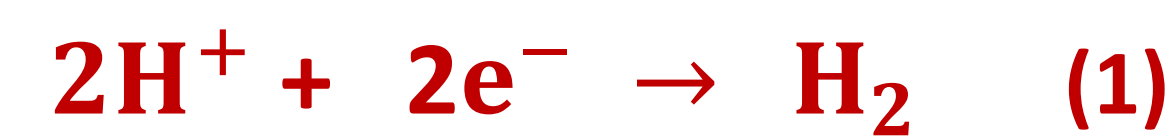


# Electronic States and H<sup>+</sup> Reduction Activity of Cobalt Complexes Supported by Viologen-like Terpyridine Ligands

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## Introduction

- Redox-active ligands are often used as a means of altering the electronic properties of metal complexes in an effort to create robust first row transition metal catalysts.
- Catalysts based on inexpensive and naturally abundant transition metals play an integral role in developing environmentally friendly methods for the production of various industrial feedstocks, processes of which currently rely on fossil fuels.
- H<sub>2</sub>, as an industrial staple, has a number of uses including the refinement of crude oil into fuels.<sup>1</sup> Designing energy efficient catalysts for electrocatalytic H<sub>2</sub> production (Eq1), through the use of renewable sources of electricity, is of increasing interest.<sup>2</sup>

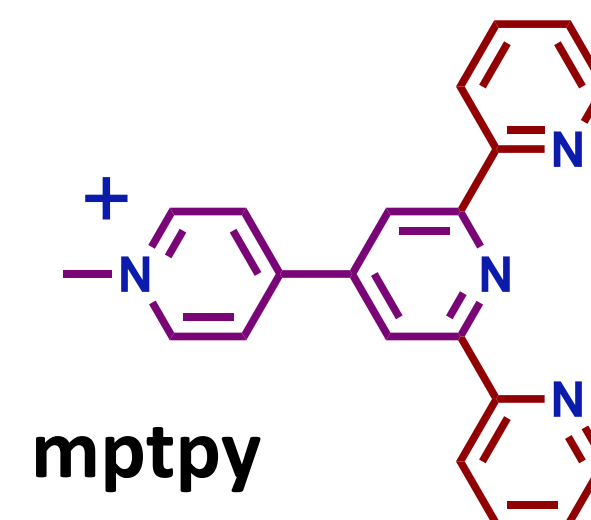


## Ligand Design

- Redox-Active Ligands:** We aim to influence the redox properties of metal catalysts by employing ligands that behave as electron acceptors.
- Inspiration:** The *N,N'*-dialkyl-4,4'-bipyridinium dications (Eq2) exhibit three stable oxidation states that are accessible at comparatively mild potentials due to conjugation between the two pyridinium rings.<sup>3</sup>



- Metal complexes featuring the viologen-like 4'-(*N*-Me-4''-pyridinium)-2,2':6',2''-terpyridine ligand (**mptpy**, Figure 1) were synthesized and were found to incorporate the electronic properties of the bipyridinium dications.
- We have identified a Co(II) complex that appears to exhibit strong interactions between the cobalt center and the π\* orbitals of the ligand, greatly altering the electronic properties of the complex.

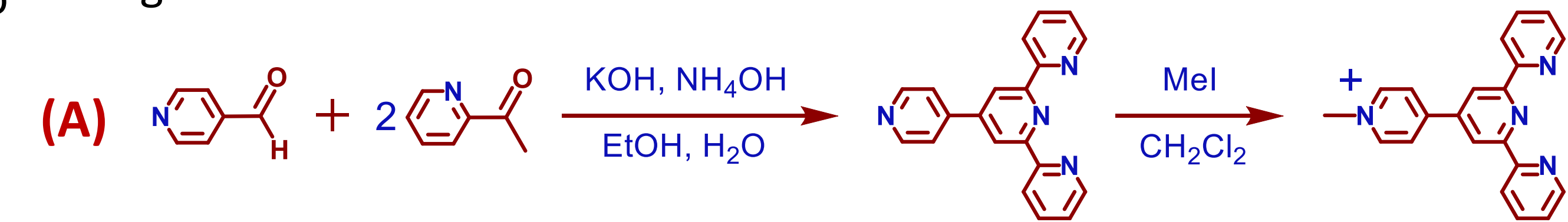


- We examined the redox capabilities of the supporting mptpy ligand by isolating and structurally, spectroscopically, and electrochemically characterizing four of the seven accessible oxidation states of the metal complex

Figure 1: Mptpy = 4'-(*N*-Me-4''-pyridinium)-2,2':6',2''-terpyridine ligand.

