Supporting Information for

Lattice-Directed Stabilization of Different Spin-State Phases in Metallo-Supramolecular Chains on Au Surfaces

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Supporting Discussion

1. Fano-fitting of the d*I*/d*V* spectra

The d*I*/d*V* spectrum of the HS-Ni atom on Au(100) measured at zero magnetic field (red in Figure 1b) is fitted by a linear combination of two Fano functions as follow,[1,2]

$$\frac{\mathrm{d}I}{\mathrm{d}V}(\mathrm{e}V) = A_1 F_1(\mathrm{e}V) + A_2 F_2(\mathrm{e}V) + B$$

$$F_i(\mathrm{e}V) = \frac{(\varepsilon_i + q_i)^2}{1 + \varepsilon_i^2} \qquad (i = 1, 2)$$

$$\varepsilon_i = (\mathrm{e}V - \varepsilon_{0_i})/\Gamma_i$$

where A_1, A_2 and B are the constants, q_i, ε_{0_i} and Γ_i are the Fano asymmetry parameter, the energy shift with respect to the Fermi level and the half width at half maximum (HWHM) of the *i*th Kondo resonance, respectively.

The d*I*/d*V* spectrum of the HS-Ni atom on Au(110) (red in Figure 3c) is fitted by adding a linear term to a single Fano function to deal with the influence of the background resonance in the spectroscopic region as follow,[3,4]

$$\frac{\mathrm{d}I}{\mathrm{d}V}(\mathrm{e}V) = a\frac{(\varepsilon + q)^2}{1 + \varepsilon^2} + b\mathrm{e}V + c$$

$$\varepsilon = (\mathrm{e}V - \varepsilon_0)/\Gamma$$

where *a*, *b* and *c* are the constants.

The Kondo temperature T_K can be extracted from Γ as follow,[5]

$$k_\mathrm{B}T_\mathrm{K} = \sqrt{\Gamma^2 - (1.75k_\mathrm{B}T)^2 - (0.87\mathrm{e}V_\mathrm{m})^2 - (\alpha k_\mathrm{B}T)^2}$$

where k_B is the Boltzmann's constant, V_m is the modulation voltage used for the d*I*/d*V* measurements, T is the temperature, and α is a parameter being equal to π as predicted by the Fermi-liquid theory.[6]

2. Comparison of the experimental wide-range d*I*/d*V* spectrum and the calculated DOS of the LS-Ni on Au(100)

The wide-range d*I*/d*V* spectrum acquired at a dark LS-Ni atom in the coordination chain on Au(100) shows a strong resonance centered at ~1.0 V and a shoulder located at ~-0.3 V (Figure S3a). In comparison with the calculated DOS of the Ni atom (Figure S3b), we assign the peak at 1.0 V to the calculated electronic state at 1.5 eV (solid black arrow in Figure S3b), and the shoulder at -0.3 V to the calculated state at 0.6 eV (dashed black arrow) in consideration of the Fermi level offset and the underestimation of energy gap in the DFT method.

3. Comparison of the experimental wide-range d*I*/d*V* spectrum and the calculated DOS of the HS-Ni on Au(110)

The wide-range d*I*/d*V* spectrum acquired at a bright HS-Ni atom in the coordination chain on Au(110) shows a peak at the Fermi level based on a background broad resonance (Figure S7a). The peak stems from the Kondo effect of the HS-Ni atom. The broad resonance is assigned to the calculated electronic state around the Fermi level, as shown by the theoretical DOS curves (Figure S7b).

Supporting Figures

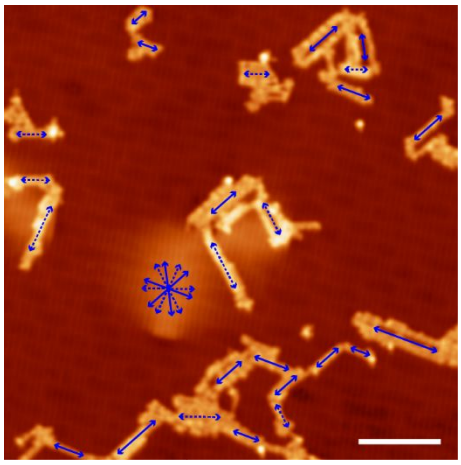

Figure S1. Large-area STM image of the coordination chains formed on Au(100) (scanning conditions: bias $V = 100$ mV, feedback current $I = 50$ pA, temperature $T = 4.9$ K). The six extending orientations of the molecular chains are highlighted by the solid and dashed blue arrows. Scale bar: 20 nm.

