Supporting Information

Reactive Intermediates Involved in Cobalt Corrole Catalyzed Water Oxidation (and Oxygen Reduction)

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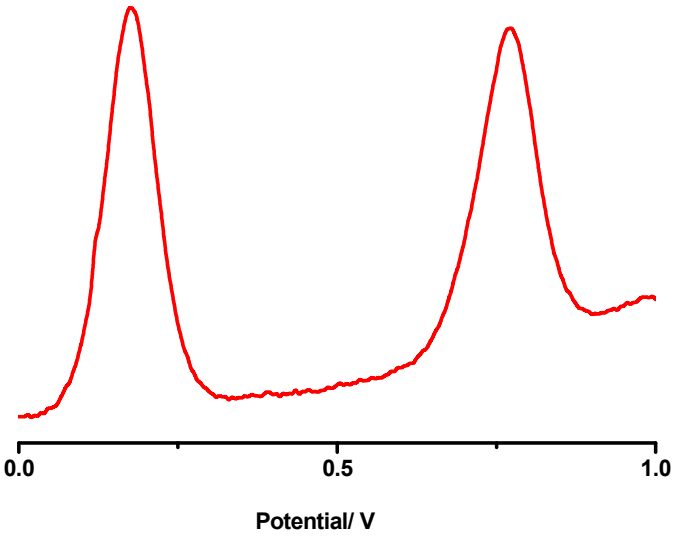

Figure S1 Square wave voltammogram of 0.5 mM Co(tpfc) in 0.2 M TBAP solution of acetonitrile, under Ar atmosphere at a scan rate of 250 mV/ sec. Working electrode: Glassy carbon, Reference electrode: Ag/AgCl, Counter electrode: Platinum wire; TBAP as the supporting electrolyte (0.2 M). The potentials are versus ferrocene/ ferrocenium.

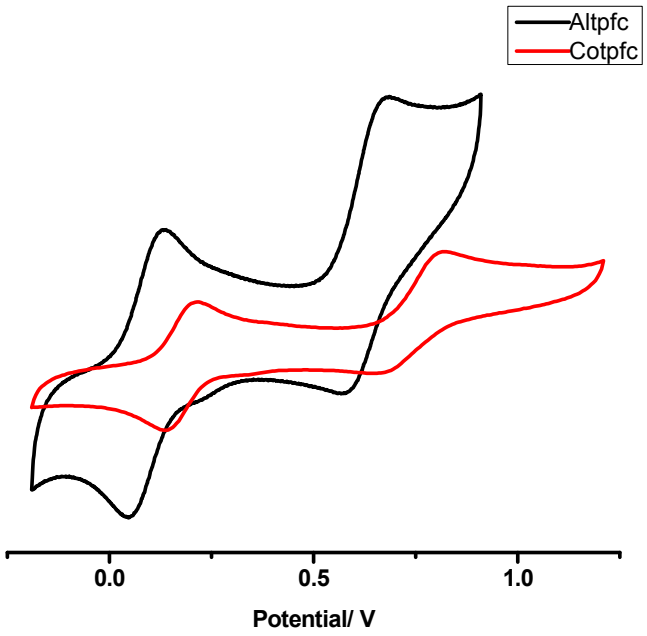

Figure S2 Cyclic voltammograms of 0.5 mM Co(tpfc) (—) and Al(tpfc) (—) in acetonitrile solutions under Ar atmosphere at a scan rate of 0.1 V/s and other conditions as in Figure S1.