## Preparation and Synthesis

- The mptpy ligand was prepared by the condensation of 2-acetylpyridine, pyridine-4-carboxaldehyde, and ammonia in basic ethanol, followed by alkylation using methyl iodide to provide the monocationic ligand as its iodide salt.



- A salt metathesis was conducted to convert the iodide salt to the more soluble chloride salt of the ligand, which was then combined with cobalt(II) chloride in methanol to form the [(mptpy)<sub>2</sub>Co]<sup>4+</sup> complex. The complex was isolated as its PF<sub>6</sub><sup>-</sup> salt upon addition of NH<sub>4</sub>PF<sub>6</sub>.

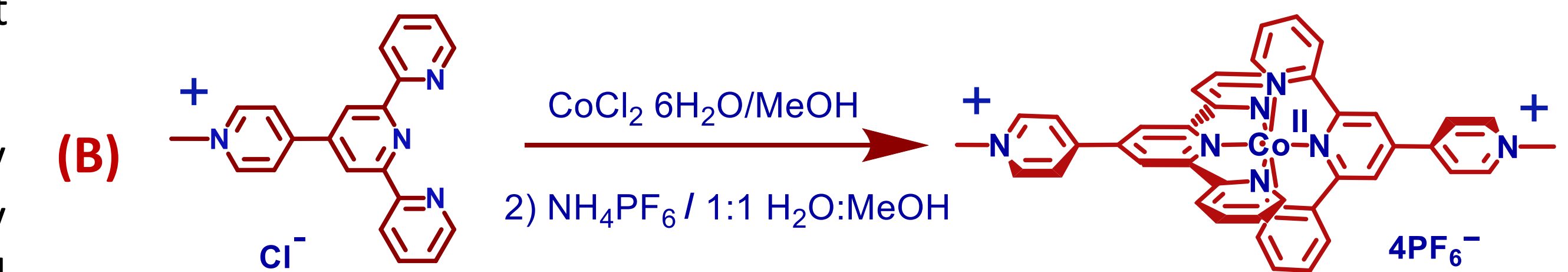


Figure 2: Synthesis of (A) the 4'-(*N*-Me-4''-pyridinium)-2,2':6',2''-terpyridine ligand (**mptpy**) and (B) the [(mptpy)<sub>2</sub>Co]<sup>4+</sup> complex of interest.

## Electrochemical and Spectroscopic Characterization

The [(mptpy)<sub>2</sub>Co]<sup>4+</sup> complex and its respective [(mptpy)<sub>2</sub>Zn]<sup>4+</sup> control complex, based on a redox-inactive metal center, were characterized by cyclic voltammetry (Figures 3A-3B), UV-vis-NIR spectroscopy (Figures 3C-3D), and solid state single crystal X-Ray diffraction (Figure 3E) to determine their electrochemical and structural properties.

