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On-Surface Atom by Atom Assembled Aluminium Bi-Nuclear Tetrabenzophenazine Organo-Metallic Magnetic Complex

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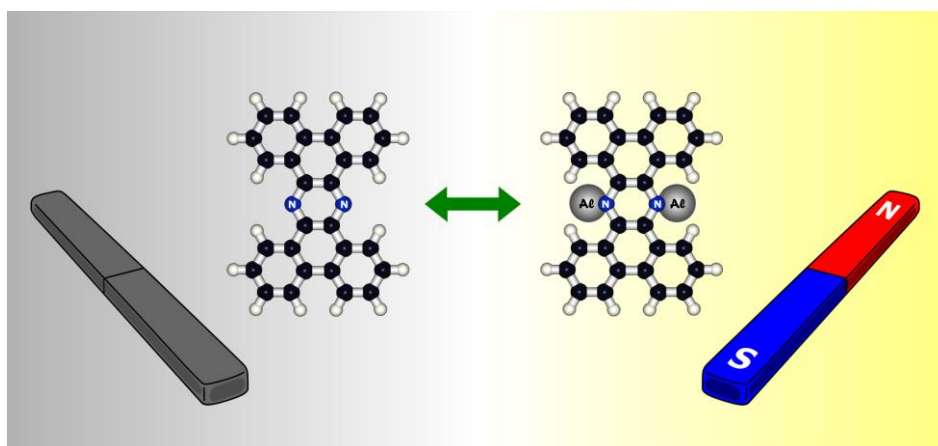
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KEYWORDS: Single molecule magnet, Kondo resonance, Aluminum-organic molecule complex,
LT-UHV STM, Molecule manipulation.

ABSTRACT: The Kondo effect results from the interactions of the conduction electrons in a metal bulk with localized magnetic impurities.^{1,2} While adsorbed atop a metallic surface, the on-surface nanoscale version of this effect is observed when a single magnetic atom³ or a single magnetic molecule (SMM)^{4,5} is interacting with the conduction electrons. SMM are commonly organo-metallic complex incorporating transition metal atoms in different oxidation states.⁶⁻⁸ We demonstrate how a single non-magnetic neutral tetrabenzo[a,c,j,h]phenazine molecule can be on-surface coordinated with exactly two aluminum metal atoms (Al(III) oxidation state on the Au(111) surface) by low-temperature scanning tunneling microscope (LT-STM) single atom manipulation. It results a Kondo measurable localized molecular magnetic moment. This opens a new way to design SMM complex without the need of heavy transition metal atom and complex ligand to stabilize the molecular coordination sphere.

TOC



On an Au(111) surface, single Al₂-tetrabenzo[a,c,j,h]phenazine organo-metallic complexes were constructed using aluminium atom by atom LT-STM single atom/molecule manipulation protocols. The Kondo effect was characterized by measuring the local differential conductance (dI/dV) scanning tunneling spectra (STS). DFT calculations confirm the stabilization of the Al₂-complex magnetic moment on the Au(111) surface. Figure 1(b) is presenting the LT-UHV STM constant current topographic image of tetrabenzo[a,c,j,h]phenazine molecules co-adsorbed with single Al atoms on an Au(111) metallic surface. The molecules (chemical structure Fig. 1(a)) are imaged having the shape of an ‘H’ letter. Single Al ad-atoms are clearly identified as well as the underlying herringbone reconstruction of the Au(111) surface. The two Al atoms are coordinated by manipulating the H-molecule towards those Al’s using the STM in a pushing manipulation mode forming the Al₂ organo-metallic complex (Ref. 9.⁹) A single Al atom invariably binds to one nitrogen of the central pyrazine ring as anticipated by design. Attempts by STM manipulations to coordinate an Al atom on other parts of the H-molecule result in the Al atom always binding to one of those nitrogen’s central pyrazine ring. This on-surface coordination experiment was also attempted with a single Au atom. As expected, an Au atom manipulated towards the pyrazine central ring is showing a lower affinity with the nitrogen’s as compared to Al. It always settled underneath one of the four off-center phenyl rings (see Suppl. Info. S1).

