed in a flat-lying position.

Lower panel: In this work, flexible NHCs were prepared by functionalization of the NHCs with chemically active nitro groups (marked by red spheres). The NHCs changed their geometry from standing into flat-lying position following reduction of the nitro group.
at low temperature (−20 °C), but after annealing to 90 °C the NHCs geometry was changed into a flat-lying position.[6] These changes indicated that at an intermediate size of substituents the NHC adsorption geometry can represent a local minimum and the optimized orientation is achieved following annealing.

Chemical derivatization of the NHCs’ side groups allows the formation of functional NHC-based SAMs,[10,11] which can be utilized as biosensors[12] or as local chemical probes.[13] Considering that the anchoring geometry of NHCs is directly controlled by the steric properties of their side groups, it is expected that chemical transformations that change the steric properties of the side groups will influence the NHCs anchoring geometry, thus providing a new route for the formation of flexible SAMs (Scheme 1, bottom panel). In this work, we demonstrate the feasibility of this approach by using NO2-functionalized NHCs that were anchored on Au (111) surface and show that these NHCs change their anchoring geometry from horizontal into parallel position upon nitro group reduction. Moreover, it was identified that the Au surface properties can be tuned following trigger-induced chemical and structural changes in the surface-anchored NHCs.

Results and Discussion

Nitrophenyl-functionalized NHCs were prepared, activated and deposited on the surface of a clean Au (111) single crystal (Scheme 2).[9c] The NHC-coated Au sample was transferred to a ultra-high vacuum (UHV) chamber for X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structures (NEXAFS) measurements at the ALOISA beamline of the ELETTRA synchrotron (Trieste, Italy).[10]

![Scheme 2. NO2-functionalized imidazolium salt was activated by mixing it with a strong base (KOTBu = potassium tert-butoxide) in THF. The activated NHCs were anchored on Au (111) surface.](image)

N 1s XP spectra of the NHC-coated Au surface revealed two peaks centered at 400.5 and 405.9 eV, with an area ratio of 2.4:1 (Figure 1a). The high energy N 1s XPS peak was fit by one Gaussian and was correlated to NO2 species.[11] The wider (FWHM = 3.5 eV) low-energy peak was constructed of two Gaussians centered at 399.3 and 401.3 eV, which were assigned to amine (N–H) and pyrrolic (N=C) nitrogen, respectively.[12]

The presence of an amine signature in the XP spectra of the as-deposited NHCs indicated that partial nitro reduction had occurred on the surface. Infrared reflection absorption spectroscopy (IRRAS) measurement of the supported NO2-functionalized NHCs solely detected the presence of NO2 groups with no N–H signature (Supporting Information, Figure S1), specifying that the partial nitro reduction was not initiated by surface-anchoring of the NHCs but occurred following exposure to X-ray radiation.[13]

Polarized nitrogen k-edge NEXAFS measurements were performed to elucidate the chemical and geometrical properties of NO2-functionalized NHCs on Au (111) (Figure 1b).[14] The p-polarized NEXAFS spectrum of the as-deposited NHCs (solid line spectrum in Figure 1b) displayed three main peaks. The peak at 403.6 eV was correlated to N 1s → π* (NO2) transition.[14] The peak at 401.5 eV was assigned to N 1s → π* (N–C) transition. This assignment was based on NEXAFS measurement of surface anchored NHCs that were not functionalized with NO2 groups (Supporting Information, Figure S2).[14] The peak at 398.7 eV was correlated to another π* resonance and was assigned to N 1s → π* (C=N–H) transition. The detection of this peak indicates that partial reduction of the nitro group occurred in the as-deposited NHCs and led to the formation of a dehydrogenated amine,[12b] as has been previously reported.[15] The strong interaction between the nitrogen atoms and the Au surface circumvented the complete nitro-to-amine reduction. The wide peak at 407 eV was correlated to N 1s → α* (N=C, N–H) transitions.[14]
The NHCs anchoring-geometry was assigned by identifying the variations in the peak amplitudes between the p- and s-polarized NEXAFS spectra. The s-polarized spectrum (dotted line spectrum in Figure 1b) depicted similar transitions to the one obtained in the p-polarized but with lower intensities, except for the \( \pi^*_{\text{N-C}} \) transition, which showed a similar intensity in the two spectra. On the basis of these differences, it can be concluded that the NHCs were anchored in a tilted position toward the Au surface.