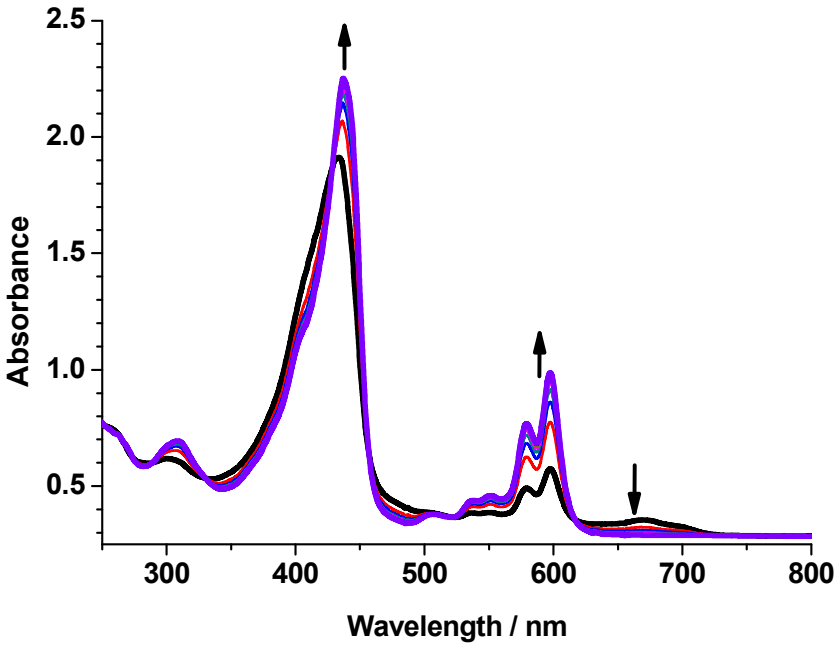

Figure S3 Spectroelectrochemical measurements during reduction of the solution of 0.5 mM Co(tpfc) oxidized at 0.51 V, in 0.2 M TBAP solution of acetonitrile, under argon atmosphere at an applied potential of -0.19 V (vs. Fc/Fc^{+}).

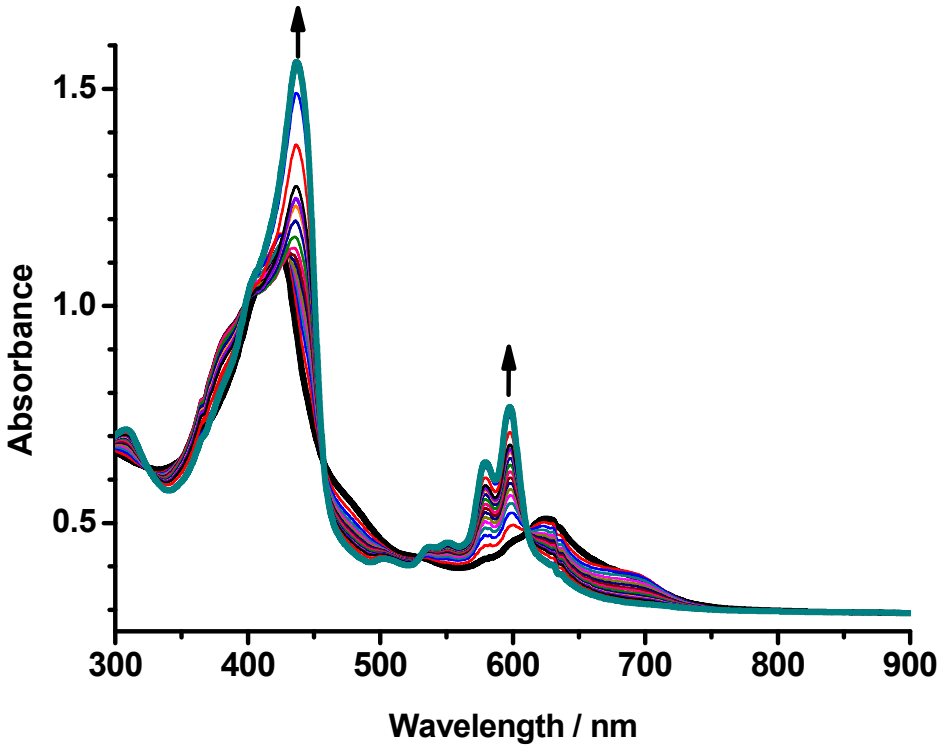

Figure S4 Spectroelectrochemical measurements during reduction of the solution of 0.5 mM Co(tpfc) oxidized at 1.11 V, in 0.2 M TBAP solution of acetonitrile under argon atmosphere without any application of potential (vs. Fc/Fc^{+}).

