Abrupt Switching of Crystal Fields during Formation of Molecular Contacts

Jinjie Chen,*,† Hironari Isshiki,†,‡ Clemens Baretzky,† Timofey Balashov,† and Wulf Wulfhekel†

Physikalisches Institut, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Straße 1, 76131 Karlsruhe, Germany

E-mail: jinjie.chen@kit.edu

Supporting Information

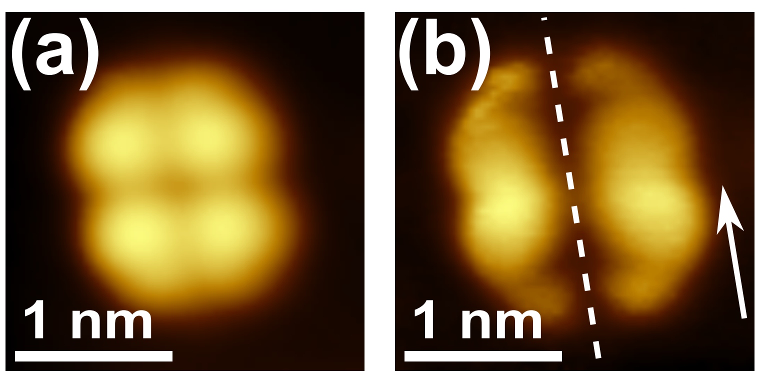

Figure S1: Topography of a $Co(thd)_2$ molecule (a) presents a four-fold symmetry, while the corresponding map of dI/dV signal on same molecule (b) shows a $C_{1\mathrm{v}}$ symmetry with a mirror plane (white dashed line). The white arrow indicates the [110] direction of Cu(100) surface. Set point: 720 mV, 400 pA, modulation of lock-in: 10 mV.

*To whom correspondence should be addressed

†Physikalisches Institut, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Straße 1, 76131 Karlsruhe, Germany

‡Current address: ISSP, Wakashiba 226-1, Kashiwa-shi, Chiba-ken, 277-8581, Japan

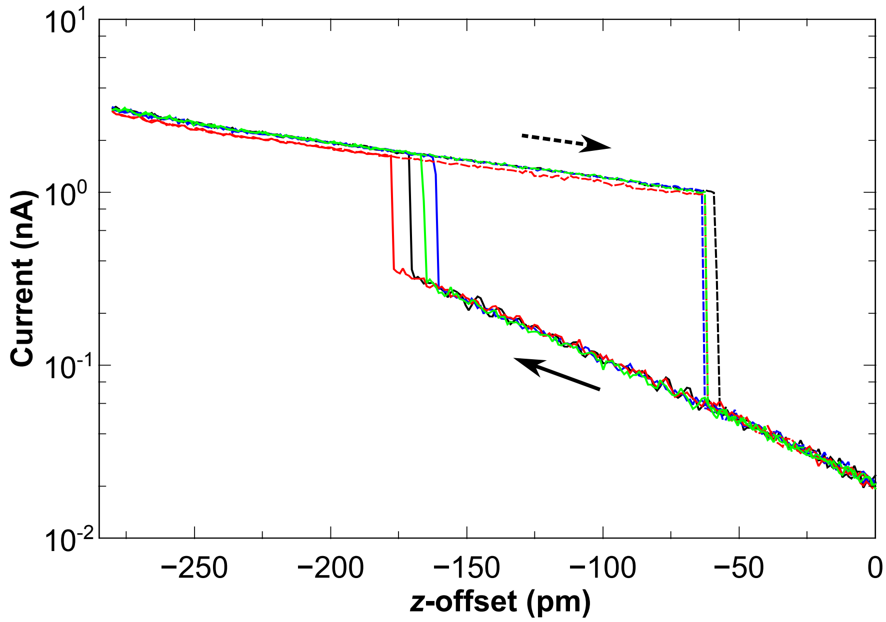

Figure S2: Four $I(z)$ curves scanned on the center of the very same $Co(thd)_2$ molecule repeatedly. Negative z-offsets represent a decrease of the tip-sample distance from the initial set point: 20 mV, 20 pA. The arrows indicate the directions, approaching and retracting the tip. The current is on a logarithmic scale.

