Two-Orbital Kondo Screening in a Self-Assembled Metal–Organic Complex

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ABSTRACT: Iron atoms adsorbed on a Cu(111) surface and buried under polyphenyl dicarbonitrile molecules exhibit strongly spatial anisotropic Kondo features with directionally dependent Kondo temperatures and line shapes, as evidenced by scanning tunneling spectroscopy. First-principles calculations find nearly full polarization for the half-filled Fe 3d_{xz} and 3d_{yz} orbitals, which therefore can give rise to Kondo screening with the experimentally observed directional dependence and distinct Kondo temperatures. X-ray absorption spectroscopy and X-ray magnetic circular dichroism measurements confirm that the spin in both channels is effectively Kondo-screened. At ideal Fe coverage, these two-orbital Kondo impurities are arranged in a self-assembled honeycomb superlattice.

KEYWORDS: Kondo effect, organometallic complex, self-assembly, scanning tunneling spectroscopy, X-ray absorption spectroscopy, X-ray magnetic circular dichroism, density functional theory

The interaction between a magnetic impurity and the conduction electrons of a nonmagnetic host can give rise to a many-body singlet state manifesting itself as a sharp resonance near the Fermi energy (E_F). This is known as the Kondo effect1 and was originally observed in bulk solids containing magnetic impurities. Subsequently, it has been reported for various low-dimensional systems, such as surface-adsorbed magnetic atoms2–4 and semiconductor quantum dots.5,6 In recent years, great attention was devoted also to organic and metal–organic molecules, owing to their potential for single-molecule spintronic applications.7,8 Moreover, the Kondo effect in molecular systems can be manipulated in a controlled way. In particular, it can be turned on and off by adsorbing atoms or small molecules,9–13 by detaching peripheral hydrogen atoms,14 by supramolecular interactions,15,16 or by modifying the molecular conformation with voltage pulses.17–19 The study of more complex Kondo systems, for example, those with more than one available screening channel, can give further insight into Kondo physics and possibly lead to different tools for the control of magnetism and spintronics at the nanoscale. To date, however, molecular systems in which more than one orbital can contribute to Kondo screening have rarely been investigated.20–23

Here, we report on a Kondo effect with two orbital contributions, each of them having distinct Kondo temperature and location, as evidenced by scanning tunneling spectroscopy (STS) measurements. We obtain this system by the combination of magnetic atoms with purely organic molecules; namely, we adsorb Fe atoms under NC-Ph_3-CN molecules in (NC-Ph_3-CN)_2Cu_2 networks on Cu(111). The Kondo effect arises from the presence of two singly occupied Fe d orbitals with different spatial distribution and hybridization with the molecular orbitals, as evidenced by density functional theory (DFT) calculations. The spatial distribution of the Kondo features reflects the anisotropy of the Fe-molecule hybridization. X-ray magnetic circular dichroism (XMCD) reveals that the spin in both Kondo channels is fully screened. Adjusting the Fe coverage, we obtain samples where exactly one Fe atom is buried under one NC-Ph_3-CN molecule and thus create an ordered superlattice of two-orbital Kondo species. Moreover, we discuss the results obtained replacing Fe with Co, known to be a Kondo impurity when adsorbed on Cu(111). In the metal–organic complex, its Kondo signature disappears, coherently with the d orbital occupation obtained from our DFT calculations.

