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Addressing Multiple Resistive States of Polyoxovanadates: Conductivity as a Function of Individual Molecular Redox States

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ABSTRACT: The sustainable development of IT-systems requires a quest for novel concepts to address further miniaturization, performance improvement and energy efficiency of devices. The realization of these goals cannot be achieved without an appropriate functional material. Herein, we target the technologically important electron modification using *single* polyoxometalate (POM) molecules envisaged as smart successors of materials that are implemented in today's complementary metal-oxide-semiconductor (CMOS) technology. Lindqvist-type POMs were physisorbed on the Au(111) surface, preserving their structural and electronic characteristics. By applying an external voltage at room temperature, the valence state of the single POM molecule could be changed multiple times through the injection of up to 4 electrons. The molecular electrical conductivity is dependent on the number of vanadium 3d electrons, resulting in several discrete conduction states with increasing conductivity. This fundamentally important finding illustrates the far-reaching opportunities for POM molecules in the area of multiple-state resistive (memristive) switching.

INTRODUCTION

Memory elements based on reversible switching of the internal electrical resistance as a function of an external voltage and current are considered as a serious competitor for the actually dominating charge based memories such as Flash and DRAM^{1,2}. The simple "electrode/insulator/electrode"-cell setup of these resistive switching memories offers a typical low power consumption, high scalability and low switching time in combination with CMOS compatibility, which makes them very appealing for the usage in the next-generation information technology, including neuromorphic computing³. However, when exploiting common transition-metal-oxide-layers (e.g. TiO₂⁴, HfO₂⁵ or SrTiO₃⁶) as switching units with dimensions significantly lower than the actual possible limit of 10 nm, growing technical issues emerge due to quantum physical effects that can only be eased by tremendous efforts in case of big industrial production lines. Elaboration of chemical and physical approaches at the level of molecules can therefore help reaching the ultimate scalability, also granting access to not-yet-developed functionalities.

Metal-oxo clusters (so-called POMs^{7,8,9,10}) and their inorganic–organic hybrid derivatives¹¹ meet in principle the requirements necessary for a possible implementation¹² in resistive switching devices. The as-yet-undeveloped utilization of *single*, spatially clearly defined POM molecules¹³ remains, however, the key challenge to achieving the fundamental breakthrough in the resistive memory-based computer technology. It allows first to circumvent the problem of <10 nm electron tunneling effects known from microelectronics, i.e. to transit from top down to bottom up approach and second to implement discrete energy levels of POMs instead of the band structure of a dielectric solid-state material. These points are beneficial for developments in the area of neuromorphic computing where the fundamentally important memristive functionality operates with multiple resistive states (MRS) that are manifested by changes in the many stable, metal-centered redox states. Due to the unique interplay between the molecular

charge, the redox properties (associated to $V^{IV/V}$) and the spin degrees of freedom (existence of { V^{IVO} }²⁺ with spin-½), polyoxovanadates^{14,15} — a subfamily of POMs — have emerged as the most promising prototypes for molecular memory devices. Furthermore, some polyoxovanadate structures such as Lindqvist-type hexavanadates^{16,17} allow altering these characteristics without significant geometric perturbations¹⁸.

Herein, the resistive switching cell is represented by embedding fully-oxidized hexavanadate molecules into a model setup, in which the bottom electrode is represented by the Au(111) surface and the top electrode is the platinum tip of a scanning tunneling microscope (STM). Although STM in resistive switching studies is a rarely used technique, it has already been successfully applied both for the mechanistic elaboration of classical thin film systems^{19,20} as well as for new approaches such as the atomic switch²¹ and superionic conductive solids²². The choice of the Lindqvist-type hexavanadate was also prompted by its low molecular charge (2-), solubility in organic solvents and thermodynamic stability in air that is all precious for immobilization procedures on electrode surfaces. Especially, the charge of this POM enables to circumvent the highly relevant problem of agglomeration illustrated e.g. for the [V^{IV}₁₀V^V₈O₄₂(I)]⁵⁻ polyoxoanion²³ on Au(111). Using different experimental and computational techniques, we show that the individual hexavanadate molecule displays MRS on Au(111) under unprecedented conditions, room temperature and low operating voltage. This is so far a remarkable observation at the level of single molecules and thus a promising way to establish a new kind of molecular resistive switching cells.