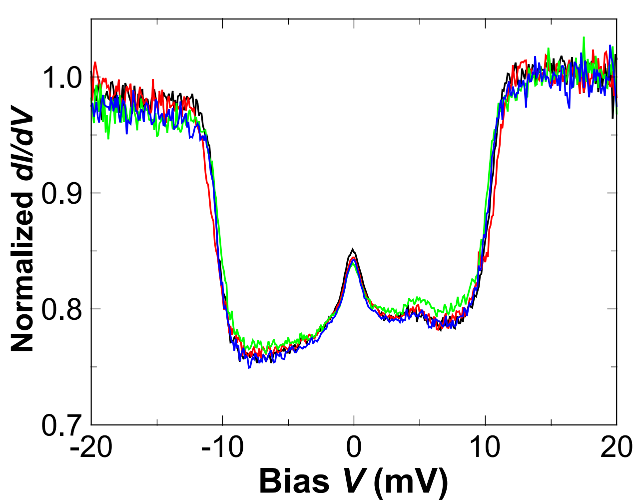

Figure S3: Four reproducible dI/dV spectra scanned respectively after each time when the tip contacted the center of a $Co(thd)_2$ molecule with a same z-offset of -240 pm from the same initial set point (U=20 mV, I=20 pA).

Kondo resonances and inelastic spin excitations were only clearly observed when contacting the molecule in the center at the location of the metal ion. Figure S4 shows an example of dI/dV curves obtained when contacting the molecules in the center and on a ligand.

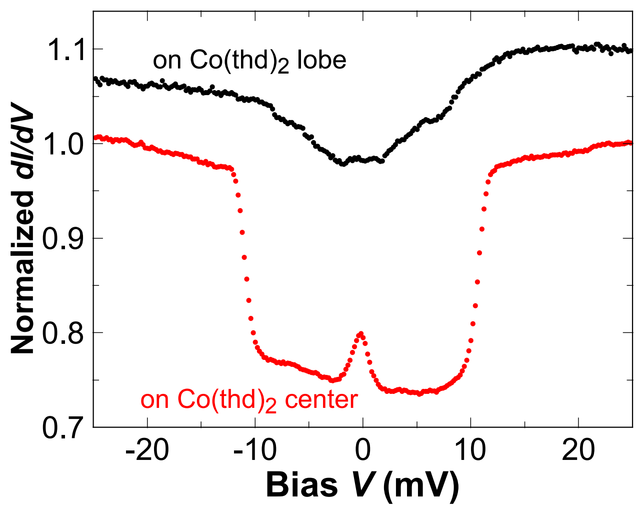

Figure S4: A comparison of normalized dI/dV spectra scanned when contacting the ligand (black) and the center (red) of a $Co(thd)_2$ molecule with a same set point (U=25 mV, I=1 nA). The spectrum on the ligand is vertically offset by 0.1 for clarity.

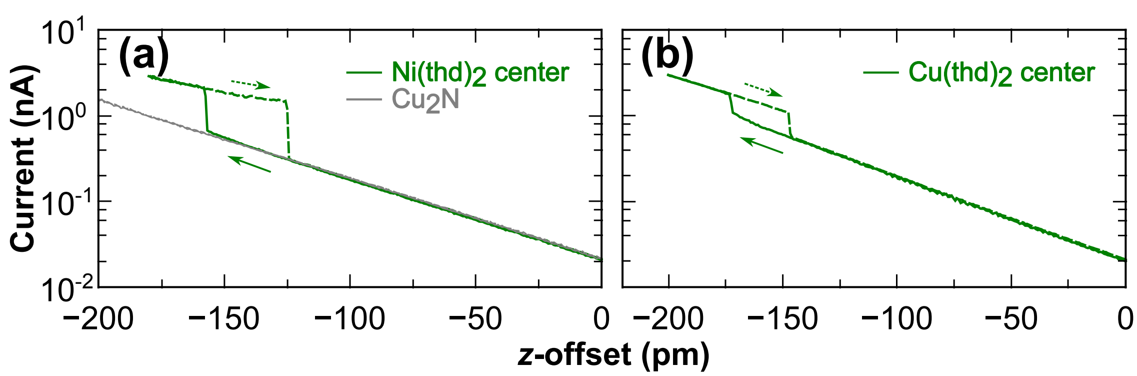

Figure S5: $I(z)$ curves on $Ni(thd)_2$ (a) and $Cu(thd)_2$ (b) molecules. Negative z-offsets represent a decrease of the tip-sample distance from the initial set point: 20 mV, 20 pA. The arrows indicate the directions, approaching and retracting the tip. Note that the current is on a logarithmic scale.

