

SUPPORTING INFORMATION

Sulphur vs NH Group: Effects on the CO₂ Electroreduction Capability of Phenylenediamine-Cp Cobalt Complexes

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SUMMARY

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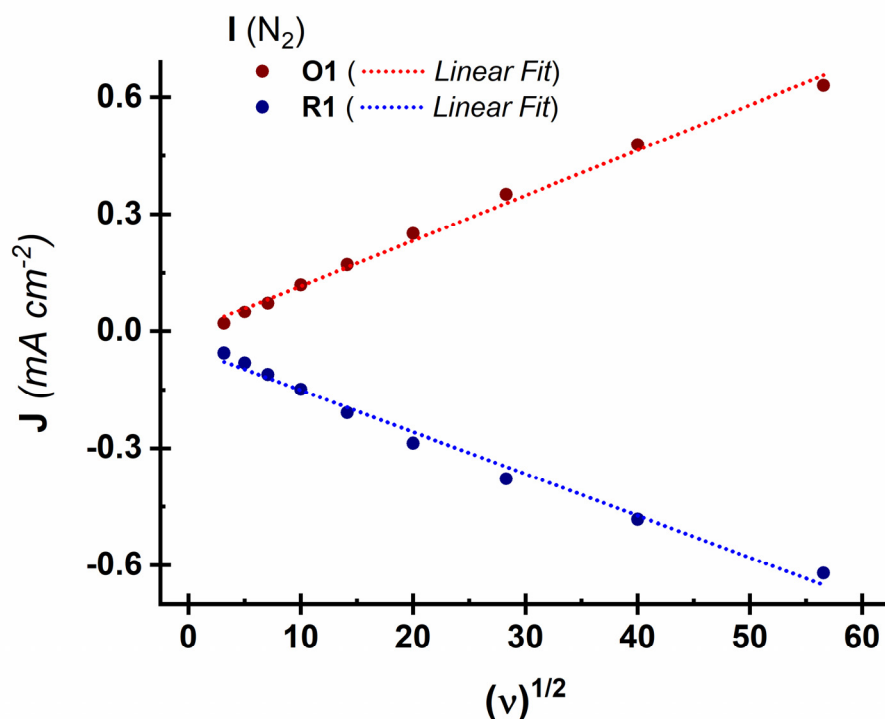


Figure S1 – Plot of oxidation (red) and reduction (blue) current densities vs $(v)^{1/2}$ for complex I.

KF CALCULATION

The rate constant k_f of the chemical step for compound II was determined using eq S1,[1] which correlates the potential shift occurring at different scan rates with the rate constant k_f .

$$(Eq. S1) \quad E_p = E_{\frac{1}{2}} - 0,78 \frac{RT}{nF} + \frac{RT}{2nF} \ln \left(k_f \frac{RT}{nF} \right) + \frac{RT}{2nF} \ln \left(\frac{1}{v} \right)$$

Then, plotting the difference $E_p - E_{1/2}$ vs $\ln(1/n)$, the value of the rate constant can be determined from the intercept of the linear fit. Data points for $\ln(1/n) > 2$ have

been excluded from the linear fit, as the reversibility is already reached. According to **eq. 1**, the plot in Figure S2 is expected to have a slope of 12.8 mV for single-electron processes. In the case of complex **II**, the observed slope is 13.4 ± 1.6 mV for scan rates ranged between 0.2 and 3.2 V s⁻¹; an intercept of 0.05883 led to a **k_f** of **1.90 s⁻¹** and, consequently, a **t_{1/2}** equal to **364.8 s** for compound **II**.