Once a single Al is on-surface complexed with one of the 2 available central nitrogens of the H-molecule (see below for discussion), the central part of this Al₁-complex is STM imaged with a brighter contrast than the center of a bare molecule as presented in Fig. 1(d). After a second STM tip molecule manipulation, another Al can be coordinated to the remaining free central nitrogen leading to an on-surface Al₂-molecule complex not stable in solution. STM imaged, this new

complex presents an even brighter central contrast than the Al₁-complex one as presented in Fig. 1(e).

The detailed electronic structures of the bare H-molecule, of the Al₁- and Al₂-complexes were characterized using local STS dI/dV measurements completed by DFT calculations. When the STM tip is located between two corner phenyls and near one of the nitrogen sites of the bare molecule, three distinct tunneling electronic resonances are observed. In first approximation, they can be attributed to the H-molecule |S₀⁺> (hole) and |S₁⁻> (electron) tunneling resonances of the molecular electronic |S₀> ground and |S₁> first excited singlet states respectively. They are captured at applied voltages higher than 1.5 V on each polarity (See the STS spectrum in Figure 2(a)). When the tip is located at the center of the bare molecule, those resonances are not existing in the [-1.0 V, +1.0 V] narrow voltage window as also presented in Fig. 2(b). Here, the STS spectra recorded on an Au(111) terrace (black line) and on this molecule (red) are identical.

In this [-1.0 V, +1.0 V] bias voltage interval, the STS spectrum recorded on the Al₁-molecule complex demonstrates that the Au(111) surface state was smoothed and shifted below its usual -500 mV energy location. This is because the single Al atom of the Al₁-complex is a strong scattering center for the surface electron standing waves nearby the Al₁-molecule complex center¹⁰ as presented in Fig. 2(b) by the blue STS spectrum. Another distinctive feature of this tunneling spectrum is a notable increase of the differential conductance for a positive bias voltage coming from a down shift of the +1.9 V Fig. 2(a) |S₁⁻> tunneling resonance. **New Ref. A^{ref}**

After the construction of the Al₂-molecule complex by molecule manipulation and as presented by the Fig. 2(b) green spectrum, a new very sharp peak is recorded exactly at a zero bias voltage.

According to its sharp symmetric shape, this is the signature of a Kondo resonance with a Kondo temperature of 30.3 K (see Suppl. Info. S2) indicating that the Al₂-molecule complex is magnetic on the Au(111) surface (new Ref. B R. Zitko PRB 84, 195116 (2011)).¹¹

Self-consistent field (SCF) DFT calculations were performed with one H-molecule per unit cell on the Au(111) surface (see Methods). With an adsorption energy of 3.38 eV, the H-molecule adsorbs flat on Au(111) with its central pyrazine stabilized on a bridge site. For this lowest-energy surface conformation, each pair of terminal phenyl rings is matching with two Au top surface atoms (see Suppl. Info. Fig. S3(a)). When forcing the pyrazine to adsorb atop an Au site, the adsorption energy increase only by 29 meV indicating a very low lateral diffusion barrier on Au(111). Using a Bader analysis, there is only a small 0.16 electrons small donation to the surface and the H-molecule HOMO-LUMO gap (highest occupied - lowest unoccupied molecular orbitals) is centered around the Au(111) Fermi level. Notice that HOMO and LUMO are the main mono-electronic states entering respectively in the composition of the $|S0^+\rangle$ and $|S1^-\rangle$ quantum states required to describe the recorded electronic resonances in Fig. 2(a).

One and two Al (respectively Au) single ad-atoms were also adsorbed in the unit cell (see Methods). When one Al ad-atom is located next to the phenanthrazine molecule, it stabilizes underneath, next to a nitrogen and on a bridge site. The molecule minimizes its surface energy by approaching the Al site. It shifts its central pyrazine slightly away from its original bridge site (see Fig. S3(b)). During this on-surface stabilization, the H-molecule captures a tiny amount of charge (0.04 electrons). This charge transfer induces a shift down of the LUMO energy in $|S1^-\rangle$ state as

shown in Fig. 2(c). Altogether, the Al atom had lost 1.86 electrons mainly transferred to the Au(111) surface without developing a local magnetic moment in the Al₁-molecule complex.

