# SUPPORTING INFORMATION FOR

# Lanthanide-Porphyrin Species as Kondo Irreversible Switches through Tip-induced Coordination Chemistry

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# 1. Au-2H-4FTPP species on Au(111).



**Figure S1. Identification of minority Au-2H-4FTPP species on Au(111)**. a) and b) show the appearance of the premetallated Au-2H-4FTPP species encircled (yellow), at negative and positive bias voltage, respectively (width= 10 nm,  $V_b = -0.75$  V,  $I_t = 25$  pA; width= 10 nm,  $V_b = 1.0$ V,  $I_t = 25$  pA). c) Side and top view of the relaxed structure of the Au-2H-4FTPP, with the Au adatom below the molecular backbone, and the four-lobed appearance of the Keldish-Green theoretical STM image at 1V. d) STS of both species acquired in the positions depicted in b with green and yellow arrows, showing a shift of ~0.5 eV (Feedback conditions for STS:  $I_t = 200$  pA,  $V_b = -1.25$  V, modulation: 10 mV, frequency= 773 Hz, integration time = 36 ms per point, sampling energy= 3.5 meV).

2. Controlled tautomerization of 2H-4FTPP species on Au(111).



**Figure SI2. Spatially controlled and uncontrolled tautomerization of 2H-4FTPP species on Au(111).** a) STM image of an island displaying two distinct porphyrin tautomers, to be termed tautomer 1 and 2. Tautomer 1 is highlighted with the black arrow ( $I_t = 35 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 4.6 nm). b) Tunneling current versus time spectrum featuring a telegraphic signal corresponding to the switch between tautomer 1 and 2, applied on green cross of a. c) Topographic image showing that the target monomer is now tautomer 2 ( $I_t = 35 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 4.6 nm). d) Zoomed-in image with tautomers 1 and 2 ( $I_t = 35 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 4.6 nm). e) Scanning at perturbative conditions shows spikes in the STM images as monomers are changing while the image is being recorded ( $I_t = 35 \text{ pA}$ ,  $V_b = 1.8 \text{ V}$ , width= 3.5 nm). f) Scanning the same area after the perturbation reveals that some monomers changed from 1 to 2 or vice-versa ( $I_t = 35 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 3.5 nm).

### 3. Deprotonation of 2H-4FTPP species on Au(111).



**Figure SI3. Tip-induced deprotonation of 2H-4FTPP species on Au(111).** a-b) STM images showing where a 2.1 V voltage pulse is applied (green cross) to transform an intact 2H-4FTPP species into a 1H-4FTPP monomer by removing one proton ( $I_t = 100 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 7 nm). c) Same area at negative bias, where a subsequent 2.4 V pulse is applied in the same monomer ( $I_t = 100 \text{ pA}$ ,  $V_b = -0.8 \text{ V}$ , width = 7 nm). d) The applied pulse resulted in the full deprotonation (0H-4FTPP) of the original monomer and the collateral deprotonation of an adjacent species ( $I_t = 100 \text{ pA}$ ,  $V_b = -0.8 \text{ V}$ , width = 7 nm). e) Tunneling current versus time spectrum applied over 40 s on the blue cross, displaying a telegraphic signal corresponding to different positions of the inner proton. f ) Scanning the area again shows that the inner hydrogen has been displaced to the opposite pyrrole moiety (c-f:  $I_t = 100 \text{ pA}$ ,  $V_b = -0.8 \text{ V}$ , width = 7 nm).

4. High resolution images at positive and negative bias of intermediate Dy-1H-4FTPP species on Au(111).



Figure SI4. Visualization of asymmetric Dy-1H-4FTPP species on Au(111). a)  $I_t = 100 \text{ pA}$ ,  $V_b = 0.25 \text{ V}$ , width = 6.6 nm. b) Ball-and-stick model of partial metallated species. c)  $I_t = 100 \text{ pA}$ ,  $V_b = 0.7 \text{ V}$ , width = 6.6 nm.