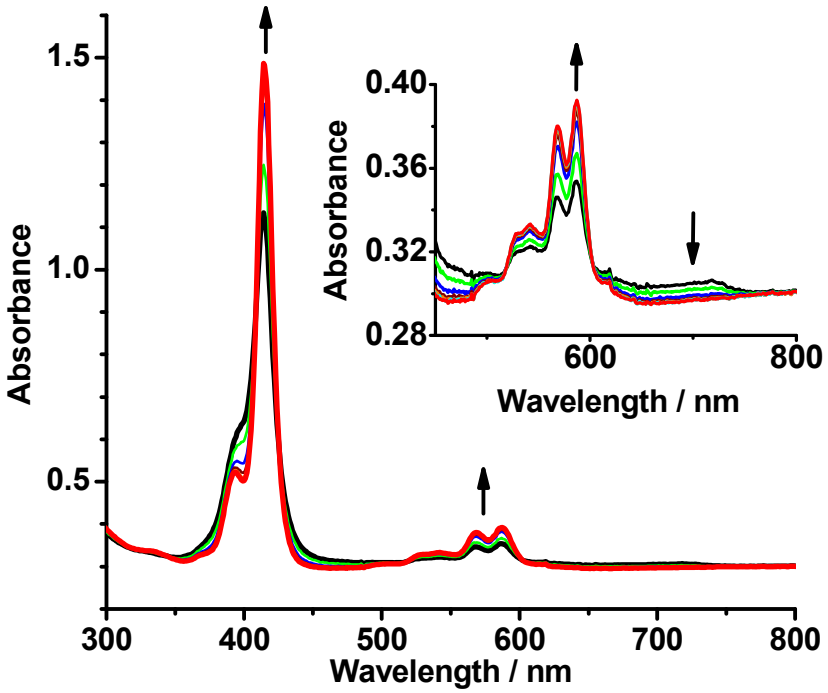

Figure S5 Spectroelectrochemical measurements during reduction of the solution of 0.05 mM Al(tpfc) oxidized at 0.41 V in 0.2 M TBAP solution of acetonitrile, under argon atmosphere at an applied potential of -0.19 V (vs. Fc/Fc^{+}).

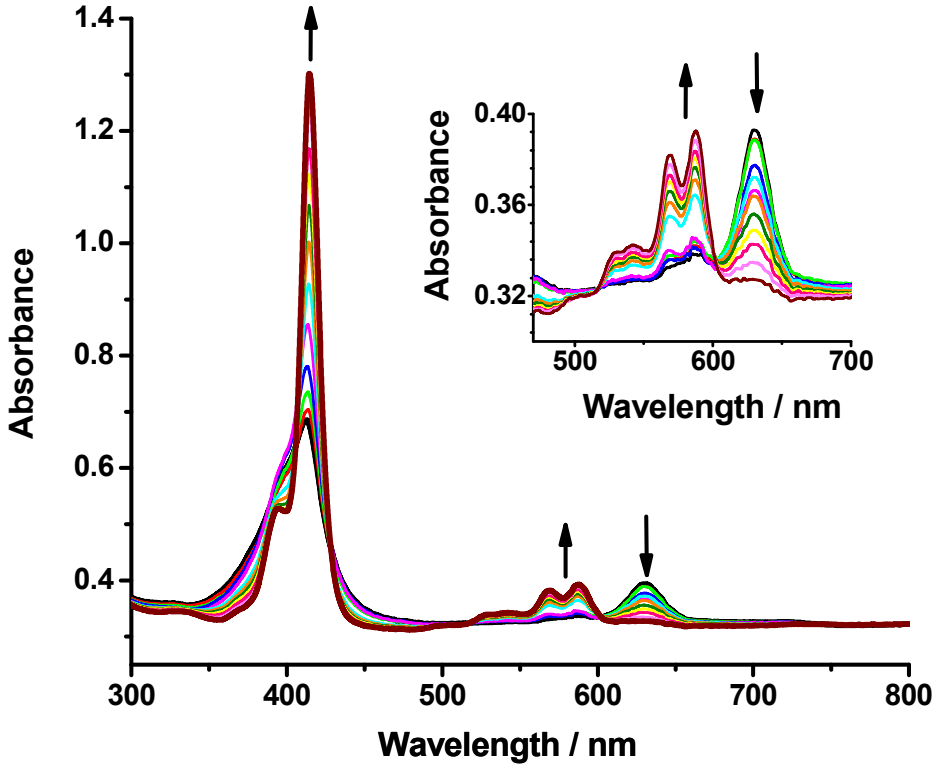

Figure S6 Spectroelectrochemical measurements during reduction of the solution of 0.05 mM Al(tpfc) oxidized at 0.91 V in 0.2 M TBAP solution of acetonitrile, under argon atmosphere at an applied potential of -0.19 V (vs. Fc/Fc^{+}).

