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Charge retention by organometallic dications on self-assembled monolayer surfaces

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ABSTRACT

Charge retention by mass-selected ruthenium trisbipyridine dications, or $Ru(bpy)_3^{2+}$, soft-landed onto self-assembled monolayer (SAM) surfaces of 1H, 1H, 2H, 2H-perfluorodecane-1-thiol (FSAM), 11-mercaptoundecanoic acid (COOH-SAM), and 11-amino-1-undecanethiol (HSAM) on gold was examined using *in situ* time-resolved secondary ion mass spectrometry in a Fourier transform ion cyclotron resonance apparatus (FT-ICR SIMS). FT-ICR SIMS analysis was performed during ion soft-landing and for 8–15 h after the ion beam was switched off. Our results demonstrate efficient retention of the doubly charged precursor ion on the FSAM and COOH-SAM surfaces manifested by the abundant $Ru(bpy)_3^{2+}$ ions in the SIMS spectra. In contrast, only the singly charged $Ru(bpy)_3^+$ and $Ru(bpy)_2^+$ ions were observed on HSAM, indicating rapid loss of at least one charge by the deposited dications. The signal of $Ru(bpy)_3^{2+}$ on COOH-SAM remained almost constant for more than 8 h after the end of ion soft-landing, while a relatively fast decay followed by a plateau region was observed on the FSAM surface. However, we found that SIMS analysis of $Ru(bpy)_3^{2+}$ ions soft-landed onto FSAM is complicated by facile ion-molecule reactivity occurring either on the surface or in the SIMS plume, making it difficult to accurately measure the charge reduction kinetics. Efficient retention of the doubly charged $Ru(bpy)_3^{2+}$ ions on COOH-SAM is remarkably different from facile neutralization of protonated peptides deposited onto this surface reported in previous studies. Our results indicate different mechanisms of charge reduction of protonated molecules and permanent ions, such as $Ru(bpy)_3^{2+}$, on SAM surfaces. Thus, we propose that proton loss is the major charge reduction channel for the protonated species, while electron transfer through the insulating SAM is responsible for the charge loss by permanent ions. Fundamental understanding of charge reduction phenomena is essential for controlled preparation of catalytically active substrates using ion soft-landing.

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1. Introduction

Collisions of hyperthermal (<100 eV) ions with surfaces play an important role in applications ranging from structural characterization of large biomolecules in mass spectrometry [1–5] to controlled surface modification [6–14] to understanding the dynamics of ion-surface collisions [15–22] and plasma-wall interactions in fusion reactors [23–28]. Physical and chemical processes occurring during the interaction of hyperthermal ions with surfaces, including elastic and inelastic scattering, charge transfer, dissociation, and soft- and reactive-landing, have been extensively reviewed [7–14,29–32]. Soft- and reactive-landing of ions, the hyperthermal analogs of

physisorption and chemisorption in thermal systems, are widely used for immobilization of mass-selected ions on surfaces with or without charge retention [6,10,33–47].

Charge retention has a significant effect on both the structure and reactivity of deposited complex molecules [32,35,36,48–56]. Partial charge retention has been unambiguously proven for small, closed-shell ions and peptide ions deposited onto fluorinated self-assembled monolayer (FSAM) surfaces [35,50,57–59]. It also has been demonstrated that charge reduction following soft-landing of protonated molecules on self-assembled monolayer (SAM) surfaces involves proton loss to the surface [59]. This process efficiently acidifies the SAM and may induce proton-mediated reactions between soft-landed species [54]. In contrast, charge reduction of ions that carry a permanent charge involves capture of low-energy electrons transferred through an insulating SAM layer [56]. It has been demonstrated that this process is controlled by the surface properties, the ion's charge state, and surface coverage [55,56,60]. For example, at low surface coverage, ligand-capped gold clusters

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deposited onto partially fluorinated SAMs efficiently retain their charge [55]. However, efficient charge reduction resulting from electron tunneling through FSAM was observed at higher surface coverage [56]. These observations were rationalized assuming that the tunneling is induced by the potential built across the layer following ion deposition.