#### 5. Spin-polarized calculations.



**Figure SI5.** Spin polarized density calculations and computed spin-density of (0H/1H/2H)-4FTPP species on Au(111). a) Computed Projected Density of Electronic States (PDOS) for both spin-up (blue line) and spin-down (red-line) channels onto the three (0H/1H/2H)-4FTPP molecules within the formed interfaces as a function of the energy (in eV) referred to the Fermi level. b) Computed spin-density (in eV<sup>-1</sup>), obtained as the difference between the spin-up and spin-down PDOS channels of panel a), for the three (0H/1H/2H)-4FTPP molecules up to the Fermi level as a function of the energy (in eV) referred to the Fermi level. c) Different views of the 3D isosurface corresponding to the difference of electronic densities between the formed 2H-4FTPP@Dy/Au(111) interface and the isolated 2H-4FTPP molecule and substrate by separate (red: charge depletion region, blue: charge gain region; isovalue: 0.005 e<sup>-</sup> Å<sup>-3</sup>), which reflects the charge redistribution on the molecule after the formation of the interface, including the charge transfer from the substrate of 0.85 e<sup>-</sup>.

In order to make a direct comparison with the STS experiments shown in the main text for the three different lanthanide porphyrin species (see Fig. 2), we have carried out a battery of calculations to compute the Projected Density of Electronic States (PDOS) for both spin-up and spin-down channels onto the three (0H/1H/2H)-4FTPP molecules within the formed interfaces (cf. Figure SI5). Due to the sequential increase of electronic saturation of the molecules from the 0H-4FTPP to the 2H-4FTPP cases, the molecular LUMO gets closer to the Fermi level, almost pinning into it for the 2H-4FTPP case. This effect is also clearly observed in the Figure 3 of the main text, reflecting the good agreement regarding electronic properties between the experimental evidence and the result of the calculation.

Regarding the magnetic properties of the molecular species, rationalizing from a theoretical atomistic perspective the occurrence of a Kondo resonance in this kind of interfaces turns into a difficult challenge, especially in those involving 4f-electrons as it is the present case. Nonetheless, herein we have tried to shed some light from the calculations in the elucidation of the origin of the Kondo resonance observed in the experiments. For that purpose we have computed the spin density within the molecules as the difference between the spin-up and spin-down PDOS channels of Figure SI5a (cf. Figure SI5b). What we observe is that a net integration of the obtained spin-density profiles up to the Fermi energy yields values of 0.02, 0.14 and 0.64 spin-down electrons from the 0H-4FTPP to the 2H-4FTPP cases. Highest value of electronic unpairing of 0.64 e<sup>-</sup> scattered by the Dy atom towards the molecule is obtained for the 2H-4FTPP species (considering the 0.85 e<sup>-</sup> transferred from the substrate to the molecule for this interface), which points it up as the best potential candidate to yield a Kondo resonance from the theoretical point of view, agreeing with the experimental observation. Notice the very low values of electronic unpairing for the 1H-4FTPP and 0H-4FTPP cases, which do not manifest any trace of Kondo resonance in experiments.

Additionally, to visualize the redistribution of the charge within the 2H-4FTPP molecules after the interface is formed we have obtained the 3D isosurface corresponding to the difference of electronic densities between the formed 2H-4FTPP@Dy/Au(111) interface and the isolated 2H-4FTPP molecule and substrate by separate, which reflects the charge redistribution on the molecule after the formation of the interface, including the charge transfer from the substrate of 0.85 e<sup>-</sup>. As we can observe, for this case, yielding a Kondo resonance, the redistribution of the electronic charge is quite delocalized on all over the molecule. This observation reinforces this interface as candidate interface to manifest a Kondo resonance. 6. Lateral manipulation and transformation of Dy-2H-4FTPP into Dy-0H-4FTPP.



