Self-Assembled Monolayers of Nitron: Self-Activated and Chemically Addressable N-Heterocyclic Carbene Monolayers with Triazolone Structural Motif

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Abstract

N-heterocyclic carbenes (NHCs) have emerged as a unique molecular platform for the formation of self-assembled monolayers (SAMs) on various surfaces. However, active carbene formation requires deprotonation of imidazolium salt precursors, which is mostly facilitated by exposure of the salt to exogenous base. Base residues were found to be adsorbed on the metal surface and hindered the formation of well-ordered carbene-based monolayers. Herein, we show that nitron, a triazolone-based molecule that freely tautomerizes into carbene, can spontaneously self-assemble into monolayers on Pt and Au surfaces, overcoming the necessity for base-induced deprotonation for active carbene formation. SAMs of nitron were found thermally stable and could not be displaced by thiols, demonstrating their high chemical stability. The addressable amine group in surface-anchored nitron was shown to be chemically available for SN2 reaction, making the surface-anchored nitron a chemically-addressable cross-linking reagent for surface modifications.

Introduction

The strong affinity of N-heterocyclic carbenes (NHCs) to coinage metals enabled their self-assembly into monolayers on metal,^[1] metal-oxide^[2] and semimetal^[3] surfaces. These self-assembled monolayers (SAMs) were characterized with high thermal and chemical stability^[1d, 4] and were utilized for diverse applications,^[5] e.g. as co-catalysts,^[1a, 2, 6] molecular probes for surface reactivity,^[1e, 7] surface patterning reagents^[8] and biosensors.^[9] The common molecular motif in surface-anchored NHCs is the imidazolium backbone, in which the carbene carbon is located between two nitrogen atoms^[4b, 5] and stabilized by the σ withdrawing and π donating properties of the adjacent nitrogen atoms.^[10]

In a typical deposition process an active carbene, which can be anchored to metal surfaces, is formed following deprotonation of the imidazolium salt by using a strong base such as potassium tert-butoxide (KO^tBu) (Scheme 1, top panel).^[1d, 11] Alternatively, the halide anion of the imidazolium salt can be replaced with a hydrogen carbonate anion which functions as a base for deprotonation and enables NHCs' deposition under vacuum conditions^[4a, 11b, 12] or under ambient conditions while using methanol as a solvent.^[4a] Active carbene can be also formed by using NHC–CO₂ adducts as precursors.^[1c, 8, 12c] The free carbene is made, along with CO₂ as a byproduct, by annealing the NHC–CO₂ adduct under vacuum condition. Thus, base-induced deprotonation for active carbene formation can be circumvented by using NHC–CO₂ adducts or NHC(H)[HCO₃] salts as precursors. However, it should be noted that both NHC–CO₂ adducts and NHC(H)[HCO₃] salts are not commercially available and their preparation involves synthetic steps that are characterized with low yield.

In a similar way to imidazoles, triazole-based NHCs^[13] were utilized as ligands in NHC-catalyzed reactions^[14] and complexation of transition metals.^[15] It was recently demonstrated^[16] that nitron, a commercially available triazole-based reagent^[17] is in equilibrium with its diaminocarbene tautomer (Scheme 1, bottom panel). The NHC-type tautomer plays a crucial role in nitron activation for its

complexation as a ligand with various metal atoms or ions.^[18] The carbene tautomer was found to be less energetically stable, by 2.3-5.7 kcal/mol, than the nitron tautomer.^[19] However, consumption of the carbene tautomer by its complexation with a metal enabled to maintain a constant concentration of free carbenes in the solution by nitron-to-carbene tautomerization.

Previous Works

This Work

Scheme 1. Top panel: Free carbene formation, which can be anchored on various metal surfaces, requires base-induced deprotonation of imidazolium salts precursors. **Bottom panel:** The two tautomeric conformations of nitron (left and middle) enabled its spontaneous anchoring on metal surfaces, as demonstrated in this work.

In this work we show that the spontaneous tautomerization of nitron to carbene can be utilized for the formation of nitron-based SAMs on Pt and Au surfaces (Scheme 1). Nitron transformation to carbene does not require the addition of a strong base or ion exchange procedures, making its surface-anchoring a self-activated process. The absence of base or halides in the deposition process prevented the adsorption of salt or base residues on the surface, which can hinder the formation of a dense monolayer. Ligand exchange experiments revealed that nitron was strongly anchored to the metal surface and could not be displaced by thiols. Furthermore, it is demonstrated that the secondary amine of the nitron functions as a nucleophile in base-activated $\text{S}_{\text{N}}2$ reactions and can be utilized as a chemical handle for functionalization of the SAM.