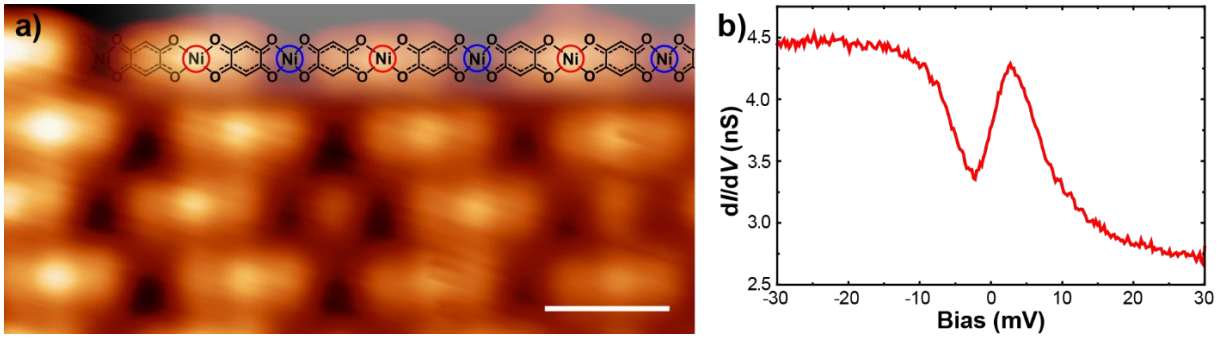

Figure S2. (a) STM image of the antiferroelastic phase of the coordination chains formed on Au(111) with the chemical structure superimposed (in constant height mode, $V = 3$ mV, $I = 416$ pA at maximum, $T = 4.9$ K). The HS-Ni ($S = 1$) and LS-Ni ($S = 0$) atoms are marked by the blue and red circles, respectively. (b) A representative dI/dV spectrum acquired at a HS-Ni atom in the coordination chain on Au(111). The dI/dV measurement is conducted by using a lock-in amplifier with a modulation of $V_{rms} = 1$ mV and a frequency of $f = 800$ Hz at $T = 2$ K.

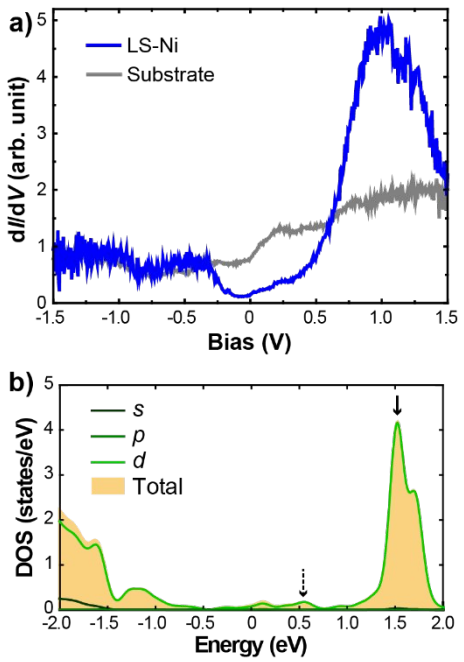

Figure S3. (a) Experimental dI/dV spectra acquired on the bare Au(100) substrate (grey) and at a dark LS-Ni atom in the chain on Au(100) (blue). The dI/dV spectra are acquired by using a lock-in amplifier with a modulation of V_{rms} = 10 mV and a frequency of f = 973 Hz at T = 4.9 K. (b) Calculated DOS curves of the LS-Ni atom in the coordination chain on Au(100).

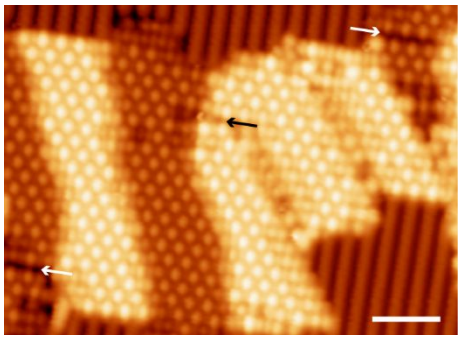

Figure S4. STM image of the coordination chains formed on Au(110) (V = 100 mV, I = 3.1 nA, T = 4.9 K). The linear defects between the neighboring chains are marked by the arrows. Scale bar: 3 nm.

