

Supporting Information

for

**Photoinitiated Multi-step Charge Separation and Ultrafast Charge  
Transfer Induced Dissociation in a Pyridyl-Linked  
Photosensitizer-Cobaloxime Assembly**

Brad S. Veldkamp, Won-Sik Han, Scott M. Dyar, Samuel W. Eaton, Mark A. Ratner, and

Michael R. Wasielewski\*

*Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center,*

*Northwestern University, Evanston, IL 60208-3113*

E-mail: [m-wasielewski@northwestern.edu](mailto:m-wasielewski@northwestern.edu)

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## I. Experimental details

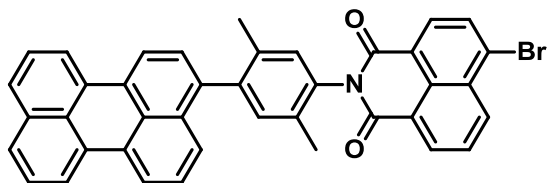
### a. General

Unless stated otherwise, all reagents were purchased from Sigma-Aldrich and used without further purification. Perylene (98+%) and 1,4-dioxane (99%) were from Alfa Aesar. Bis(pinacolato)diboron (99%) and 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride were from Frontier Scientific. Dichloromethane, hexanes, hydrochloric acid, ethanol (absolute), and acetone were from Macron Chemicals. Toluene ( $\geq 99.5\%$ ) and silica gel for column chromatography (chromatography grade, 400-230 mesh) were from VWR. 4-pyridinylboronic acid ( $>97\%$ ) was from Boron Molecular. Tetrakis(triphenylphosphine)palladium(0) (99%) was from Strem Chemicals, Inc.

Dichloromethane, used for spectroscopy and electrochemistry, and tetrahydrofuran were passed over two packed columns of neutral alumina with a Glass Contour solvent system prior to use. *N,N*-dimethylformamide was passed over two packed columns of activated molecular sieves with a Glass Contour solvent system prior to use. Benzonitrile was treated with concentrated HCl, dried over  $K_2CO_3$ , filtered, and then distilled from  $P_2O_5$  prior to use.<sup>1</sup>

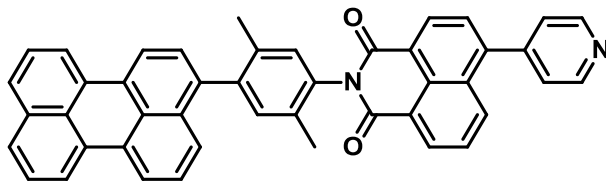
<sup>1</sup>H nuclear magnetic resonance spectra were recorded on a Bruker Avance III 500 MHz instrument. *J* values are given in Hz. High resolution mass spectrometry was performed on an Agilent 6210 ToF LC/MS mass spectrometer. For all compounds except Per, positive ion electrospray ionization (ESI) mode was used with direct infusion of the sample using an Agilent 1100 pump stack. For Per, atmospheric pressure photoionization (APPI) was used.

**b. Synthesis.** 3-bromoperylene (**PerBr**) and 3-(4'-amino-2',5'-dimethylphenyl)perylene (**PerXyNH<sub>2</sub>**) were synthesized as before.<sup>2</sup>



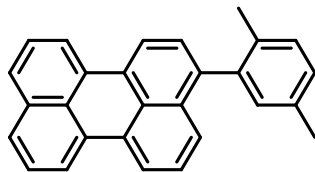
**PerXyNMIBr**

**PerXyNMIBr.** To a round bottom flask equipped with a reflux condenser were added **PerXyNH<sub>2</sub>** (205 mg, 0.552 mmol), 4-bromo-1,8-naphthalic anhydride (1.53 g, 5.52 mmol), 95 mL of ethanol, and 5 mL of pyridine. The reaction mixture was heated to reflux for 66 h. Following removal of the solvent under reduced pressure, the product was purified by elution with dichloromethane on a silica gel column and then by elution with dichloromethane on an aluminum oxide column (neutral, Brockman I, deactivated with 6% added H<sub>2</sub>O by weight). To the resulting yellow solid, 100 mL of dichloromethane was added and 100 mL of ethanol layered on top. The solution was cooled to -15 to -20 °C and stored overnight. The precipitate was collected by vacuum filtration and washed with 5 mL of cold ethanol yielding **PerXyNMIBr** (307 mg, 88%) as a yellow solid.  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 8.77 (1 H, d, *J* 7.2, *ArH*), 8.68 (1 H, d, *J* 8.5, *ArH*), 8.52 (1 H, d, *J* 7.8, *ArH*), 8.28 – 8.22 (4 H, m, *ArH*), 8.14 - 8.11 (1 H, m, *ArH*), 7.95 – 7.91 (1 H, m, *ArH*), 7.70 (2 H, apparent d, *J* 8.1, *ArH*), 7.53 – 7.42 (5 H, m, *ArH*), 7.33 (1 H, s, *ArH*), 7.21 (1 H, s, *ArH*), 2.20 (3 H, s, CH<sub>3</sub>), 2.10 (3 H, s, CH<sub>3</sub>). ESI-HRMS (*m/z*) M<sup>+</sup> = 629.0995 (calculated 629.0985).



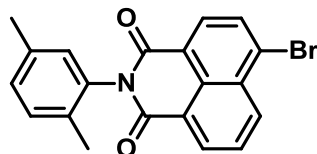
**Per-NMI**

**Per-NMI.** To a round bottom flask equipped with a reflux condenser, **PerXyNMIBr** (150 mg, 0.238 mmol), 4-pyridinylboronic acid (99 mg, 0.805 mmol), and 75 mL of tetrahydrofuran were added and purged with nitrogen prior to the addition of a nitrogen-purged 25 mL solution of 2 M aqueous potassium carbonate and finally tetrakis(triphenylphosphine)palladium(0) (55 mg, 0.0476 mmol). The reaction mixture was heated to reflux for 3 h under nitrogen. After cooling to room temperature, the water layer was removed. The solution was diluted with 150 mL of dichloromethane and washed three times with 100 mL of water. The organic layer was dried under reduced pressure and the resulting crude material purified by column chromatography on silica gel using an eluent gradient of 0 – 15% acetone by volume in dichloromethane. Further purification was obtained by passing the material through an aluminum oxide column (neutral, Brockman I, deactivated with 6% added H<sub>2</sub>O by weight) with dichloromethane as an eluent and a second silica gel column using an eluent gradient of 0 – 20% acetone by volume in dichloromethane. **Per-NMI** (91 mg, 61%) was obtained as a yellow solid.  $\delta_{\text{H}}$ (500 MHz; CDCl<sub>3</sub>) 8.86 – 8.85 (2 H, m, ArH), 8.79 – 8.77 (2 H, m, ArH), 8.29 – 8.23 (5 H, m, ArH), 7.86 – 7.82 (1 H, m, ArH), 7.79 (1 H, apparent dd, *J* 7.5, *J* 4.0, ArH), 7.71 (2 H, apparent d, *J* 8.1, ArH), 7.52 – 7.43 (7 H, m, ArH), 7.35 (1 H, s, ArH), 7.23 (1 H, s, ArH), 2.23 (3 H, s, CH<sub>3</sub>), 2.11 (3 H, s, CH<sub>3</sub>). ESI-HRMS (*m/z*) [M+H]<sup>+</sup> = 629.2234 (calculated 629.2224).