Figure SI6. Lateral and vertical manipulation of an intact 2H-4FTPP and a Dy-2H-4FTPP species on Au(111). Scanning parameters: a)  $I_t = 150 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width = 8.8 nm. b)  $I_t = 150 \text{ pA}$ ,  $V_b = -1 \text{ V}$ , width = 8.8 nm. c)  $I_t = 100 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width= 12 nm. d)  $I_t = 100 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width = 12 nm. e)  $I_t = 100 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width= 12 nm. f)  $I_t = 100 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width = 12 nm. g)  $I_t = 100 \text{ pA}$ ,  $V_b = -0.8 \text{ V}$ , width = 12 nm. h)  $I_t = 100 \text{ pA}$ ,  $V_b = 1 \text{ V}$ , width = 12 nm. i)  $I_t = 180 \text{ pA}$ ,  $V_b = 0.4 \text{ V}$ , width = 7 nm.

#### 7. Theoretical Modelling and Computational Details.

In order to theoretically analyze the structural and STM-imaging properties of the 2H-4FTPP and Dy-(0/1/2)H-4FTPP on Au(111) interfaces we have used two complementary DFT-based simulation packages: (i) the accurate plane-wave code QUANTUM ESPRESSO<sup>1</sup> that we used for determination of the complex interfacial atomic geometries and (ii) the efficient local-orbital code FIREBALL<sup>2</sup> used to simulate of the theoretical STM images. In the calculations carried out using the plane-wave QUANTUM ESPRESSO code1 one-electron wave-functions were expanded in a plane-waves basis with energy cutoffs of 500 and 600 eV for the kinetic energy and the electronic density, respectively. Exchange and Correlation (XC) effects have computed in the revised generalized gradient corrected approximation (GGA) PBESol.<sup>3,4</sup> Kresse-Joubert Projector Augmented Wave (KJPAW) pseudopotentials<sup>5</sup> have been adopted to model the ionelectron interaction for all the involved atoms (H, C, N, F, Dy and Au). At this point it is important to remark that 20 valence electrons have been accounted for the Dy atom, which permits to include the role of the lanthanoid  $4f^{10}$  electrons in the subtle interfacial chemistry. In all the calculations, Brillouin zone (BZ) has been sampled using optimal [4×4×1] Monkhorst-Pack grids,<sup>6</sup> guaranteeing a full convergence in energy and electronic density. A perturbative van der Waals (vdW) correction was used to check the reliability of the adsorbed molecular ad-layer configurations. For this purpose, we have used an empirical vdW R<sup>-6</sup> correction to add dispersive forces to conventional density functionals (DFT+D3).7 Spin-polarized fashion has been considered in all the calculations. Atomic relaxations were carried out using a conjugate gradient minimization scheme until the maximum force on any atom was lower than 0.02 eV/Å. The Fermi level was smeared out using the Methfessel–Paxton approach<sup>8</sup> with a Gaussian width of 0.01 eV, and all energies were extrapolated to T=0 K. Self-consistency in the electron density was converged to a precision in the total energy better than  $10^{-6}$  eV.

On the other hand, in the FIREBALL code<sup>2</sup> we use a local-orbital formulation in such a way that self-consistency is implemented on the orbital occupation numbers, which were calculated using the orthonormal Löwdin orbitals.<sup>9</sup> In these calculations we used a basis set of optimized single and double numerical atomic orbitals (NAOs)<sup>10</sup>: sp<sup>3</sup>d<sup>5</sup> for C, N and Au, sp<sup>3</sup>s\*p\*<sup>3</sup> for F, ss\* for H, and sp<sup>3</sup>d<sup>5</sup>f<sup>7</sup> for Dy. In these calculations we used the local density approximation (LDA) functional<sup>11</sup> and the ion–electron interaction has been modeled by means of norm-conserving scalar-relativistic pseudopotentials.<sup>12</sup> This local-orbital formulation has been adopted for the

STM-imaging simulations, where tunnelling currents for the STM images have been computed by using the Keldysh-Green function formalism, together with the first-principles tight-binding Hamiltonian obtained from the FIREBALL code, as explained in full detail elsewhere.<sup>2,13,14</sup> Our STM theoretical simulation approach includes a detailed description of the electronic properties of both the W-tip and the sample simultaneously. All computed theoretical STM images have been obtained at constant-current scanning conditions, moving the W-tip perpendicularly to the sample in each STM scanning-step to search a pre-selected fixed value of the tunnel current, in order to mimic the experimental procedure.