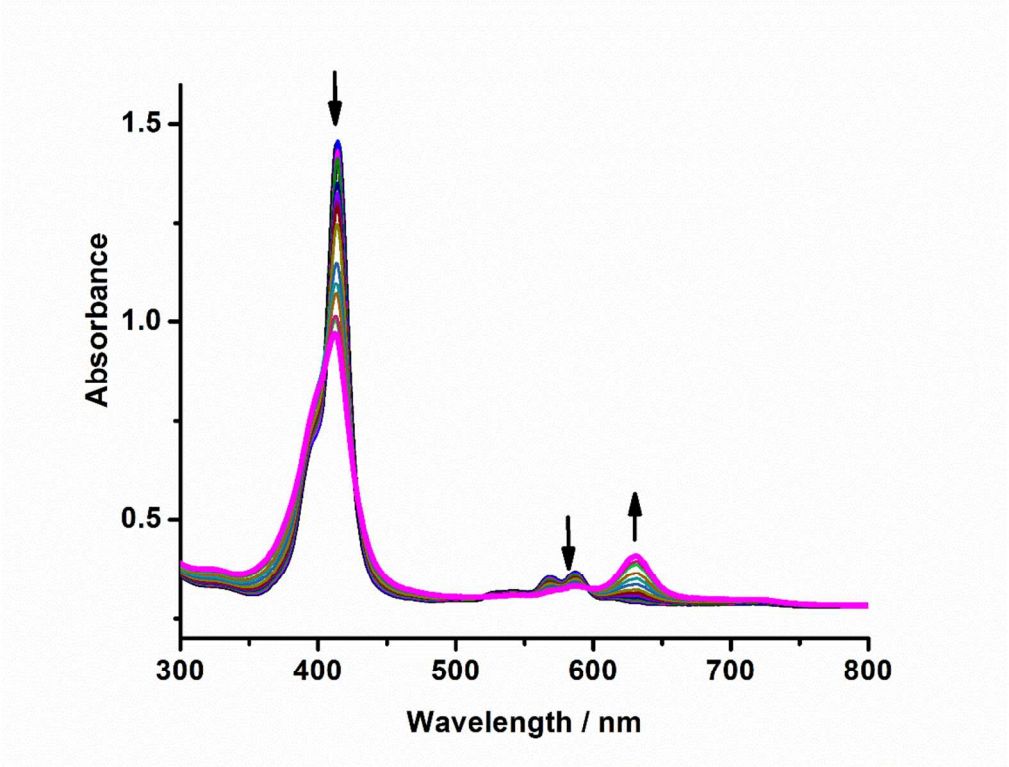

Figure S7 Spectroelectrochemical measurement of 0.05 mM Al(tpfc), starting after the first oxidation performed at 0.41 V (300 sec), and changing the potential to 0.91 V (350 sec). All values are vs. Fc/Fc+ in 0.2 M TBAP solutions of acetonitrile, under argon atmosphere.