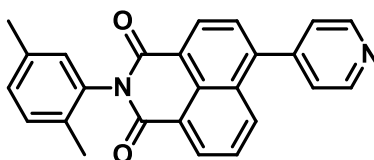
**Per**

**Per.** To a round bottom flask equipped with a reflux condenser, **PerBr** (30.8 mg, 0.0930 mmol) as a solid mixture with perylene, 2,5-dimethylphenyl boronic acid (41.8 mg, 0.279 mmol), cesium carbonate (303 mg, 0.930 mmol), and 25 mL of tetrahydrofuran were added and purged with nitrogen prior to the addition of 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride (7.2 mg, 0.0093 mmol). The reaction mixture was heated to reflux for 16 h under nitrogen. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was extracted with 50 mL of dichloromethane and washed three times with 50 mL of water. The organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered, and evaporated to dryness under reduced pressure. Column chromatography of the residue on silica gel using dichloromethane as an eluent followed by recrystallization from hexanes gave crude product. Column chromatography on silica gel using gradient elution with 2% – 10% toluene by volume in hexanes gave **Per** (12 mg, 36%) as a yellow solid.  $\delta_{\text{H}}$ (500 MHz;  $\text{CD}_2\text{Cl}_2$ ) 8.28 – 8.22 (4 H, m, ArH), 7.72 (2 H, apparent d,  $J$  8.2, ArH), 7.52 (2 H, apparent td,  $J$  7.8,  $J$  4.4, ArH), 7.40 (1 H, t,  $J$  7.9, ArH), 7.34 (1 H, d,  $J$  7.6, ArH), 7.30 (1 H, d,  $J$  8.4, ArH), 7.24 (1 H, d,  $J$  7.2, ArH), 7.18 (1 H, dd,  $J$  7.1,  $J$  1.4, ArH), 7.09 (1 H, s, ArH), 2.37 (3 H, s,  $\text{CH}_3$ ), 2.03 (3 H, s,  $\text{CH}_3$ ). APPI-HRMS (m/z)  $[\text{M}+\text{H}]^+ = 357.1635$  (calculated 357.1638).



**XyNMIBr**

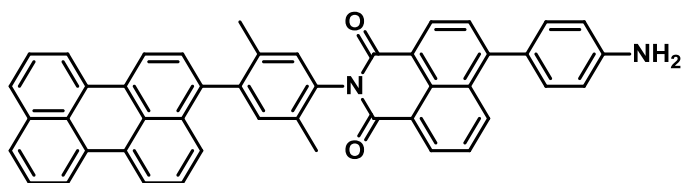
**XyNMIBr.** To a round bottom flask equipped with a reflux condenser, 2,5-dimethylaniline (0.218 g, 1.80 mmol), 4-bromo-1,8-naphthalic anhydride (0.500 g, 1.80 mmol), 57 mL of ethanol, and 3 mL of pyridine were added. The reaction mixture was heated to reflux under nitrogen for 45 h. After cooling to room temperature, the solvent was removed under reduced pressure. The product was isolated by column chromatography on silica gel with dichloromethane as an eluent to give **XyNMIBr** (0.172 g, 25%) as a white solid.  $\delta_{\text{H}}$ (500 MHz;  $\text{CD}_2\text{Cl}_2$ ) 8.68 – 8.65 (2 H, m, ArH), 8.44 (1 H, d,  $J$  7.9, ArH), 8.11 (1 H, d,  $J$  7.9, ArH), 7.91 (1 H, dd,  $J$  4.9,  $J$  7.3, ArH), 7.30 (1 H, d,  $J$  7.8, ArH), 7.23 (1 H, dd,  $J$  7.3,  $J$  1.0, ArH), 7.02 (1 H, s, ArH), 2.38 (3 H, s,  $\text{CH}_3$ ), 2.08 (3 H, s,  $\text{CH}_3$ ). ESI-HRMS ( $m/z$ )  $[\text{M}+\text{H}]^+ = 380.0288$  (calculated 380.0281).



**NMI**

**NMI.** To a round bottom flask equipped with a reflux condenser, **XyNMIBr** (100 mg, 0.263 mmol), 4-pyridinylboronic acid (100 mg, 0.814 mmol), and 75 mL of tetrahydrofuran were added and purged with nitrogen prior to the addition of a nitrogen-purged 25 mL solution of 2 M aqueous potassium carbonate solution and finally tetrakis(triphenylphosphine)palladium(0) (60.8 mg, 0.0526 mmol). The reaction mixture was heated to reflux under nitrogen for 19 h. After

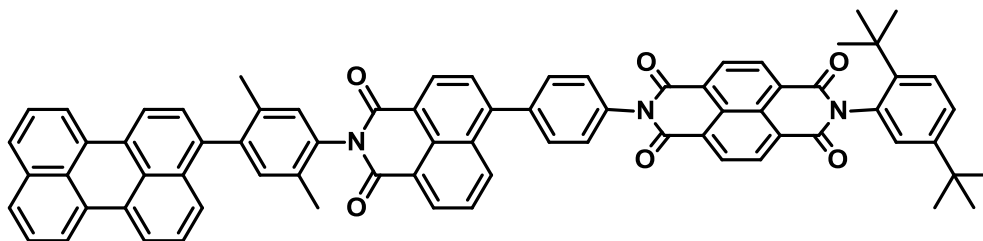
cooling to room temperature, the water layer was removed. 150 mL of dichloromethane was added and the organic layer washed three times with 100 mL of water. The solvent was evaporated under reduced pressure and the product purified by column chromatography on silica gel using gradient elution with 7 – 10 % acetone by volume in dichloromethane. Recrystallization from 2-propanol gave **NMI** (34 mg, 34% yield) as a white powder.  $\delta_{\text{H}}$ (500 MHz;  $\text{CD}_2\text{Cl}_2$ ) 8.81 – 8.80 (2 H, m, *ArH*), 8.69 – 8.66 (2 H, m, *ArH*), 8.27 (1 H, dd, *J* 8.0, *J* 1.1, *ArH*), 7.80 (1 H, dd, *J* 7.3, *J* 4.9, *ArH*), 7.77 (1 H, d, *J* 7.5, *ArH*), 7.50 – 7.49 (2 H, m, *ArH*), 7.31 (1 H, d, *J* 7.8, *ArH*), 7.24 (1 H, dd, *J* 7.2, *J* 1.1, *ArH*), 7.05 (1 H, s, *ArH*), 2.39 (3 H, s,  $\text{CH}_3$ ), 2.11 (3 H, s,  $\text{CH}_3$ ). ESI-HRMS (*m/z*) [ $\text{M}+\text{H}$ ] $^+$  = 379.1444 (calculated 379.1441).



**PerXyNMIAAn**

**PerXyNMIAAn.** To a round bottom flask equipped with a reflux condenser, **PerXyNMIBr** (160 mg, 0.254 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine<sup>3</sup> (61 mg, 0.28 mmol), sodium carbonate (81 mg, 0.76 mmol), and mixed solvent (THF/ $\text{H}_2\text{O}$  = 9 mL/3 mL) were added and purged with nitrogen prior to the addition of tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol). The reaction mixture was heated to reflux for 20 h under nitrogen. The reaction mixture was cooled to room temperature and poured into  $\text{H}_2\text{O}$ . The crude product was extracted twice with 50 mL of dichloromethane and washed twice with 50 mL of water. The combined organic phases were dried over anhydrous  $\text{MgSO}_4$  and filtered. The filtrates were dried under reduced pressure and purified by column chromatography on silica gel using ethyl acetate/hexane (*v/v* = 1:1) as an eluent to give

**PerXyNMIAn** (0.14 g, 86%) as an orange solid.  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ) 8.73 (2 H, m, ArH), 8.48 (1 H, apparent d,  $J$  8.5, ArH), 8.22–8.29 (4 H, m, ArH), 7.70–7.79 (2 H, m, ArH), 7.72 (2 H, d,  $J$  8.1, ArH), 7.42–7.53 (5 H, m, ArH), 7.38 (2 H, d,  $J$  7.8, ArH), 7.34 (1 H, s, ArH), 7.23 (1 H, s, ArH), 6.88 (2 H, d,  $J$  7.8, ArH), 3.94 (2 H, s,  $\text{NH}_2$ ), 2.23 (3 H, s,  $\text{CH}_3$ ), 2.11 (3 H, s,  $\text{CH}_3$ ). ESI-HRMS (m/z)  $[\text{M}+\text{H}]^+ = 643.2379$  (calculated 643.2386).



