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Switching the Spin on a Ni Trimer within a Metal-Organic Motif by Controlling the On-Top Bromine Atom

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ABSTRACT

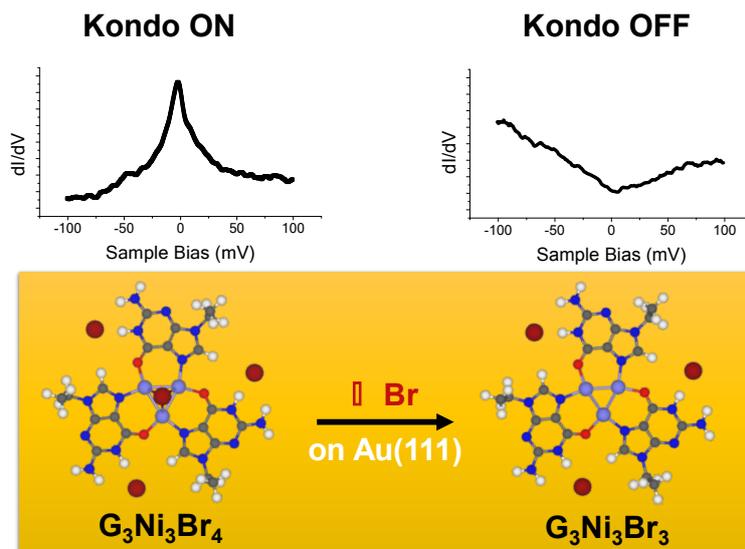
Controlling the spin of metal atoms embedded in molecular systems is a key step towards the realization of molecular electronics and spintronics. Many efforts have been devoted to explore the influencing factors dictating the survival or quenching of a magnetic moment in a metal-organic molecule, and among others, the spin control by axial ligand attachments is most promising. Herein, from the interplay of high-resolution STM imaging/manipulation and STS measurements together with DFT calculations, we successfully demonstrate that a Ni trimer within a metal-organic motif acquires a net spin promoted by the adsorption of an on-top Br atom. The spin localization in the tri-metal centers bonded to Br was monitored *via* the Kondo effect. The removal of the Br ligand resulted in the switch from **a** Kondo ON to **a** Kondo OFF state. The magnetic state induced by the Br ligand is theoretically attributed to the enhanced Br 4p_z and Ni 4dz² states due to the charge redistribution. The manipulation strategy reported here provides the possibility to explore potential applications of spin-

tunable structures in spintronic devices.

KEYWORDS: scanning tunneling microscopy, scanning tunneling spectroscopy, Kondo effect, spin switching, ligand attachment, density functional theory

Controlling the charge and spin at single molecular scale is a key step towards the realization of molecular electronics and spintronics.¹⁻⁵ When a molecular spin lies in the proximity of a metal substrate, it may exhibit the Kondo effect,^{6, 7} originating from the screening of the localized spin by conducting electrons. This fundamental effect provides an ideal workbench for identifying magnetic atomic and molecular species on surfaces,^{8, 9} in break junctions,^{10, 11} as well as in single-electron transistors.¹²⁻¹⁷ Its detection has been used as a fingerprint of paramagnetism in systems such as in C₆₀,¹⁷ carbon nanotubes,¹⁸ graphene¹⁹ and different edge states of graphene nanoribbons²⁰ obtained by on-surface synthesis. Scanning tunneling microscopy has been proven to be a powerful tool in the characterization of the spin state in magnetic systems.²¹⁻²⁷ Many efforts have been devoted to understanding the influencing factors behind the survival of a molecular spin in contact with a metal surface²⁸ and determining basic rules for their manipulation. For example, numerous studies of organo-metallic species with a single metal center, such as metallo-porphyrins and -phthalocyanines molecules, reported that the molecular spin can be manipulated by tuning the periphery chemical environment,²⁹⁻³³ conformational change,³⁴⁻³⁶ the adsorption site on a substrate,³⁷⁻³⁹ the structure of the self-assembled domain,^{35, 40, 41} and the axial coordination^{5, 42-46}. In particular, the possibility of modifying the Kondo state of a magnetic molecule by changing its axial ligand coordination with the attachment of small molecules such as atomic hydrogen,⁵ Cl,⁴² CO,^{43, 44} NO,⁴³ NH₃,⁴⁵ and alkali metals⁴⁶ attracts a lot of attentions due to the potential applications as gas sensors. However, the study of the magnetic ground state of multiple metal centers into complex assemblies is still elusive, as well as the development of possible manipulation routes that could enable/disable their Kondo screening with the substrate. These would entitle the design of novel devices for electrical sensing chemical signals.