RESULTS AND DISCUSSION

Materials Design. The target hexavanadates $[V_6O_{13}\{(OCH_2)_3CCHR'SR\}_2]^{2-}$ (1–7) were prepared from pentaerythrithol-based ligands that were augmented with thioether –SR groups at the molecular periphery (R = Me (L1, L2), Pr (L3), C₅H₉ (L4), Ph (L5), 2-C₁₀H₇ (L6), CF₃ (L7), R' = H (L1, L3–L7), Me (L2)) to provide a certain degree of stabilization on gold surfaces. The molecular structures of 1–3 and 5–7 were revealed by single-crystal Xray diffraction and display the hexavanadate core capped by two (tris)alkoxo ligands in a transoid (*anti*-) fashion, as illustrated in Figure 1 (see Supporting Information for details of synthesis and X-ray diffraction structural analysis). The bond valence sum analysis and ⁵¹V-NMR spectroscopy (signal at *ca.* –495 ppm²⁴) show that the hexavanadate unit in these compounds is fully oxidized ($\{V^{IV}_0V_6\}$).



Figure 1. Conceptual chart and absorption/photoemission spectra. a Schematic representation of hexavanadate single-molecule **5** adsorbed on Au(111) with the above spotted STM tip. The DFT geometry optimizations of **5** on Au(111) give the Au–S distances of 3.36/4.14 Å (face) and 4.80/5.03 Å (edge). The phenyl rings in DFT-optimized **5** cap the gold surface with Au···Ph contacts of *ca.* 3.72/4.89 Å (face) and *ca.* 4.04/5.14 Å (edge). The Au···Ph contacts are expected to provide additional stabilization as implied by the IRRAS data. **b,c** IRRAS (b) and IR spectra (c) of **5** with correlated stretching vibrations. **d,e,f,g** XPS spectra of **1** (d: V 2p; f: S 2p) and **5** (e: V 2p; g: S 2p) on Au(111).

Proof-Of-Concept Adsorption Properties. The infrared reflection-absorption spectroscopy (IRRAS) was first used to assess the propensity of thermally stable 1-7 to retain the single-molecule structural integrity when adsorbed on the gold surface (see Supporting Information for details). The IRRAS spectra exhibit typical (tris)alkoxo (ca. 1110, 1050 cm⁻¹) and terminal / bridging V–O (*ca.* 950, 810–790 cm⁻¹) stretching vibrations of the hexavanadate cage which are, in comparison with the polycrystalline bulk materials, not significantly influenced by adsorption of 1-7 on Au (Figure 1). A weakening of the arylic C–H stretching vibrations in the 3080–3010 cm⁻¹ region, as observed for 5, points out that the phenyl rings are planarly-oriented to the Au surface due to dispersive interactions. From these data it can be concluded that the hexavanadate structures remain remarkably unaffected by the contact with the metallic surface.

To shed light on their adsorption geometries and the corresponding energetics, density functional theory (DFT) calculations were performed for two representative cases of **1–7**, that is for **1** (R = Me) and **5** (R = Ph). The DFT geometry optimizations indicate that the edge-orientation is slightly more favorable than the face-orientation for **1** and **5** by 0.15 eV and 0.23 eV, respectively (see Supporting Information for details). In line with the calculations of the Keggin-type polyoxoanion $[SiW_{12}O_{40}]^{4-}$ on Ag(111)²⁵ and Ag(100)²⁶, the main properties of **1** and **5** are neither strongly impacted by the adsorption site nor by orientation of the hexavanadate structure with respect to the surface.

Molecular Valence State and Adsorption Type On the Surface. Further insights into the immobilization and electronic properties of **1** and **5** on Au(111) were gained by X-ray photoelectron spectroscopy (XPS) and STM (see Supporting Information for details). The XPS measurements (Figure 1) were performed on samples with a low submonolayer coverage exhibiting isolated single molecules, as evidenced by STM. For **1** and **5**, only the electron population { $V^{IV}_0V^{V}_6$ } could be detected (**1**: 98 %, **5**: 99 %), which is in accordance with the fully-oxidized nature of these compounds in solution and in the solid state. The

DFT results also indicate that the chemical integrity of the hexavanadate dianion is preserved in its adsorbed form. The Bader analysis of the adsorbed molecules assigns a charge of -1.9 to the {V₆} unit and the projected density of states (PDOS) of **1** and **5** also reveal only minor changes in the electronic structure when comparing the isolated molecules to their face- and edge-oriented forms. The PDOS of the POM–Au hybrid system is nearly independent of the adsorption mode.