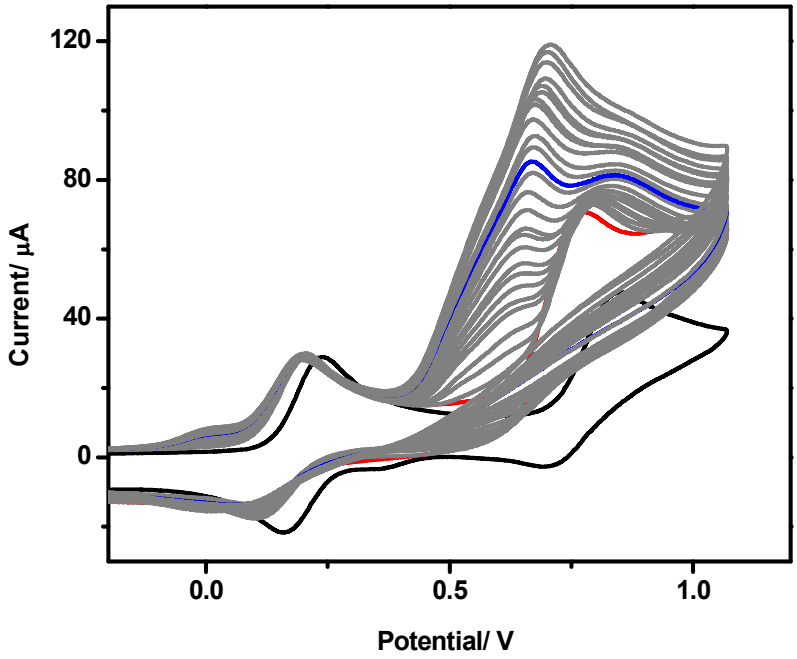

Figure S8 Cyclic voltammograms of 1 mM Co(tpfc) in acetonitrile solutions (—), 4.8% water (v/v) (—) & increasing concentration of TBAOH (15.0 - 310.0 µM) at a scan rate of 0.1 V/s under the conditions as in Figure S1. Results obtained with 0 µM and 196 µM TBAOH are emphasized by red and blue colors respectively.

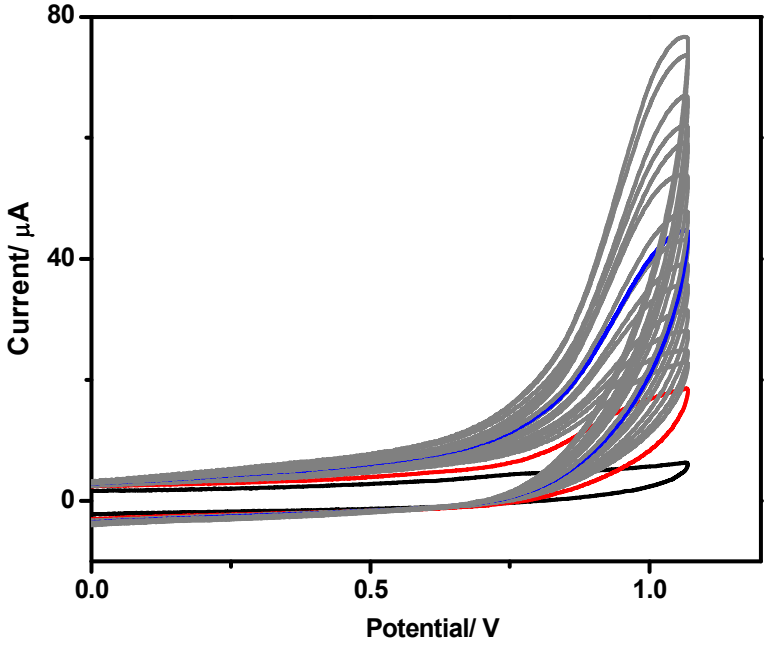

Figure S9 Cyclic voltammograms in acetonitrile solutions (—), 4.8% water (v/v) (—) & increasing concentration of TBAOH (15.0 - 310.0 μM) at a scan rate of 0.1 V/s under the conditions as in Figure S1. Results obtained with 0 μM and 196 μM TBAOH are emphasized by red and blue colors respectively.