Experimental

Nitron (98%), heptanethiol (98%), potassium tert-butoxide (99.99%) and bromonitromethane (90%) were purchased from Sigma-Aldrich and used without further purification. Para-nitrothiophenol (p-NTP) (96%) was purchased from Alfa-Aesar and used without further purification. Pt films were prepared by evaporation of 10 nm Cr film on a piranha cleaned Si (110) wafer, followed by evaporation of 100 nm Pt. Au films were prepared by evaporation of 200 nm Au on piranha cleaned glass slides. The slides were flame annealed following the deposition.

Nitron was dissolved in THF (70 mM) in a glove box. The freshly prepared solution was transferred to a vial in which the metal-coated Si wafers were deposited. After 18 hours, the wafers were removed from the glove box and rinsed three times with tetrahydrofuran, three times with distilled water and two times with ethanol. The samples were then flushed with N₂ for 5 minutes. Ligand exchange experiments were conducted by immersing the nitron-coated surfaces in a solution of 5 mM heptanethiol or p-NTP in ethanol for 24 hours. The samples were afterward rinsed with ethanol and dried under N₂ flow.

SN2 reactions were conducted in a glove box by immersing the nitron-coated metal surfaces in a 30 mM solution of Potassium tert-butoxide in THF. After 24 hours, the surface was rinsed 5 times with THF and then immersed in 50 mM bromonitromethane in THF. The solution was removed after 2 hours and the surface was rinsed with THF and ethanol and then dried under N₂ flow.

X-ray photoelectron spectroscopy (XPS) measurements were performed by using 5600 multi-technique (AES/XPS) system (PHI) and an Al K α (1486.6 eV) X-ray source. Spectra analysis was performed with CasaXPS software. The error values in the XPS peaks area ratio analysis were deduced based on XPS measurements of three different samples.

Polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements were performed at room temperature under positive nitrogen pressure in a reflection-absorption cell (Harrick,

Inc.) with a PM-FTIR spectrometer (PMA-50 coupled to Vertex 70, Bruker). 1,024 scans were performed with a resolution of 4 cm^{-1} while using a mercury-cadmium-telluride (MCT) detector.

Atomic force microscope infrared (AFM-IR) measurements were performed on nitron-coated Pt nanoparticles. Pt nanoparticles were prepared by evaporation of a 15 nm thick Pt layer on a highly doped silicon wafer, followed by annealing to $550\text{ }^{\circ}\text{C}$ for 5 hours. AFM-IR measurements were performed in tapping mode on a nanoIR3 system (Bruker) equipped with Bruker Hyperspectral QCL laser source ($800\text{--}1800\text{ cm}^{-1}$), using gold-coated Si probes with a nominal diameter of $\sim 25\text{ nm}$, resonance frequency values of $75 \pm 15\text{ kHz}$ and spring constant values of $1\text{--}7\text{ N/m}$. Averaged spectral acquisition time was 5 sec/spectra with a spectral resolution of 4 cm^{-1} . All spectra were averaged and smoothed using Savitzky-Golay filter.

Results and Discussion

SAM of nitron was prepared on Pt film (see experimental section for details). The influence of surface anchoring on the chemical and structural properties of nitron molecules were identified by comparing the N1s XP spectra and IR spectra of non-coordinated nitron (Fig 1a and 1b, respectively, spectra i) with that of the surface-anchored nitron (Fig 1a and 1b, respectively, spectra ii). Surface-anchoring of the nitron molecules eliminated the high energy N1s XPS peak (402.0 eV), which was detected in the non-coordinated species (Fig. 1a, spectrum i). This peak was correlated to a more electron depleted state, such as the positively-charged nitrogen atom in the non-carbene tautomer. Thus, its elimination provides indication for surface-anchoring of the nitron.^[16] The positions of the two other N1s XPS peaks of the surface-anchored nitron, located at 399.9 eV and 398.3 eV and correlated to the triazolic nitrogen groups and the secondary amine,^[20] respectively, were unchanged following surface-anchoring of nitron.

Figure 1. a. N1S XPS signal of the nitron precursor (i) and SAM of nitron on Pt (ii). **b.** ATR-IR and PM-IRRAS spectra of the nitron precursor (i) and SAM of nitron on Pt film (ii), respectively.