Adding the second Al on the central pyrazine leads to a stabilization of the Al₂-molecule complex with its shift to a hollow site (see Fig. S3(c)). As compared with the Al₁-complex, the coordination of two Al triggers a large electronic structure transformation. Each Al ad-atom has now lost about two electrons and one electron was transferred to the H-molecule explaining the observed molecular local magnetic moment leading to the zero voltage Kondo resonance. The SCF value of this magnetic moment is 0.41 Bohr magnetons with a filling of about 0.65 electrons spin-up and 0.24 electrons spin-down at the Fermi energy.

The main oxidation state of aluminum is well-known and defined as Al(III). When Al is chemisorbed on the metal surface, this oxidation number is no more valid. For a single isolated Al chemisorbed on Au(111), DFT calculations give an oxidation state between Al(I) and Al(II) and low-valent aluminum compounds had been already obtained in solution.¹² About 1.82 electrons are missing from the Al 3p and the 3s native orbitals. This intermediate oxidation state beneficiaries to the observed coordination between the neutral H-molecule and the 2 STM manipulated Al atoms. Notice that in solution, the closest known compound is (Al(Methyl)₃)₂-pyrazine.¹³ On the Au(111) surface, the consequence of this intermediate oxidation state is that the Al₂-molecule complex is magnetic as probed using the Kondo effect. Indeed, the analysis of the spin distribution on the Al₂-complex (see Fig. 2c and Fig. 3(d)) indicates that its central pyrazine is spin polarized. To understand this distribution, we have calculated different Al₂-molecule complex oxidation states away from its stabilizing surface while keeping its surface optimized conformation. We first considered Al₂-molecule complex with two neutral Al atoms. Far away from the surface, this

artificial molecule has no magnetic moment. As indicated by our charge analysis of the Al₂-molecule complex on the Au(111) surface, removing three electrons from this Al₂-complex produces a large spin polarization but not comparable with the adsorbed complex one (Fig. 3(e)). However, the spin distribution of a H-molecule anion alone (Fig. 3(f)) is showing a very good agreement with the adsorbed Al₂-molecule complex experimental Kondo map Fig. 3b. This confirms that the 2 Al atoms are partially charging negatively the H-molecule because of their adsorption on the Au(111) surface. They serve as spin donor for the molecule electronic cloud. The advantage of this on-surface coordination chemistry is that the surface Al₂-molecule constructed complex is magnetic as compared with the (Al(Methyl)₃)₂-pyrazine molecule.¹³

Using Au ad-atoms on the Au(111) surface do not lead to a spin polarization of the H-molecule. The molecule-to-surface charge transfer is slightly increasing (0.24 electrons for two Au ad-atoms) to the molecule instead of the electron transfer in the case of Al ad-atoms. This can be rationalized observing that Au ad-atoms do not change locally the Au(111) work function and the local electrostatic balance on the surface.

CONCLUSION

Light metallic ad-atoms can be on-surface **coordinated** to partially charge a neutral organic molecule on a noble metal surface, spin polarize this molecule and create an on-surface single molecule magnet organo-metallic complex. We have used exactly two Al atoms pre-positioned on an Au(111) surface. At a zero bias voltage, a Kondo resonance with a temperature of 30.3 K was STS measured. The magnetism of our Al₂-tetrabenz[a,c,j,h]phenazine complex rationalizes by comparing the electron affinity and ionization energies of the different partners involved: the

surface, the Al ad-atom and the neutral molecule. The Au(111) surface has a work function larger than the H-molecular affinity and smaller than its ionization energy. As a consequence, almost no charge transfer takes place between the molecule and the surface. With its small oxidation energy, Al ad-atoms are efficiently transferring electrons to the Au(111) surface and the molecule becomes spin polarized. On a surface and having the possibility to use light metal atoms with a neutral small organic molecule open the way to design new and light organo-metallic magnetic molecular materials.

