

SUPPORTING INFORMATION

FOR

**Redox Non-Innocent Bis(2,6-diimine-pyridine) Ligand-Iron Complexes as Anolytes for
Flow Battery Applications**

Gabriel Martins da Silva Almeida Duarte^[a,b], Jason D. Braun^[a,b], Patrick K. Giesbrecht^[a] and
David E. Herbert^{[a]*}

[a] Department of Chemistry and the Manitoba Institute of Materials, University of Manitoba,
144 Dysart Road, Winnipeg, MB, R3T 2N2, Canada

[b] These authors contributed equally to this work

* david.herbert@umanitoba.ca

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General methodology: charge/discharge measurements

Cycling measurements were carried out inside an N₂-filled glovebox. Potential was applied by a potentiostat and recorded over time using a CHI760C electrochemical workstation. In order to perform battery tests, both the electrolyte and active species solutions were placed in a custom-built air-tight H-cell made up of two chambers separated by a fine porosity glass frit. In one of the chambers, a solution made up of the active species (2 mM) and the electrolyte *n*Bu₄PF₆ (0.4 M) was stored along with the working and reference electrodes inserted in two outputs. In the other chamber, the 0.4M *n*Bu₄PF₆ solution was placed as well as the counter electrode. Reticulated vitreous carbon (RVC) counter and working electrodes were used, with a non-aqueous Ag/Ag⁺ quasi-reference electrode. Potential cutoffs, voltages at which the reversible couples start and finish, were set according to CV results. Cycling experiments were executed at a variety of anodic and cathodic currents (0.5, 1.1, 1.5 and 2.2 mA) with different (dis)charge times (3600 or 7200 s), corresponding to 0.5, 1, and 2 C charging rates assuming a 2e⁻ reduction process.

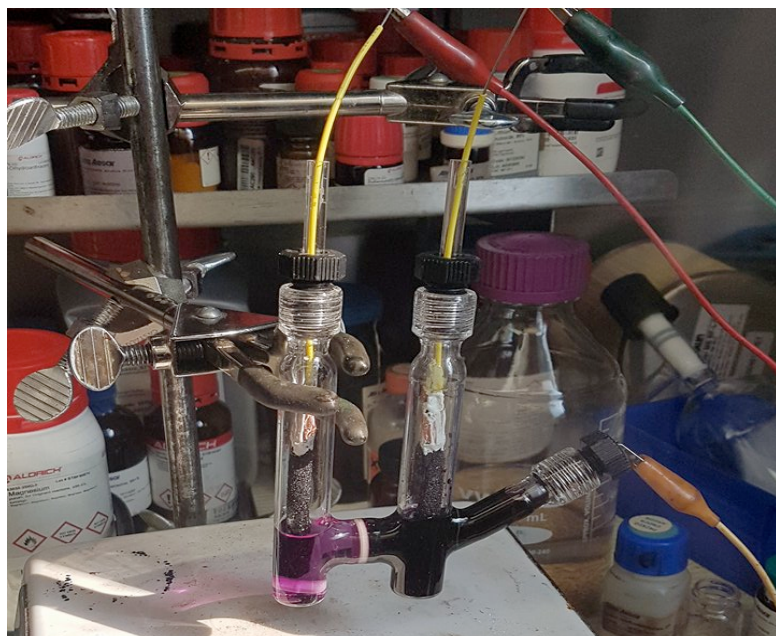


Figure S1. H-cell^[1] used for cycling measurements.

Cycling Measurements / Coulombic Efficiency / Capacitance Figures

Cycling of **1** at 2.2 mA, (dis)charge time = 1 h, 2.0 C charging rate, potential cut-offs: 1 V to -2.6 V, cathodic charging

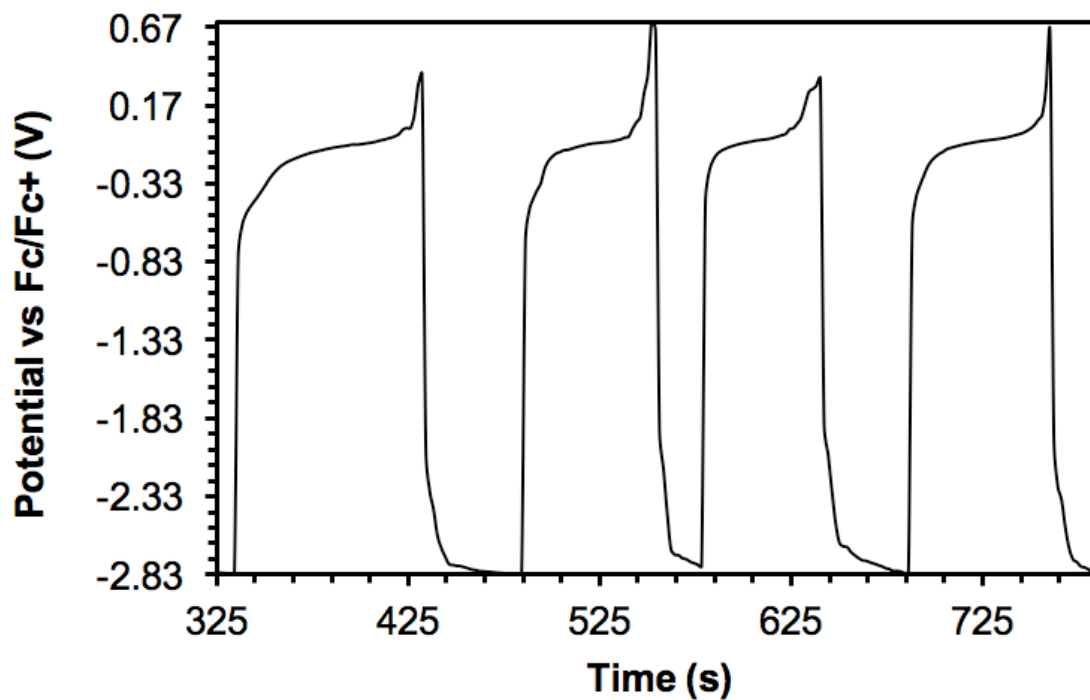


Figure S2. Potential curves for **1** (1 V to -2.6 V, cathodic charging at 2 C).