### Per-NMI-NDI

**Per-NMI-NDI.** To a round bottom flask equipped with a reflux condenser **PerXyNMIAn** (0.12 g, 0.20 mmol), *N*-(2,5-di-*tert*-butylphenyl)-1,5-dicarboxy-4,8-naphthalenedicarboximide anhydride<sup>4</sup> (0.1 g, 0.22 mmol), and pyridine (10 mL) were added and heated to reflux in the absence of light for 24 h. The reaction mixture was cooled to room temperature and pyridine was removed under reduced pressure. The product was purified by column chromatography on silica gel using dichloromethane/acetone ( $v/v = 100:1$ ) as an eluent to give **Per-NMI-NDI** (0.16 g, 74%) as a green solid.  $\delta_{\text{H}}$ (500 MHz;  $\text{CDCl}_3$ ) 8.92 (4 H, q,  $J$  8.1, ArH), 8.82 (1 H, dd,  $J$  14.2,  $J$  8.1, ArH), 8.79 (1 H, d,  $J$  7.8, ArH), 8.51 (1 H, apparent d,  $J$  7.8, ArH), 8.23–8.30 (4 H, m, ArH), 7.90 (1 H, q,  $J$  10.1, ArH), 7.84–7.88 (1 H, m, ArH), 7.81 (2 H, d,  $J$  8.5, ArH), 7.63 (1 H, d,  $J$  8.5, ArH), 7.59 (2 H, d,  $J$  8.9, ArH), 7.45–7.54 (6 H, m, ArH), 7.36 (1 H, s, ArH), 7.25 (1 H, s, ArH), 7.10 (2 H, d,  $J$  8.0, ArH), 7.05 (1 H, d,  $J$  7.1, ArH), 2.25 (3 H, s,  $\text{CH}_3$ ), 2.12 (3 H, s,  $\text{CH}_3$ ), 1.35 (9 H, s,  $(\text{CH}_3)_3$ ), 1.29 (9 H, s,  $(\text{CH}_3)_3$ ). ESI-HRMS (m/z)  $\text{M}^+ = 1079.3927$  (calculated 1079.3934).



### c. Fitting of transient absorption data

Femtosecond transient absorption spectroscopy data were fit to sequential  $A \rightarrow B$ ,  $A \rightarrow B \rightarrow C$ , or  $A \rightarrow B \rightarrow C \rightarrow D$  models using the following procedure. The chirp, or variation in the pump to probe time delay as a function of probe wavelength, was measured using the Kerr effect – rotation of the probe pulse polarization as a result of spatial and temporal overlap with the pump pulse. By placing a polarizer set perpendicular to the probe pulse polarization after a sample cell containing dichloromethane, light which passed through the polarizer as a result of the Kerr effect was measured as function of pump to probe time delay and probe wavelength.

Using Surface Xplorer Pro<sup>5</sup> a chirp correction file was generated by fitting the pump to probe time delay variation as function of probe wavelength and then the following analysis was performed for each data set. A scattered light background was subtracted. The chirp was corrected. Singular value decomposition was performed with up to three components. For the  $A \rightarrow B$ ,  $A \rightarrow B \rightarrow C$ , or  $A \rightarrow B \rightarrow C \rightarrow D$  models, the principal kinetics were then respectively globally fit to a sum of one to three exponential decays and a constant to generate a kinetic model of the form:

$$\Delta A(\lambda) = A_0(\lambda) + A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} + A_3(\lambda)e^{-t/\tau_3} \quad (\text{S1})$$

where  $\Delta A(\lambda)$  is the calculated absorbance change as a function of wavelength,  $\lambda$ ;  $A_0$ ,  $A_1$ ,  $A_2$ , and  $A_3$  are pre-exponential coefficients that vary with  $\lambda$ ;  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are time constants that do not depend on  $\lambda$ ;  $t$  is time; the  $A_2$ , and  $A_3$  terms are used as needed; and the expression is convoluted with a Gaussian instrument response function.

From the above model,  $A \rightarrow B$  fits were derived using the following equations:

$$A(\lambda) = A_0(\lambda) + A_1(\lambda) \quad (\text{S2})$$

$$B(\lambda) = A_0(\lambda) \quad (\text{S3})$$

$$\tau_{A \rightarrow B} = \tau_1 \quad (\text{S4})$$

where  $A(\lambda)$  and  $B(\lambda)$  are the difference spectra of species A and B as a function of wavelength and  $\tau_{A \rightarrow B}$  is the inverse of the rate at which A forms B.

$A \rightarrow B \rightarrow C$  fits were derived using the following equations:

$$A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_0(\lambda)(Q_2 - Q_1) \quad (\text{S5})$$

$$B(\lambda) = \frac{-A_2(\lambda)}{Q_1} + A_0(\lambda) \quad (\text{S6})$$

$$C(\lambda) = A_0(\lambda) \quad (\text{S7})$$

$$Q_1 = \frac{\frac{1}{\tau_1}}{\frac{1}{\tau_2} - \frac{1}{\tau_1}} \quad (\text{S8})$$

$$Q_2 = \frac{\frac{1}{\tau_2}}{\frac{1}{\tau_2} - \frac{1}{\tau_1}} \quad (\text{S9})$$

$$\tau_{A \rightarrow B} = \tau_1 \quad (\text{S10})$$

$$\tau_{B \rightarrow C} = \tau_2 \quad (\text{S11})$$

where  $A(\lambda)$ ,  $B(\lambda)$ , and  $C(\lambda)$  are the difference spectra of species A, B, and C as a function of wavelength and  $\tau_{A \rightarrow B}$  and  $\tau_{B \rightarrow C}$  are the inverse of the rates at which A forms B and B forms C, respectively.

$A \rightarrow B \rightarrow C \rightarrow D$  fits were derived using the following equations:

$$A(\lambda) = A_0(\lambda)(Q_4 + Q_5 - Q_6 - Q_7) + A_1(\lambda) + A_2(\lambda) \quad (\text{S12})$$

$$+ A_3(\lambda) \left( \frac{Q_4 + Q_5}{Q_3} \right)$$

$$B(\lambda) = A_0(\lambda) \left( \frac{Q_7 - Q_4}{Q_1} \right) - A_2(\lambda) \left( \frac{1}{Q_1} \right) - A_3(\lambda) \left( \frac{Q_4}{Q_1 Q_3} \right) \quad (\text{S13})$$

$$C(\lambda) = A_0(\lambda) + A_3(\lambda) \left( \frac{1}{Q_3} \right) \quad (\text{S14})$$

$$D(\lambda) = A_0(\lambda) \quad (\text{S15})$$

$$Q_3 = \frac{1}{\tau_1 \tau_2} \left[ \left( \frac{1}{\tau_1} - \frac{1}{\tau_3} \right) \left( \frac{1}{\tau_2} - \frac{1}{\tau_3} \right) \right]^{-1} \quad (\text{S16})$$

$$Q_4 = \frac{1}{\tau_1 \tau_2} \left[ \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \left( \frac{1}{\tau_2} - \frac{1}{\tau_3} \right) \right]^{-1} \quad (\text{S17})$$

$$Q_5 = \frac{1}{\tau_1 \tau_2} \left( \frac{1}{\tau_1 \tau_2} + \frac{1}{\tau_1 \tau_3} - \frac{1}{\tau_2 \tau_3} - \frac{1}{\tau_1^2} \right)^{-1} \quad (\text{S18})$$

$$Q_6 = Q_5 \left( \frac{\tau_1}{\tau_3} \right) \quad (\text{S19})$$

$$Q_7 = Q_4 \left( \frac{\tau_2}{\tau_3} \right) \quad (\text{S20})$$

$$\tau_{A \rightarrow B} = \tau_1 \quad (\text{S21})$$

$$\tau_{B \rightarrow C} = \tau_2 \quad (\text{S22})$$

$$\tau_{C \rightarrow D} = \tau_3 \quad (\text{S23})$$

where  $A(\lambda)$ ,  $B(\lambda)$ ,  $C(\lambda)$ , and  $D(\lambda)$  are the difference spectra of species A, B, C, and D as a function of wavelength and  $\tau_{A \rightarrow B}$ ,  $\tau_{B \rightarrow C}$ , and  $\tau_{C \rightarrow D}$  are the inverse of the rates at which A forms B, B forms C, and C forms D, respectively. All reported time constants are the average value from two experimental runs.