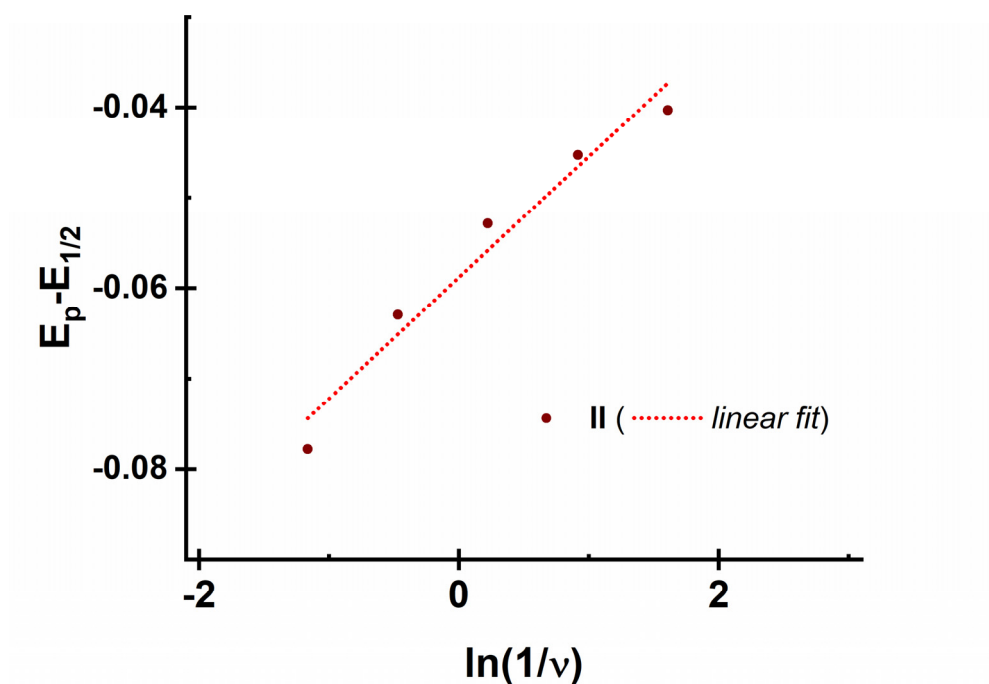


Figure S2 – Graph $E_p - E_{1/2}$ vs $\ln(1/v)$ for derivative **II**.

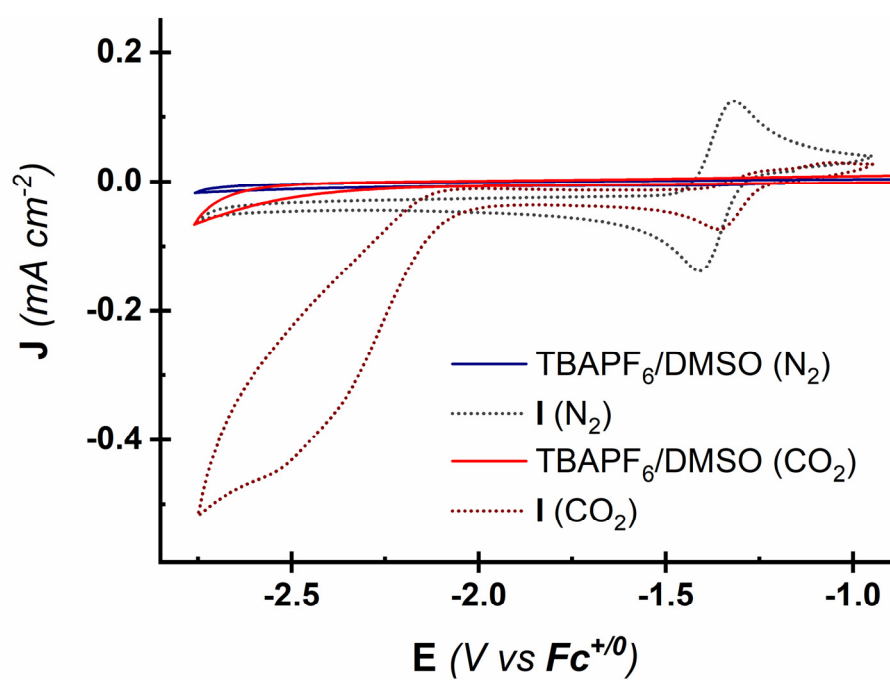


Figure S3 – CV of TBAPF₆/DMSO 0.1 M under N_2 (solid blue line) and CO_2 (solid red line). CVs of complex I under the same conditions are reported for comparison (dotted lines).