ATR-IR spectrum of the nitron precursor (Fig. 1b, spectrum i) revealed a sharp peak at 1242 cm⁻¹ which was correlated to a C=N stretch while the peaks at 1500-1600 cm⁻¹ were associated with C=C stretches of the aromatic rings. PM-IRRAS spectra of surface-anchored nitron (Fig. 1b, spectrum ii) showed a dominant peak at 1223 cm⁻¹, correlated to the C=N stretch. Interestingly, a relatively small feature was detected in the C=C region (1597 cm⁻¹). PM-IRRAS measurements are highly sensitive to dipoles that are perpendicular to the surface. Thus, the strong C=N signal and the weak C=C signal that were detected in the PM-IRRAS spectrum (Fig. 1b, spectrum ii) can indicate a preferred upright position of the triazole ring and a flat-lying position of the nitron's phenyl rings.

AFM-IR measurements were conducted to identify the spatial distribution of surface-anchored nitron on the metal surface.^[21] These localized measurements were performed on Pt nanoparticles in order to probe the selective adsorption of nitron on various surface sites. AFM-IR spectrum (1250-1650 cm⁻¹) was measured on the surface of nitron-coated Pt nanoparticle (Supp. Info. Fig. S1). The most dominant peak in this spectral range was detected at 1492 cm⁻¹ and correlated to C=C stretches of the nitron's aromatic

rings (Fig. 1b, spectrum i). This peak was therefore chosen as a marker for probing the IR signature of surface-anchored nitron molecules on Pt nanoparticles and the AFM-IR mapping was conducted at this energy (Fig. 2). AFM topography measurement of nitron coated Pt nanoparticles (Fig. 2a) was followed by AFM-IR mapping at 1490 cm^{-1} (Fig. 2b). The AFM-IR measurements identified a relatively homogeneous distribution of the vibrational signature across the surface of Pt nanoparticles.^[22] No vibrational signature was detected on the Si wafer, demonstrating the selective chemisorption of nitron on the metal surface.

Figure 2. AFM topography mapping (a) and the corresponding AFM-IR mapping at 1490 cm^{-1} (b) of nitron-decorated Pt nanoparticles.

The influence of surface annealing on the stability, chemical properties and anchoring geometry of nitron monolayer were probed by conducting N1s XPS and PM-IRRAS measurements (Fig. 3a and Fig. 3b, respectively). Annealing of nitron-coated Pt film to $100\text{ }^{\circ}\text{C}$ led to 24 and 8% decrease in the N1s and C1s XPS peaks area, respectively, with relatively minor changes in the XPS signal profile (Fig. 3a and Supp. Info. Fig. S2). The decrease in the peaks area can be attributed to desorption of a minority physisorbed nitron species from the surface.

Figure 3. N1s XPS (a) and PM-IRRAS (b) signals of nitron SAM on Pt film before (i) and following annealing to 100 (ii) and 200 °C (iii).

Annealing of the sample to 200 °C induced noticeable changes in the N1s XPS signal pattern (Fig. 3a, spectrum iii). An increase was detected in the intensity of the N1s XPS peak that was centered at 398 eV, while the location of the high energy XPS peak shifted from 399.9 to 399.4 eV. These changes were associated with stronger interactions between the surface-anchored nitron and Pt surface. The N1s/Pt4f XPS peaks area ratio was not changed once the annealing temperature was increased from 100 to 200 °C, implying that surface annealing did not lead to desorption of surface-anchored molecules.

PM-IRRAS measurements showed a gradual decrease in the C=N (1223 cm^{-1}) and C=C (1597 cm^{-1}) peak intensities along with the annealing temperature (Fig. 3b). These changes in the PM-IRRAS spectra can specify a gradual shift in the nitron orientation into a more flat-lying position. The gradual variation in the orientation of surface-anchored nitron enabled the formation of stronger interaction with the Pt surface, as identified by the noticeable changes in the XPS signal pattern (Fig. 3a, spectrum iii).

Ligand exchange experiments of surface-anchored nitron were performed with heptanethiol and p-nitrothiophenol (p-NTP). N1s and S2p XPS signals were measured (Fig. 4a and Fig. 4b, respectively) prior and following exposure of the nitron-coated Pt film to heptanethiol or p-NTP. Relatively small changes were detected in the N1s XPS pattern following ligand exchange experiments with heptanethiol (Fig. 4a, spectrum i and ii). This result indicates that nitron was not removed from the surface due to exposure to thiols. S2p XPS measurement identified that although nitron was not removed from the surface, heptanethiol was co-adsorbed on the nitron-coated Pt surface (Fig. 4b, spectrum ii).