In this study, we report on the manipulation of the magnetic state of a multiple-metal center in a molecular assembly by addition/removal of Br atoms. Based on our previous study,⁴⁷ we chose a derivative of the guanine molecule (9-ethylguanine, abbreviated as G) and a NiBr₂ salt with the aim of fabricating a three-metal-center (i.e., Ni trimer, shortened as Ni₃) metal-organic system on the Au(111) surface. Through a combination of high-resolution scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), density functional theory (DFT) calculations and STM image simulations, we demonstrate that this system shows an intermediate configuration with a Br atom sitting on top of the hollow site of the central Ni₃ cluster, which modifies the electronic configuration of the three-metal center. Annealing to higher temperatures, the G₃Ni₃Br₄ metal-organic network is transformed into G₃Ni₃Br₃, where the on-top Br atom is vanished. Moreover, *in-situ* removal of the on-top Br atom by STM manipulation is also achieved. Differential conductance (dI/dV) spectra on the G₃Ni₃Br₄ structures show a pronounced zero-bias peak at Fermi level assigned to the signature of Kondo effect, which is absent on the G₃Ni₃Br₃ structures (cf. Scheme 1); thus, removal of on-top Br atoms of the G₃Ni₃Br₄ structure through annealing or *in-situ* STM manipulation removes the zero-energy Kondo resonance. Such an on-top Br adsorption induced Kondo effect on a Ni₃ cluster within a metal-organic structure is theoretically interpreted by a charge redistribution over *d* orbitals of Ni leading to the gain of a net magnetization.



Scheme 1. Schematic illustration of the on-top Br atom induced Kondo effect on a three-metal center within a metal-organic structure. Kondo effect is generated by the attachment of a Br atom above the Ni₃ cluster within the G₃Ni₃Br₄ motif on the Au(111) surface. After annealing or STM manipulation, the on-top Br atom is removed and the Kondo effect vanishes in the resulted G₃Ni₃Br₃ motif.

RESULTS AND DISCUSSION

The co-deposition of G molecules and NiBr₂ on the Au(111) surface held at room temperature (RT) results in close-packed islands like the one shown in Figure 1a. A close-up STM image allows us to identify the elementary structural motifs, depicted by white contours in Figure 1b. The characteristic motifs (Figure 1c) are composed of a bright dot at the center, assigned to an on-top Br atom, and six peripheral protrusions around the triangular base.⁴² This assignment is also confirmed by the Br removal experiment discussed below. The structural motif beneath the central Br atom coincides in size and shape with the structure of the basic motif of G₃Ni₃I₃ assemblies, reported previously.⁴⁷ Thus, we tentatively assign the G₃Ni₃Br₄ motif (Figure 1c) to a structure formed by a G₃Ni₃Br₃ base with an additional Br atom sitting on the hollow site of the central Ni₃ cluster. This structure is successfully reproduced by DFT structural simulations for a G₃Ni₃Br₄ cluster on the Au(111) surface, resulting in the optimized structural model superimposed on the STM image in Figure 1c, and depicted in Figure

1d. According to this, the motif is composed of three homochiral G molecules coordinated with three Ni atoms located at the hollow sites of the Au(111) surface. Three peripheral Br atoms are uniformly located at the specific hydrogen-rich harbors *via* electrostatic interactions. Importantly, the top Br atom sits on top of the hollow site of the Ni₃ cluster, with an adsorption energy of -1.40 eV. The corresponding ESQC calculated STM image, shown in Figure 1e, reproduces the major details of our STM images with a large central spot corresponding to the Br-Ni₃ motif, which is brighter than both the lateral ethyl groups and the on-surface Br atoms. The G₃Ni₃Br₄ motifs are then linked together by hydrogen bonds and van der Waals interactions to form extended metal-organic islands, as shown in Figure 1f.