To fit the nanosecond transient absorption decay kinetics shown in Figure 8B for a

solution of  $8.27 \times 10^{-5}$  M Per-NMI and  $1.65 \times 10^{-4}$  M  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  in dichloromethane two different rate laws were considered:

$$\text{rate} = k[A] \quad (\text{S24})$$

$$\text{rate} = k[A][B], \quad [A]_0 = [B]_0 \quad (\text{S25})$$

where  $[A]$  and  $[B]$  are the concentration of A and B, and  $[A]_0$  and  $[B]_0$  are the initial concentrations of A and B. For the first rate law,  $[A]$  is given by:

$$[A] = [A]_0 e^{-kt} \quad (\text{S26})$$

where  $k$  is the rate constant and  $t$  is time. For the second rate law,  $[A]$  is given by:

$$[A] = \left[ \frac{1}{[A]_0} + kt \right]^{-1} \quad (\text{S27})$$

In both cases these expressions were convoluted with a Gaussian instrument response function with a full width at half the maximum height of 7 ns. Also, an exponential rise convoluted with the same Gaussian response function was added as needed to each fitting expression to account for the response of an electronic noise filter. Reported rate constants are the average of fits from two experimental runs.

To use the above functions to fit the decay of the  $\text{Per}^{+\bullet}$  and  $\text{Co(I)}$  signals at 550 nm (Figure 8B), the  $\Delta A$  vs. time data was used to calculate  $[\text{Per}^{+\bullet}]$  vs. time (or equivalently  $[\text{Co(I)}]$  versus time). At 550 nm, where the absorbance of  $^3\text{Per}$  is negligible compared to the strong combined  $\text{Per}^{+\bullet}$  and  $\text{Co(I)}$  absorption,  $\Delta A$  is given by:

$$\Delta A = \varepsilon_{\text{Co(I)}} b [\text{Co(I)}] + \varepsilon_{\text{Per}^{+\bullet}} b [\text{Per}^{+\bullet}] \quad (\text{S28})$$

where  $\varepsilon_{\text{Co(I)}}$  is the extinction coefficient of the dissociated  $\text{Co(I)}$  catalyst in units of  $\text{M}^{-1} \text{cm}^{-1}$ ,  $b$  is the pathlength in units of cm,  $[\text{Co(I)}]$  is the molar concentration of the dissociated  $\text{Co(I)}$

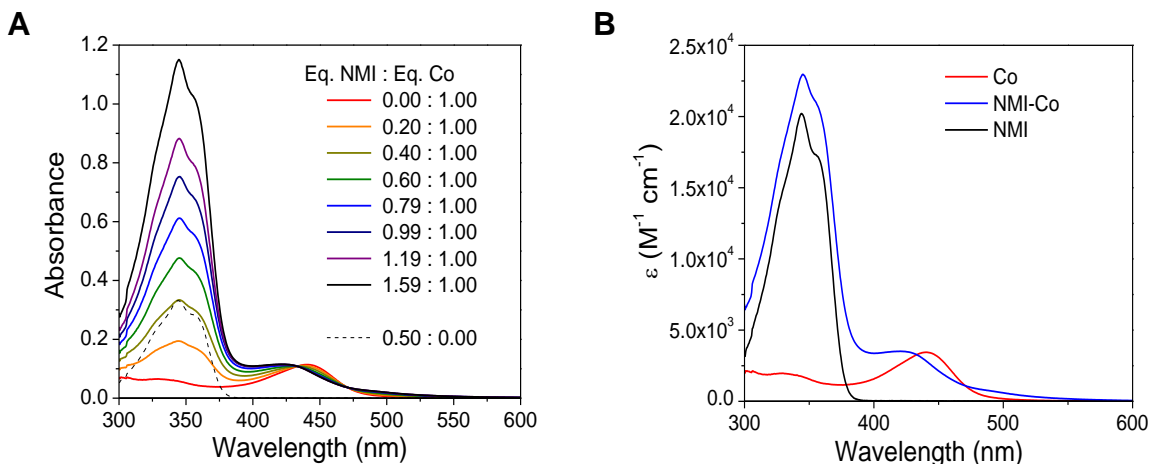
catalyst,  $\epsilon_{Per^+}$  is the extinction coefficient of the perylene cation in units of  $M^{-1} cm^{-1}$ , and  $[Per^+]$  is the molar concentration of the perylene cation. Since electron transfer generates an equal amount of the Co(I) catalyst and perylene cation, in this case  $[Per^+] = [Co(I)]$  and the concentration of these species are given by:

$$[Per^+] = [Co(I)] = \frac{\Delta A}{b(\epsilon_{Co(I)} + \epsilon_{Per^+})} \quad (S29)$$

The pathlength,  $b$ , for the experiment was 0.2 cm. The value of  $\epsilon_{Co(I)}$  at 550 nm where the decay of the absorbance was fit has been previously reported as  $4.7 \times 10^3 M^{-1} cm^{-1}$ .<sup>6</sup> The value of  $\epsilon_{Per^+}$  at 550 nm can be estimated from the data in Figures 2 and S5. First, from Figure 2, the extinction coefficient of Per-NMI at the maximum of the lowest energy perylene transition near 445 nm is  $4.4 \times 10^4 M^{-1} cm^{-1}$ . Since the perylene cation is reported to have comparatively negligible absorption near this transition,<sup>7</sup> the perylene cation extinction coefficient at 550 nm can be estimated by comparing the ratio of absorbance gain at 550 nm in Figure S5 as perylene is oxidized compared to the absorbance loss at the peak of the lowest energy perylene transition. From this analysis  $\epsilon_{Per^+}$  at 550 nm is estimated to be  $2.7 \times 10^4 M^{-1} cm^{-1}$ . Using the expression above for  $\Delta A$ , the resulting fits were converted to absorbance units and graphed in Figure 8 to show how well each rate equation modeled the observed kinetic data.

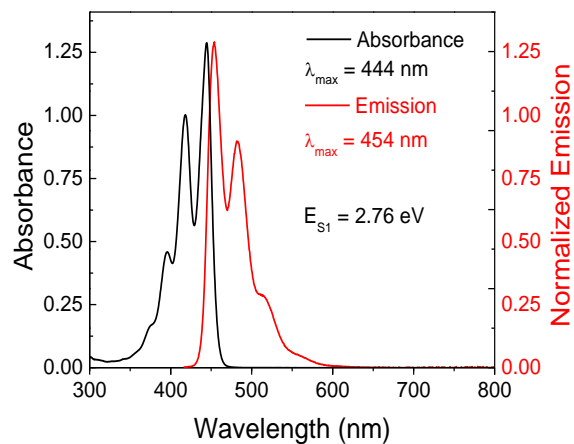
The nanosecond transient absorption decay kinetics of Per-NMI-NDI in dichloromethane (See Figure S12) were fit to a sum of two exponentials convoluted with a Gaussian instrument response function with a full width at half the maximum height of 7 ns. The reported value is the average of separate kinetics measurements at 555 nm, 560 nm, and 565 nm.

## II. NMI to catalyst binding study



**Figure S1.** A.) UV-Vis absorption spectra of [Co(dmgBF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and NMI in dichloromethane in varying concentrations reported here as  $1.65 \times 10^{-4}$  M equivalents (eq.). B.) Molar extinction coefficients for the Co catalyst, ligand bound catalyst (NMI-Co), and free ligand (NMI) determined by SIVVU as a model for the absorbance data (SIVVU is available from Dr. Douglas Vander Griend at Calvin College in Grand Rapids, Michigan).