The orientation and adsorption energy of NO\(_2\)-functionalized NHCs were analyzed by DFT calculations. Energetically favorable position (\(-3.30 \text{ eV}\)) was the atop adsorbed NHC in which the imidazole ring was slightly tilted toward the Au surface and the bulky NO\(_2\)-decorated phenyl rings were mostly oriented parallel to the surface (Figure 1c). Notably, the Au atom that binds the NHC was slightly pulled out of the Au surface, indicating the strong interaction between the anchored NHC molecule and the surface Au atom. Similar behavior was recently observed for other surface-anchored NHC species.[16]

The adsorption energy was increased to \(-3.36 \text{ eV}\) once the NHC was anchored on Au ad-atom [Au-ad/Au (111)] (Figure 1d). The enhanced adsorption energy is a result of stabilization of the bulky molecule on the defected surface.[80] It should be noted that in both adsorption scenarios (with and without ad-atom) the adsorption geometry was similar; the central NHC ring slightly tilted toward the surface, whereas the bulky NO\(_2\)-decorated phenyl rings oriented parallel to the surface. Interestingly, additional stable adsorption conformations of NHCs, with varying orientations of the NO\(_2\) groups, were detected (Supporting Information, Figure S3). However, all these conformations showed the imidazole ring positioned in a preferred perpendicular orientation relative to the Au surface. Thus, the experimental results and theoretical calculations support a structure in which the as-deposited NHCs possess an imidazole ring in a tilted position and the NO\(_2\)-functionalized phenyl rings in a favorable parallel orientation to the Au surface.

The influence of nitro reduction on the adsorption geometry of surface-anchored NHCs was studied by annealing the surface to various temperatures and identifying the correlations between the chemical and structural properties of the NHCs, based on XPS and NEXAFS measurements (Figures 2 and 3, respectively). X-Ray measurements were conducted in a UHV chamber with H\(_2\) base pressure of \(1 \times 10^{-6} \text{ torr}\). The sample was held at each temperature for 15 minutes enabling exposure to \(1 \text{ L} = 1 \times 10^{-6} \text{ torr sec}\) of H\(_2\) molecules prior to X-ray measurement.

N1 s XPS measurements were conducted following annealing of the NHCs-coated Au (111) crystal (Figure 2a). The high energy N1 s XPS peak area (centered at 405.9 eV and correlated to NO\(_2\) species) continuously decreased as function of the annealing temperature (Figure 2a). The low energy N1 s XPS peak (397–403.5 eV), which was constructed of two Gaussian fittings, showed a different trend. The area of the Gaussian that was centered at 401.3 eV and correlated to N–H species did not change noticeably up to annealing temperature of 300 °C, whereas the area of the Gaussian centered at 399.3 eV and correlated to N-H species continuously increased along with the annealing temperature.

Quantitative analysis of the area of the three Gaussians that construct the N1 s XPS spectra (Figure 2b) showed that, up to an annealing temperature of 300 °C, there is a correlated decrease in the area of the NO\(_2\) species and an increase in the area of the NH\(_3\) species. These coupled changes indicated that surface annealing led to reduction of the NO\(_2\) functional groups. Once the annealing temperature was increased to 400 °C, the Gaussian correlated to NH\(_3\) species was negatively
shifted by 1 eV (Figure 2a). The shift in the peak position of the Gaussian correlated to NH along with the increase in the area of the Gaussian correlated to N=C species suggest that partial decomposition of the surface-anchored NHCs has occurred at this temperature.\textsuperscript{[14b,17]}

Both p- and s-polarized nitrogen k-edge NEXAFS spectra showed a continuous decrease in the nitro-correlated peak (403.6 eV) along with an increase in the dehydrogenated amine peak (398.7 eV) as the annealing temperature was increased to 300°C (Figure 3). This trend matches the one detected by XPS measurements and specifies that nitro groups were reduced as the annealing temperature was elevated.

Large differences between the p- and s-polarized NEXAFS spectra were detected as the annealing temperature was raised (Figure 3). The amplitude of the $\pi^*$ region (397–405 eV) in the p-polarized spectra increased as function of the annealing temperature, whereas the amplitude of the same region was decreased in the s-polarized spectra. An opposite trend, albeit in lower magnitude, was detected in the $\sigma^*$ region (405–415 eV), in which an increase was obtained in the s-polarized spectra and a decrease in the p-polarized spectra as function of the annealing temperature. These changes show that the surface-anchored NHCs were gradually reoriented from a tilted position at room temperature into a flat-lying position at 300°C.