Methods

Tetrabenz[a,c,j,h]phenazine molecules were sublimated using free evaporation by heating a quartz crucible at 240°C. The evaporation parameters were selected to deposit a minute amount of molecules to produce a sub-monolayer coverage to avoid molecules from clustering and to provide enough space in between the deposited Al atoms and molecules to perform the STM molecule manipulations. The H-molecules were deposited on an Au(111) mono-crystal which was cleaned using standard methods consisting of several cycles of Ar⁺ ion sputtering and subsequent annealing. During the molecules deposition, the gold substrate temperature was kept below 40 °C. The sample was cooled down with liquid helium before its transfer to the STM chamber. An aluminum source mounted in the STM chamber was used to deposit Al atoms on the gold surface. During this deposition, the sample was kept at cryogenic temperatures. All STM imaging, tunneling spectroscopy measurements and molecule manipulations were done at ~7 K using a Createc LT-UHV-STM.

The VASP code¹⁵ was used to evaluate the geometry and electronic structure of the H-molecule adsorbed on Au(111) in the presence of Al and Au ad-atoms. The calculations were performed using the PBE generalized-gradient approximation. The plane wave basis set was converged to

400 eV of cutoff energy and the k-point sampling was $7 \times 7 \times 1$ for an orthogonal $7 \times 4 \sqrt{3}$ unit cell of the Au (111). This $7 \times 4 \sqrt{3}$ unit cell is an almost square cell of (20.36 x 20.15) Å. The PBE functional was completed by semi-empirical van-der-Waals interactions as parametrized by Thatchenko and Scheffler.¹⁶

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

The Frota fitting of the STS Kondo resonance and the theoretically observed minimum energy configurations (PDF)

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Author contributions

W.–H.S. was responsible for planning and conducting the whole STM experiments with C.M. R.R. and N.L. were responsible for the calculations and the interpretation of the experiments with C.J.

Notes

The authors declare no competing financial interest.

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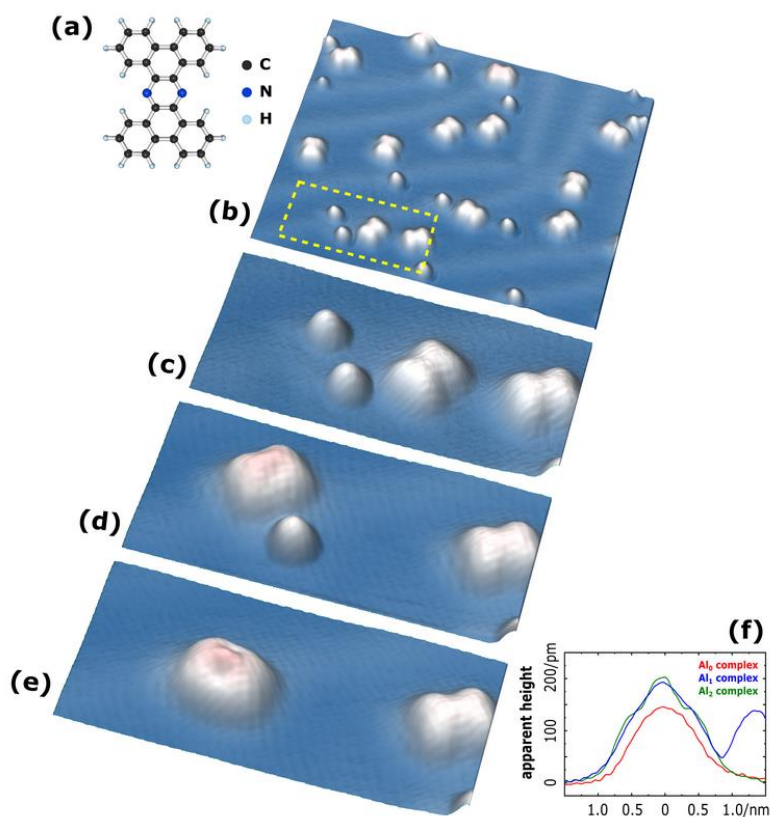