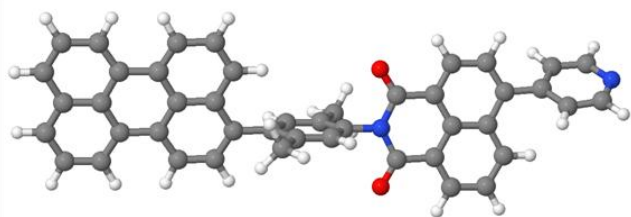
## III. Steady state absorbance and emission spectra



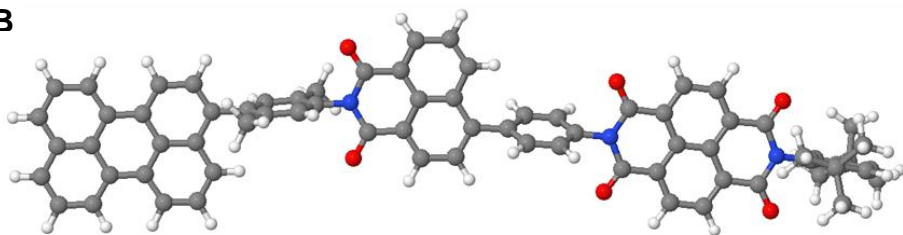
**Figure S2.** Steady state absorbance spectrum of Per in dichloromethane (black,  $\lambda_{\max} = 444$  nm) and steady state emission spectrum of Per with  $\lambda_{\text{ex}} = 396$  nm in dichloromethane (red,  $\lambda_{\max} = 454$  nm). Based on the average of the absorption and emission maxima, the S<sub>1</sub> energy of Per is 2.76 eV.

#### IV. Calculated geometries of Per-NMI and Per-NMI-NDI

A



B



**Figure S3.** A.) Structure of Per-NMI at the B3LYP/6-31G(d,p) level of theory. B.) Structure of Per-NMI-NDI at the B3LYP/6-31G(d,p) level of theory.

**Table S1:** Geometry in Å of Per-NMI optimized with B3LYP/6-31G(d,p). The absolute energy is  $-1991.7637081612 E_h$ . There are 0 imaginary frequencies.

| Atom Type | X        | Y        | Z        |
|-----------|----------|----------|----------|
| C         | 10.3215  | -1.07315 | 0.636725 |
| C         | 9.702374 | 0.173582 | 0.36798  |
| C         | 8.27941  | 0.236827 | 0.196271 |
| C         | 7.506664 | -0.96381 | 0.307237 |
| C         | 8.169415 | -2.15971 | 0.565827 |
| C         | 9.564655 | -2.21774 | 0.730562 |
| C         | 10.47254 | 1.359391 | 0.266697 |
| C         | 9.860497 | 2.563039 | 0.005645 |
| C         | 8.466368 | 2.62892  | -0.16682 |
| C         | 7.659371 | 1.498004 | -0.08074 |
| C         | 6.194551 | 1.561249 | -0.25795 |
| C         | 5.415686 | 0.363722 | -0.12866 |
| C         | 6.040779 | -0.89462 | 0.154118 |
| C         | 3.986926 | 0.432938 | -0.27341 |
| C         | 3.19739  | -0.75087 | -0.11701 |
| C         | 3.835902 | -1.94478 | 0.15835  |
| C         | 5.231935 | -2.01713 | 0.285048 |

|   |          |          |          |
|---|----------|----------|----------|
| C | 5.540235 | 2.755828 | -0.53962 |
| C | 4.145167 | 2.819531 | -0.68438 |
| C | 3.378357 | 1.685453 | -0.54722 |
| C | 1.702957 | -0.7081  | -0.17755 |
| C | 0.995408 | -0.69579 | 1.030768 |
| C | -0.39943 | -0.65911 | 1.090015 |
| C | -1.08381 | -0.63888 | -0.13056 |
| C | -0.40162 | -0.66899 | -1.34311 |
| C | 0.994898 | -0.7047  | -1.39667 |
| N | -2.53161 | -0.58549 | -0.14021 |
| C | -3.23076 | -1.80546 | -0.25013 |
| C | -4.71431 | -1.72832 | -0.20621 |
| C | -5.37421 | -0.48054 | -0.0614  |
| C | -4.61618 | 0.711519 | 0.05369  |
| C | -3.13176 | 0.67775  | 0.028062 |
| C | -6.80397 | -0.43057 | -0.01104 |
| C | -7.44309 | 0.845976 | 0.137385 |
| C | -6.66047 | 1.986003 | 0.262775 |
| C | -5.25667 | 1.924411 | 0.220433 |
| C | -5.44422 | -2.90058 | -0.28198 |
| C | -6.84935 | -2.86277 | -0.20305 |
| C | -7.51357 | -1.66065 | -0.06803 |
| C | -8.92402 | 0.992783 | 0.160573 |
| C | -9.73784 | 0.547613 | -0.89156 |
| C | -11.1139 | 0.762448 | -0.82283 |
| N | -11.7265 | 1.371742 | 0.200227 |
| C | -10.9463 | 1.796782 | 1.201462 |
| C | -9.56131 | 1.637918 | 1.22925  |
| O | -2.45022 | 1.682926 | 0.157183 |
| O | -2.63151 | -2.86228 | -0.36423 |
| C | 1.707061 | -0.74439 | -2.72835 |
| C | -1.12001 | -0.6232  | 2.413987 |
| H | 11.40012 | -1.10515 | 0.764367 |
| H | 7.611993 | -3.08475 | 0.647535 |
| H | 10.03689 | -3.17437 | 0.933908 |
| H | 11.54931 | 1.298187 | 0.398148 |
| H | 10.44922 | 3.472519 | -0.0698  |
| H | 8.028778 | 3.599533 | -0.36811 |
| H | 3.243091 | -2.8458  | 0.28602  |
| H | 5.667295 | -2.98592 | 0.500442 |
| H | 6.103863 | 3.674107 | -0.64932 |
| H | 3.674051 | 3.774579 | -0.89755 |



|   |          |          |          |
|---|----------|----------|----------|
| H | 2.299104 | 1.738676 | -0.63833 |
| H | 1.557898 | -0.70832 | 1.960329 |
| H | -0.97533 | -0.66888 | -2.26529 |
| H | -7.14595 | 2.950749 | 0.370868 |
| H | -4.65279 | 2.820791 | 0.311082 |
| H | -4.90938 | -3.83827 | -0.38613 |
| H | -7.41416 | -3.78895 | -0.24011 |
| H | -8.59462 | -1.65189 | 0.011379 |
| H | -9.30573 | 0.063966 | -1.76163 |
| H | -11.7563 | 0.430601 | -1.63637 |
| H | -11.4531 | 2.288634 | 2.029537 |
| H | -8.98589 | 1.997725 | 2.076147 |
| H | 1.000421 | -0.91808 | -3.5444  |
| H | 2.45994  | -1.53859 | -2.75275 |
| H | 2.232323 | 0.195863 | -2.93207 |
| H | -1.60809 | 0.345952 | 2.567358 |
| H | -0.42024 | -0.78134 | 3.238654 |
| H | -1.89208 | -1.39765 | 2.474846 |

**Table S2:** Geometry in Å of Per-NMI-NDI optimized with B3LYP/6-31G(d,p). The absolute energy is -3467.6981288439  $E_h$ .

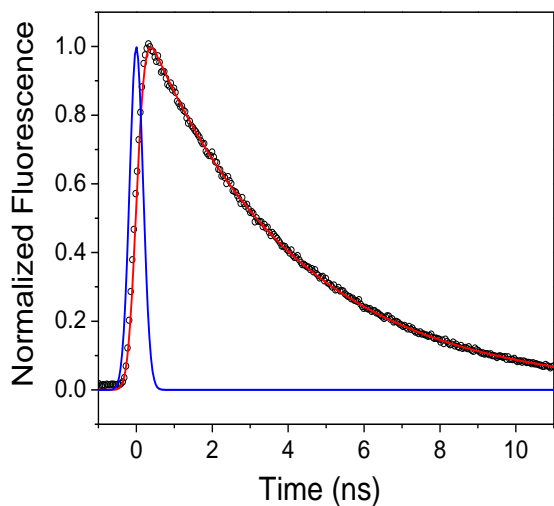
| Atom Type | X        | Y        | Z        |
|-----------|----------|----------|----------|
| C         | 18.5524  | -1.27385 | 1.167147 |
| C         | 17.99637 | -0.0307  | 0.772635 |
| C         | 16.5821  | 0.07515  | 0.553325 |
| C         | 15.75489 | -1.0793  | 0.738801 |
| C         | 16.35709 | -2.27306 | 1.124725 |
| C         | 17.7432  | -2.37283 | 1.338457 |
| C         | 18.82003 | 1.109132 | 0.59234  |
| C         | 18.26744 | 2.309477 | 0.210931 |
| C         | 16.88225 | 2.417613 | -0.00487 |
| C         | 16.0246  | 1.33316  | 0.155115 |
| C         | 14.56875 | 1.442477 | -0.06607 |
| C         | 13.73697 | 0.289877 | 0.12384  |
| C         | 14.29918 | -0.96694 | 0.522666 |
| C         | 12.31874 | 0.402849 | -0.08017 |
| C         | 11.47548 | -0.73838 | 0.115665 |
| C         | 12.05374 | -1.93141 | 0.504355 |
| C         | 13.43962 | -2.04467 | 0.699715 |