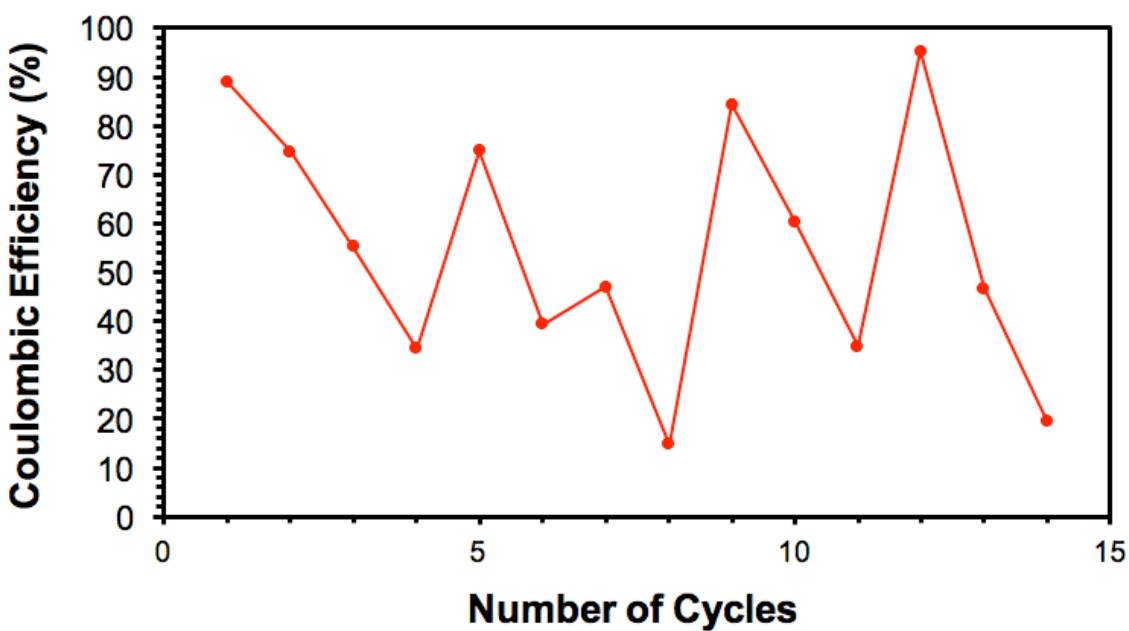


Figure S3. Coulombic Efficiency for **1** (1 V to -2.6 V, cathodic charging at 2 C).

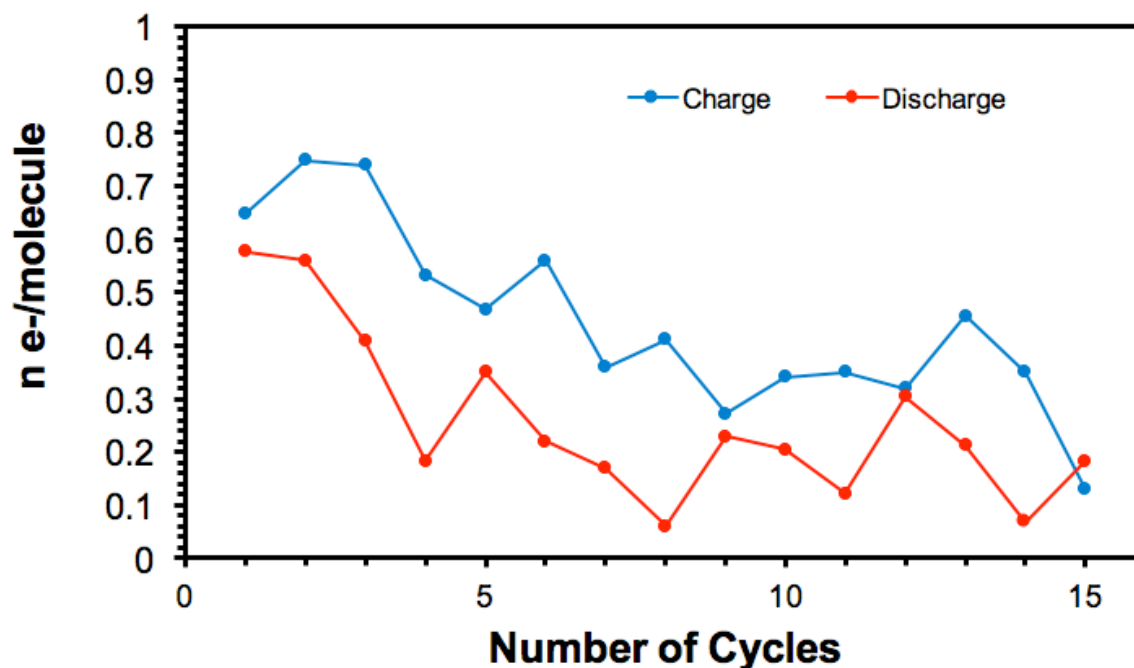


Figure S4. Capacitance for **1** (1 V to -2.6 V, cathodic charging at 2 C).

Allowing the cell to reach -2.6 V led to irreversible reduction of the MCC, consistent with the cyclic voltammogram shown in Figure S5. The absence of significant plateaus in Figure S2 suggests no redox processes were accessed in the experiment. Additionally, the time span to cover each cycle was roughly 150 seconds, which despite the accelerated C-rate, is fast, having an unsatisfactory impact on the capacitance, as confirmed by the low number of electrons per molecule on Figure S6.

