

Supplementary materials to:

Conductance Fluctuations in Cobalt Valence Tautomer Molecular Thin Films

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Synthesis of [Co(SQ)₂(3-tpp)₂]. The synthetic procedures were carried out under an inert atmosphere of dry nitrogen gas using standard Schlenk techniques. Commercial HPLC-grade solvents were obtained from Fisher Scientific and additionally purified by passing through a double-stage drying/purification system (Pure Process Technology, Nashua, NH, USA). Elemental analyses were carried out by Atlantic Microlab, Inc. (Norcross, GA, USA). Co₂(CO)₈ (with 1-10 wt.% of hexane) and 3-thiopheneboronic acid (>98%) were purchased from Millipore Sigma and VWR, respectively. The compounds [Co₄(SQ)₈] (SQ = 3,5-di-tert-butylsemiquinonate)¹ and 4-(3-thienyl)pyridine (3-tpp)² were synthesized according to the previously published procedures.³ The complex [Co(SQ)₂(3-tpp)₂] was synthesized by layering a solution of [Co₄(SQ)₈] (270 mg, 0.135 mmol) in 8 mL of toluene on top of a 5 mL dichloromethane solution of 3-tnp (172 mg, 1.07 mmol). Dark-blue crystals that formed after 2 weeks were washed with toluene and dried under vacuum at 100 °C for 24 h to produce a dark-green solid. Yield = 180 mg (42%). *Elem. Anal.* (%): Calcd. (Found) for C₄₆H₅₅CoN₂O₄S₂ (= [Co(SQ)₂(3-tpp)₂): C, 67.13 (66.84); H, 6.74 (6.73); N, 3.40 (3.31), as previously described.³

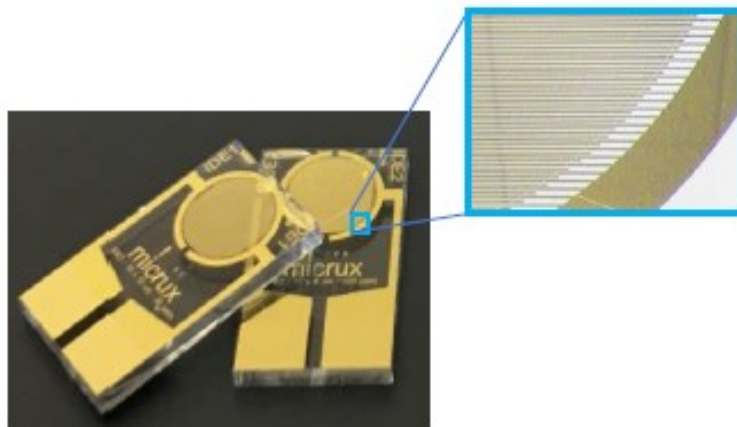


Figure S1. Micrux interdigitated electrodes. Each gold electrode pair measures 200 nm high with a 5 μm gap.

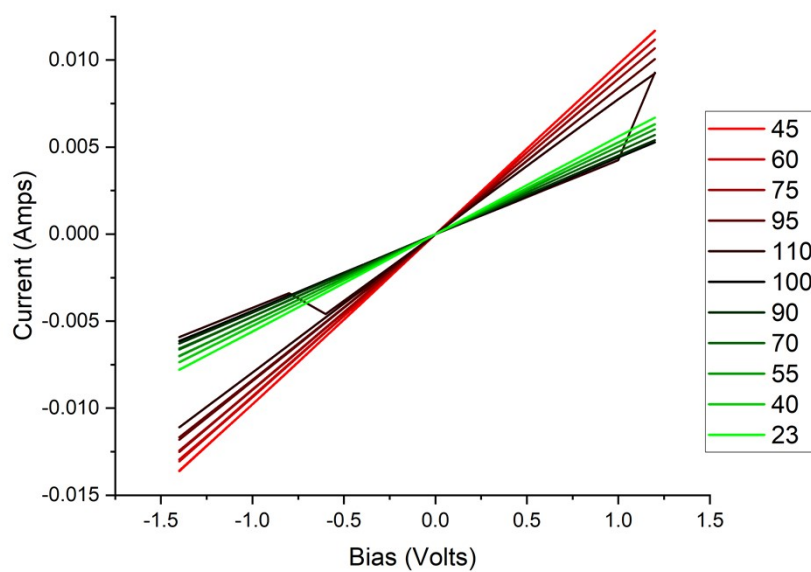


Figure S2. Temperature dependent IV raw data of thin film of $[\text{Co}(\text{SQ})(\text{Cat})(3\text{-tpp})_2]$ measurement under incandescent light irradiation. The temperature is indicated in Celsius.