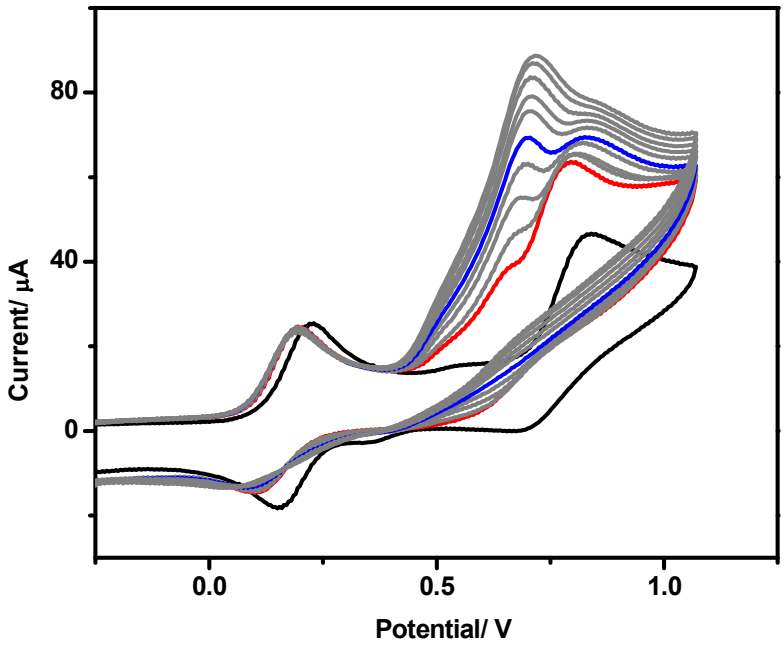

Figure S10 Cyclic voltammograms of 1 mM Co(tpfc) in acetonitrile solutions (—), 4.8% water (v/v) (—) & increasing concentration of TBAF (15.0 - 124.0 µM) at a scan rate of 0.1 V/s under the conditions as in Figure S1. Results obtained with 0 µM and 58 µM TBAF are emphasized by red and blue colors respectively.

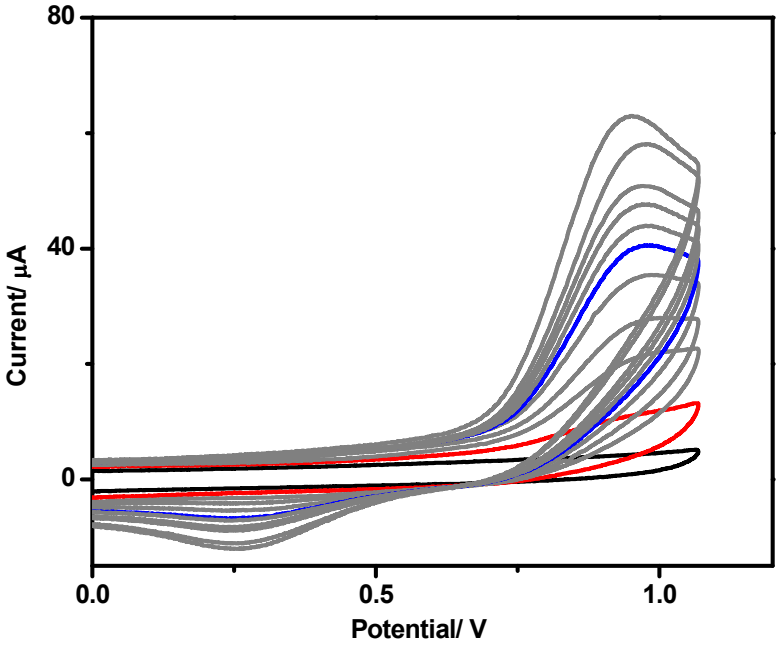

Figure S11 Cyclic voltammograms in acetonitrile solutions (—), 4.8% water (v/v) (—) & increasing concentration of tetrabutyl ammonium fluoride (TBAF) (15.0 - 124.0 µM) at a scan rate of 0.1 V/s under the conditions as in Figure S1. Results obtained with 0 µM and 58 µM TBAF are emphasized by red and blue colors respectively.