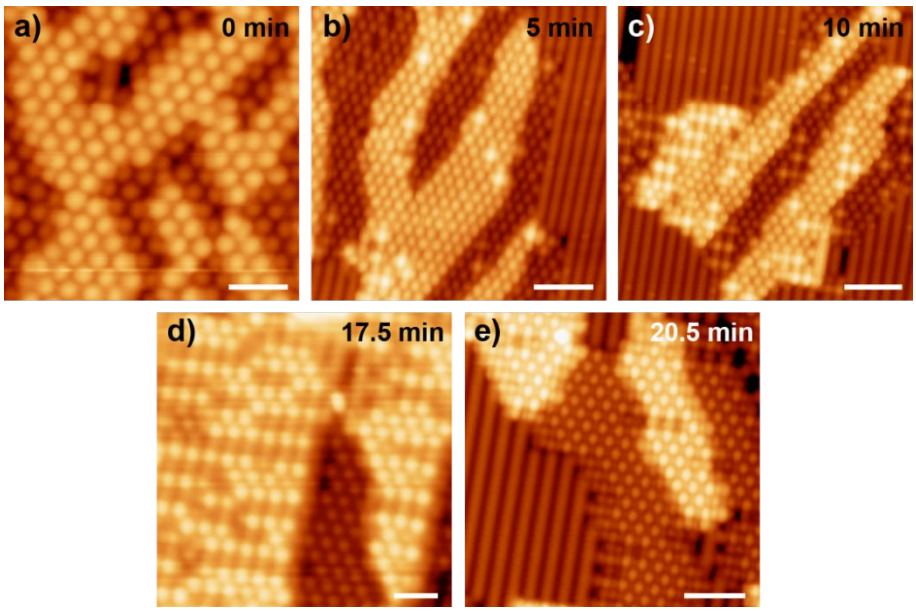

Figure S5. STM images of the samples obtained by depositing Ni at 1420 K for (a) 0 min (V = -50 mV, I = -100 pA, T = 78 K), (b) 5 min (V = -60 mV, I = -90 pA, T = 78 K), (c) 10 min (V = -50 mV, I = -100 pA, T = 78 K), (d) 17.5 min (V = -100 mV, I = -100 pA, T = 78 K) and (e) 20.5 min (V = 100 mV, I = 2.5 nA, T = 4.9 K) to the Au(110) surface with pre-covered THB molecules. the samples were heated to about 450 K after deposition of the molecules and Ni. Scale bars: (a) 2 nm, (b) 4 nm, (c) 4 nm, (d) 2 nm and (e) 3 nm.

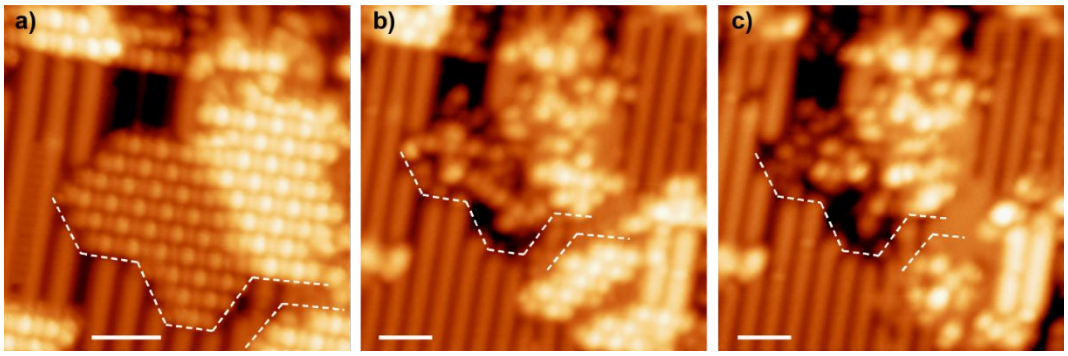

Figure S6. STM images of the same area (a) before (V = 300 mV, I = 1 nA, T = 4.9 K) and (b,c) after removing the molecular structures by sequentially parking the tip with a large bias (*e.g.*, 4.3

V) above the molecular islands (V = 300 mV, I = 1 nA, T = 4.9 K). The dashed lines highlight the initial boundaries of the molecular islands. The non-reconstructed substrate surface beneath the molecular chains is exposed after the treatment. Scale bars: 2 nm.