RESULTS AND DISCUSSION

Deposition of NC-Ph_3-CN polyphenyl molecules24 on the Cu(111) substrate at 300 K yields a (NC-Ph_3-CN)_2Cu_2 honeycomb network.25 Subsequent Fe deposition at 10 ± 2 K leads to the coexistence of three Fe-related species, as demonstrated by the scanning tunneling microscopy (STM) image of Figure 1a. Atoms landing in the hexagonal cavities

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stick on their site of impact without thermal diffusion toward the molecules, similar to what has been observed for Fe deposition on (NC-Ph3-CN)3Cu2/Cu(111) networks.26 The Fe atoms appear as well localized protrusions (turquoise dashed circle). On the organic ligands, two Fe-related features are discerned by their apparent height. The very bright features (yellow full circle) readily disappear through repeated STM imaging (see Supporting Information). We systematically observe after such an event that empty cavities in the immediate vicinity of the displaced element become occupied by a single Fe atom. Thus, the bright protrusions are identified as Fe atoms adsorbed onto the organic molecules. In contrast, the less bright features (red dotted circle) are very robust against manipulation with the STM tip and attributed to Fe atoms below the organic molecules.

When Fe is deposited at higher temperature (18 K < T_{dep} < 50 K), Fe diffusion within the cavities and down from the molecules is activated, and all atoms are found under the molecules (Figure 1b,c). From these observations, we infer that the buried adsorption site is the most stable one, whereas the other two are metastable.27 In Figure 1c, the Fe coverage corresponds to one Fe atom per molecule: in most cases, there is exactly one Fe atom below one molecule, and there are only few molecules that have no or two Fe atoms underneath. Therefore, we are able to create a regular lattice of buried Fe atoms.

The electronic structure of Fe atoms adsorbed on the substrate and under the molecules has been characterized by means of STS. The differential conductance spectra (dI/dV) acquired on Fe/Cu(111) (see Figure 2a) show no noteworthy spectral features around $E_F$, similar to the spectra acquired on undecorated molecules and on Fe atoms on top of molecules reported in the Supporting Information. In contrast, spectra acquired on molecules covering an Fe adatom show large variations of the differential conductance close to $E_F$, with a marked spatial variation across the molecule; see the symbols in Figure 2b for the location of the spectra. The conductance exhibits an intense peak on one side (○), a dip above the molecule (△), and a smaller peak on the other side of the molecule (+).

The spatial distribution of the two types of resonances can be seen in more detail in the dI/dV map shown together with the
constant current image in Figure 2b. The image shows the NC-Ph3-CN in the honeycomb network, with some molecules presenting an Fe atom below the central phenyl ring. The $dI/dV$ map was acquired on the region highlighted by the white rectangle, thus comprising two molecules burying Fe atoms. A large bright spot is visible on one side of each molecule and a smaller, less bright one on the respective other side. For each molecule, a darker region is detected between the bright spots. Comparison with the spectra shown in Figure 2a reveals that the brightest and largest spot in the $dI/dV$ map corresponds to the intense peak ($\Delta$). The dip ($\langle \Delta \rangle$) appears as a depression in the map, whereas the peak with smaller amplitude ($\langle \Delta \rangle$) is related to the less bright and smaller feature on the other side of each molecule. The higher intensity observed on one side of the molecules is ascribed to the tilt of the phenyl rings with respect to the surface and to each other.\textsuperscript{25,28,29} Notice that very similar results have been obtained for Fe atoms buried by NC-Ph3-CN molecules (see Supporting Information).

We attribute these different spectral features to a manifestation of spatially varying Kondo screening. To substantiate this interpretation, we fit the spectra with a Fano function\textsuperscript{30}

$$\Phi(E) = \frac{(q\Gamma + E - E_0)^2}{\Gamma^2 + (E - E_0)^2}$$

(1)

with $E_0$ being the energy position of the resonance and $\Gamma$ its half-width at half-maximum; $q$ determines the line shape of the curve. $\Gamma$ has a characteristic dependence on temperature expressed by $2\Gamma = [(\alpha k_B T)^2 + (2\Gamma_0)^2]^{1/2}$.\textsuperscript{31,32} $\Gamma_0$, the half-width at 0 K, is related to the Kondo temperature $T_K$ by $\Gamma_0 = k_B T_K$. The fit with eq 1 agrees very well with experiment in the relevant energy interval around $E_F$ (see Figure 2a). The peaks on both sides of the molecule yield consistent Kondo temperatures of $T_K = 63 \pm 4$ and $62 \pm 3$ K, whereas the dip gives a significantly higher value of $T_K = 114 \pm 5$ K (see Supporting Information for the fitting parameters). From these results, we deduce that the Kondo features left and right of the molecular axis belong to one class and the one on the axis to another.