Figure 1. Construction of the aluminum metal complexes based on a tetrabenzo[a,c,j,h]phenazine molecule. (a) the molecule structure is presented by a ball and stick model. (b) An STM image taken after deposition of both ‘H’ shape tetrabenzo[a,c,j,h]phenazine molecules and Al atoms. Image size is 20 nm x 16 nm and bias voltage and tunneling current were set as 500 mV and 30 pA. (c)-(e) A sequence of the zoomed-in images constructing the metal complexes by STM molecule manipulation technique. From (c) to (e), the STM junction tunnel resistance set up was between 1 to 2 M Ω to manipulate the molecule. Others manipulations sequences are presented in Supp. Info. S4. After the metal-molecule complex formation, a protrusion emerges at the center of molecule instead of the Al ad-atom features. Apparent height of center protrusion is slightly higher and sharper for the Al₂-complex than for an Al₁-complex as shown in cross-section profiles (f) recorded while scanning the STM tip apex across the molecule (red across (c), blue across (d) and green across (e)).

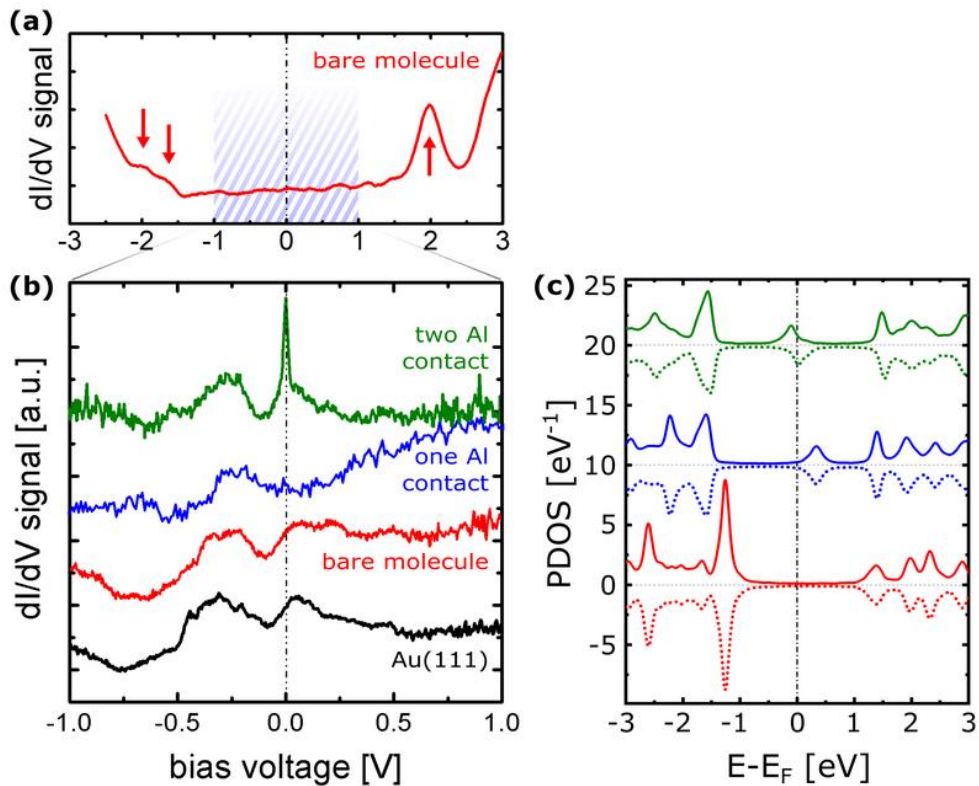


Figure 2. scanning tunneling spectra observed on the tetra benzo[a,c,j,h]phenazine molecule and its metal complexes. (a) The spectrum taken on a bare H shaped molecule on the Au(111) surface with a wide bias voltage range. Two peaks are distinguished for each polarity corresponding to the first and second reduced states (positive) and the first and second oxidation states (negative) respectively. (b) Spectra obtained in the gap of the Al-complex molecular electronic states. The STM-bare molecule junction is showing no resonances. The spectrum from the Al1-molecule complex shows relatively higher differential conductance according to the voltage increase (blue). This is a tail