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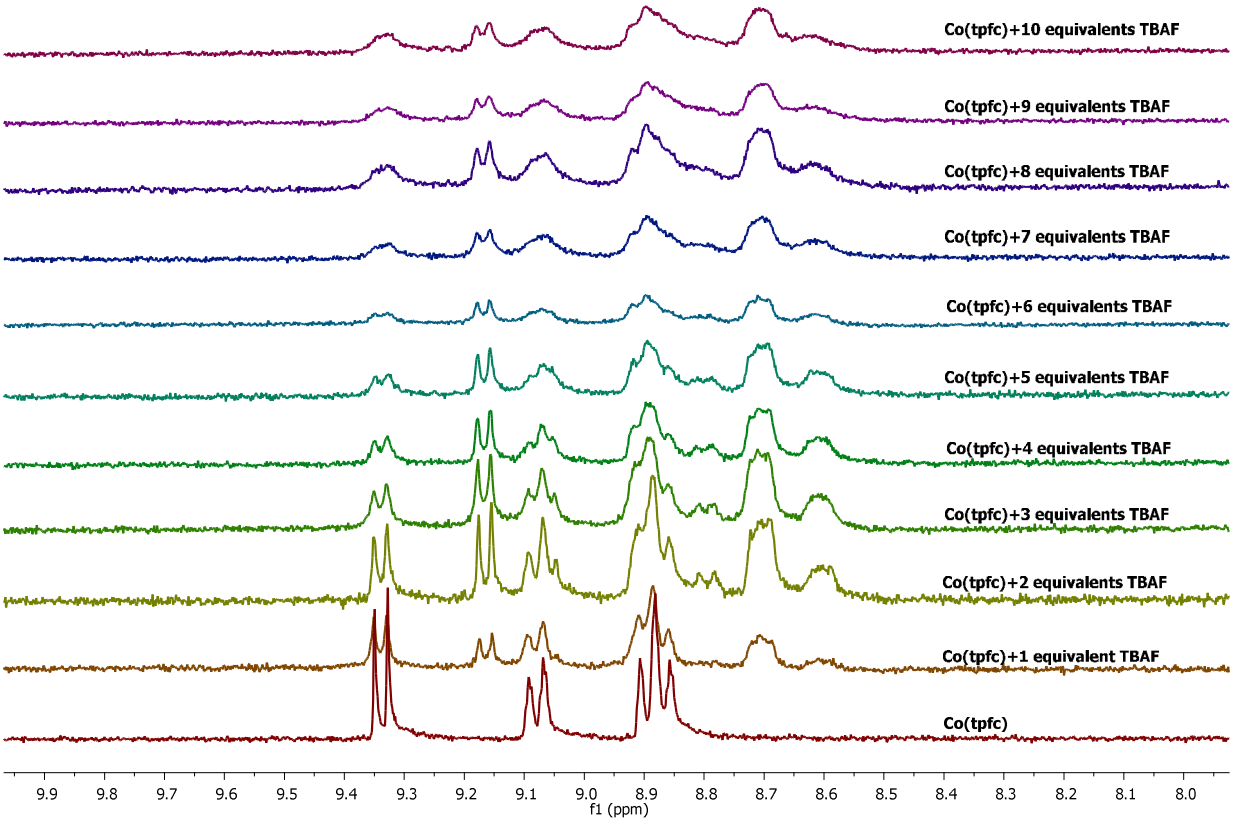

Figure S12 ^{1}H NMR spectral changes of Co(tpfc) in the aromatic region on increasing the concentration of TBAF in CD_3CN at room temperature (200 MHz).