|   |          |          |          |
|---|----------|----------|----------|
| C | 13.974   | 2.639525 | -0.45075 |
| C | 12.5881  | 2.748243 | -0.6443  |
| C | 11.77155 | 1.65691  | -0.45772 |
| C | 9.991146 | -0.63351 | -0.03804 |
| C | 9.207221 | -0.55718 | 1.119913 |
| C | 7.8184   | -0.40562 | 1.084557 |
| C | 7.220729 | -0.34275 | -0.17932 |
| C | 7.978169 | -0.44593 | -1.34289 |
| C | 9.366415 | -0.59594 | -1.30203 |
| N | 5.790039 | -0.14441 | -0.29811 |
| C | 5.343341 | 1.157322 | -0.61032 |
| C | 3.874748 | 1.346868 | -0.72765 |
| C | 2.98197  | 0.266783 | -0.5036  |
| C | 3.492541 | -1.02015 | -0.19816 |
| C | 4.953302 | -1.25661 | -0.08641 |
| C | 1.568521 | 0.479034 | -0.59547 |
| C | 0.687001 | -0.62511 | -0.33778 |
| C | 1.233644 | -1.8734  | -0.06769 |
| C | 2.622643 | -2.07604 | -0.00078 |
| C | 3.389343 | 2.598444 | -1.06061 |
| C | 2.003645 | 2.804214 | -1.1962  |
| C | 1.114618 | 1.772273 | -0.97249 |
| C | -0.79384 | -0.47868 | -0.32836 |
| C | -1.59149 | -1.3532  | -1.08344 |
| C | -2.98042 | -1.27571 | -1.03748 |
| C | -3.59362 | -0.32686 | -0.22157 |
| C | -2.82157 | 0.549086 | 0.539211 |
| C | -1.43235 | 0.474939 | 0.481868 |
| O | 5.425482 | -2.35005 | 0.186089 |
| O | 6.139568 | 2.069268 | -0.76662 |
| N | -5.03627 | -0.25931 | -0.15885 |
| C | -5.70597 | -1.3349  | 0.469071 |
| C | -7.18968 | -1.25618 | 0.512045 |
| C | -7.86185 | -0.15028 | -0.06103 |
| C | -7.14718 | 0.907764 | -0.67226 |
| C | -5.66177 | 0.873623 | -0.72844 |
| C | -7.91239 | -2.27581 | 1.110908 |
| C | -9.31862 | -2.22891 | 1.146312 |
| C | -9.99936 | -1.16111 | 0.583915 |
| C | -9.28251 | -0.10261 | -0.0237  |
| C | -9.95678 | 1.00097  | -0.59815 |
| C | -9.23569 | 2.025675 | -1.1891  |

|   |          |          |          |
|---|----------|----------|----------|
| C | -7.82951 | 1.979291 | -1.22633 |
| C | -11.4882 | -1.13737 | 0.610318 |
| N | -12.1127 | -0.02946 | 0.007201 |
| C | -11.4438 | 1.063384 | -0.57677 |
| O | -12.0604 | 2.000376 | -1.05504 |
| O | -12.1431 | -2.03773 | 1.109736 |
| O | -5.0863  | -2.27185 | 0.941226 |
| O | -5.00419 | 1.764493 | -1.23764 |
| C | -13.5653 | 0.035576 | 0.071832 |
| C | -14.416  | -0.54957 | -0.88094 |
| C | -15.7893 | -0.39171 | -0.60616 |
| C | -16.2774 | 0.305521 | 0.489662 |
| C | -15.4168 | 0.899806 | 1.423476 |
| C | -14.0555 | 0.736868 | 1.180955 |
| C | -15.9749 | 1.676741 | 2.627064 |
| C | -14.8591 | 2.184692 | 3.558176 |
| C | -16.7814 | 2.893245 | 2.113774 |
| C | -16.9072 | 0.754187 | 3.448026 |
| C | -14.0212 | -1.388   | -2.12477 |
| C | -14.954  | -1.03998 | -3.31345 |
| C | -14.1885 | -2.88323 | -1.76124 |
| C | -12.5845 | -1.16816 | -2.6458  |
| C | 10.16024 | -0.71392 | -2.58198 |
| C | 7.012123 | -0.31952 | 2.355287 |
| H | 19.62451 | -1.34131 | 1.329148 |
| H | 15.7568  | -3.16278 | 1.270844 |
| H | 18.16756 | -3.32607 | 1.639617 |
| H | 19.88944 | 1.016088 | 0.759342 |
| H | 18.89648 | 3.184017 | 0.073751 |
| H | 16.49157 | 3.384036 | -0.3005  |
| H | 11.42207 | -2.80084 | 0.661363 |
| H | 13.82733 | -3.01142 | 0.999044 |
| H | 14.57967 | 3.524195 | -0.60419 |
| H | 12.1629  | 3.704192 | -0.93529 |
| H | 10.6993  | 1.745498 | -0.58954 |
| H | 9.703926 | -0.59595 | 2.085253 |
| H | 7.470625 | -0.40311 | -2.30164 |
| H | 0.566008 | -2.70524 | 0.133395 |
| H | 3.034513 | -3.05372 | 0.224488 |
| H | 4.098043 | 3.403092 | -1.22396 |
| H | 1.632746 | 3.782813 | -1.48419 |
| H | 0.05179  | 1.942546 | -1.09911 |

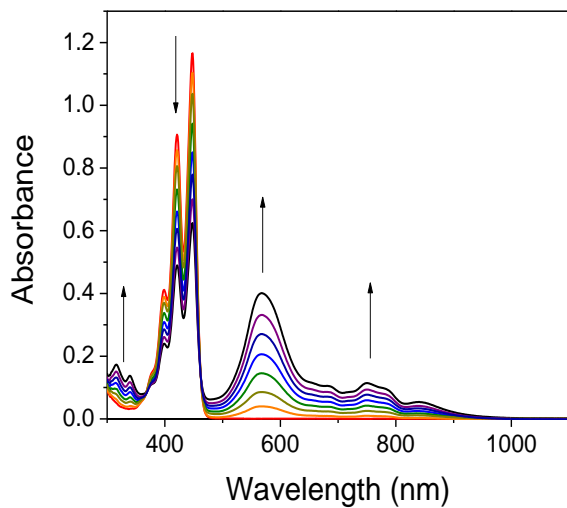
|   |          |          |          |
|---|----------|----------|----------|
| H | -1.11673 | -2.09129 | -1.72225 |
| H | -3.5872  | -1.9538  | -1.62782 |
| H | -3.30578 | 1.280998 | 1.176435 |
| H | -0.83736 | 1.144515 | 1.094605 |
| H | -7.37177 | -3.10866 | 1.546473 |
| H | -9.89148 | -3.0248  | 1.609113 |
| H | -9.77814 | 2.85771  | -1.62392 |
| H | -7.25799 | 2.775601 | -1.69013 |
| H | -16.5163 | -0.83313 | -1.27769 |
| H | -17.3533 | 0.382435 | 0.612637 |
| H | -13.3216 | 1.156226 | 1.858734 |
| H | -15.2996 | 2.716526 | 4.407197 |
| H | -14.1857 | 2.881067 | 3.047858 |
| H | -14.2621 | 1.358074 | 3.956524 |
| H | -17.2078 | 3.452453 | 2.954259 |
| H | -17.6058 | 2.585423 | 1.463723 |
| H | -16.1421 | 3.572812 | 1.541062 |
| H | -17.3225 | 1.296388 | 4.304782 |
| H | -16.3635 | -0.11685 | 3.828046 |
| H | -17.7478 | 0.387153 | 2.852017 |
| H | -14.6343 | -1.59289 | -4.20247 |
| H | -14.9114 | 0.029015 | -3.54537 |
| H | -15.9973 | -1.30641 | -3.13226 |
| H | -13.9331 | -3.51538 | -2.61991 |
| H | -15.2191 | -3.10661 | -1.46971 |
| H | -13.5392 | -3.15267 | -0.92351 |
| H | -12.4747 | -1.70546 | -3.59293 |
| H | -11.8186 | -1.56279 | -1.97692 |
| H | -12.3814 | -0.11207 | -2.84155 |
| H | 9.497356 | -0.80523 | -3.4467  |
| H | 10.81771 | -1.58901 | -2.56097 |
| H | 10.80156 | 0.160151 | -2.74074 |
| H | 6.386368 | 0.579244 | 2.375209 |
| H | 7.66752  | -0.29157 | 3.229493 |
| H | 6.350803 | -1.18696 | 2.454242 |