The spatial distribution of the Kondo temperature is shown in Figure 2c. The map was derived from fitting with eq 1 a set of point spectra acquired across the molecule. It shows two distinct $T_K$ values with a sharp transition from one to the other, as evidenced by the profile taken perpendicular to the molecular axis and through the center of the molecule, indicated by the gray line. The bright areas seen on the $dI/dV$ map at $E_F$ (Figure 2b) display the lower $T_K$ value and the peak-like line shape, whereas along the molecular axis, $T_K$ doubles and the Kondo effect leads to a dip. Therefore, there is a correlation between line shape and width: peaks correspond to lower $T_K$ and dips to higher $T_K$. Spatial variations of $T_K$ were reported for TBrPP-Co molecules on Cu(111)\textsuperscript{33} and for Fe(II) P on Au(111).\textsuperscript{23} These systems displayed a smooth increase of $T_K$ from the center to the periphery of the molecule, that is, over a distance greater than 0.3 nm. Moreover, no significant changes in the line shape were observed, with all spectra showing a dip. In contrast, our system shows a sharp transition within a distance of 0.1 nm, without intermediate values of $T_K$. This abrupt transition between the two $T_K$ values and line shapes hints toward the coexistence of two Kondo channels with different coupling to the conduction electrons of the substrate.

To gain more insight into the Kondo effect observed upon formation of the metal–organic complex, we replaced Fe with Co. As for Fe, Co atoms, three possible adsorption positions for $T_K = 10$ K are present: on the substrate, on top of molecules, and under molecules. Co is known to be a Kondo impurity on the bare Cu(111) substrate,\textsuperscript{3,34} and our STS measurements, shown in Figure 2a, reproduce the reported Fano dip with $T_K = 52 \pm 3$ K. However, this Kondo signature disappears when Co atoms are under molecules (Figure 2a) or on top of them (see Supporting Information). Therefore, Fe is Kondo-screened only when buried under the molecules and Co only as an adatom. The disappearance of the Kondo effect upon formation of metal–organic complexes was reported also for Co bound to TCNE molecules on Cu$_2$N.\textsuperscript{35}

To rationalize our findings, we performed DFT calculations employing the generalized gradient approximation with a mean-field Hubbard correction (GGA+U) with $U = 4$ eV\textsuperscript{36} as implemented in the Quantum-ESPRESSO package.\textsuperscript{37} To take into account the van der Waals interaction between molecule and substrate, we included the semimicrospherical long-range dispersion correction proposed by Grimme.\textsuperscript{38,39} The considered slab model consisted of a $6 \times 6$ supercell of three layers of Cu(111) with a NC-Ph3-CN molecule attached to two Cu adatoms with an Fe or Co atom located below the central phenyl ring (see inset in Figure 3a). After relaxation, both...
transition metal adatoms are located in a bridge position of the Cu(111) substrate at ≈1.6 Å above the surface. The central ring of the NC-Ph3-CN molecule is located at ≈3.1 Å above the substrate, and the molecule is slightly tilted.

The GGA+U calculations predict an atomic magnetic moment of 2.1 and 0.6 μB for the buried Fe and Co atoms, respectively. The orbital moments are strongly quenched, indicating that the calculated magnetic moments have mainly spin character. This implies that the Fe atom is in a S = 1 ground state. Table 1 shows the Löwdin spin-up and spin-down occupations of the s and d orbitals for the buried Fe and Co atoms. The x and y coordinates are parallel and perpendicular, respectively, to the long molecular axis in the surface plane. Only orbitals that are partially filled and polarized can lead to a Kondo effect, that is, to screening of the unpaired spin by the conduction electrons, and the resonance is expected to be the most intense for orbitals with only one spin state occupied. The values in Table 1 show that the d orbitals of Co are all almost completely filled, which explains the absence of a Kondo effect for this system. In the case of Fe, on the other hand, the diagonal orbitals dxy and dyz are both nearly singly occupied and fully polarized and can thus yield a Kondo effect. Owing to hybridization, the actual wave functions of the system cannot have a pure atomic character, thus explaining the small spin polarization of the dxy and dyz planar orbitals.