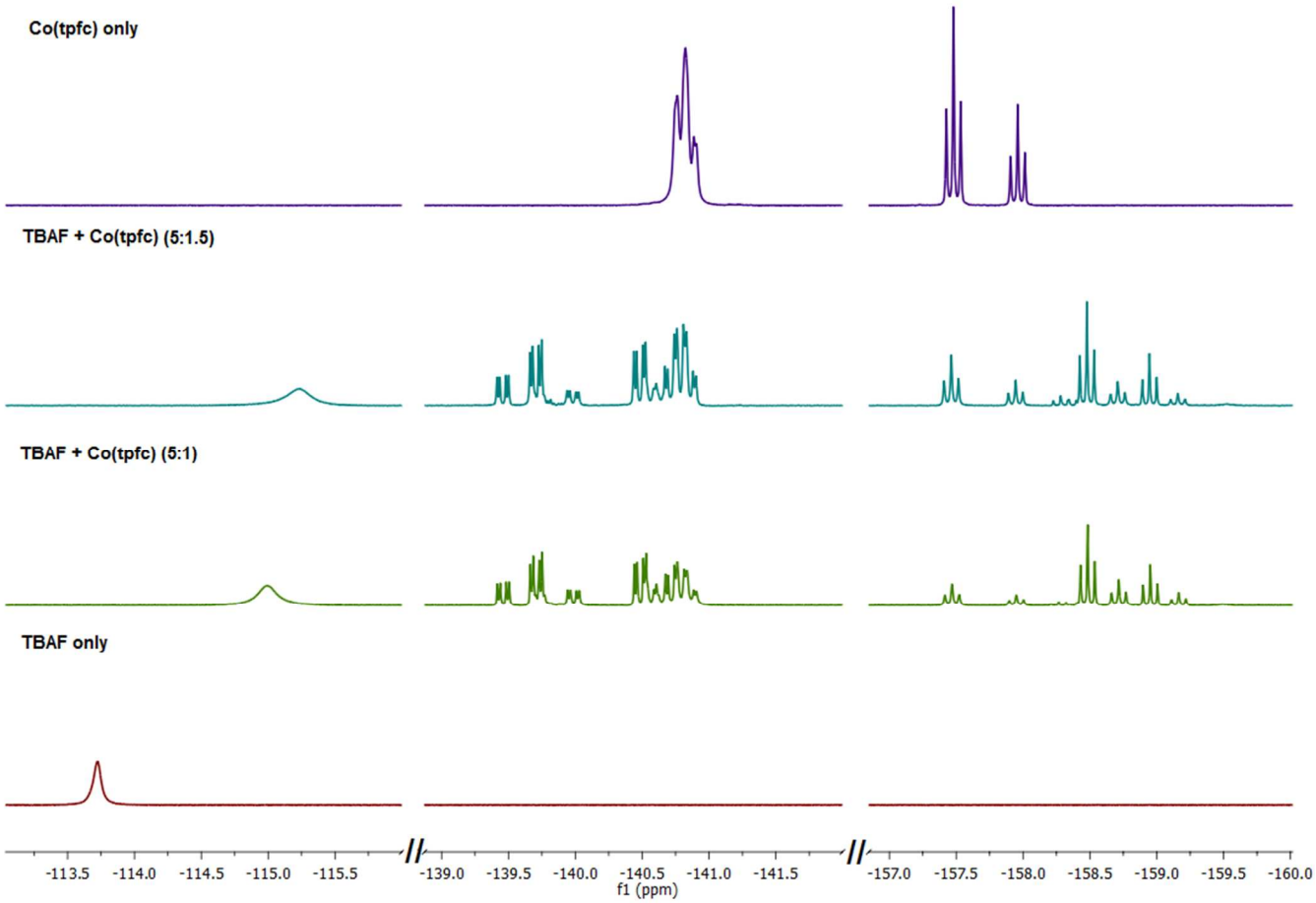

Figure S13 The ^{19}F NMR (376.75 MHz) spectral changes on adding increasing amounts of Co(tpfc) to a solution of TBAF in CD_3CN.

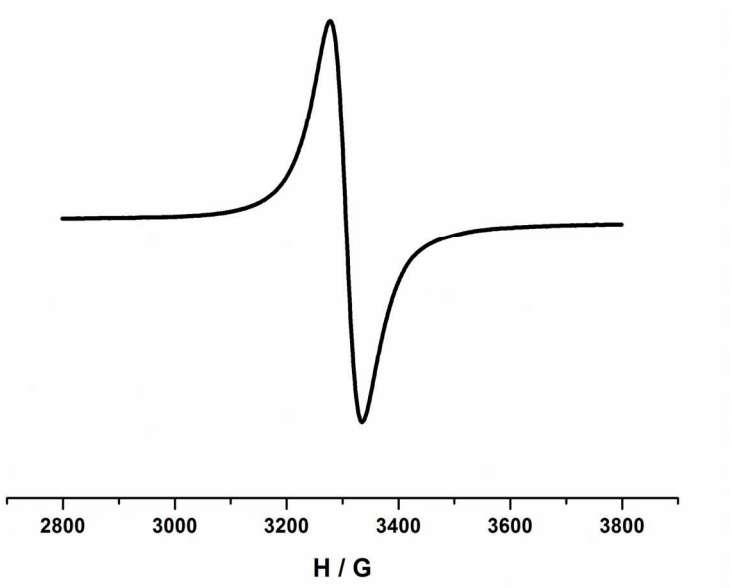

Figure S14 EPR spectrum of Co(tpfc) (precipitated from hexane) by addition of bromine (filtered and inserted into a capillary) and measured as such.