Fitting of the S 2p peaks^{27,28} in the XPS spectra suggests that for **1** and **5**, the sulfur atoms of the (tris)alkoxo ligands are predominately oriented to the gold surface ($E_B = ca$. 163.3 eV). Signals attributed to non-coordinated (free) thioethers (*ca*. 164.7 eV) or covalently grafted sulfur species as a consequence of a homolytic C–S bond cleavage (*ca*. 161.7 eV) were not or only marginally observed (< 5%). These XPS data provide evidence that the hexavanadate molecules are weakly physisorbed, fully oxidized and lay flat on Au(111).

Single-Molecule Imaging. Next, high resolution STM images of **1** (R = Me) and **5** (R = Ph) on Au(111) were recorded. From the deposition of a 7.5 \cdot 10⁻³ mM acetonitrile solution on the substrate it can be concluded that only a submonolayer coverage with discrete single molecules was attained. The measured three-dimensional electron densities (E_{BIAS} = 1.00 V, p = 1 \cdot 10⁻⁹ mbar) of the discrete hexavanadates show a homogeneous distribution with no long-range ordering effects. The mean lateral dimensions of **1** (4.3±0.3 x 3.8±0.3 nm) differ significantly from those of **5** (5.5±0.4 x 4.9±0.5 nm) with the higher steric nature. The measured height of the deposited hexavanadates (0.80±0.05 nm) is in good agreement with the measured edge-to-edge electron-density (*ca.* 0.8 nm) of the polyoxoanion cage in crystal structures of **1** and **5** as well as with the calculated height (*ca.* 0.76 nm) of the energetically favored edge-orientation indicated by DFT. Notably, both POMs are characterized by a continuous parabola- (and not "hilly"-like) height profile and estimated ellipsoid dimensions (Figure 2). In consistency with a study of POMs on highly

ordered pyrolytic graphite (HOPG)²⁹, the length and width of **1** and **5** in the STM images is significantly greater than the measured electron density of their crystal structures. This is due to the pronounced overestimation³⁰ of charged molecules on a polarizable surface^{31,32} by the STM tip. Here, the repulsive interactions between the negatively charged tip and the polyoxoanion with its enlarged electronic density extension provoke van der Waals interactions of the single molecules with the substrate. These polarization and charge-balancing effects propagate parallel to the surface with an insignificant influence on the molecule height and they are only present directly around the charged adsorbate. This is also supported by the fact that the physical dimensions of the immobilized hexavanadates are independent of their concentration ($7.5 \cdot 10^{-2}$ to $7.5 \cdot 10^{-3}$ mM) and the deposition procedure (drop- or dip-coating). As a result, both investigated **1** and **5** are discretely immobilized on Au(111) as single molecules.



Figure 2. Immobilized single molecules and conductivity response. a,b,c,d STM images of drop-coated $(7.5 \cdot 10^{-3} \text{ mM})$ 1 (a) and 5 (c) recorded on Au(111) with $E_{\text{BIAS}} = 1.0 \text{ V}$ ($I_{\text{set}} =$ 100 pA) at room temperature and the corresponding line profiles for 1 b) and 5 (d). e,f,g Experimental single-point STS data of single scans (gray) of 1 (e) and 5 (f) at room temperature and of 5 (g) at 100 K on Au(111), shown with the corresponding electron population for each transition; fitted data (dose-response function) are indicated in red. f,h The d*l*/d*E* of the *l*-*V* curve (h) is depicted for fitted data of 5 (f).