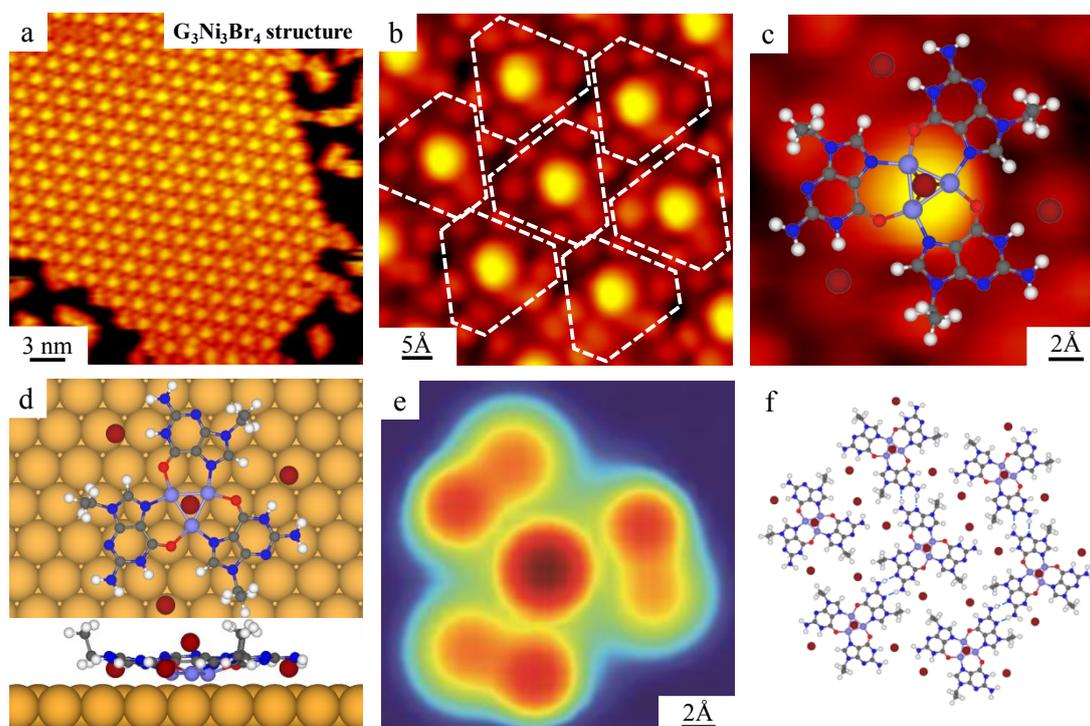


Figure 1. Formation of the G₃Ni₃Br₄ network structure after the deposition of G molecules and NiBr₂ on Au(111) held at RT. (a) Large-scale STM image showing the close-packed island composed of the G₃Ni₃Br₄ structure. (b) Close-up STM image showing the details of the structure in which G₃Ni₃Br₄ structures are indicated by white contours. (c) A further zoomed-in STM image of the G₃Ni₃Br₄ motif superimposed with the DFT-optimized gas-phase model. (d) Top and side views of the DFT-relaxed model of the G₃Ni₃Br₄ motif on Au(111). H: white, C: gray, N: blue, O: red, Ni: light blue, Br:

brown, Au: yellow. (e) The ESQC calculated STM image of the $G_3Ni_3Br_4$ motif at E_f . (f) DFT-optimized gas-phase model of the $G_3Ni_3Br_4$ network structure. Hydrogen bonds are depicted by blue dashed lines.

As we will show next, the axial attachment of a Br atom on top of the Ni_3 cluster has important consequences on their electronic configuration. First, STS measurements uncover a net magnetization of the $G_3Ni_3Br_4$ metal organic moiety. Figure 2b shows a representative dI/dV point spectrum taken on-top of the central Br atom (*cf.* the black cross in Figure 2a), which shows a pronounced, narrow peak centered at zero bias. Based on both the bias position and the logarithmic-like shape of the peak we attribute it to an Abrikosov-Suhl resonance due to the Kondo effect,²¹ and named as Kondo resonances herein. The coupling between the magnetic center and surrounding free electrons has further been quantified by fitting the Kondo resonance with a Fano function^{48, 49} (see details in the Supporting Information), obtaining a Kondo temperature of $T_K \sim 124$ K. The extension of the Kondo signal in STM experiments has been related to the spin localization.^{50, 51} Accordingly, we conducted 20 dI/dV point spectra along a line between two adjacent on-top Br atoms (black line indicated in Figure 2a). The resulting spectral map along the line (shown as a vertical axis in Figure 2c, with the colors representing the dI/dV intensity) shows that the zero-bias resonances are localized within the range of the metal centers. Furthermore, these resonances are unaffected by the proximity of edges or defects, suggesting that the coupling between neighboring metal-organic motifs is negligibly small.⁴¹