In order to establish a connection of the Fe d orbitals with the spatial variation detected in STS, we show in Figure 3a the spin-resolved projected density of states (PDOS) projected onto the Fe and the molecule states, calculated for the slab described above and shown in the inset. The PDOS projected onto the Cu(111) states is omitted for clarity. From Fe 3d orbital-resolved PDOS, we deduce that the states derived from the Fe dxy (labelled A and A') and dyz (B and B') orbitals have most of their weight in the energy regions identified by the cyan boxes for majority and minority spins. However, owing to hybridization with the substrate states, they are spread over several electronvolts and the corresponding spatial charge distribution is blurred.

A clearer picture can be obtained from GGA+U calculations for a free-standing NC-Ph3-CN molecule with an Fe atom attached to the central phenyl ring (see Figure 3b). The PDOS calculated for the free-standing and the surface-supported system presents similarities as, for example, the features of the states corresponding to the planar (star) and d2z orbital of Fe orbitals. States A (A') and B (B'), originating mainly from the Fe dxz and dyz orbitals, respectively, are now clearly identified in the PDOS. The d orbital occupations are similar for the two systems (see Tables 1 and 2), indicating that the occupations mostly result from the interaction with the molecule and the Cu(111) substrate plays a minor role. From these observations, we deduce that, for the identification of the atomic orbitals, the free-standing Fe-molecule system is a simplified but appropriate representation of the surface-supported one. Therefore, we use it to describe the contribution of each orbital to the spatial charge distribution.

In Figure 3c, we present the isosurface density plots for the free-standing Fe-molecule system corresponding to states A, B and A', B'. By inspecting the PDOS in Figure 3b and the isosurface density plots, we conclude that A and A' are almost pure Fe states, with little or no hybridization with the molecule and extending perpendicularly to the molecular axis, whereas B and B' have a higher degree of hybridization and are delocalized on the molecular axis. The asymmetry of the resulting hybridized orbitals reflects the spatial dependence observed in STS measurements. Thus, the observed Kondo effect arises from the presence of two screening channels, A and B, one originating mainly from the Fe atomic dxz orbital and the other from the dyz one.

To confirm this interpretation, we estimate the Kondo temperature expected for the states derived from these d orbitals by using

\[
\Gamma = k_B T_K \approx \frac{2\Delta}{\pi} \exp \left[ -\frac{\pi}{2\Delta} \left( \frac{1}{\epsilon_F} + \frac{1}{\epsilon + U} \right) \right]^{-1}
\]

where the level binding energy, \(\epsilon_F\), the Coulomb repulsion energy, \(U\), and the hybridization energy between the level and continuum of states in the metal substrate, \(\Delta\), appear as parameters. \(\Delta\) is required to be small with respect to \(\epsilon_F\). Qualitatively, state B, being closer to \(E_F\) than state A, is expected to yield a higher \(T_K\) for a given value of \(\Delta\). Considering our results for the free-standing Fe-molecule system, the energies of states A and B are \(\epsilon_F = -1.0\ eV\) and \(\epsilon_F = -0.9\ eV\). The Coulomb repulsion energy corresponds to the difference between the energy of the occupied and the unoccupied states, \(U_A = 2.6\ eV\) and \(U_B = 2.2\ eV\). We use a typical value of the hybridization energy \(\Delta \approx 0.2\ eV\), yielding \(T_{KA} = 68\ K\) and \(T_{KB} = 116\ K\). These values are in agreement with the experimental Kondo temperatures deduced from the dI/dV spectra, supporting our interpretation of the presence of two distinct Kondo channels, associated with the states derived from dxz (A and A') and from dyz (B and B').