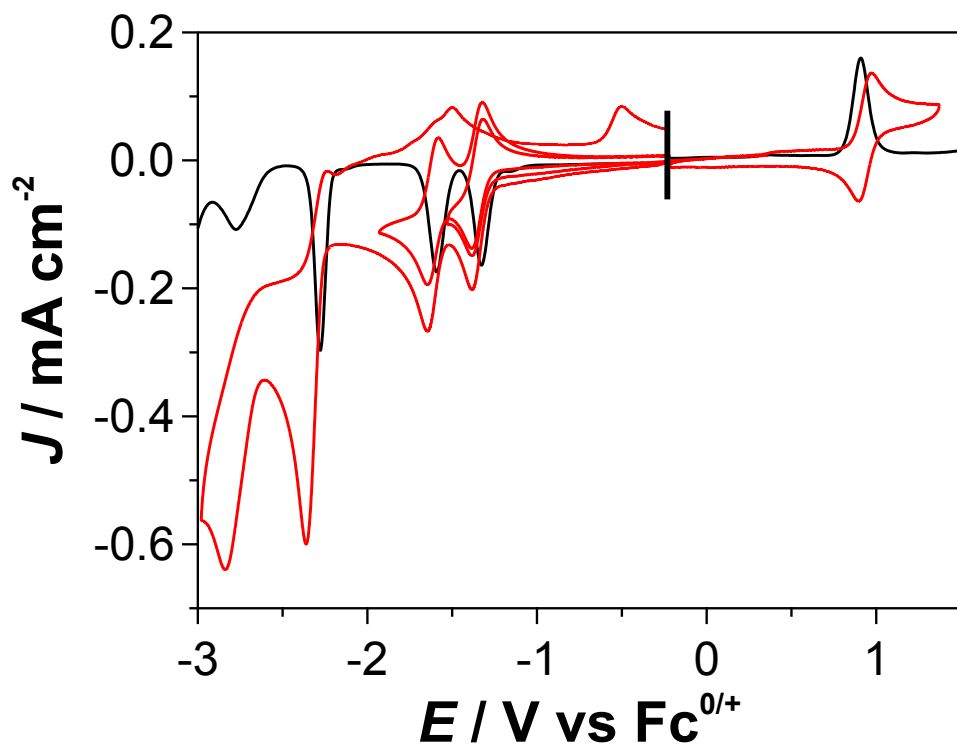


Figure S5. Wide CV of **1** confirming irreversible redox processes below -2.2 V.

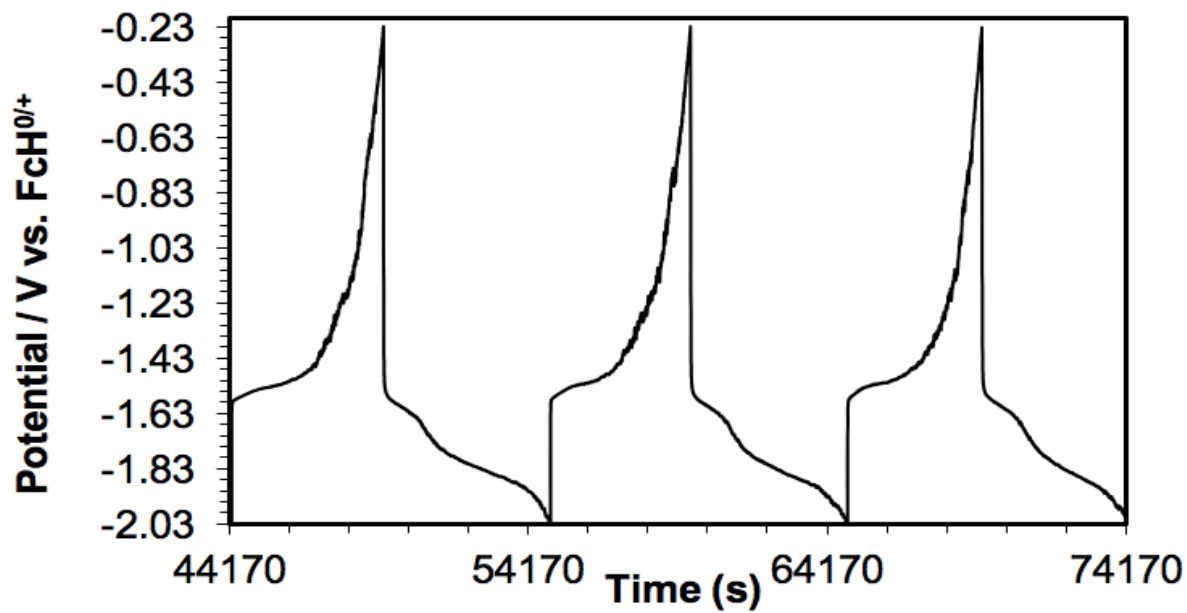


Figure S6. Potential curves for **1** (-0.2 to -2 V, cathodic charging at 0.5 C).

Cycling of **2** at 0.5 mA, (dis)charge time = 2h, rate of 0.5 C; potential cutoffs: 0.23 V to -2.03 V, cathodic charging

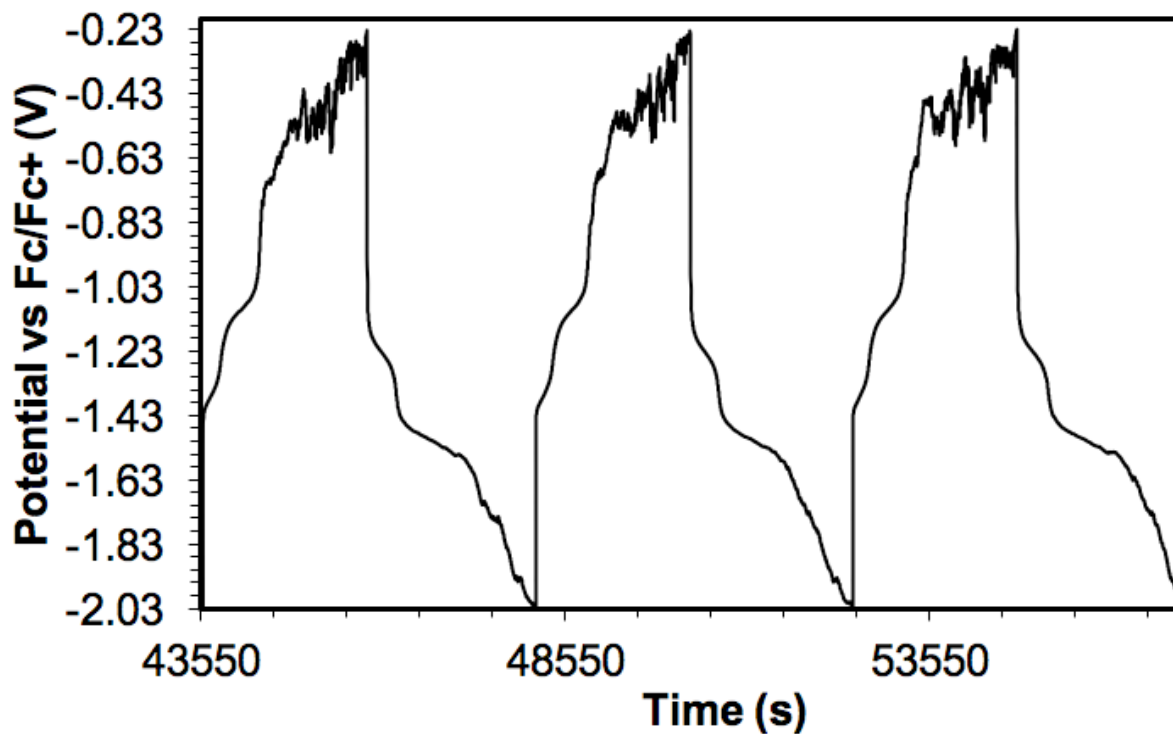


Figure S7. Potential curves for **2** (-0.2 V to -1.8 V, cathodic charging at 0.5 C).