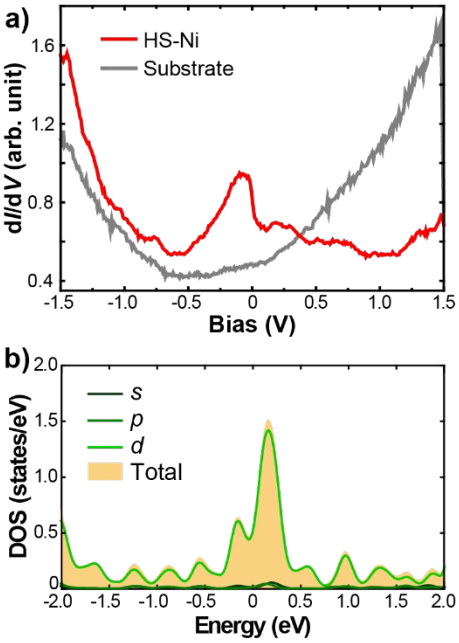

Figure S7. (a) Experimental dI/dV spectra acquired on the bare Au(110) substrate (grey) and at a bright HS-Ni atom in the chain on Au(110) (red). The dI/dV spectra are acquired by using a lock-in amplifier with a modulation of V_{rms} = 20 mV and a frequency of f = 1.992 kHz at T = 4.9 K. (b) Calculated DOS curves of the HS-Ni atom in the coordination chain on Au(110).

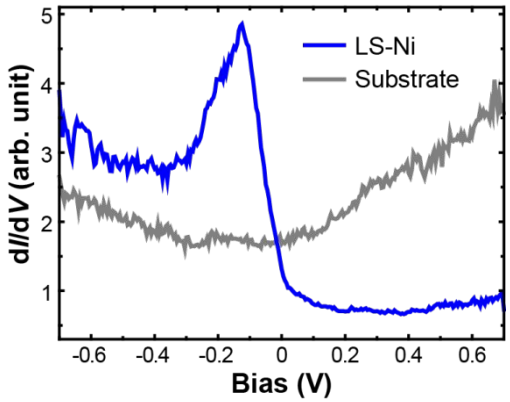

Figure S8. dI/dV spectra acquired on the bare Au(110) substrate (grey) and at a dark LS-Ni atom at the chain ending on Au(110) (blue) showing a resonance centered at ~-0.15 V. The dI/dV spectra are acquired by using a lock-in amplifier with a modulation of V_{rms} = 10 mV and a frequency of f = 1.992 kHz at T = 4.9 K.

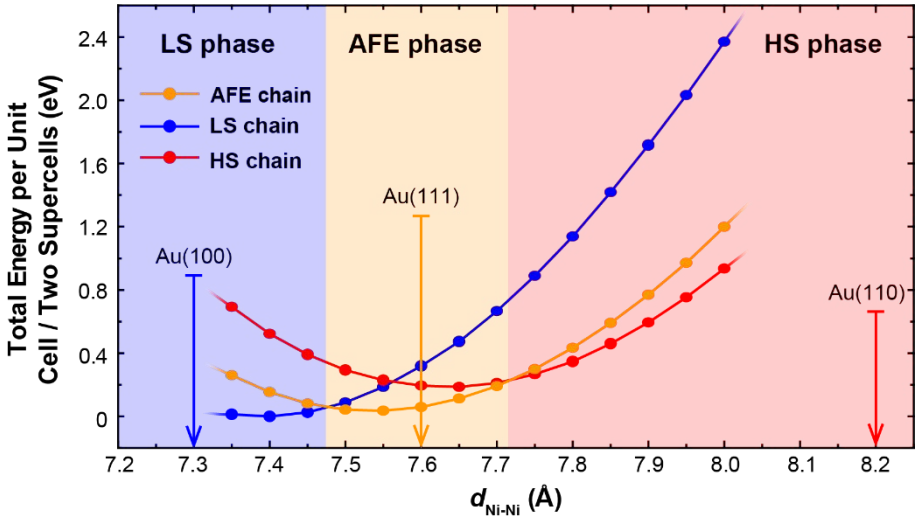

Figure S9. Total energy per unit cell for the AFE phase (yellow) or per two supercells for the LS (blue) and HS (red) phases versus d_{Ni-Ni} of the coordination chain. The reference point of energy is the energy minimum of the LS phase at d_{Ni-Ni} = 7.40 Å. The d_{Ni-Ni} values of the chains formed on Au(100), Au(111) and Au(110) are marked by the colored arrows. The diagram is adapted with permission from Ref. 5. Copyright 2020 American Chemical Society.

References

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