It is interesting to note that Fe atoms buried by the molecules have \(S = 1\) with two singly occupied orbitals, as Co atoms on Cu(111). However, in the case of Co/Cu(111), the two orbitals are degenerate, resulting in a single value for \(T_K\).

To investigate the degree of screening of both Kondo channels, we performed X-ray absorption spectroscopy (XAS) and XMCMD measurements at the EPFL/PSI X-Treme beamline at the Swiss Light Source. Since the Fe deposition temperature controls the Fe abundance in the three adsorption sites on the (NC-Ph3-CN)Cu2/Cu(111) surface, we can produce samples with the Fe adatoms predominantly adsorbed on the substrate (sample A, \(T_{dep} = 3\ K\)) and samples where they are mostly below the molecules (sample B, \(T_{dep} = 40\ K\). Figure 4a,b compares XAS and XMCMD recorded at the Fe L3 edge absorption edges of two such samples. As expected, the spectra

| Table 1. Löwdin Populations of the s and d Atomic Orbitals for Fe and Co Atoms Adsorbed under NC-Ph3-CN on Cu(111) |
|---|---|---|---|---|---|
|          | s   | dxy | dxz | dyz | dxy',dyz' |
| Fe spin-up | 0.31 | 0.98 | 0.92 | 0.92 | 0.90 | 0.89 |
| Fe spin-down | 0.28 | 0.93 | 0.18 | 0.20 | 0.50 | 0.74 |
| Co spin-up | 0.30 | 0.97 | 0.87 | 0.88 | 0.86 | 0.85 |
| Co spin-down | 0.30 | 0.95 | 0.68 | 0.60 | 0.80 | 0.80 |

| Table 2. Löwdin Populations of the s and d Atomic Orbitals for the Free-Standing Fe-Molecule System |
|---|---|---|---|---|---|
|          | s   | dxy | dxz | dyz | dxy',dyz' |
| Fe spin-up | 0.08 | 0.98 | 0.97 | 0.98 | 0.86 | 0.86 |
| Fe spin-down | 0.08 | 0.96 | 0.12 | 0.11 | 0.59 | 0.69 |

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of sample A are very similar to those measured for Fe atoms on Cu(111). In contrast, the XAS spectra of sample B show a broader $L_2$ absorption peak and a strongly reduced XMCD signal. As the shapes of the magnetization curves of samples A and B are identical (see inset in Figure 4b), implying an equal response to the external magnetic field, we can conclude that most of the remaining magnetic signal of sample B originates from residual Fe atoms on Cu(111). This is further corroborated by the observation that depositing additional Fe at 3 K results in an increase of the XAS and XMCD intensities, as one atom per Cu(111) unit cell.

To reveal the signature of the Fe atoms adsorbed under molecules, we removed the contribution of the residual Fe atoms adsorbed on Cu(111). To estimate their amount, we subtracted from the XAS spectrum of sample B in Figure 4a the one Fe on bare Cu(111) rescaled such that the difference does not become negative at any energy (see Supporting Information). With this method, we estimate the residual Fe atoms on the Cu surface to be 20 ± 3% of the total Fe coverage. The resulting XAS and XMCD signals are shown in Figure 4c,d. Applying sum rules to these spectra, using the number of holes $n_\pi = 2.85$ found by the DFT calculations, we obtain a spin magnetic moment of only 0.15 ± 0.1 $\mu_B$. A nonscreened $S = 1$ state would result in a magnetic moment of $\approx 1.9 \mu_B$ at $T = 2.5$ K, as estimated using the Brillouin function. Therefore, the magnetic moment of the buried Fe atoms is to a very good approximation entirely Kondo-screened.