The potential curves shown in Figure S7 clearly exhibit two plateaus on both charging and discharging segments, indicating that the two redox couples are being accessed. An increase in capacitance is observed when compared to a charging rate of 0.5 C.

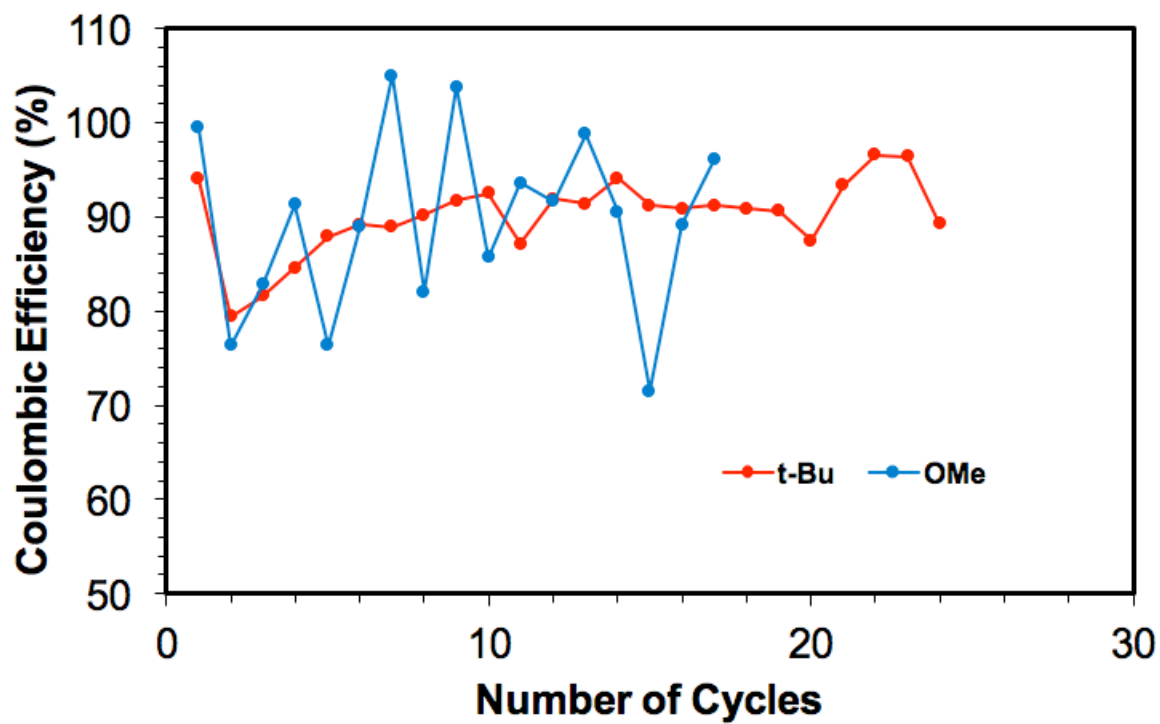


Figure S8. Coulombic efficiency at charging rate of 0.5 C.

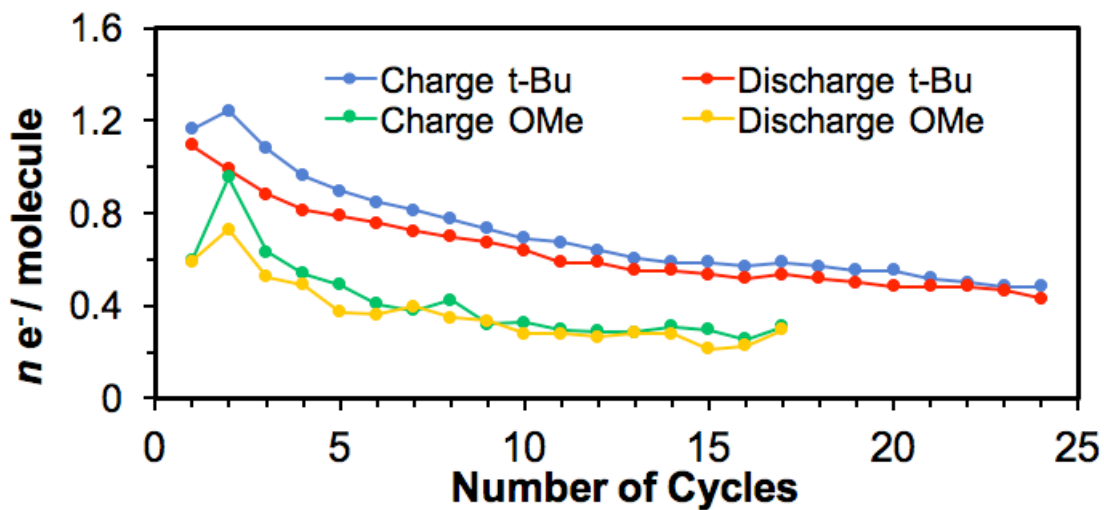


Figure S9. Capacitance at charging rate of 0.5 C.