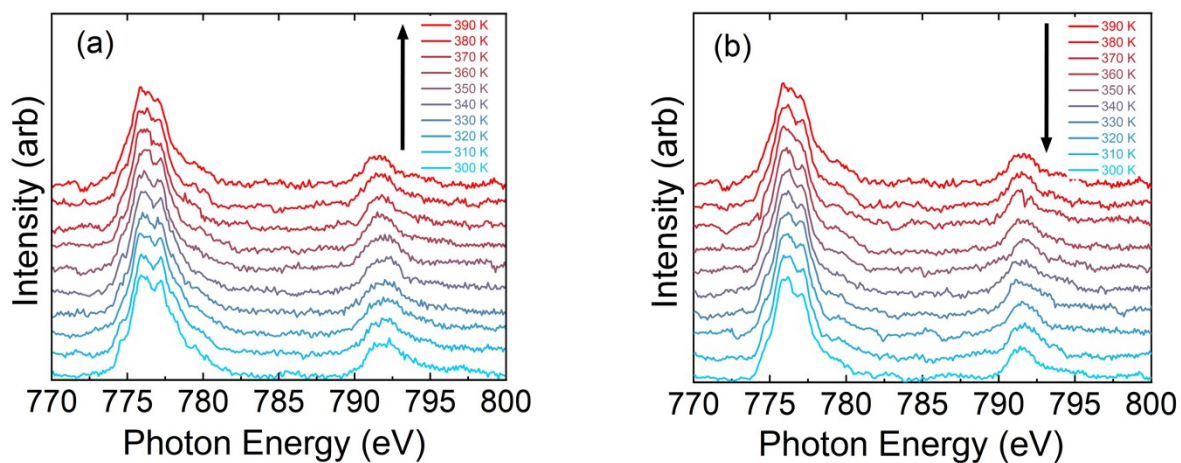


Figure S3. Temperature dependent X-ray absorption spectra of a 75 nm thin film of $[\text{Co}(\text{SQ})(\text{Cat})(3\text{-tpp})_2]$ on a HOPG substrate taken with (a) an increasing temperature cycle (b) and the subsequent decreasing temperature cycle.

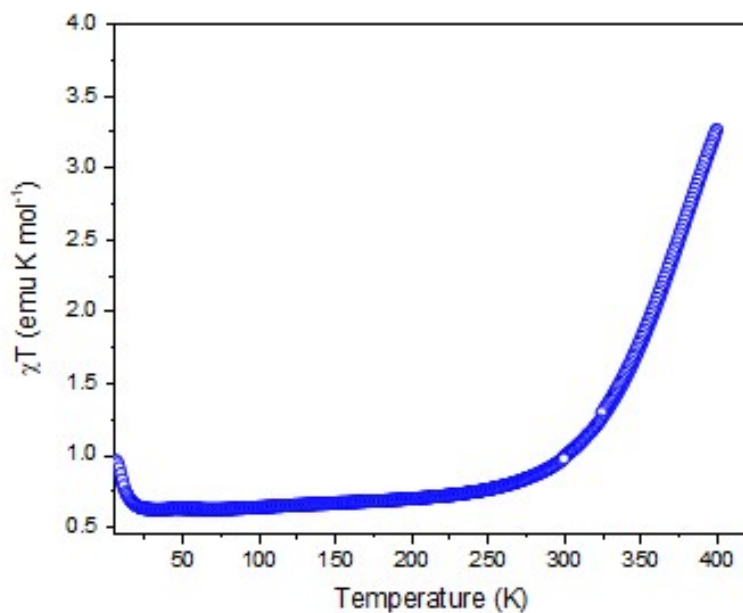


Figure S4: Temperature dependent magnetic susceptibility of $[\text{Co}(\text{SQ})(\text{Cat})(3\text{-tpp})_2]$ powder.

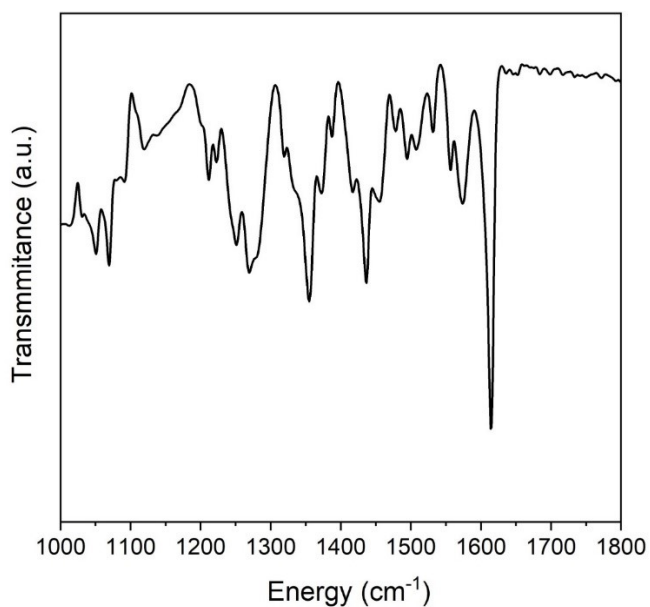


Figure S5: Infrared spectrum of $[\text{Co}(\text{SQ})(\text{Cat})(3\text{-tpp})_2]$ [published in a previous manuscript³].

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2. C. Hertzog-Ronen, E. Borzin, Y. Gerchikov, N. Tessler and Y. Eichen, Detection and identification of alkylating agents by using a bioinspired "Chemical Nose". *Eur. J. Chem.*, 2009, **15**, 10380-10386.
3. Ping Wang, Sandugash Yergeshbayeva, Xinsong Lin, Shubham Bisht, Miguel Gakiya-Teruya, and Michael Shatruk, "Structural and Magnetic Investigation of Cobalt Valence Tautomeric Complexes with Sulfur-Containing Ligands", *Cryst. Growth Des.* 2023, **23**, 2384–2394; <https://doi.org/10.1021/acs.cgd.2c01373>