Ideally, by performing temperature-dependent measurements, successive suppression of the screening channels should be observed with increasing temperature: the system is expected to turn first into an underscreened impurity, and then the magnetic moment associated with both orbitals is expected to be recovered. However, since XMCD measures the magnetic moment projected onto the photon beam direction, which is parallel to the external magnetic field, the gain of magnetic moment due to the disruption of the Kondo state is in competition with the temperature-induced decrease of its projection expected for a paramagnetic system. Measurements at 40 K show that the projected spin magnetic moment of the Fe atoms adsorbed under molecules does not change significantly with respect to the value obtained at 3 K (see Supporting Information). This observation indicates that the absolute value of the magnetic moment must have increased, thus confirming that the screening effect is partially lost at 40 K.

**CONCLUSIONS**

In conclusion, we have shown that the combination of transition metal atoms and organic molecules can suppress the Kondo effect in the case of Co, while inducing it for Fe, leading to a regular array of Kondo impurities. In addition, these impurities have two distinct screening channels that originate from nondegenerate orbitals and give rise to a Kondo effect with different signatures in the directions parallel and perpendicular to the molecular axis. The effective screening of the spin in both channels is finally demonstrated through XAS and XMCD measurements.

**METHODS**

**Sample Preparation.** The Cu(111) substrate was prepared by Ar$^+$ sputtering (2 $\mu$A/cm$^2$, 800 V, 20 min) and annealing (800 K, 20 min) cycles. NC-Ph$_3$-CN molecules were evaporated from a molecular effusion cell at 418 K onto the Cu(111) substrate at 300 K. The obtained (NC-Ph$_3$-CN)$_3$Cu$_2$ honeycomb network has a period of 3.51 nm.

Fe and Co were evaporated from an e-beam evaporator, while the sample was placed in the STM. One monolayer of Fe or Co is defined as one atom per Cu(111) unit cell.

**STM.** STM and STS experiments were performed with a 5 K ultrahigh vacuum STM$^{46}$ using W tips. Indicated bias voltages, $V_B$ refer to the sample.

In all STS measurements, the voltage modulation refers to peak-to-peak values. All spectra are averaged over several measurements, and a reference spectrum acquired on the substrate has been subtracted. The differential conductance map is extracted from a grid of 32 × 16 $dI/dV$ spectra.

**DFT.** The DFT calculations were performed within the density functional theory framework employing the generalized gradient approximation (GGA) with a mean-field Hubbard correction (GGA + $U$)$^{38}$ as implemented in the Quantum-ESPRESSO package.$^{37}$ We used ultrasoft pseudopotentials, a planewave cutoff of 30 Ry, and a Hubbard parameter $U$ of 4 eV for the Fe and Co d orbitals. We checked the convergence with respect to the cutoff and tested different values of $U$ (namely, $U = 2$ and 3 eV), which give very similar results. The structure was fully relaxed using a 2 × 2 × 2 k-point mesh until all residual forces were below $10^{-3}$ Ha/Å. The density of states and magnetic properties were then computed self-consistently on a 4 × 4 × 4 k-point mesh. The atomic magnetic moment and the Löwdin population of the Fe and Co orbitals were obtained by projecting the Kohn–Sham wave functions onto a set of localized atomic orbitals.

**XMCD.** We recorded the $L_3$ absorption edges of Fe in the total electron yield mode. The Cu(111) preparation and the molecule deposition were performed in the preparation chamber of X-Treme,$^{44}$ and Fe was deposited after the sample had been transferred in situ into the cryostat. Molecule and Fe coverages were calibrated by cross-correlating XAS spectra with in situ STM measurements. The STEM was also employed to check the quality of the metal–organic honeycomb structure. The magnetization curves were obtained as the amplitude of the $L_3$ XMCD peak intensity at 703.5 eV divided by the pre-edge signal at 701.5 eV. The spectra are normalized to the XAS area.