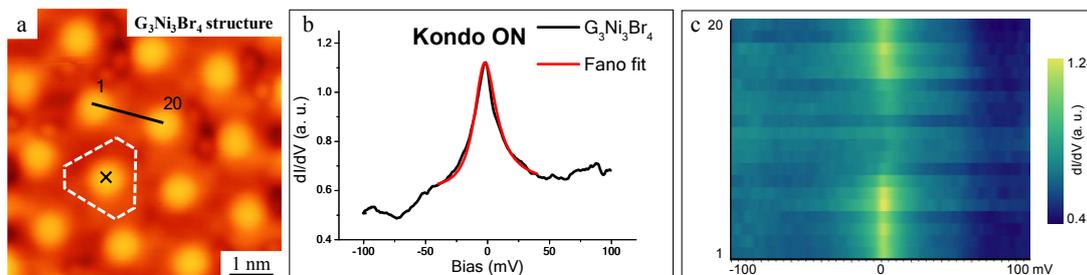


Figure 2. Characterization of the electronic properties of the $G_3Ni_3Br_4$ structure. (a) An STM image with a $G_3Ni_3Br_4$ motif highlighted by the white contour. (b) A

representative experimental dI/dV point spectrum (the black curve) obtained at the black cross shown in (a), which shows a pronounced peak at the Fermi level representing the signature of Kondo effect (open-feedback parameters: $V_t = 1.0$ V, $I_t = 1$ nA, modulation voltage $V_{rms} = 0.4$ mV, lock-in frequency: 760 Hz); the corresponding Fano fit curve (the red one) ($q=10$, $\Gamma=10.8$ mV) shows a good agreement. The flat density of states of the STM tip is checked before and after on the bare Au(111) surface, where it only displays the well-known surface state onset (cf. Figure S1). (c) The spectral map of 20 spectra taken along the black line in (a) stacked vertically with colors corresponding to dI/dV intensity.

After a thermal treatment of the sample at 390 K for 10 min, a honeycomb network like the one shown in Figure 3a is observed instead. Close-up STM images resolve that these structures are formed by the elementary triangular motifs, depicted by white contours in Figure 3b. These motifs are assigned to $G_3Ni_3Br_3$ clusters, according to the identical configuration of $G_3Ni_3I_3$ honeycomb network structure in our previous study.⁴⁷ Also note that this structure coincides with the $G_3Ni_3Br_4$ motif from above, but with the on-top Br atoms removed probably due to the annealing process. A further zoomed-in STM image superimposed with the DFT-optimized gas-phase model is shown in Figure 3c. It is noticeable that the electronic density of states of the Ni_3 cluster within the $G_3Ni_3Br_3$ motif is less pronounced in comparison with the case of $G_3Ni_3I_3$. The top and side views of the DFT optimized structural model of $G_3Ni_3Br_3$ on Au(111) are shown in Figure 3d. We find that here the Ni_3 cluster lies 0.3 Å closer to the Au(111) surface than in the $G_3Ni_3Br_4$ motif, presumably suffering a larger hybridization with metal states. The corresponding ESQC calculated STM image is shown in Figure 3e, assigning the peripheral bright spots to ethyl groups pointing upwards and to the close-by Br adatoms. The elementary $G_3Ni_3Br_3$ motifs further interact with each other by double hydrogen bonds resulting in the formation of the honeycomb network shown in Figure 3f.