In this study, we examine the kinetics of charge retention following soft-landing of ruthenium trisbipyridine dications, or $Ru(bpy)_3^{2+}$, onto SAM surfaces terminated with $-CF_3$ (FSAM), $-CH_3$ (HSAM), and $-COOH$ (COOH-SAM) functional groups. We previously have demonstrated strong binding of this organometallic dication to COOH-SAM, resulting in covalent binding of a fraction of deposited molecules to the surface [61]. Here, we compare the kinetics of charge loss on this surface and inert FSAM and HSAM surfaces. Charge reduction and desorption kinetics during and after mass-selected ion deposition are explored using time-resolved *in situ* secondary ion mass spectrometry (SIMS) in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer specially configured for studying ion-surface collisions [57,59,62]. We demonstrate efficient retention of two charges by $Ru(bpy)_3^{2+}$ on COOH-SAM and FSAM, as well as the loss of at least one charge on HSAM. The result obtained for the COOH-SAM surface is in sharp contract with complete neutralization of protonated peptides observed in previous studies [50,58], which indicates that the mode of ionization of the projectile ion is another important parameter for determining the efficiency of charge retention/reduction by soft-landed ions.

2. Experimental

Experiments were performed using a specially designed 6 Tesla FT-ICR instrument configured for studying ion-surface interactions [62]. The experimental approach for soft-landing experiments is described in detail elsewhere [57,59] and only briefly outlined here. It involves normal-incidence collision of externally produced ions with a SAM surface positioned at the rear trapping plate of the ICR cell. Ions are produced in a high-transmission electrospray source, efficiently thermalized in the collisional quadrupole, and mass-selected prior to acceleration and collision with the surface. Ion kinetic energy controlled by varying the voltage difference between the collisional quadrupole of the ion source and the surface was maintained at 40 eV in these experiments. During soft-landing, the surface is exposed to a continuous beam of mass-selected ions for approximately 60 min. In this study, typical ion currents of 50 pA of mass-selected $Ru(bpy)_3^{2+}$ ions were delivered onto an approximately 3.5-mm diameter spot on the target. The maximum coverage of soft-landed ions obtained in these experiments was less than 6% of a monolayer, suggesting that the total ion dose is well below the saturation threshold for SIMS experiments [57,58].

In situ analysis of surfaces following soft-landing is performed by combining 8 keV Cs$^+$ SIMS with FT-ICR detection of the sputtered ions [57–59]. Primary Cs$^+$ ions are generated using a Model 101502 HWIG-250F cesium ion gun (HeatWave Labs Inc., Watsonville, CA) installed on-axis with the soft-landing target. The Cs ion gun incorporates electrostatic deflection plates for pulsing and deflecting the Cs$^+$ beam, as well as an Einzel lens for additional focusing. The Cs$^+$ beam is transmitted through the FT-ICR instrument's electrostatic bending quadrupole and the remaining part of the instrument's electrostatic ion guide into the surface mounted just behind the ICR cell. The bending quadrupole is located at the intersection of the ion beam generated by the electrospray ionization (ESI) source and the Cs$^+$ beam, which enables simultaneous transmission of both ion beams to the surface for monitoring the soft-landing process during and immediately following ion deposition. Static SIMS conditions with a total ion flux of about 2×10^{10} ions/cm^2 (current 4 nA,

duration 80 μs, spot diameter 4.6 mm, 15 shots per spectrum, 100–200 data points) were used in these experiments that typically lasted for 8–15 h. The following potentials were applied to various focusing elements: Cs$^+$ gun floating voltage, +8 kV; extraction, +7 kV; lens, +5 kV; and Einzel lens, ($L_1 = L_2 = -250$ V; $L_3 = +3$ kV). The Cs$^+$ ion beam was pulsed by alternating the potential applied to one of the deflection plates between 0 and -400 V with the high value blocking the Cs$^+$ beam from reaching the surface. Data acquisition was accomplished using a MIDAS data station [63].