**Figure 4.** (a) Fe $L_{2,3}$ XAS for samples A and B ($B = 6.8$ T, $T = 2.5$ K, $\Theta = (7 \pm 1) \times 10^{-3}$ ML). (b) XMCD of spectra in (a). Inset: Magnetization curves of samples A and B. Curves are scaled to the same saturation value. (c) XAS signal resulting from the subtraction of the contribution of residual Fe atoms on Cu(111) from spectra of sample B and (d) corresponding XMCD. All spectra are normalized to the XAS area.
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Supporting information for:

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STM and STS

Manipulation of Fe adatoms

Figure S1 demonstrates that the very bright features observed on STM images (indicated by yellow arrows) are single atoms adsorbed on molecules. Indeed, after repeated imaging, these objects disappear and single atoms, marked by the turquoise dashed circles, are found in close-by cavities.

![Figure S1](image-url)

Figure S1: Consecutive images showing the successive descent of Fe atoms from ontop of the molecules in the (NC-Ph$_3$-CN)$_3$Cu$_2$/Cu(111) honeycomb network down to the substrate. Fe deposition: $\Theta = (6 \pm 1) \times 10^{-3}$ ML, $T_{\text{dep}} = 10 \pm 2$ K. ($V_t = -300$ mV, $I_t = 50$ pA, $T_{\text{STM}} = 5$ K).

Fe on (NC-Ph$_5$-CN)$_3$Cu$_2$/Cu(111)

Figure S2 shows results for Fe deposition on honeycomb networks built with a longer polyphenyl molecules, namely, (NC-Ph$_5$-CN)$_3$Cu$_2$/Cu(111). Deposition between 20 and 50 K leads to diffusion of the Fe atoms under the molecules. Different to the result obtained with NC-Ph$_3$-CN molecules, in this case small clusters are often formed, visible as the brightest spots in the STM image in Fig. S2(a). Buried single Fe atoms appear as smaller, dimmer features, as the one encircled. Figure S2(b) shows an STM image and the corresponding $dI/dV$ map at $E_F$. The images show several NC-Ph$_5$-CN molecules, some of them with an Fe atom below a phenyl ring (white arrows). The bottom-left molecule also hosts a bigger object, identified as an Fe cluster (green arrow). For each buried Fe atom, the $dI/dV$ map at $E_F$ shows a large bright spot on one side of the molecular axis and a less bright, smaller one on the opposite side; a depression is observed in correspondence of the molecular axis. Notice that these spectroscopic features are absent for the buried Fe cluster (green arrow).
Figure S2: (a) STM image of the (NC-Ph$_5$-CN)$_3$Cu$_2$ honeycomb network on Cu(111) for $\Theta = (6 \pm 1) \times 10^{-3}$ ML of Fe deposited at $T_{\text{dep}} = 32$ K. The red circle indicates a buried Fe atom ($V_t = -50$ mV, $I_t = 300$ pA, $T_{\text{STM}} = 5$ K). (b) Smaller scale STM image, white arrows indicate buried Fe atoms, the green arrow points at an Fe cluster ($V_t = -300$ mV, $I_t = 800$ pA, $T_{\text{STM}} = 5$ K); corresponding $dI/dV$ map at $E_F$ ($V_{\text{mod}} = 2$ mV at 523 Hz).

STS spectroscopy on related systems

Figure S3(a) shows the $dI/dV$ spectra acquired on Co atoms adsorbed on NC-Ph$_3$-CN molecules. In Fig. S3(b) spectra measured on Fe atoms on NC-Ph$_3$-CN and on the pristine molecules are presented. None of the spectra show Kondo features.