Figure 4: N1s (a) and S2p (b) XPS signals of nitron-coated Pt film before (i) and after exposure to heptanethiol (ii) or p-NTP (iii).

A similar pattern of thiols' co-adsorption on the nitron-coated Pt surface was demonstrated with p-NTP molecules. Immersion of the nitron-coated Pt film in p-NTP led to the appearance of a high-energy peak (404-408 eV) in the N1s XP spectrum (Fig. 4a, spectrum iii). The detection of this peak was correlated to the -NO_2 group of p-NTP. Surface anchoring of p-NTP changed as well the low energy (396-402 eV) N1s XPS peak pattern and led to the appearance of a peak in the S2p XP spectrum (Fig. 4b, spectrum iii). C1s XPS measurements showed an increase in the carbon peak area following exposure of the nitron-coated surface to thiols, providing another indication that thiols were co-adsorbed on the Pt film (Supp. Info. Fig. S3).

The influence of surface anchored nitron molecules on the adsorption of thiols and the ways by which thiols' adsorption impact the anchored nitron molecules was assessed by comparing the S2p/Pt4f and N1s/Pt4f XPS peaks area ratio for thiols that were adsorbed on bare and nitron-coated Pt surfaces (Table 1). The S2p/Pt4f XPS peaks area ratio for heptanethiol and p-NTP on Pt were 0.009 and 0.007, respectively, while the N1s/Pt4f XPS peaks area ratio for nitron on Pt was 0.015. Since there are four nitrogen atoms in each nitron molecule, it can be estimated that the surface density of heptanethiol and p-NTP on Pt were higher by 2.4 and 1.9, respectively, than that of nitron.

Table 1: XPS peaks area ratio analysis

	S2p/Pt4f		N1s/Pt4f	
	Thiols	Thiols + Nitron	Nitron (without thiols)	Thiols + Nitron
Heptanethiol	0.009±0.002	0.011±0.002	0.015±0.002	0.014±0.002
p-NTP	0.007±0.002	0.005±0.002		0.021±0.003

The S2p/Pt4f XPS peaks area ratio for heptanethiols and p-NTPs that were anchored on nitron-coated Pt surface were 0.011 and 0.005, respectively. Thus, an up to 25% difference was measured in the S2p/Pt4f XPS peaks area ratio once thiols were adsorbed on nitron-coated Pt surface, instead of the bare Pt surface. Fluctuations at this magnitude are within the measurement error, as identified by multiple XPS measurements of the same surface. Therefore, it can be deduced that the presence of nitron molecules on the Pt surface did not block the adsorption sites of thiols and did not noticeably change their surface density.

The N1s/Pt4f XPS peaks area ratio was 0.014 following adsorption of heptanethiols on the nitron-decorated Pt surface. The small change in the N1s/Pt4f XPS peaks area ratio following heptanethiols' adsorption indicates that co-adsorption of heptanethiols did not induce desorption of nitron molecules from the surface. The N1s/Pt4f XPS peaks area ratio increased by 40% following p-NTP adsorption on nitron-coated Pt surface. From the increase in the N1s/Pt4f XPS peaks area ratio it can be deduced that

the surface density of p-NTPs was 1.6 times higher than that of nitron. This value is smaller than the one measured for p-NTPs on the bare Pt surface, but still within the measurement error. Thus, the ligand exchange experiments revealed that the presence of nitron molecules on the Pt surface did not noticeably influence the surface density of heptanethiol and p-NTPs. Additionally, the adsorption of both thiols on nitron-coated Pt surface did not lead to desorption of nitron molecules from the surface. These results demonstrate the strong adsorption of nitron on Pt surface and show that nitron molecules do not form a highly dense monolayer on the surface.

The secondary amine in surface-anchored nitron provides a chemical handle for functionalization of the SAM by SN2 reactions.^[1d, 24] In order to activate the secondary amine for coupling reactions it was deprotonated with a strong base, making it a nucleophile for SN2 reaction with bromonitromethane (Scheme 2). Base addition was found essential for activation of the secondary amine for SN2 reaction.

Scheme 2. SN2 reaction of surface-anchored nitron with bromonitromethane.