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Molecular Current-Voltage Characteristics. The stable scanning with positive bias voltage and the convenient STM depiction of single hexavanadate molecules of 1 and 5 allowed us to assess their current-voltage (I-V) characteristics via single-point scanning tunnelling spectroscopy (STS) at room temperature (~ 295 K), which is a favored operating condition in the field of molecular electronics and spintronics³³. In addition, the I-V curves at 100 K were acquired for compound 5 with improved stabilization attributes on Au(111). The substrates with immobilized 1 and 5 were scanned continuously by employing the STM measurement parameters ($E_{BIAS} = 1.0 \text{ V}$, $I_{set} = 100 \text{ pA}$, scanning range: 100x100 nm) to localize the deposited single molecules. The single-point I-V measurements were performed during the ongoing scanning procedure by spotting the STM tip above one of the heretofore localized single molecules. It was found that the best I-V curves could be recorded for a positive bias potential in the range of 0.0-2.0 V with a linear scan rate of $dE/dt = 1.0 \text{ V} \text{ s}^{-1}$. At 100 K the tip positioning of **5** became more fragile due to a setupspecific temperature gradient between the tip and the cooled sample. To clarify the spectra, the I-V data were fitted by using a dose-response function for compounds 1 and 5. In contrast to classical step functions, this function type clearly represents the noninfinite slopes and the horizontal parts of all steps. The I-V curves presented in Figure 2 show a Coulomb staircase-like potential-dependent increase of the current with clearly distinct current steps for **1** at 0.66, 1.08 and 1.48 V and for **5** at *E* = 0.61, 1.09 and 1.55 V. Further implied steps are observed at ca. 1.90 and 1.97 V for 1 and 5, respectively. The reduction potentials of **5** are only slightly shifted (E = 0.57, 0.97, 1.33 and 1.86 V) upon lowering the temperature (100 K).

To elucidate the distinct resistive states, the deviations of the fitted *I–V* data (d*E*/d*I*) were calculated, resulting in four distinct electron transitions for **1** and **5**. As **1** and **5** remain fully oxidized when adsorbed on gold, each step in the recorded *I–V* curves can be attributed to a single-electron reduction of the hexavanadate core, that is $\{V^{IV}_0V^V_6\} \rightarrow$

 $\{V^{IV}_{1}V^{V}_{5}\} \rightarrow \{V^{IV}_{2}V^{V}_{4}\} \rightarrow$ etc. Substantial statements about the retention time of the simulated switching cells cannot be given because the direct contact of the POM with the metallic substrate prevents the stabilization of the tip induced charge within an accessible time scale.



Figure 3. Projected density of states (PDOS). a PDOS of isolated molecules 1 and 5. b PDOS of molecules 1 and 5 adsorbed on Au(111) in the face- and edge-orientation. c 1-, 2and 3-electron reduced molecule 5 adsorbed in the edge-orientation. d Adsorbed molecule 5 with an applied field of $E_{ext} = 0.5 \text{ eV} \text{ Å}^{-1}$. All energies refer to the Fermi level. The highest occupied band, located between -1.0 and 0.0 eV below the Fermi level (E_F), corresponds to S and C atoms of the ligands, whereas the polyoxovanadate (POV) oxo band (red line) lies lower in energy, E < -1.0 eV. Empty d-vanadium bands (blue line), essential for the molecular conductivity, appear slightly above E_F .

Upon one-electron reduction, the partial filling of the vanadium d-levels in PDOS (Figure 3) is corroborated by the Mulliken atomic spin densities (ASDs). If an external electric field $E_{\text{ext}} = 0.5 \text{ eV} \text{ Å}^{-1}$ is applied to **1** and **5** on Au(111), the lowest vanadium d-band downshifts in energy, fully hitting the Fermi level and accepting electronic density from gold. Bader analysis proves the reduction of adsorbed molecules, with an increase of the molecular charge of roughly one unit, up to -2.72 for **5** in the *face* orientation and a concomitant oxidation of the gold slab by 0.94 e. The Mulliken ASDs also indicate that the extra electron transferred upon application of the electric field is accepted by vanadium atoms (see Supporting Information for details). This illustrates the fundamental role of the vanadium d-levels in the conductivity of the herein explored POMs on Au.

CONCLUSIONS

We showcased the potential of a molecular system to display MRS at room temperature and low bias voltages in a technologically relevant resistive switching model setup. This remarkable finding thus paves the way for neuromorphic computing at the level of single molecules. Although, it is noteworthy that our experiments and computations demonstrate presently the fundamental effect of detecting several discrete and stable reduction states of a single POM molecule. The eventual industrial implementation will indeed require the electrical contacting of individual molecules which remains a great challenge in the fields of molecular electronics and spintronics. Further studies will in particular have to focus on an increased charge stabilization by molecular and/or interface tuning in order to realize non-volatile switching.

ASSOCIATED CONTENT

Supporting Information. Details of synthesis and analytical characterization of organic ligands L1–L7 and hexavanadate compounds 1–7. The crystal data and details of structure refinements are described in the CIF files: CCDC 1854538–1854543. Data of IRRAS, XPS and STM/STS measurements at hybrid molecule–surface interfaces. Details of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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