Figure S3: $dI/dV$ spectra acquired on the indicated systems on Cu(111): (a) Co on NC-Ph$_3$-CN; (b) bare NC-Ph$_3$-CN and Fe on NC-Ph$_3$-CN; spectra are offset for clarity. Setpoint: $V_t = -50$ mV, $I_t = 300$ pA, $V_{\text{mod}} = 2$ mV peak-to-peak at 523 Hz.
Fitting parameters

Values of $\Gamma_0$ and $q$ obtained from the fits in Fig. 2(a) in the main text (using $\alpha = 5$):

- main peak: $\Gamma_0 = 5.4 \pm 0.3$ meV, $q = 10$
- less intense peak: $\Gamma_0 = 5.3 \pm 0.2$ meV, $q = 3$
- dip: $\Gamma_0 = 9.8 \pm 0.5$ meV, $q = -0.6$

Co/Cu(111): $\Gamma_0 = 4.5 \pm 0.3$ meV and $q = 0.4$

XAS and XMCD

Dependence on the deposition temperature

Most of the Fe atoms on sample B in the main paper ($T_{\text{dep}} = 40$ K) are buried under the molecules. This sample shows a much weaker XMCD signal (red in Fig. 4 and Fig. S4) than sample A ($T_{\text{dep}} = 3$ K, blue in Fig. 4). To explain the origin of this difference, we have added Fe atoms at 3 K on sample B (Fig. S4, green). At this deposition temperature, Fe atoms come to rest on their impact site which is predominantly bare Cu(111). This results in an increase of the XAS and XMCD intensities, see Figs. S4(a) and (b), with both spectral shapes approaching the ones measured on the sample with all of the Fe deposited at 3 K.

Figure S4: XAS (a) and corresponding XMCD (b) spectra of a sample on which Fe was evaporated at 40 K (red, sample B), $\Theta = (7 \pm 1) \times 10^{-3}$ ML and further Fe was added at 3 K (green), final coverage $\Theta = (1.4 \pm 0.2) \times 10^{-2}$ ML. The spectra are normalized to the XAS area for the first deposition.
Subtraction of the signal of residual Fe/Cu(111)

We estimate for sample B the relative amount of Fe present on bare Cu(111) and buried under the molecules by subtracting the spectrum of Fe on bare Cu(111)\textsuperscript{S4} from the XAS spectrum of sample B. The amount of Fe on bare Cu(111) is then given by the scaling factor needed for the Fe/Cu(111) spectrum such that the difference does not become negative for any energy, see Fig. S5(a). The green circle highlights the part of the spectra that would result in a negative XAS in the difference spectrum if the signal coming from Fe on bare Cu(111) was overestimated. We find that the amount of Fe adsorbed on the bare Cu in sample B is $20 \pm 3 \%$. The result of the subtraction is shown in Fig. S5(b). In Fig. 4 in the main text we report the two polarizations as well as the XMCD signal.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s5.png}
\caption{(a) Total XAS of sample B in the main text (red) and total XAS of Fe atoms on Cu(111) (black). Gray: spectrum of Fe on Cu rescaled by a factor 0.2. Fe coverage is $\Theta = (7 \pm 1) \times 10^{-3}$ ML for both samples. The spectra are normalized to the XAS area. (b) Result of the difference to extract the total XAS of Fe atoms buried by molecules.}
\end{figure}

Temperature-dependent measurements

Figure S6(a) shows XAS spectra of the Fe atoms under molecules obtained with the procedure described above from spectra acquired at 40 K and at 3 K. For the 40 K data, the procedure is applied keeping for the Fe/Cu an unmodified XAS value and reducing the XMCD by a factor of 3.7. This factor corresponds to the ratio of the Fe moment at 3 K and 40 K as derived from moments and anisotropy values given in Ref.\textsuperscript{S4} For this sample we
deduce a spin magnetic moment of $0.3 \pm 0.1 \mu_B$ at 3 K and of $0.4 \pm 0.1 \mu_B$ at 40 K.

Figure S6: (a) Total XAS and (b) XMCD of Fe under molecules for the same sample measured at 40 K and 3 K. Fe coverage is $\Theta = (7 \pm 1) \times 10^{-3}$ ML. The spectra are normalized to the XAS area.

References