The acquisition of SIMS spectra followed procedures described in detail elsewhere [59]. A typical event sequence includes a quench pulse (51 ms), Cs$^+$ pulse (80 μs), recoil (60 μs), Au substrate ions ejection (2.5 ms), delay (60 ms), Cs ejection (5.2 ms), gated trapping (100 ms), broadband chirp excitation (2.6 ms), delay (3 ms), and detection (102 ms). The soft-landed ion beam was deflected during SIMS analysis by switching the potential applied to one pair of electrostatic bending quadrupole rods. The time delay between switching off the Cs$^+$ pulse and gated trapping of sputtered ions—the recoil time—determines the range of m/z values observed in the spectrum. Spectra obtained using relatively short recoil time are dominated by low-mass peaks, while long recoil time favors detection of higher-mass ions. In this work, we used a 60 μs recoil time that provides adequate representation of ions with $m/z > 200$. The kinetics data were obtained by sampling the surface every 4 min during and after soft-landing.

SAMs of 11-mercaptoundecanoic acid (COOH-SAM), 11-amino-1-undecanethiol (HSAM), and 1H, 1H, 2H, 2H-perfluorodecane-1-thiol (FSAM) were prepared following literature procedures [64,65]. The gold-coated silicon wafer (5-nm chromium adhesion layer and 100 nm of polycrystalline vapor-deposited gold) was purchased from SPI Supplies (Westchester, PA) and custom laser cut into 4.8-mm diameter substrates by Delaware Diamond Knives (Wilmington, DE). After thorough cleaning, the substrates were immersed in a container with 1-mM solution of the corresponding thiol in ethanol for 12 hrs. The SAM surfaces were then removed from the thiol solutions, ultrasonically washed in ethanol (acetic acid/ethanol in the case of COOH-SAM) for 5 min, quickly dried with dry nitrogen gas, and placed in the ultra-high vacuum (UHV) chamber maintained at 2×10^{-9} Torr.

1H, 1H, 2H, 2H-perfluorodecane-1-thiol was purchased from Fluorous Technologies Inc. (Pittsburgh, PA). 11-Amino-1-undecanethiol was purchased from Dojindo Molecular Technologies (Gaithersburg, MD), and 1-dodecanethiol, 11-mercaptoundecanoic acid, and tris(2,2′-bipyridine) dichlororuthenium(II) hexahydrate ($Ru^{II}(bpy)_3Cl_2 \cdot 6H_2O$) were purchased from Sigma–Aldrich (St. Louis, MO). All samples were used as received. The $Ru^{II}(bpy)_3Cl_2 \cdot 6H_2O$ sample was dissolved in methanol to a final concentration of 50 μM. A syringe pump (Cole Parmer, Vernon Hills, IL) was used for direct infusion of the electrospray samples at a flow rate of 20 μL/h.

3. Results

Fig. 1 shows FT-ICR SIMS spectra obtained after soft-landing of 5.2×10^{11}, 5.9×10^{11}, and 6.4×10^{11} ions of $Ru(bpy)_3^{2+}$ onto COOH-SAM, HSAM, and FSAM, respectively. All three spectra contain several peaks related to the soft-landed precursor ion. The spectrum of the COOH-SAM surface (Fig. 1a) is dominated by abundant peaks at m/z 414.04 and 570.11, corresponding to the singly charged $Ru(bpy)_2^+$ and $Ru(bpy)_3^+$, respectively. $Ru(bpy)_3^+$ originates from both charge reduction on the surface and charge exchange in the SIMS plume, while $Ru(bpy)_2^+$ may be produced through fragmentation of the vibrationally excited complex desorbed from the surface by the energetic Cs$^+$ ions. The doubly charged $Ru(bpy)_3^{2+}$ observed as a less-abundant peak at m/z 285.06