## Supplementary information to:

# Electronic structure of cobalt valence tautomeric molecules in different environments

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#### I. POWDER X-RAY DIFFRACTION

Powder X-ray diffraction (PXRD) data were collected at room temperature using a Panalytical X'Pert Pro X-ray diffractometer with an X'Celerator detector and a Cu- $K_{\alpha}$  source  $(\lambda = 1.54187 \text{ Å})$ . The PXRD pattern of  $[\text{Co}^{\text{II}}(\text{SQ})_2(4\text{-CN-py})_2]$ , i.e., Co-py, was recorded in the  $2\theta$  range from 5° to 55° with a step of 0.017° and the total collection time of 1 hour. The data analysis was performed with CrystalDiffract software.



Supplementary Figure 1. Power X-ray diffraction of the Co-py molecules obtained both experimentally and via simulations.

#### II. MAGNETIC SUSCEPTIBILITY

Magnetic properties of Co-tpp are analyzed in terms of the magnetic susceptibility  $\chi$  recorded with a Magnetic Property Measurement System (MPMS-XL, Quantum Design) using 17.3 mg of powder sample of Co-tpp placed in a tightly closed polycarbonate capsule. The direct-current magnetic susceptibility is measured in the presence of a bias field of 1 kOe between 50 and 400 K ( $\pm 2$  K/min) and corrected for diamagnetic contribution from the sample holder and for the intrinsic diamagnetism of the sample (Suppl. Fig. 2). Based on



Supplementary Figure 2. Product of magnetic susceptibility  $\chi$  and temperature of 17.3 mg of powder Co-tpp recorded with a Magnetic Property Measurement System (MPMS-XL, Quantum Design) in the presence of a bias field of 1 kOe.

the temperature dependence of the  $\chi T$  product, the complex is in the LS [Co<sup>III</sup>(Cat)(SQ)(3-tpp)<sub>2</sub>] state at lower temperatures, as the plateau  $\chi T$  value of  $\approx 0.6$  emu K/mol is close to the spin-only expectation value of  $\approx 0.375$  emu K/mol for the S = 1/2 state. The  $\chi T$  curve shows an increase above 300 K, indicating valence-tautomeric SCO to the HS [Co<sup>II</sup>(SQ)<sub>2</sub>(3-tpp)<sub>2</sub>] state. The conversion is incomplete even at 400 K, the highest temperature of our measurements, where the  $\chi T$  value reaches  $\approx 3.1$  emu K/mol. We note that the other complex studied in this work, Co-py, showed the average  $\chi T$  value of  $\approx 3.7$  emu K/mol in the HS state [1]. Based on the similarity of the coordination environment and electronic structure, we can assume a similar  $\chi T$  value in the HS state of Co-tpp. Comparing the  $\chi T$  value reached for this complex at 400 K to  $\approx 0.6$  emu K/mol for the LS state and  $\approx 3.7$  emu K/mol for the HS state, we can estimate that 80% of the Co-tpp molecules are in the HS state at 400 K. By the same token, the temperature at which the fractions of the LS and HS states are equal, commonly referred to as  $T_{\frac{1}{2}} \approx 370$  K.

### III. AB-INITIO CALCULATIONS OF HS AND LS STATES

As described in the manuscript, the HS state is calculated using HSE06 [2, 3] that is well suited to obtain the valence and conduction bandwidth as well as the magnitude of the HOMO-LUMO gap [4, 5]. Unfortunately, there is no easily attainable convergence of the electronic structure in the LS state. As a crude approximation, we calculated the orbitals in the framework of DFT+U calculation with U = 3.0 eV for Co (Suppl. Fig. 3). While the DFT+U is reasonably successful for understanding the Fe(II) spin crossover complexes [6], it is less successful for the cobalt tautomeric complexes [5]. Part of the problem is that the correlation energy changes with spin state in the DFT+U formalism, [6, 7]. Additionally, the conduction and valence bands are compressed towards the Fermi level. In general, it is widely acknowledged that DFT has a problem with the band gap [4, 8, 9] yielding in case of LS Co-py and Co-tpp significantly lower LUMO levels.



Supplementary Figure 3. Partial density of states for LS and HS Co-py and Co-tpp derived from abinitio hybrid functional Heyd-Scuseria-Ernzerhof calculations. Spin-up and spin-down components are displayed in the upper and lower half of the panel, respectively.

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