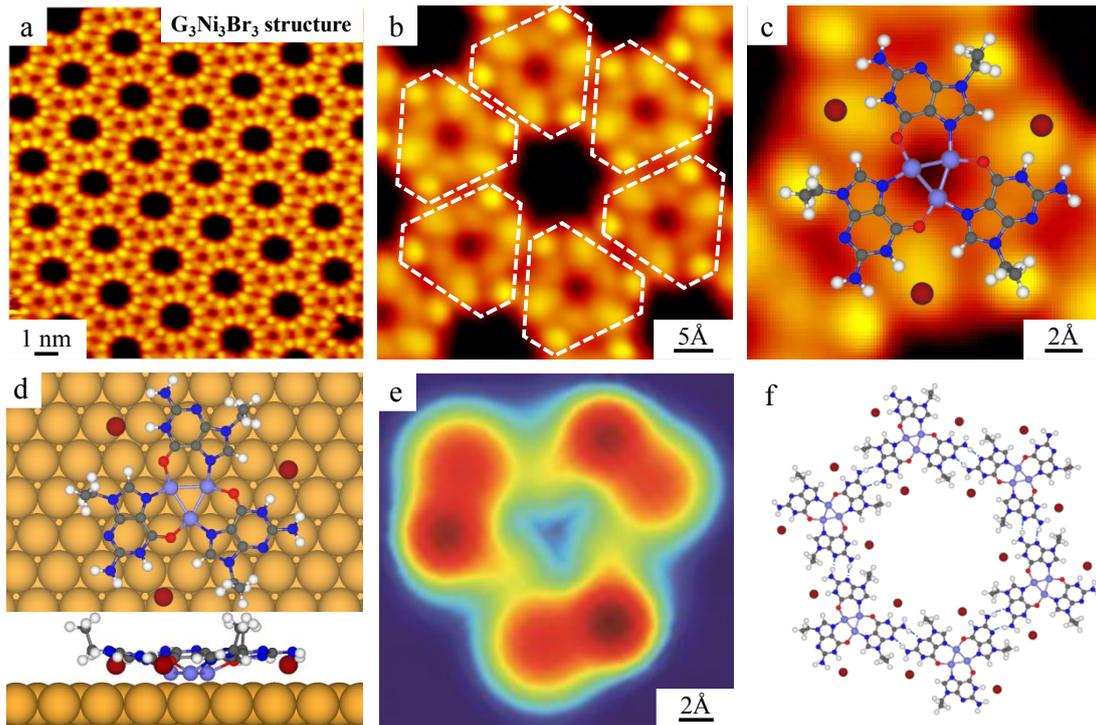


Figure 3. Formation of the $G_3Ni_3Br_3$ network structure after annealing the sample of $G_3Ni_3Br_4$ phase at 390 K on Au(111). (a) Large-scale STM image showing the honeycomb network composed of the $G_3Ni_3Br_3$ structure. (b) Close-up STM image showing the details of the structure in which $G_3Ni_3Br_3$ structures are indicated by white contours. (c) A further zoomed-in STM image of the $G_3Ni_3Br_3$ motif superimposed with the DFT-optimized gas-phase model. (d) Top and side views of the DFT-relaxed model of the $G_3Ni_3Br_3$ motif on Au(111). (e) The ESQC calculated STM image of the $G_3Ni_3Br_3$ motif at E_f . (f) DFT-optimized gas-phase model of the $G_3Ni_3Br_3$ network structure.

In contrast to $G_3Ni_3Br_4$, dI/dV spectra obtained at the center of the $G_3Ni_3Br_3$ motif (*i.e.*, the spectrum in Figure 4b taken over the black cross in Figure 4a) show a relatively featureless curve near the zero bias (*cf.* Figure 4b), which indicates the absence of a Kondo effect upon removal of the on-top Br atom. These results suggest that the magnetic moment concluded after the Kondo resonance in $G_3Ni_3Br_4$ clusters is induced by the presence of the Br atom on top of the Ni_3 moiety and vanishes when this halogen atom is removed. By delicately controlling the annealing procedure (at ~ 380 K for 10 min), an intermediate state composed of both $G_3Ni_3Br_4$ and $G_3Ni_3Br_3$ motifs can be

obtained (shown in Figure S2). In this mixed state, dI/dV spectra (Figure S3) further corroborated the coexistence of both magnetic ground states (Kondo ON or OFF) depending on the presence of the Br atom on top. This suggests that the triangular motifs remain at the annealing temperatures, and that the only transformation consists on the detachment of the Br atom from the central part of the moiety.

These results suggest that the Kondo state of a molecular $G_3Ni_3Br_4$ cluster could be switched OFF by means of atomic-scale manipulation experiments using the STM. As shown in Figure 4c and 4d, the STM tip was used to remove the on-top Br atom from a $G_3Ni_3Br_4$ motif resulting in the formation of the $G_3Ni_3Br_3$ one. Correspondingly, the characteristic Kondo peak (red curve in Figure 4e) of a $G_3Ni_3Br_4$ motif, which is acquired before the manipulation on the species marked in Figure 4c, disappears after removing the on-top Br atom (*cf.* blue curve acquired at the center of the resulting $G_3Ni_3Br_3$ motif in Figure 4d).

