Electronic Supplementary Material (ESI) for Polymer Chemistry

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, $(\mathbf{4b})_2Co^{3+}$ 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 $(\mathbf{4b})_2Co^{3+}$. A 20 mL vial was charged with 0.1 g of **(4b)**, 0.0024 g $CoCl_2*6H_2O$ and 0.0034 g $AgNO_2$. Deuterium oxide (1 mL) was then added, and the mixture stirred for 1 h. After this time, all particulates where removed via syringe filter and the solution was transferred to an NMR tube. ^{1}H NMR (D_2O): 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)$CoCl_2$ in D_2O. The complex was prepared using an existing procedure.[2] ^{1}H NMR (D_2O): 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 $(7)_2Co^{2+}$ Before and After Oxidation.

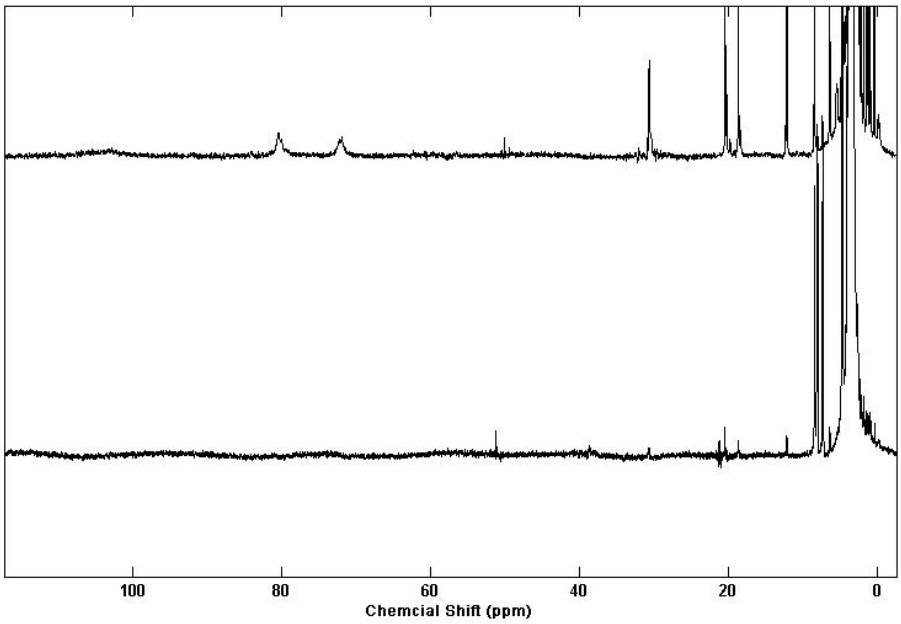

Figure S1. A ^{1}H NMR spectrum of the paramagnetic $(7)_2Co^{2+}$ species (top) shows Knight-shifted peaks between 20 and 90. The sample was gradually oxidized in air to diamagnetic $(7)_2Co^{3+}$, leading to disappearance of the Knight-shifted peaks (bottom).

(1) Mugemana, C.; Guillet, P.; Hoeppener, S.; Schubert, U. S.; Fustin, C.-A.; Gohy, J.-F. *Chemical Communications*, **46**, 1296-1298.

(2) Hogg, R.; Wilkins, R. G. *Journal of the Chemical Society (Resumed)* 1962, 341-350.

(3) Constable, E. C.; Emeléus, H. J. In *Advances in Inorganic Chemistry*; Academic Press: 1986; Vol. **30**, p 69-121.