Once the annealing temperature was increased to 400°C a new peak was obtained at 399.4 eV in the s-polarized NEXAFS spectrum (Figure 3). The formation of this peak indicated that partial decomposition of the surface-anchored NHCs has occurred at this temperature.\textsuperscript{[14b,17]} The stability of surface-anchored NHCs at high temperature (up to 300°C) can be correlated to the low hydrogen pressure (1 x 10^{-5} torr) that was used in these experiments and minimized the decomposition or desorption of surface-anchored molecules.

Complementary IRRAS measurements revealed that the IR signal was quenched following exposure of the NO$_2$-functionalized NHCs to a reducing environment. The loss of IRRAS signal can be correlated to changes in the adsorption geometry of the reduced NHCs. IRRAS measurements have low cross section toward the s-polarized component of the reflected IR light and therefore it is expected that dipoles that are parallel to the surface will not be easily detected in IRRAS measurements.

DFT calculations were performed to elucidate the energetic driving force for the experimentally observed influence of NO$_2$ reduction on NHCs’ orientation. It was identified that nitro reduction changed the orientation of the imidazole ring from 64 to 29° and significantly increased the binding energy for NO$_2$ that were anchored on ad-Au/Au (111) (Figure 4a,b). A similar effect was obtained, though of lower magnitude, for NHCs that were anchored on Au (111) surface (Supporting Information, Figure S4).

The DFT results show that the driving force for reorientation of surface-anchored NHCs arises from the lower steric hindrance between the central NHC ring and the reduced NH$_2$ groups, compared to the bulkier -NO$_2$ groups. Moreover, the lower steric hindrance enabled reorientation of the NHCs into an energetically favorable flat-lying position, thus allowing the formation of strong $\pi$ interactions between the three aromatic rings of the NHC and the Au surface.\textsuperscript{[18]} Such adsorbate-surface interactions cannot be formed with NO$_2$-functionalized NHCs due to steric hindrance.

It should be noted that the tilting angle of the imidazole ring increased and weaker NHCs adsorption energy values were detected by DFT calculations, once the dehydrogenated amine was fully reduced to amine (Supporting Information, Figure S5). These changes were correlated to both weaker interactions between the fully reduced NH$_2$ groups and the Au surface and an increase in the steric hindrance between the NH$_2$ groups, the imidazole ring and the Au surface, compared to those induced with the NH-functionalized NHCs.

Water contact angle and contact potential difference (CPD) measurements were conducted to identify the influence of nitro reduction and reorientation of the NHCs on the Au (111) surface properties (Table 1 and Figure S6 in the Supporting Information). Surface-anchoring of NO$_2$-NHCs on the Au surface changed the water contact angle from 80 to 45° and changed the work function value ($\Delta \phi$) by ~0.28 eV. An increase in the water contact angle to 60° and smaller work function values (~0.45 eV) were obtained following reduction of the NHCs’ nitro groups. Thus, reduction of the polar -NO$_2$ groups coupled with reorientation of the surface-anchored NHCs induced a more hydrophobic surface. In addition, nitro group reduction

\begin{table}[h]
\centering
\caption{Summary of water contact angle and CPD measurements.}
\begin{tabular}{|l|c|c|}
\hline
& Au & NO$_2$-NHC/Au & NH$_2$-NHC/Au \\
\hline
Contact angle [°] & 80 ± 5 & 45 ± 1 & 60 ± 2 \\
$\Delta \phi$ [eV] & – & −0.28 ± 0.01 & −0.45 ± 0.01 \\
\hline
\end{tabular}
\end{table}

Figure 4. DFT calculations of NO$_2$- and NH-functionalized NHCs (shown in a and b), respectively, anchored on Au-ad/Au (111) demonstrate the influence of nitro group reduction on the geometry and adsorption energy of the NHCs. The surface-anchored NHCs are shown in side and top views (top and bottom panels, respectively). The orientation angle was measured between the imidazole ring (black arrow) and the Au surface (green arrow).
lowered the work function value of the surface by 0.17 eV. The decrease in the work function value following -NO₂ reduction was correlated to the elimination of the negative interface dipole, which was induced by -NO₂ groups. This negative dipole partially compensated the dominant positive interface dipole of the NHCs.\(^{[16]}\)

**Conclusions**

The experimental and theoretical results described herein revealed that reorientation of surface-anchored NO₂-functionalized NHCs from tilted into a flat-lying position were induced by nitro group reduction. Contact angle and work function measurements quantified the influence of the chemical and structural changes in the NHC-based SAM on the Au surface properties. This work presents a new concept for preparation of tunable functional materials, in which the adjustable properties of chemically functionalized SAMs can be designed to modify, following exposure to a chemical trigger, the substrate properties, such as its dipole moment, work function, and electronic conductivity.