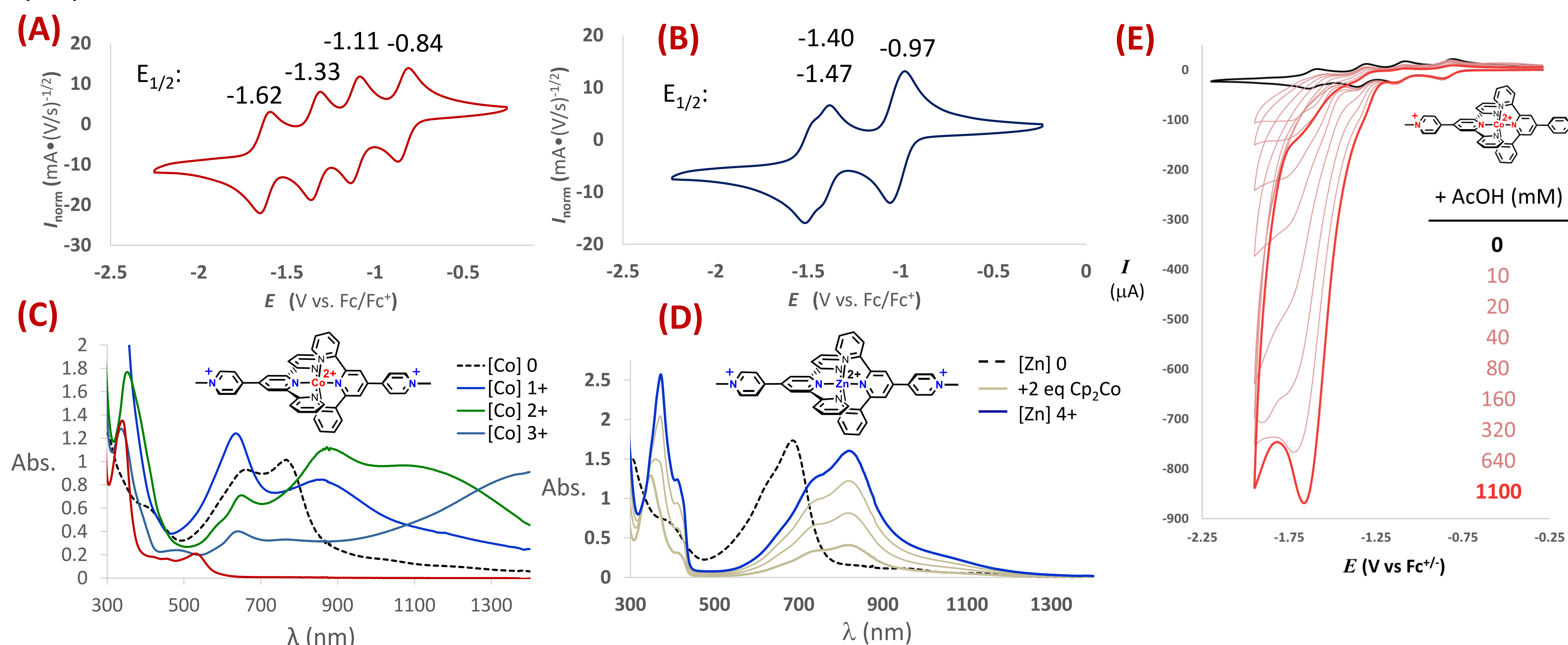


Figure 3: Cyclic voltammograms (MeCN containing 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]) at 100 mV/s scan rate using a glassy carbon working electrode) of 1 mM solutions of (A) [(mptpy)<sub>2</sub>Co(II)]<sup>4+</sup>, (B) [(mptpy)<sub>2</sub>Zn(II)]<sup>4+</sup>. UV-vis-NIR spectrum in a 1 mm path length cell of (C) 0.5 mM of [(mptpy)<sub>2</sub>Co(II)]<sup>n</sup> in MeCN (n = 1-4) reduced using Cp<sub>2</sub>Co and 0.5 mM of [(mptpy)<sub>2</sub>Co(II)]<sup>0</sup> in toluene reduced using Cp<sup>+</sup><sub>2</sub>Co. (D) 0.5 mM of [(mptpy)<sub>2</sub>Zn(II)]<sup>4+</sup> in MeCN titrated using +2 eq of Cp<sub>2</sub>Co and 0.5 mM of [(mptpy)<sub>2</sub>Zn(II)]<sup>0</sup> in toluene. (E) Cyclic Voltammograms after the addition of 20 – 1100 mM of AcOH to solutions of [(mptpy)<sub>2</sub>Co(II)]<sup>4+</sup>

## Electronic Placement and Conclusion

Paramagnetic <sup>1</sup>H NMR spectroscopy provided insight into the placement of electrons into ligand-centered vs. metal-centered orbitals, indicating the first reduction (starting from the 4+ state) is metal-centered, followed by three ligand centered reductions. Screenings of electrocatalytic activity reveal that [(mptpy)<sub>2</sub>Co]<sup>4+</sup> catalyzes the reduction of H<sup>+</sup> (from AcOH in MeCN) at milder potentials than reported for typical [(terpy)Co]<sup>2+</sup> complexes<sup>4</sup>