XPS and PM-IRRAS measurements (Fig. 5a and Fig. 5b, respectively) were conducted before and after the SN2 reaction of surface-anchored nitron with bromonitromethane. High energy feature (404.7-407.8 eV) was detected in the N1s XP spectra following SN2 reaction and attributed to the presence of nitro-groups on the surface (Fig. 5a, spectrum ii).^[25] A new peak (1324 cm⁻¹) was also detected in the PM-IRRAS spectra following SN2 reaction (Fig. 5b, spectrum ii) and correlated to the symmetric stretch of

the nitro group in bromonitromethane (Supp. Info. Fig. S4). Additional spectral changes were detected following SN2 reaction, including broadening of the low energy N1s XPS peak (Fig. 5a, spectrum ii) and a lower C-N signal (1270 cm^{-1}) in the PM-IRRAS spectra (Fig. 5b, spectrum ii). These changes can be connected with a shift in the nitron orientation, which became more flat-lying following the SN2 reaction, enabling stronger nitron-substrate interactions. The lack of CH_2Br vibration on the Pt-coated nitron surface following the SN2 reaction indicates the no reactant residues remained on the Pt surface.^[26] Exposure of nitron-coated Pt surface to strong base did not induce desorption or decomposition of nitron molecules, as identified by the lack of changes in the N1s XPS peak area or detection of deformation-related signals in the N1s XPS and PM-IRRAS spectra following the SN2 reaction (Fig. 5 and Supp. Info. Fig. S5).

Figure 5. N1s XPS (a) and PM-IRRAS (b) spectra of nitron on Pt before (i) and after SN2 reaction with bromonitromethane (ii).

In order to demonstrate the generality of nitron self-assembly on metal films, a SAM of nitron was prepared on Au film and characterized by N1s XPS measurements (Fig. 6). The N1s XPS pattern of the as-deposited nitron on Au (Fig. 6, spectrum i) was constructed of two Gaussians, centered at 399.7 and 401 eV and attributed to the nitrogen atoms of the triazole backbone and the amine group, respectively.^[20]

^{27]} The N1s XPS signal of nitron on Au was narrower than the one detected on Pt, in which a low energy component (centered at 398 eV) was detected. This difference can be attributed to the more reactive nature of Pt that led to an additional strongly-adsorbed nitrogen species on the metal surface.

Figure 6: N1s XPS signals of nitron monolayer on Au film before (i) and after annealing to 100 (ii) and 200 °C (iii).

The N1s/Au4f XPS peaks area ratio was lower by 50% than that of N1s/Pt4f. This difference indicates that nitron molecules had higher surface density on Pt in comparison to Au. N1s XPS measurements were conducted after annealing of the nitron-coated Au surfaces to 100 and 200 °C (Fig. 6, spectra ii and iii, respectively). A low energy peak (398 eV) was detected following surface annealing. This peak was obtained already at room temperature for nitron molecules that were adsorbed on Pt film. The appearance of an additional low energy XPS feature following annealing of the nitron-coated Au film shows that stronger metal-adsorbate interactions were induced after surface annealing.

Conclusions

In this work we demonstrate that nitron, a commercially-available triazole-based carbene, can spontaneously self-assemble into monolayer on Pt and Au surfaces. Unlike imidazole-based NHCs, in which either a strong base or specifically-synthesized precursors, such as NHC-CO_2 adducts and $\text{NHC(H)[HCO}_3\text{]}$ salts are needed for active carbene formation, the natural tautomerization of nitron enabled its spontaneous anchoring on metal surfaces. The nitron monolayer was thermally and chemically stable on Au and Pt films even after exposure to elevated temperature (200 °C) and could not be displaced by thiol ligands. The chemical-addressability of the secondary amine in surface-anchored nitron was demonstrated by $\text{S}_\text{N}2$ reaction, which was facilitated by base addition. This work shows that the family of carbene-based SAMs can be extended beyond the imidazolium scope to include triazole-based carbenes, such as nitron, for the formation of chemically-addressable monolayers on metal surfaces.

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Entry for the Table of Contents

RESEARCH ARTICLE

Nitron, a triazolone-based molecule, was spontaneously self-assembled on Pt and Au films, enabling the formation of well-ordered, chemically addressable monolayers.

Eianv Amit, Iris Berg and Elad Gross

Page No. – Page No.

Self-Assembled Monolayers of Nitron: Self-Activated and Chemically Addressable N-Heterocyclic Carbene Monolayers with Triazolone Structural Motif