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## Low-Spin Cobalt(II) Redox Shuttle by Isocyanide Coordination

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## **Supporting Information**



Figure S1: <sup>1</sup>H NMR of 15 mM  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  with 0.2 M DMP-CN in deuterated acetonitrile . Peaks at 7.25 – 7.00 ppm and peak at 2.35 are for DMP-CN free ligand added.



**Figure S2:** <sup>1</sup>H NMR of 15 mM [Co(PY5Me<sub>2</sub>)(DMP-CN)](PF<sub>6</sub>)<sub>3</sub> in deuterated acetonitrile with 0.2 M DMP-CN in CD<sub>3</sub>CN. Two unintegrated peaks at 7.25 - 7.00 ppm and unintegrated peak at 2.35 are for DMP-CN free ligand added. Peak at 5.5 ppm is residual dichloromethane from the synthesis.



**Figure S3:** <sup>1</sup>H NMR of 10 mM  $[Co(PY5Me_2)(ACN)](PF_6)_3$  complex in deuterated CD<sub>3</sub>CN. Peak at 5.5 ppm is residual dichloromethane from the synthesis.



**Figure S4:** Scan rate dependence of CV's for 5 mM of  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  measured with 0.2 M DMP-CN in acetonitrile with 0.1 M TBAPF<sub>6</sub>.



**Figure S5:** Peak anodic current (green) and peak cathodic (violet) as a function of the square root of scan rate (v) for  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ .



**Figure S6:** <sup>1</sup>H NMR for Evan's Method, of ferrocene proton signal (red) as a function of the concentration of  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  5.0 mM (orange), 9.0 mM (green), 13.0 mM (blue), and 16.0 mM (purple). Measured in deuterated acetonitrile with 0.2 M DMP-CN.



**Figure S7:** <sup>1</sup>H NMR for Evan's Method, of ferrocene signal as a function of  $[Co(PY5Me_2)(ACN)](PF_6)_2$  complex blue (0 mM), violet (5.1 mM), green (9.4 mM), orange (13.0 mM), and red (16.0 mM).



**Figure S8** ATIR spectrum of the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  complex (green) and of the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_3$  complex (purple).

The C=N stretching modes were analyzed by infrared spectroscopy using the attenuated total reflection (ATIR) configuration on crystals of each complex. Upon inspection of the IR spectrum for  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  complex, one signal is present at 2166 cm<sup>-1</sup> for the isocyanide stretch of the complex which is shifted from the signal of the free DMP-CN ligand (2118 cm<sup>-1</sup>), (Figure S8 ATIR spectrum of the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$  complex (green) and of the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_3$  complex (purple).). The increase in C=N frequency is due to the antibonding character of the lone pair of the carbon being reduced by sigma donation to the Co(II) metal center which has a larger contribution than the weakening  $\pi$  backdonation. Upon oxidation,

the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_3$  complex has three visible signals in the region that is typical to cyanide functional groups. The signal at 2211 cm<sup>-1</sup> can be attributed to the cyanide stretching mode while the two higher wavenumber signals can be attributed to acetonitrile bound in the crystal lattice which agrees with the single crystal x-ray structure.<sup>1</sup> The increase in bond strength from Cobalt (II) to Cobalt (III) is rationalized by the reduced  $\pi$  backdonation into the  $\pi^*$ antibonding orbital increasing the bond order of the C=N bond of the Cobalt (III) complex.



**Figure S9:** UV-visible spectrum of  $Co(PY5Me_2)(DMP-CN)(PF_6)_2$  (green) and of  $Co(PY5Me_2)(DMP-CN)(PF_6)_3$  (purple). Spectra were collected in acetonitrile with 0.4 DMP-CN present. Background was corrected for 0.4 M DMP-CN absorbance.

**Table S1:** Fitting parameters from TA measurements from bi-exponential equation. Results are average and error of 6 devices of each electrolyte.

Electrolyte	$\Delta A_0$	$A_1$	$k_1(10^{-3})$ (ns <sup>-1</sup> )	$A_2$	$k_2 (10^{-3}) (\text{ns}^{-1})$	$\mathbb{R}^2$
Inert	$0.12\pm0.02$	$0.35\pm0.02$	$1.2 \pm 2.1$	$0.45 \pm 0.06$	5.4 ± 3.5	$0.89\pm0.07$
$[Co(bpy)_3]^{3+/2+}$	$0.09\pm0.03$	$0.35\pm0.06$	$2.5 \pm 5.1$	$0.45\pm0.05$	$7.9 \pm 4.7$	$0.90\pm0.03$
[Co(PY5Me <sub>2</sub> )(DMP-CN)] <sup>+3/+2</sup>	$\textbf{-0.04} \pm 0.02$	$0.40\pm0.09$	$2.7\pm4.1$	$0.50\pm0.08$	$11.9 \pm 10.2$	$0.7\pm0.1$
[Co(PY5Me <sub>2</sub> )(ACN)] <sup>3+/2+</sup>	$0.06\pm0.02$	$0.42\pm0.04$	$2.0 \pm 2.5$	$0.43\pm0.04$	$5.2 \pm 3.9$	$0.93 \pm 0.02$



Figure S10: Example Nyquist plots of full DSSCs at 100 mW cm<sup>-2</sup> fitted to the equivalent circuit.



Figure S11: Equivalent circuit used to fit full dye-sensitized solar cells.



**Figure S12.:** Chemical capacitance as a function of potential applied at each light intensity. The potential is obtained by correcting the applied potential vs solution potential measured against  $Fc^+/Fc$ .



**Figure S13:** Plot of current density *vs.* applied voltage curves under varying illumination intensities for DSSCs containing the  $[Co(PY5Me_2)(DMP-CN)(PF_6)_{3/2}]$  electrolyte.



**Figure S14:** Plot of current density *vs.* applied voltage curves under illumination for DSSCs containing  $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$  and  $[Co(bpy)_3](PF_6)_{3/2}$  electrolytes with a 6.5 µm thick film of 30 nm TiO<sub>2</sub> nanoparticles. The electrolyte consisted of 0.15 M Co(II), 0.015 M Co(III), 0.1 M LiPF<sub>6</sub> and 0.2 M DMP-CN for the  $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$  electrolyte. All other device preparations were the same as that within the main text.

**Table S2.:** Device parameters extracted from 5 devices (average and standard deviation) shown in Figure S14.

Electrolyte	$V_{\rm OC}({ m V})$	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	FF	η
[Co(PY5Me <sub>2</sub> )(DMP-CN)](PF <sub>6</sub> ) <sub>3/2</sub>	$0.58\pm0.01$	$7.7 \pm 0.2$	$0.54\pm0.02$	$2.4 \pm 0.2$
$[Co(bpy)_3](PF_6)_{3/2}$	$0.48\pm0.01$	$9.2\pm0.4$	$0.44\pm0.04$	$1.9\pm0.1$

(1) Pace, E. L.; Noe, L. J. Infrared Spectra of Acetonitrile and Acetonitrile-D3. J. Chem. *Phys.* **1968**, *49* (12), 5317–5325.