## V. Time resolved fluorescence

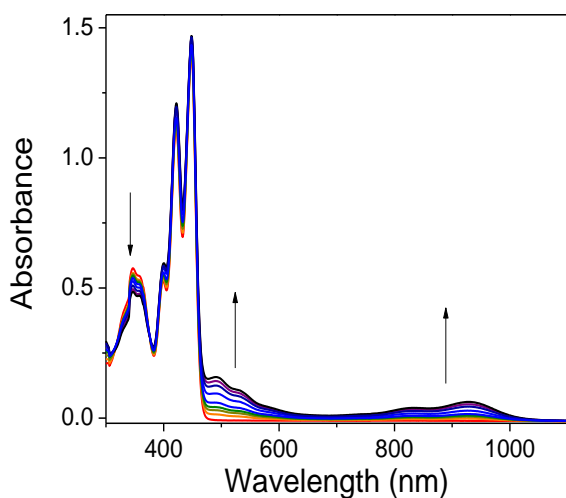


**Figure S4.** Observed fluorescence decay for Per in dichloromethane following excitation with a 390 nm laser pulse (black circles), instrument response function (blue line), and fit (red line).

## VI. Spectroelectrochemistry

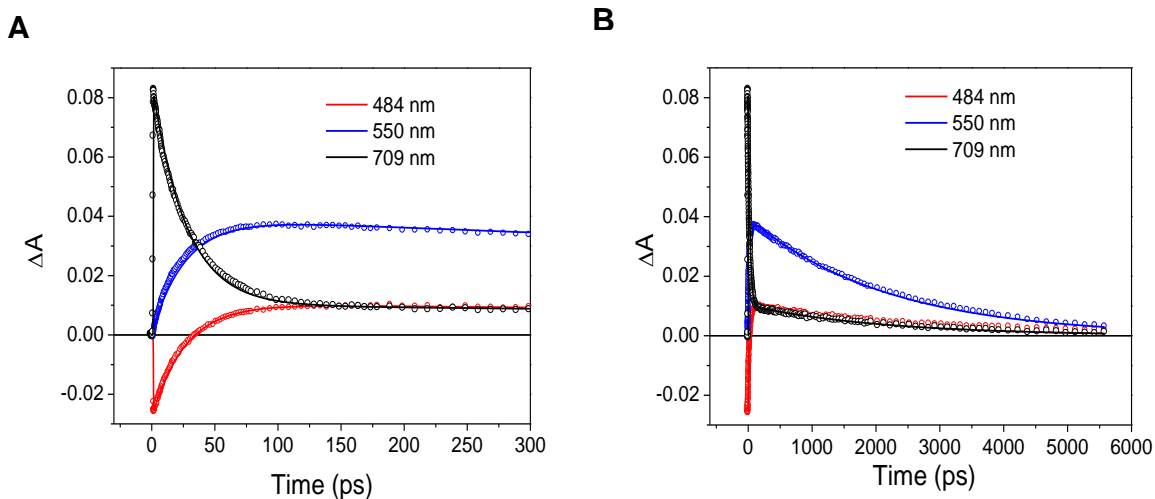


**Figure S5.** Spectral changes for Per in benzonitrile with 0.1 M TBAPF<sub>6</sub> at an applied potential increased from 0.00 to 1.12 V vs. SCE.

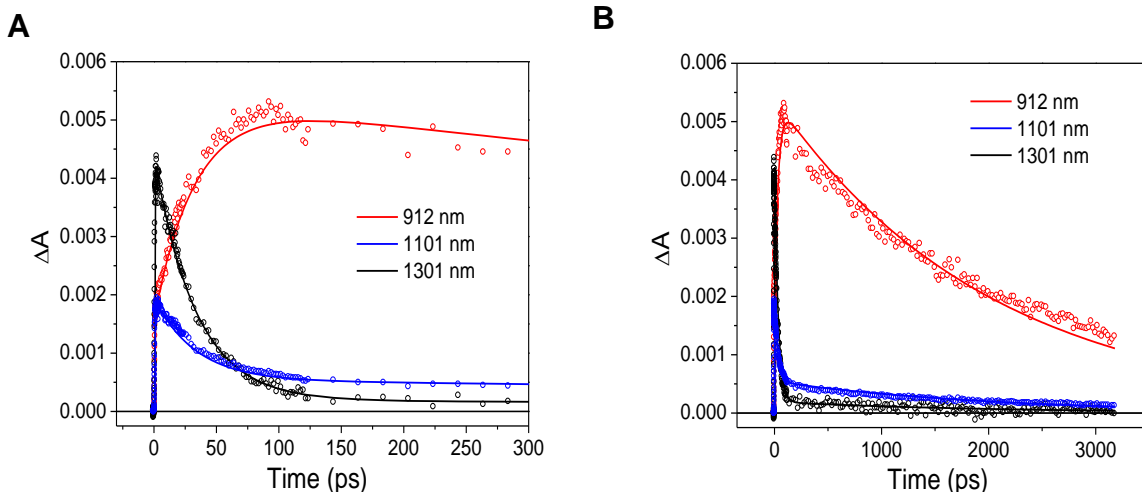


**Figure S6.** Spectral changes for Per-NMI in benzonitrile with 0.1 M TBAPF<sub>6</sub> at an applied potential decreased from 0.00V to -1.37 V vs. SCE.

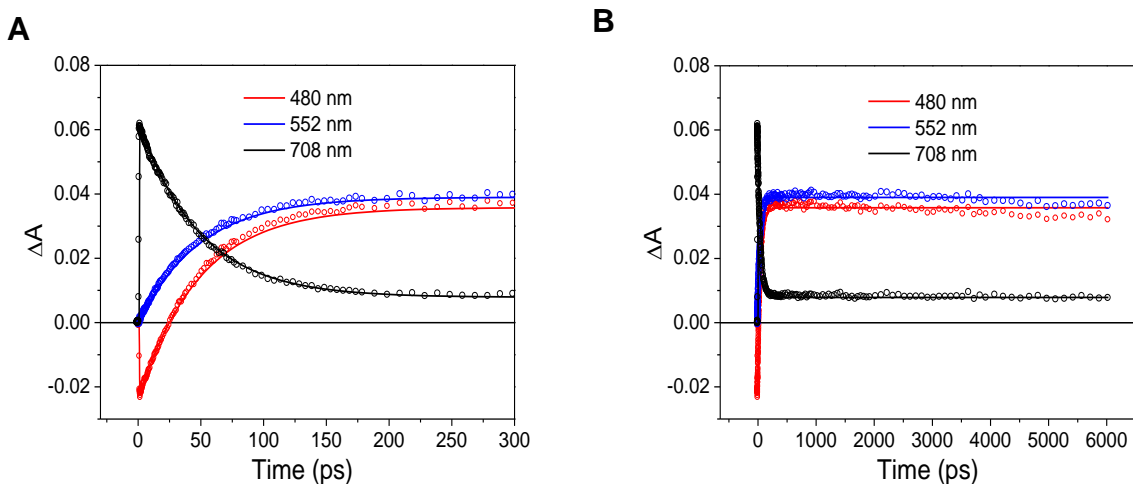
## VII. Femtosecond transient kinetics and fits



