Supplementary Information for: Substituent Effects on the
Stabilities of Polymeric and Small Molecule bis-
Terpyridine Complexes

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Model Compounds in the Investigation of Secondary Peaks

To determine whether the unexplained peaks in the NMR spectra of cobalt complexes corresponded to a Co(III) species, (4b)₂Co³⁺ was synthesized using a procedure similar to existing methods.¹ The mono complex of terpyridine with cobalt was also synthesized and investigated via NMR. For both species, the chemical shifts did not match the secondary peaks in the spectra for the 4'-modified Co(II) complexes. The possibility that impurities give rise to these secondary peaks was also ruled out by repeated recrystallization and NMR investigation of the small-molecule compounds.

Synthesis of (4b)₂Co³⁺. A 20 mL vial was charged with 0.1 g of (4b), 0.0024 g CoCl₂·6H₂O and 0.0034 g AgNO₂. Deuterium oxide (1 mL) was then added, and the mixture stirred for 1 h. After this time, all particulates were removed via syringe filter and the solution was transferred to an NMR tube. ¹H NMR (D₂O): δ = 8.56 (s, 2H), 8.52(d, 2H), 7.34 (2, 4H), 4.2-3.3 (m, 100H, polymer backbone)

NMR Shifts of (1)CoCl₂ in D₂O. The complex was prepared using an existing procedure.² ¹H NMR (D₂O): δ = 108.06 (s, 2H), 84.77 (s, 2H), 51.71 (s, 2H), 34.83 (s, 1H) 15.96 (s,2H). Note: Only five proton shifts are observed in the window examined. Since the sixth shift has recently been found to be in the range 130-170 ppm in organic solvents,³ it is conceivable that the sixth peak populates this region in aqueous solution as well.
NMR Spectra of (7)\textsubscript{2}Co\textsuperscript{2+} Before and After Oxidation.

![Figure S1](image)

Figure S1. A $^1$H NMR spectrum of the paramagnetic (7)\textsubscript{2}Co\textsuperscript{2+} species (top) shows Knight-shifted peaks between 20 and 90. The sample was gradually oxidized in air to diamagnetic (7)\textsubscript{2}Co\textsuperscript{3+}, leading to disappearance of the Knight-shifted peaks (bottom).