Solution Characterization of **1**

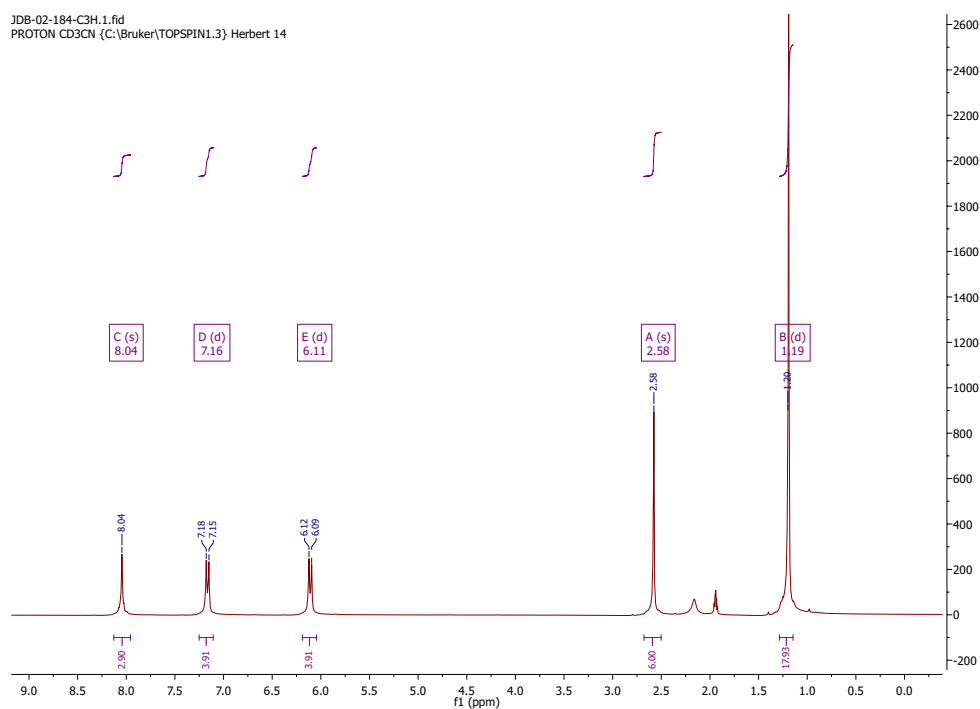


Figure S10. ^1H NMR (300 MHz, CD_3CN) of **1** $[\text{PF}_6]_2$ at 25 °C.

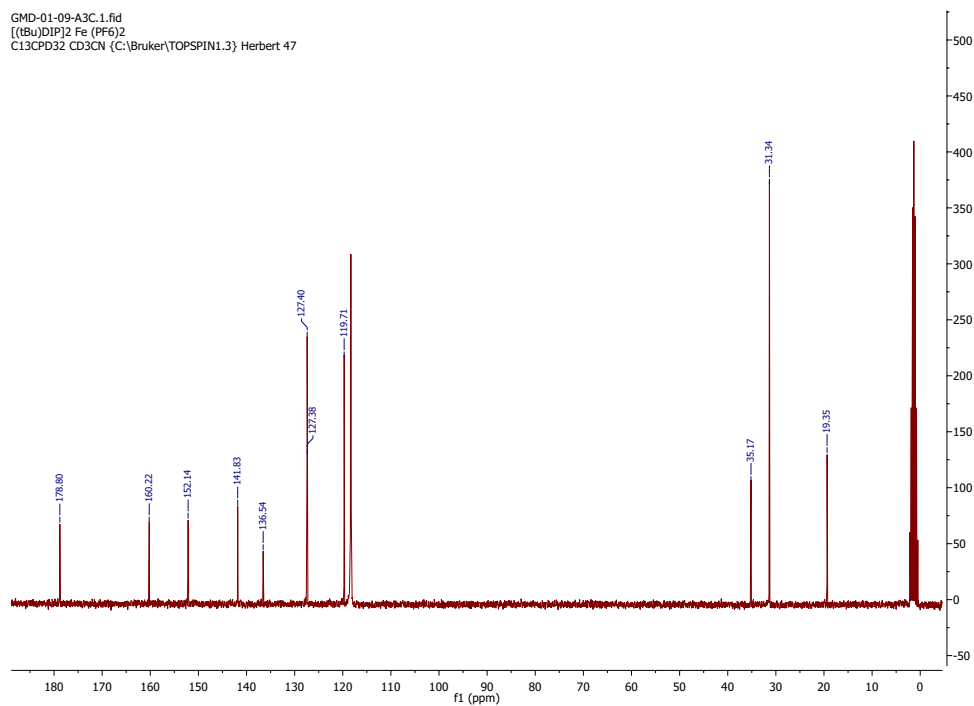


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) of **1** $[\text{PF}_6]_2$ at 25 °C.

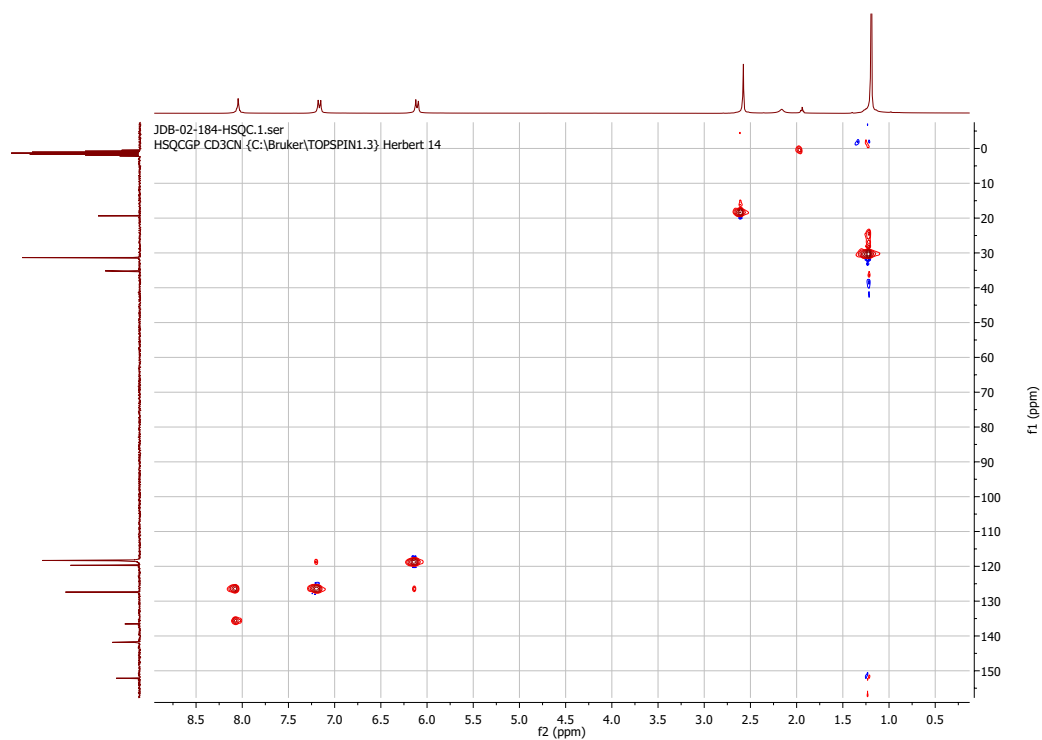


Figure S12. HSQC NMR (300/75 MHz, CD₃CN) of **1**[PF₆]₂ at 25 °C.