Table S1: Determined coefficients of Kondo resonance fits near zero bias on dI/dV spectra of Co^{2+} in both tunneling and contact conditions in Fig. 1(c) with Fano function: $y(x) = R_0(q + \frac{x - E_K}{k_B T_K})^2/(1 + (\frac{x - E_K}{k_B T_K})^2) + kx + y_0$, where T_K, q and E_K are the Kondo temperature, Fano parameter and position of Kondo resonance, respectively, $kx + y_0$ is a linear background. Note that the value of q indicates the ratio of transmission amplitudes between resonant tunneling via the Kondo state and non-resonant tunneling to the substrate, the sign of q depends on the phase shift between the two channels, which determines the resonances appearing as peaks or dips.

	tunneling	contact
T_K (K)	1.2 ± 0.5	11.4 ± 0.2
q	-0.6 ± 0.2	0.07 ± 0.02
E_K (mV)	-0.08 ± 0.03	-0.01 ± 0.03
R_0	-0.021 ± 0.006	-0.0725 ± 0.0007
k	-0.0025 ± 0.0008	0.0019 ± 0.0004
y_0	1.174 ± 0.006	0.8438 ± 0.0006

Table S2: Eigenstates and eigenenergies to spin Hamiltonians quantitated by fitting the spectra.

		eigenstate	eigenenergy (mV)
$Co(thd)_2$	tunneling	$0.4601\,\lvert 1/2\rangle + 0.0004\,\lvert -1/2\rangle - 0.8879\,\lvert -3/2\rangle$	-6.36
		$0.8879\,\lvert 3/2\rangle + 0.0004\,\lvert 1/2\rangle - 0.4601\,\lvert -1/2\rangle$	-6.36
		$0.8879\,\lvert 1/2\rangle + 0.0008\,\lvert -1/2\rangle + 0.4601\,\lvert -3/2\rangle$	1.03
		$-0.4601\,\lvert 3/2\rangle + 0.0008\,\lvert 1/2\rangle - 0.8879\,\lvert -1/2\rangle$	1.03
	contact	$0.3147\,\lvert 1/2\rangle - 0.6847\,\lvert -1/2\rangle - 0.6573\,\lvert -3/2\rangle$	-5.29
		$-0.6573\,\lvert 3/2\rangle + 0.6847\,\lvert 1/2\rangle + 0.3147\,\lvert -1/2\rangle$	-5.29
		$0.2745\,\lvert 1/2\rangle - 0.5973\,\lvert -1/2\rangle + 0.7536\,\lvert -3/2\rangle$	7.46
		$0.7536\,\lvert 3/2\rangle + 0.5973\,\lvert 1/2\rangle + 0.2745\,\lvert -1/2\rangle$	7.46
$Ni(thd)_2$	tunneling	$-0.0106\,\lvert 1\rangle - 0.9998\,\lvert 0\rangle + 0.0106\,\lvert -1\rangle$	-0.0003
		$0.7070\,\lvert 1\rangle - 0.0150\,\lvert 0\rangle - 0.7070\,\lvert -1\rangle$	1.40
		$0.7071\,\lvert 1\rangle + 0.7071\,\lvert -1\rangle$	3.51
	contact	$-0.5956\,\lvert 1\rangle + 0.5389\,\lvert 0\rangle + 0.5956\,\lvert -1\rangle$	-0.57
		$0.3811\,\lvert 1\rangle + 0.8424\,\lvert 0\rangle - 0.3811\,\lvert -1\rangle$	0.23
		$0.7071\,\lvert 1\rangle + 0.7071\,\lvert -1\rangle$	4.19