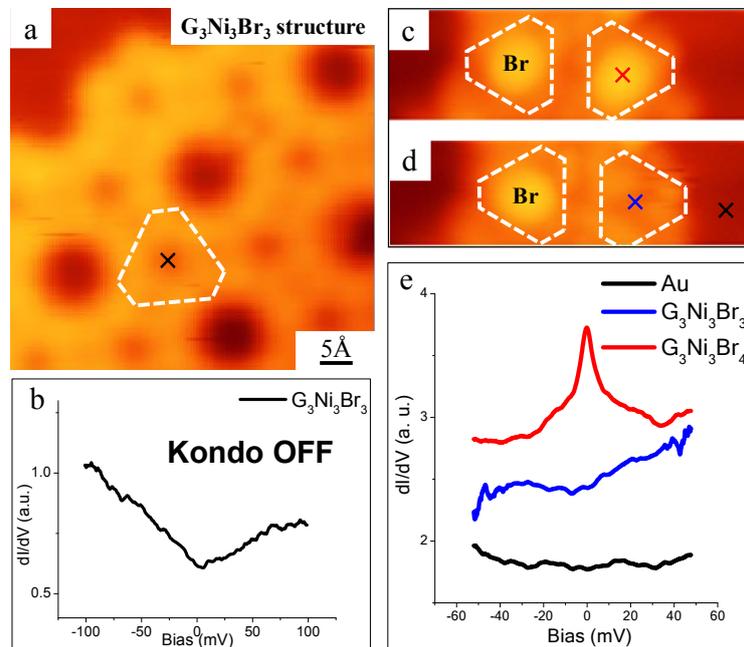


Figure 4. Characterization of the electronic properties of the $G_3Ni_3Br_3$ structure. (a) An STM image with a $G_3Ni_3Br_3$ motif highlighted by the white contour. (b) A representative experimental dI/dV point spectrum obtained at the black cross shown in (a), which shows the vanishment of the pronounced Kondo peak. (c) and (d) An *in-situ*

STM manipulation to remove the on-top Br atom in the $G_3Ni_3Br_4$ motif (by a bias ramping to ~ 3.2 V). (e) The dI/dV spectra acquired at three points, respectively, that is, with the Br atom on top (red), without the Br atom (blue), and on the bare surface (black) (open-feedback parameters: $V_t = 1.0$ V, $I_t = 1$ nA, modulation voltage $V_{rms} = 0.4$ mV, lock-in frequency: 760 Hz).

To understand the underlying mechanism behind the formation of a net magnetic moment induced by the on-top Br-atom, and its disappearance on the $G_3Ni_3Br_3$ motifs, extensive DFT calculations have been performed. The incorporation of a Br atom on-top of a $G_3Ni_3Br_3$ cluster is accompanied by a net energy gain of 1.4 eV. The Br atom binds to the three Ni atoms and slightly pulls them upwards away from the surface by 0.3 Å, thus reducing their coupling with substrate states. This distortion induces a charge redistribution and builds up a net magnetic moment in the cluster. In Figure 5a and b, the spin-densities of the $G_3Ni_3Br_3$ and $G_3Ni_3Br_4$ motifs are depicted, respectively. The spin-up and spin-down states (purple and green contours) are uniformly distributed near the Ni_3 cluster and the Au(111) surface in the $G_3Ni_3Br_3$ motif, while in $G_3Ni_3Br_4$ clusters the spin-up state is significantly more pronounced near the top Br atom. Further analysis shows that on the Au(111) surface, the magnetic moments of the $G_3Ni_3Br_3$ and $G_3Ni_3Br_4$ motifs are $-0.05 \mu_B$ and $0.88 \mu_B$, respectively. The spin polarized density of states (SPDOS) on the 4d states of the Ni_3 cluster show that the $4dz^2$ states in the $G_3Ni_3Br_4$ clearly shift upwards, partially crossing the Fermi level (cf. Figure 5d) in comparison with that in the $G_3Ni_3Br_3$ (cf. Figure 5c). Thus, the attachment of a Br atom on-top induces a charge redistribution described by a partial depopulation of dz^2 electrons, which are transferred towards Br states. In fact, the SPDOS on the p orbitals of the on-top Br atom shows a spin-polarized state as well (cf. Figure S4a, where the bonding configuration between top Br and Ni trimer is also described). Further charge differential analysis also indicates that the on-top Br atom bonds to the Ni_3 cluster with the Br $4p_z$ orbital (Figure S4b). Thus, the enhanced Br $4p_z$ and Ni $4dz^2$ states due to the formation of Br-Ni bonds may be the origin of the apparition of a net magnetic moment, explaining the observation of a Kondo resonance in our experiment.