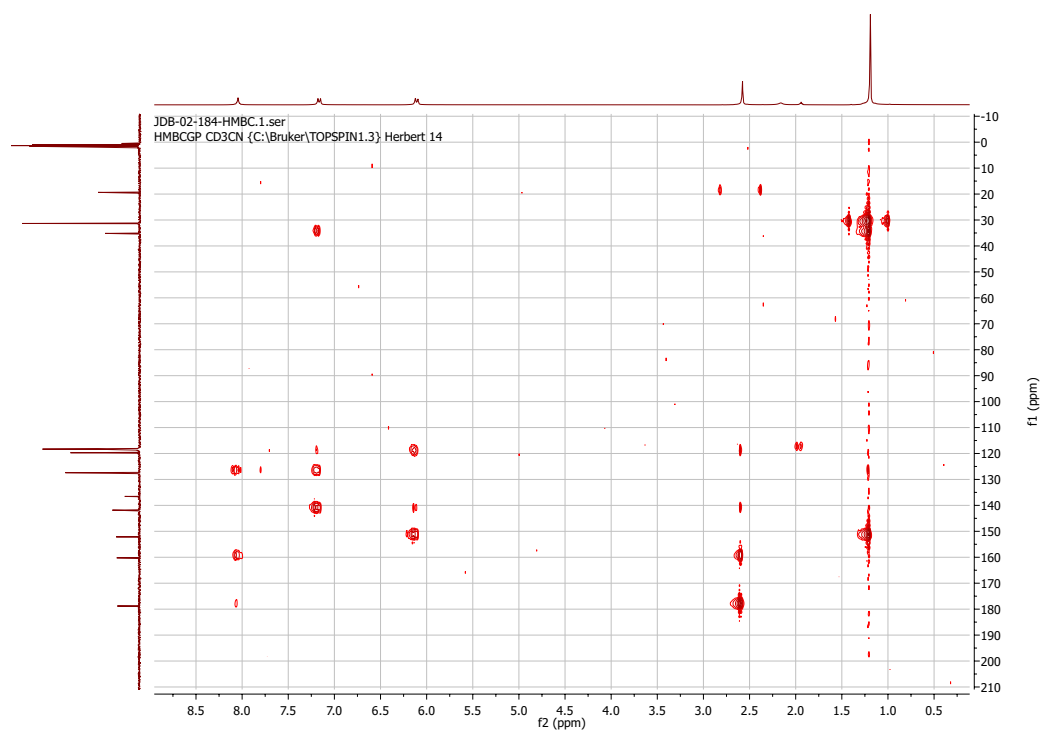


Figure S13. HMBC NMR (300/75 MHz, CD₃CN) of **1**[PF₆]₂ at 25 °C.

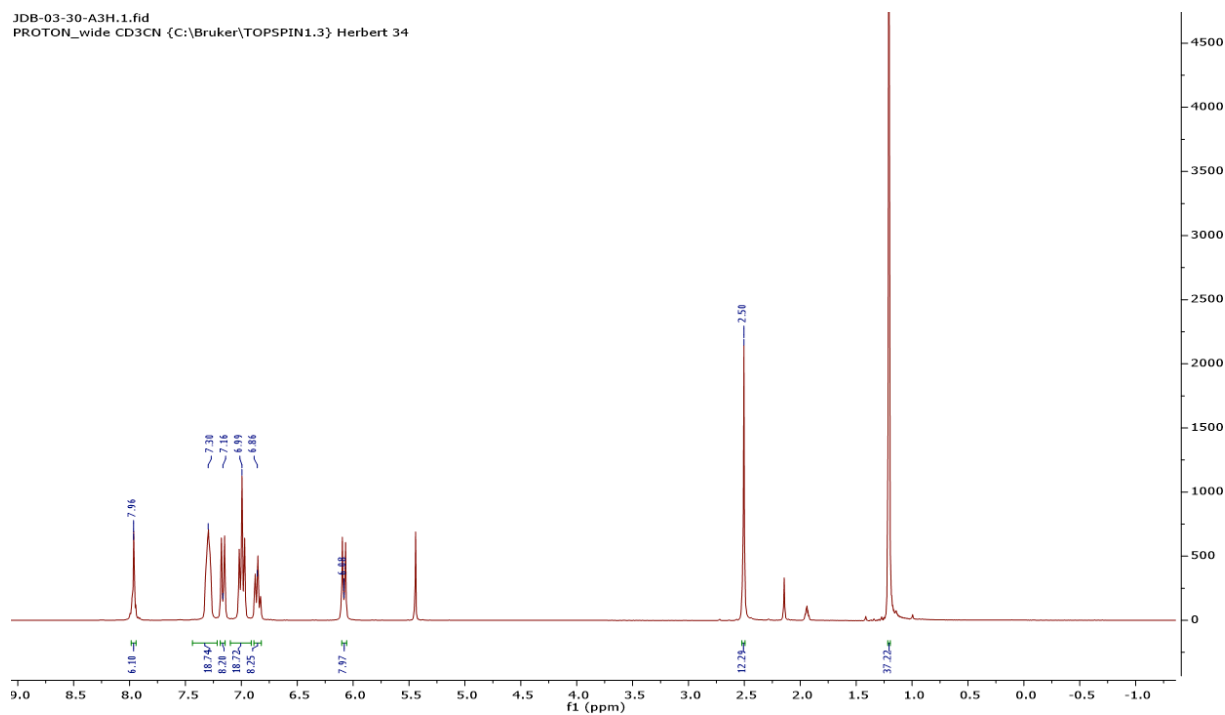


Figure S14. ^1H NMR (300 MHz, CDCl_3) of $1[\text{BPh}_4]_2$ at 25 $^\circ\text{C}$.