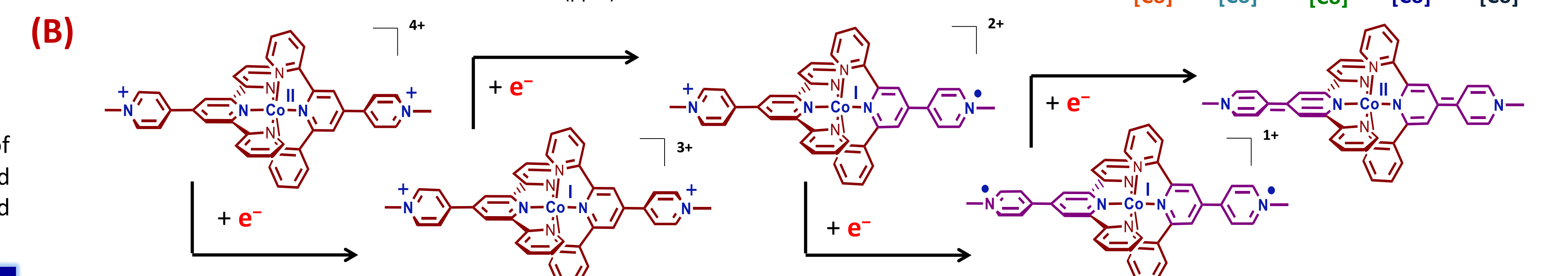
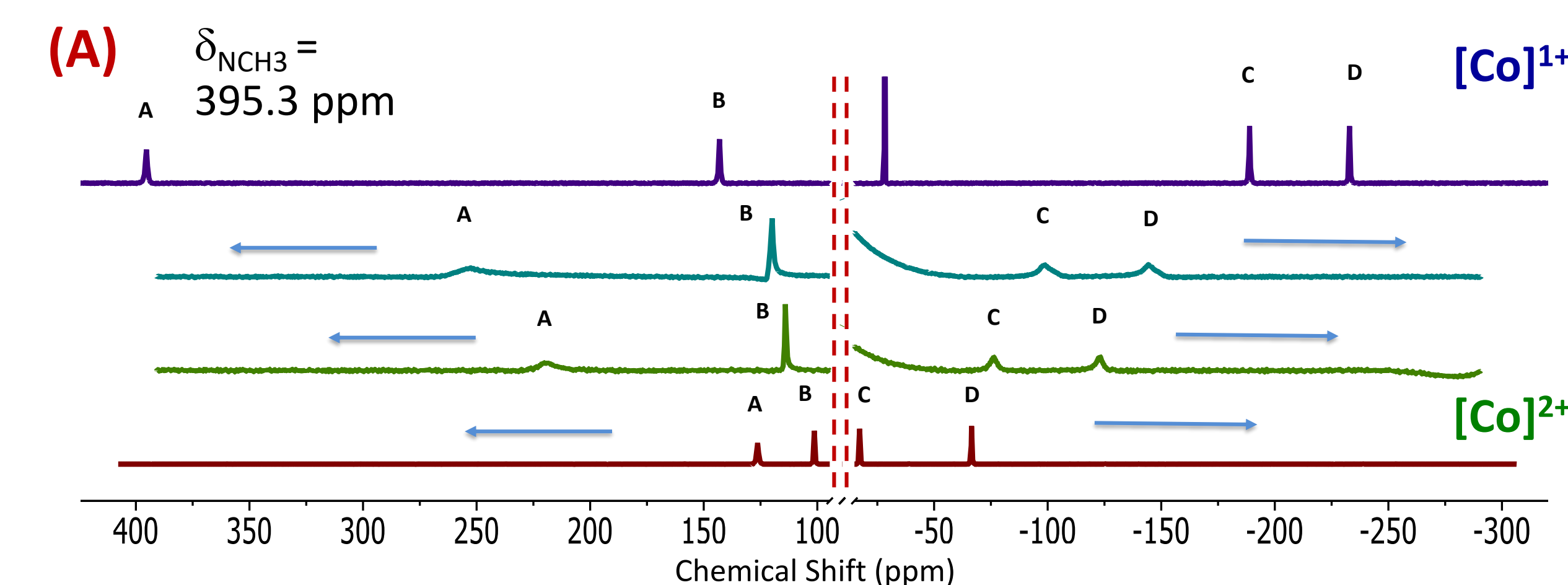


Figure 4: (A) Stacked paramagnetic <sup>1</sup>H NMR spectra (500 MHz) of [(mptpy)<sub>2</sub>Co(II)]<sup>2+</sup> gradually reduced to [(mptpy)<sub>2</sub>Co(II)]<sup>1+</sup> taken at 25°C (CD<sub>3</sub>CN, 500 MHz). Labeled signals become increasingly shielded in the same manner as the previous [Co]<sup>3+</sup> to [Co]<sup>2+</sup> reduction, indicating another ligand-centered reduction. (B) Placement of electrons with each subsequent reduction of [(mptpy)<sub>2</sub>Co(II)]<sup>4+</sup>. (C) Solid-state structure of [(mptpy)<sub>2</sub>Co(II)]<sup>4+</sup> (top) and [(mptpy)<sub>2</sub>Co(II)]<sup>1+</sup> (bottom), showing differences in bond lengths (D) Photos of [(mptpy)<sub>2</sub>Co(II)]<sup>n</sup> electrochemically reduced to oxidation states n = 4 – 0, showing subsequent darkening of colors.

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