To construct all the interfacial models we have considered: i) a slab of 3 (for relaxation purposes) and 4 (for STM-imaging simulations) physical Au(111) layers, with a minimum distance of  $\sim$ 20 Å of vacuum between neighboring cells along the axis perpendicular to the surface, and ii) full periodic boundary conditions representing an infinite Au(111) surface. For the structural optimization calculations the 2 bottommost Au(111) physical layers were kept fixed; and, as mentioned, one additional Au(111) layer was accounted for the simulation of the STM-imaging.

#### 8. Fitting of the Kondo resonance.

The spectral shape of the tunneling conductance is well described by the Fano function, which results from the interference between a discrete state (a resonance state) and a continuum state (background state). The Fano function can be expressed as:

$$\frac{dI}{dV}(V) = \frac{(q+\epsilon)^2}{1+\epsilon^2} \quad \text{with} \quad \epsilon = \frac{eV - w_0}{\Gamma}$$
(1)

Where q is the form factor,  $\epsilon$  the reduced energy, eV the applied voltage,  $w_0$  the energy shift from the Fermi level and  $\Gamma$  the half width at half maximum (HWHM). The recorded Kondo resonances are broadened by two additional factors: the finite temperature of the system and the modulation of the bias voltage applied by the lock-in amplifier. Therefore, in order to extract the intrinsic  $\Gamma$ of the Kondo resonance, we need to deconvolute the experimental signal. For the modulation of the voltage, we use:<sup>16</sup>

$$y(x) = \frac{8}{\pi \cdot (V_{pp})^2} \cdot \sqrt{\left(\frac{V_{pp}}{2}\right)^2 - x^2}$$
(2)

Where  $V_{pp}$  is the modulation of the applied voltage measured peak to peak. Finally, for the contribution of the temperature of the system we use the derivative of the Fermi function.<sup>17</sup>

## 9. References

- 1. P. Giannozzi et al., J. Phys. Condens. Matter, 2009, 21, 395502.
- 2. J. P. Lewis, P. Jelínek, J. Ortega, A. A. Demkov, D. G. Trabada, B. Haycock, H. Wang, G. Adams, J. K. Tomfohr, E. Abad, H. Wang and D. A. Drabold, *Phys. Status Solidi B*, 2011, **248**, 1989-2007.
- 3. L. A. Constantin, J. P. Perdew and J. M. Pitarke, *Phys. Rev. B*, 2009, **79**, 075126.
- 4. J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- 5. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- 6. J. D. Pack and H. J. Monkhorst, *Phys. Rev. B*, 1977, **16**, 1748-1749.
- 7. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 8. M. Methfessel and A. T. Paxton, *Phys. Rev. B*, 1989, **40**, 3616-3621.
- 9. A. A. Demkov, J. Ortega, O. F. Sankey and M. P. Grumbach, *Phys. Rev. B*, 1995, **52**, 1618-1630.
- 10. M. A. Basanta, Y. J. Dappe, P. Jelinek and J. Ortega, *Comput. Mater. Sci.*, 2007, **39**, 759-766.
- 11. P. Jelínek, H. Wang, J. P. Lewis, O. F. Sankey and J. Ortega, *Phys. Rev. B*, 2005, **71**, 235101.
- 12. M. Fuchs and M. Scheffler, Comput. Phys. Commun., 1999, 119, 67-98.
- 13. J. M. Blanco, F. Flores and R. Pérez, *Prog. Surf. Sci.*, 2006, **81**, 403-443.
- 14. J. M. Blanco, C. González, P. Jelínek, J. Ortega, F. Flores and R. Pérez, *Phys. Rev. B*, 2004, **70**, 085405.
- 15. C. González, P. C. Snijders, J. Ortega, R. Pérez, F. Flores, S. Rogge, H. H. Weltering, *Phys. Rev. Lett.* 2004, 93, 2–5
- 16. M. Ternes. Scanning tunneling spectroscopy at the single atom scale. Ph.D. thesis, SB, Lausanne (2006).
- 17. K. Nagaoka, T. Jamneala, M. Grobis, and M. F. Crommie. PRL , 2002, 88, 077205