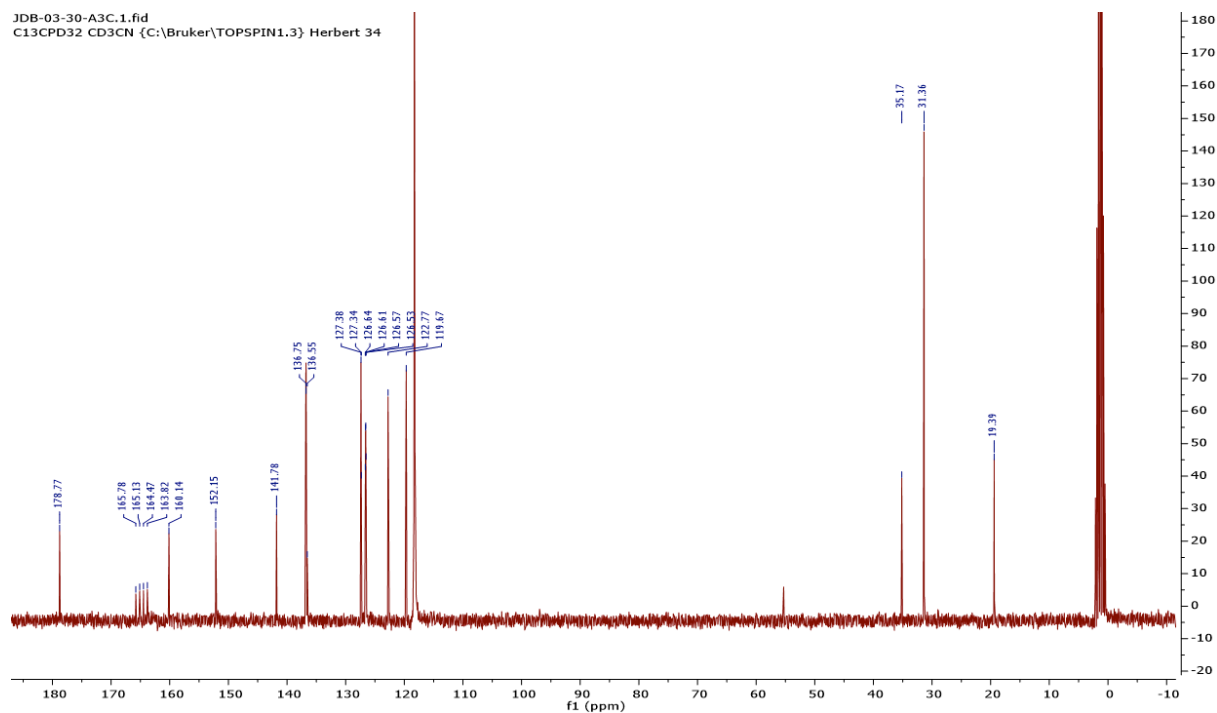


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) of $1[\text{BPh}_4]_2$ at 25 $^\circ\text{C}$.

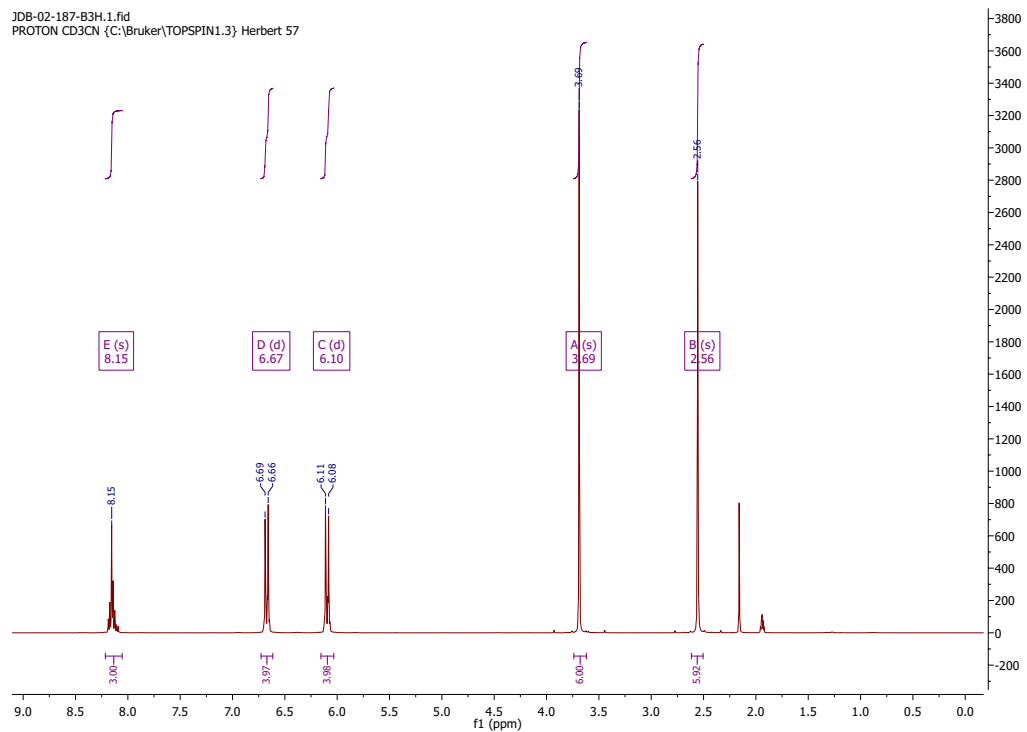


Figure S16. ^1H NMR (300 MHz, CD_3CN) of **2** at 25 °C.

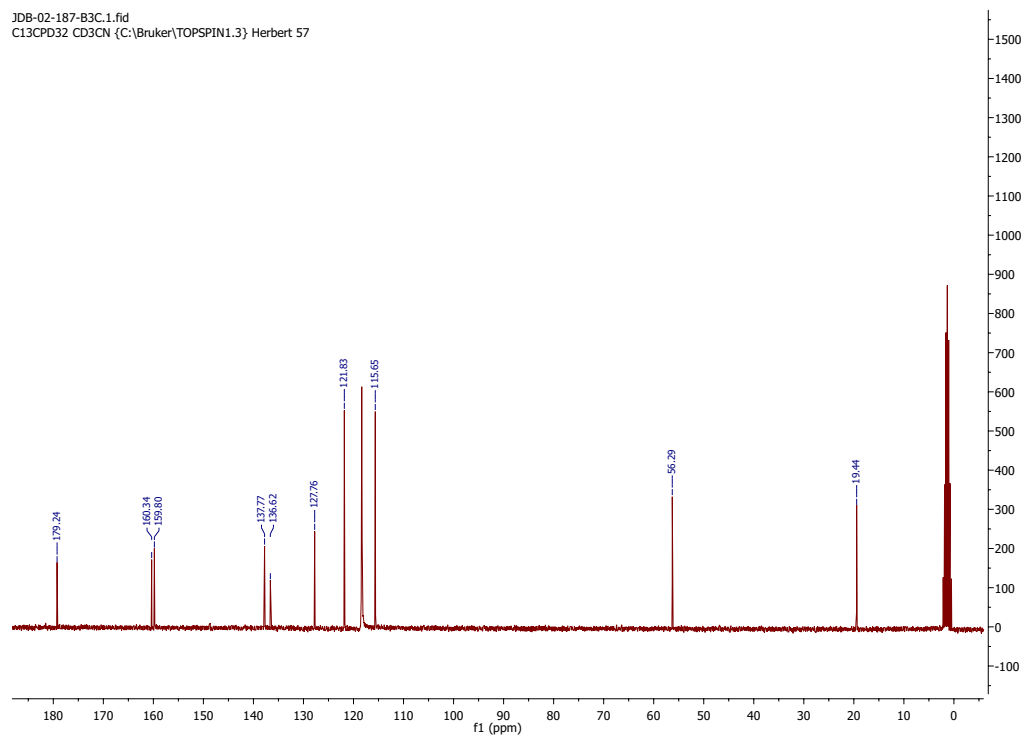


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) of **2** at 25 °C.