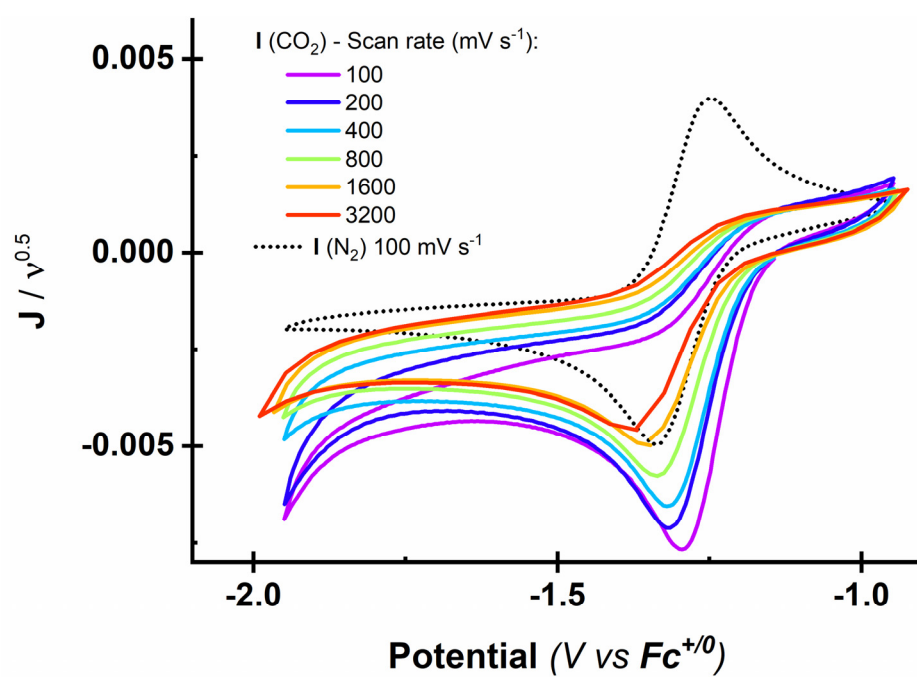


Figure S4 – CV of complex I at different scan rates. Current densities **J** are normalized by the square root of the scan rate.

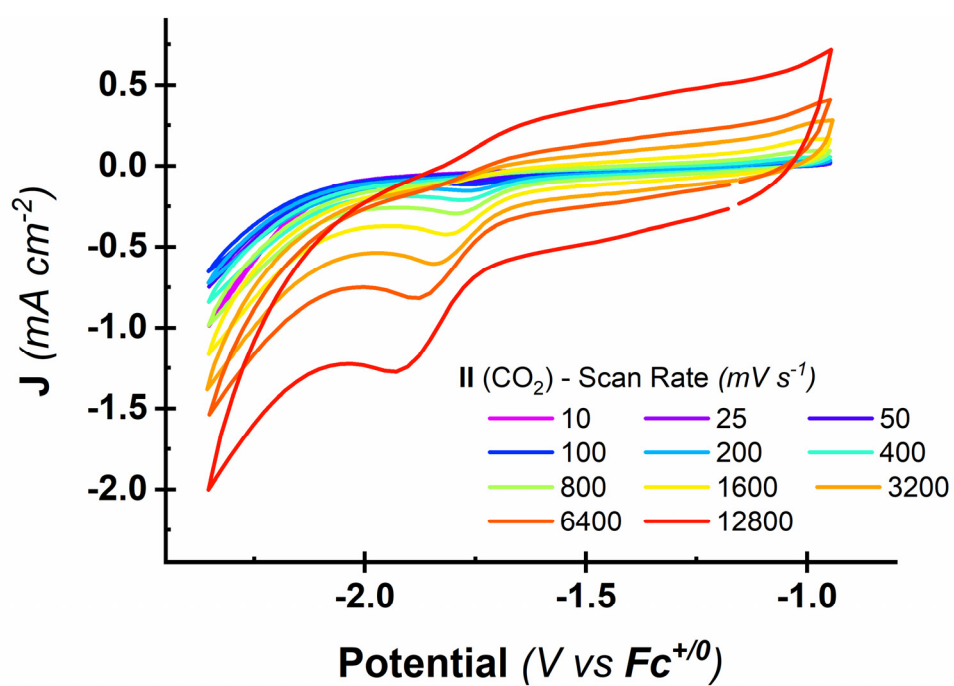


Figure S5 – CVs of complex II at different scan rates.

Reference

- [1] R.S. Nicholson, I. Shain, Theory of Stationary Electrode Polarography, Anal. Chem. 36 (1964) 1212–1212. <https://doi.org/10.1021/ac60213a053>.