**Experimental Section**

**Methods and instruments**

Au (111) single crystal (purchased from SPL) was rinsed with EtOH and dried with N₂. The crystal was then transferred to a glove box in which NHCs liquid deposition was performed. NHCs were prepared according to a recently published protocol.\(^{[9c]}\) A 30 mM solution of NO₂-functionalized NHCs in tetrahydrofuran (THF) was activated by using two equivalents of potassium tert-butoxide (KOTBu) and left for 2 h to ensure carbene formation. The mixture was syringe-filtered and transferred to vials containing the Au (111) single crystal. Ensuing 24 h immersion, the Au crystal was intermittently washed with THF and water to remove any unreacted NHCs and base remnants. Next, the sample was flushed with Ar for 15 min and stored in a glove box.

Synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) data was obtained using a p-polarized X-ray beam at a grazing incidence of \(\alpha = 4^\circ\) and close to normal emission (90°-\(\alpha\)). The spectra, taken with photon energy of 515 eV, were measured in normal emission by means of a hemispherical electron analyzer with an angular acceptance of 2° and an overall energy resolution of 200 meV. The Binding Energy (BE) was calibrated by setting the BE position of the Au 4f₇/₂ peak to 84.0 eV. All spectra were corrected by subtracting a Shirley-type background. Analysis of the XPS peaks and their fitting was performed using CasaXPS software.

Near edge X-ray absorption fine structures (NEXAFS) measurements were performed in partial electron yield using a channeltron detector equipped with a front grid biased at a negative voltage (\(-370\) V for nitrogen k-edge) to filter out the low energy secondary electrons. NEXAFS spectra at the nitrogen k-edge were measured with the resolution set to \(-80\) meV while keeping the sample at a constant grazing angle of 6°. The orientation of the surface with respect to the photon beam polarization was changed from s-polarization to close p-polarization by rotating the sample coaxially to the photon beam axis. NEXAFS spectra were reported in the form of a normalized absorption amplitude \(I_{ad}/I_{reference}\), using NEXAFS measured on the bare Au (111) surface as a reference \(I_{reference}\).

Infrared reflection absorption spectroscopy (IRRAS) measurements were conducted at room-temperature under vacuum on reflection-absorption cell (Harrick, Inc.) with FTIR spectrometer (Vertex V70, Bruker). IRRAS measurements were acquired with 1024 scans at a resolution of 4 cm\(^{-1}\) using mercury cadmium telluride (MCT) detector.

Contact potential difference (CPD) measurements were performed on a large area samples with Kelvin Probe S (DeltaPhiBesoeck, Jülich, Germany), using a vibrating gold electrode (WF 5.1 eV) in a home-built Faraday cage under argon (Ar) atmosphere.

DFT calculations were performed using the plane-wave-based Vienna ab initio simulation package (VASP)\(^{[20]}\) with the generalized-gradient approximation (GGA) and the Perdew–Burke–Erzenhof (PBE) exchange-correlation functional.\(^{[21]}\) For the description of the ionic cores we used the projector-augmented wave (PAW) method with an energy cutoff of 415 eV and a k-point sampling of Monkhorst–Pack\(^{[22]}\) with a 3 x 3 x 1 mesh. For all analyzed species, we considered dispersion interactions by using the DFT-D3 method.\(^{[24]}\) The analyzed surfaces were modeled as Au (111) and Au (111) decorated with Au adatom [Au-ad/Au(111)] by using a four-layer slab consisting of 144 and 145 Au atoms, respectively, and a vacuum slab of 27 Å between periodically repeated Au slabs. The two uppermost layers were allowed to relax whereas the lower half atoms were kept fixed at their optimized bulk positions. The adsorption energy was calculated by Equation (1):

\[
E_{ads} = E_{sur/ads} - E_{ads} - E_{sur}
\]

in which \(E_{sur/ads}\) represents the energy of the surface with an adsorbed species, \(E_{sur}\) is the optimized energy of the adsorbate calculated in the gas phase and \(E_{ads}\) is the optimized surface energy without the adsorbed molecule.

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Conflict of interest

The authors declare no conflict of interest.

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