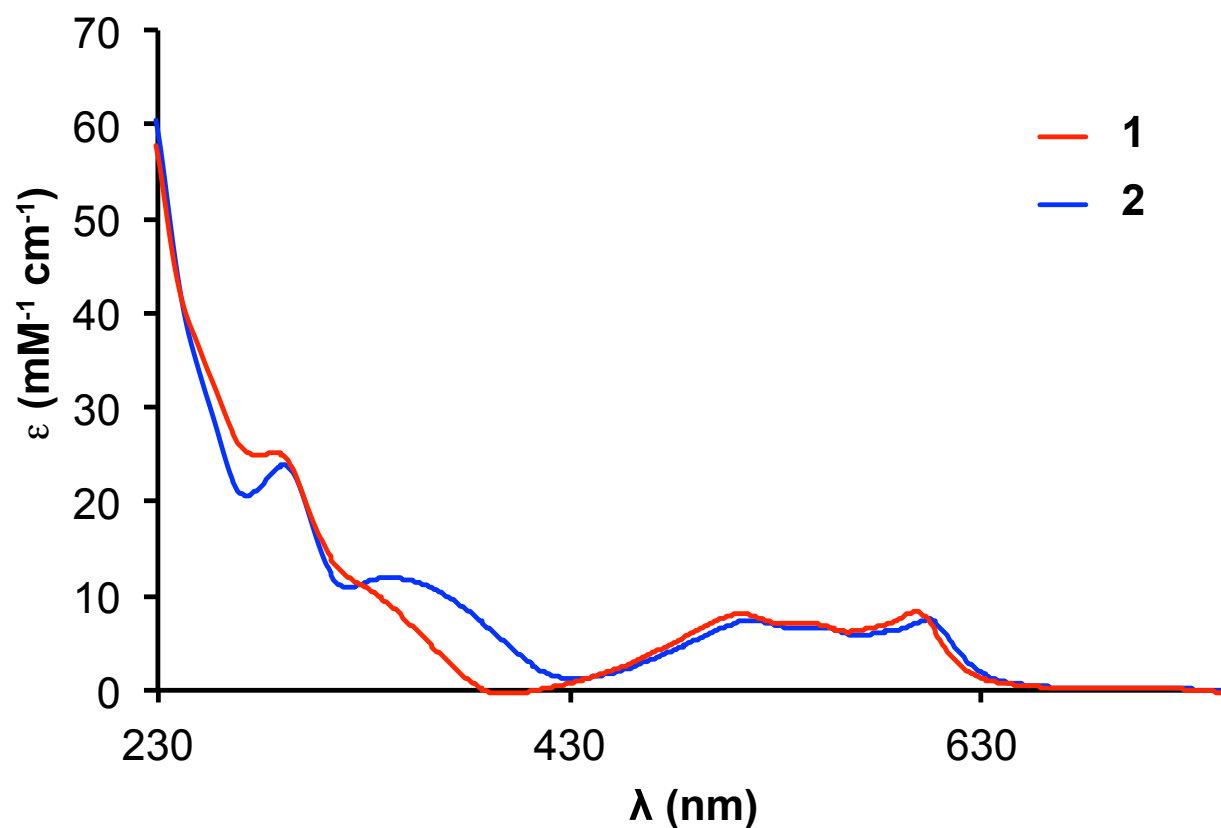


Figure S18. UV-visible spectrum of **1** and **2** in acetonitrile solution using an Agilent Technologies Cary 5000 Series spectrophotometer (range: 230 – 1600 nm).

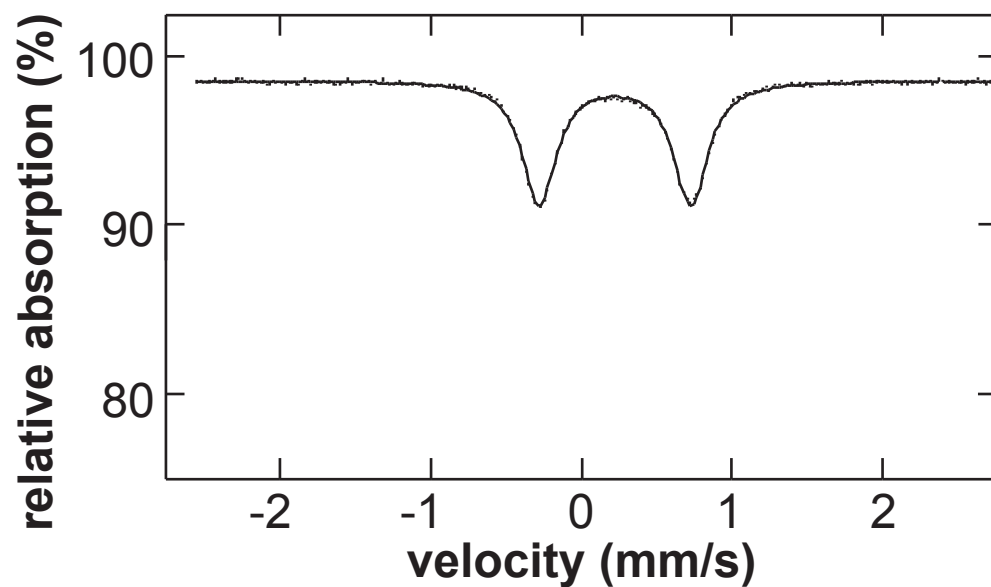


Figure S19. Mössbauer spectrum of **1** at 10 K. Data collected using an α -Fe standard at 298 K.

References

- [1] P. J. Cabrera, X. Yang, J. A. Suttill, K. L. Hawthorne, R. E. M. Brooner, M. S. Sanford, L. T. Thompson, *J. Phys. Chem. C* **2015**, *119*, 15882-15889.