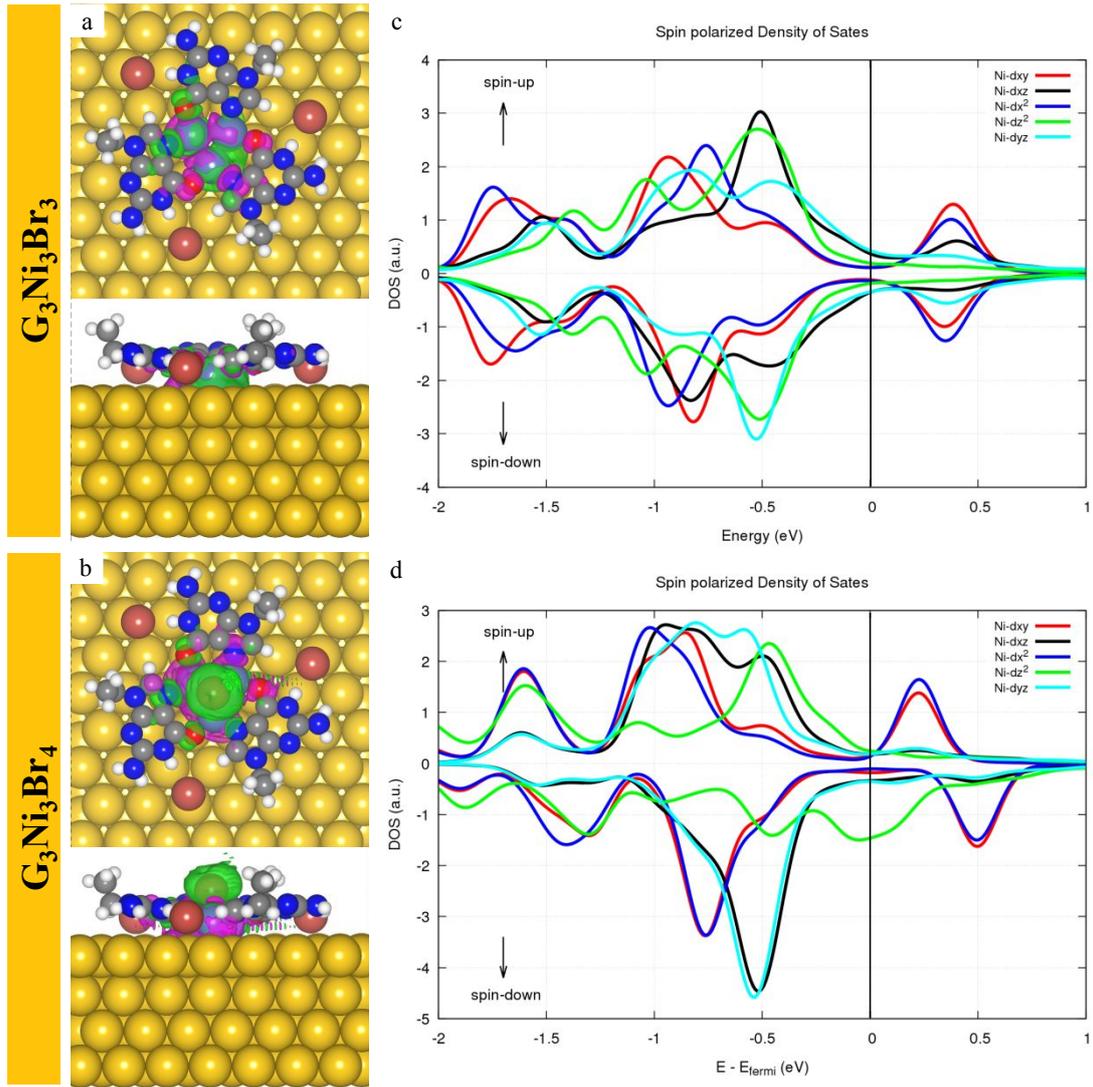


Figure 5. The top and side views of the spin-density of (a) $G_3Ni_3Br_3$ and (b) $G_3Ni_3Br_4$ motifs on the Au(111) surface. The spin-up and spin-down states are drawn as purple and green contours, respectively. The value of isosurfaces are $\pm 1 \times 10^{-4} e/\text{\AA}^3$. The SPDOS of the 4d states of the Ni_3 cluster within the (c) $G_3Ni_3Br_3$ and (d) $G_3Ni_3Br_4$ motifs.

CONCLUSIONS

In summary, here we presented an STM manipulation strategy for controlling the spin of the metallic clusters embedded in a metal-organic structure consisting in the attachment of halogen atoms on top. From a combination of high-resolution STM imaging/manipulation and STS measurements, we have demonstrated that the metal-

organic motifs containing Ni trimers lies in a magnetic ground state, and exhibits a zero-bias Kondo resonance. Comparing with a related structure appearing at higher temperatures with no magnetic fingerprint, we deduce that the magnetic state is promoted by the presence of a Br atom on top of the Ni trimer. Controllable removal of the on-top Br atom leads to the disappearance of the magnetic fingerprint from the spectra. Such an experimentally observed Kondo ON state is theoretically attributed to the enhanced Br $4p_z$ and Ni $4dz^2$ states due to the charge redistribution upon the on-top Br adsorption. The finding of the magnetic state for Ni trimer could be the basis for the bottom-up assembly of high-spin systems, stabilized by a metal-organic framework (MOF) structure. The spin-manipulation strategy presented here provides the possibility to explore the halogen-driven spin switch in more generalized situations. Utilizing such coordinative interactions of axial halogen atoms to manipulate spin states opens the door to designing spin-tunable interfaces composed of well-defined metal-organic structures with potential applications for spintronic devices.