of the first reduced state of this complex. Only in case of two Al atoms interacting with the molecule, a new sharp peak appears at a zero bias voltage. (c) The respective SCF-DFT density of states projected on the molecule for the 3 cases. Line colors are corresponding to experimentally recorded (b) dI/dV spectra. Experimental and calculated Data are shifted vertically for clarity. Solid- and dotted lines are corresponding to the up- and down-spins respectively.

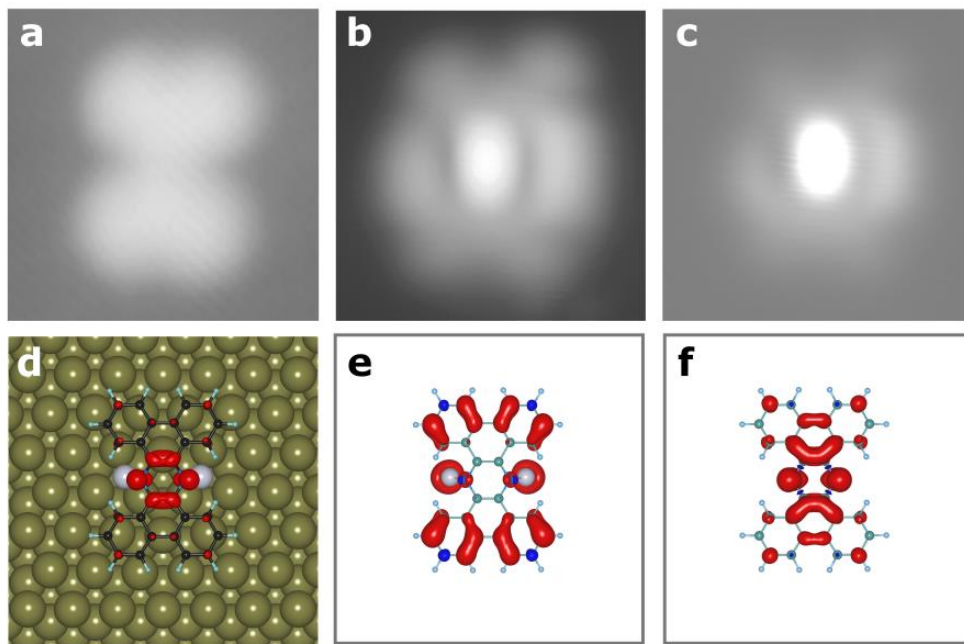


Figure 3. Experimental conductance maps vs. theoretical spin density map. STM constant current topographic images of (a) the bare tetrabenzo[a,c,j,h]phenazine molecule at 100 mV as a reference and (b) Al₂-molecule complex at 5 mV. (c) STS constant height differential conductance map at 5 mV using 1 mV of modulation, and (d) spin density distribution calculated by DFT. 5 mV of bias voltage was chosen to avoid lateral displacement of molecule during imaging due to tip-molecule interaction. The constant height mode was selected because 5 mV is at the foot of the zero bias peak and a constant current differential conductance map at this voltage gave an indirect information about molecular states.¹⁴ Localizing spin density to the pyrazine part of the molecule creates the Kondo resonance due to the coupling with the Au(111) conduction electrons. (e) Spin density of the Al-molecule-Al system without Au(111) surface when three electrons have been removed to mimic charge transfer to the substrate cannot retrieve the adsorbed distribution. (f) The anion distribution of H-molecule without Al atoms agrees with the distribution of the adsorbed system. This points at the decoupling of the molecule from the Au(111) substrate and Al ad-atoms. All image sizes are 2 nm x 2 nm.