METHODS

The Au(111) substrate was prepared by several cycles of 1.5 keV Ar^+ sputtering followed by annealing at 820 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The 9eG molecules (purchased from Sigma-Aldrich, purity >98%) and salt NiBr_2 (purchased from Sigma-Aldrich, purity >99%) were loaded into separate cells of the crucible in the molecular evaporator oriented to the substrate. After a thorough degassing, the molecules and salt were deposited onto the Au(111) substrate by thermal sublimation at 440 K and at 580 K, respectively. The sample was thereafter transferred within the UHV chamber to the STM.

STM images in Figure 1, Figure 3, Figure S2 were acquired in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature, fast scanning “Aarhus-type” STM using electrochemically etched W tips purchased from SPECS^{52, 53} where measurements were carried out at ~ 100 – 150 K. Scanning conditions: $I_t = 0.5$ – 0.8 nA, $V_t = \sim 1200$ mV. The other STM images and all spectra are taken on a home-built, low-temperature STM under UHV at pressures $\sim 1 \times 10^{-11}$ mbar and a base temperature of

4.8 K. Scanning conditions: $I_t = 20$ pA, $V_t = \sim 1000$ mV. All of the STM images were further smoothed to eliminate noises. The dI/dV measurements were acquired using lock-in amplifier technique. Analysis of STS data was performed with Origin and SpectraFox software packages.⁵⁴

The structural optimizations and electronic structures of all systems were obtained with the spin-polarized DFT calculations by using the Vienna *Ab initio* Simulation Package (VASP).⁵⁵ The electron-ion interactions were described with the Projector Augmented-Wave (PAW) potentials.⁵⁶ The exchange-correlation interactions of electrons were taken account using the Perdew-Burke-Enzerhof (PBE) of Generalized Gradient Approximation (GGA) pseudopotentials.⁵⁷ The van der Waals interactions were described with the vdW-D3 method.⁵⁸ The cutoff energy of plane wave basis was set as 400 eV. The gold surfaces were modelled with a periodic slab consisting of four atomic Au layers, in which the bottom two layers were fixed. All other atoms were optimized until the atomic force was less than 0.01 eV per Angstrom. A vacuum layer of 20 Å was used to avoid the periodic image interactions. The Brillouin zone of reciprocal space was modeled based on the Γ centered Monkhorst-Pack scheme, where a $3 \times 3 \times 1$ grid was adopted in geometry optimizations and calculations of electronic properties.⁵⁹

The calculated STM images are obtained by using the Elastic Scattering Quantum Chemistry (ESQC) code.⁶⁰ Here, the STM junction comprising the substrate, the adsorbates, the tip apex and the tip support is fully described at the atomic level. A set of semi-empirical extended Hückel orbitals is assigned on each atom site. The scattering of tunnel electrons through the junction is calculated that allows the evaluation of the tunneling current with the Landauer formula. This technique has already proven its reliability with small^{61, 62} and large^{63, 64} molecular systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

The dI/dV spectra for Kondo ON and OFF states with reference curves taken on the bare Au(111) surface; Fano fitting for Kondo resonance; Coexistence of the G₃Ni₃Br₄ and G₃Ni₃Br₃ motifs; The corresponding dI/dV spectra on the coexistent motifs; Bonding manner between on-top Br and Ni trimer; PDOS of the p_x, p_y and p_z states of the top Br atom in a G₃Ni₃Br₄ motif and differential charge density of the G₃Ni₃Br₄ motif.

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The authors declare no competing financial interests.

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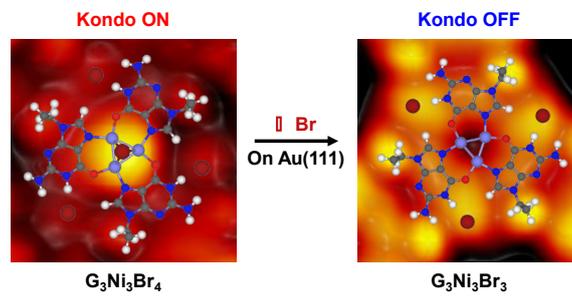
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Table of Contents



From the interplay of scanning tunneling microscopy/spectroscopy and density functional theory calculations, we successfully demonstrate that the spin of a Ni trimer within a metal-organic motif can be switched by controlling the attachment of on-top Br atom, which is monitored *via* Kondo effect.