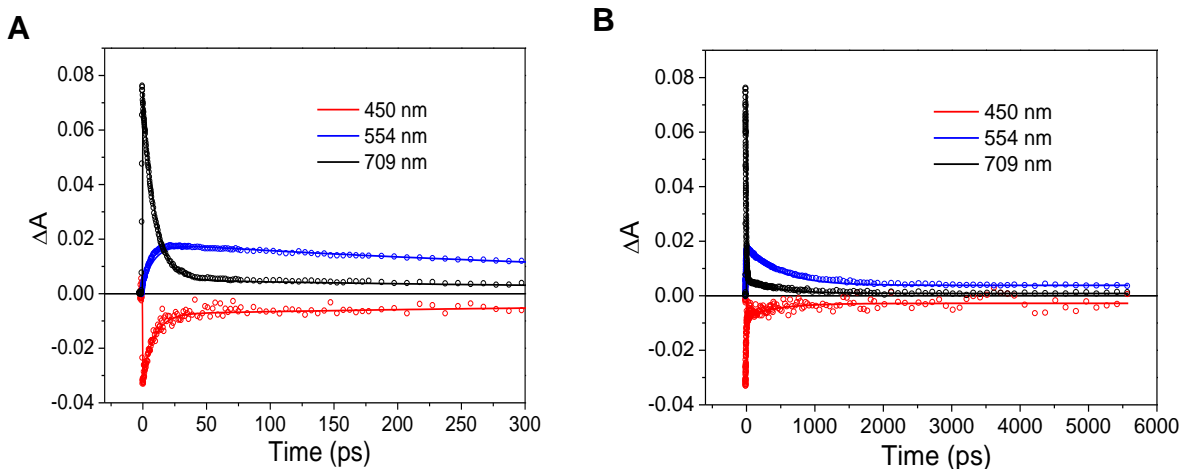
**Figure S7.** Femtosecond transient absorption kinetics of Per-NMI in dichloromethane following excitation with a 416 nm laser pulse (circles) and fits obtained by singular value decomposition and global fitting to an A  $\rightarrow$  B  $\rightarrow$  C mechanism (solid lines) for A.) short pump-to-probe time delays and B.) the entire data collection time window.



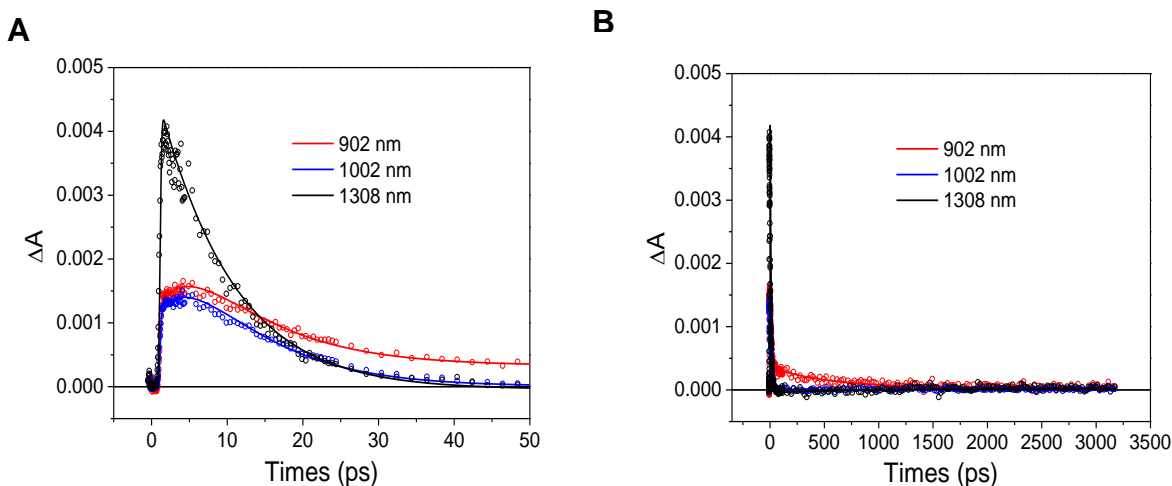
**Figure S8.** Femtosecond near-infrared transient absorption kinetics of Per-NMI in dichloromethane following excitation with a 416 nm laser pulse (circles) and fits obtained by singular value decomposition and global fitting to an  $A \rightarrow B \rightarrow C$  mechanism (solid lines) for A.) short pump-to-probe time delays and B.) the entire data collection time window.



**Figure S9.** Femtosecond transient absorption kinetics of Per-NMI-NDI in dichloromethane following excitation with a 416 nm laser pulse (circles) and fits obtained by singular value decomposition and global fitting to an  $A \rightarrow B$  model (solid lines) for A.) short pump-to-probe time delays and B.) the entire data collection time window.



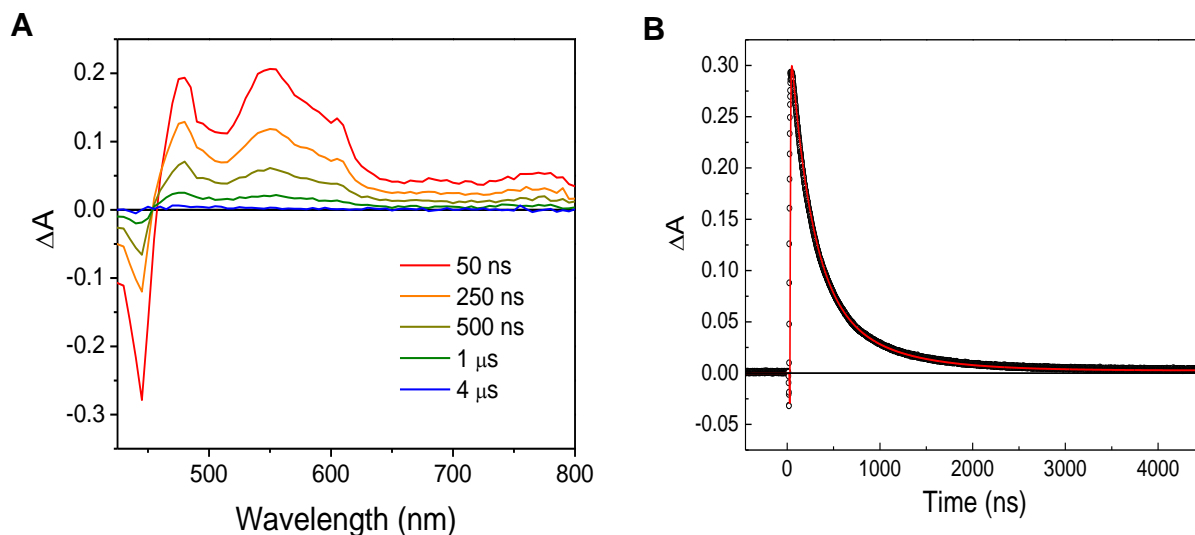
**Figure S10.** Femtosecond transient absorption kinetics of  $8.27 \times 10^{-5}$  M Per-NMI and  $1.65 \times 10^{-4}$  M  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  in dichloromethane following excitation with a 416 nm laser pulse (circles) and fits obtained via singular value decomposition and global fitting to an  $A \rightarrow B \rightarrow C$  model (solid lines) for A.) short pump-to-probe time delays and B.) the entire data collection time window.



**Figure S11.** Femtosecond near-infrared transient absorption kinetics of  $8.27 \times 10^{-5}$  M Per-NMI and  $1.65 \times 10^{-4}$  M  $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$  in dichloromethane following excitation with a 416 nm laser pulse (circles) and fits obtained via singular value decomposition and global fitting using an  $A \rightarrow B \rightarrow C \rightarrow D$  model with the  $A \rightarrow B$  rate fixed to  $\tau = 9.0$  ps and the  $C \rightarrow D$  rate fixed to  $\tau = 520$  ps based on the results from the 450 – 800 nm region (solid lines) for A.) short pump-to-probe time delays and B.) the entire data collection time window.

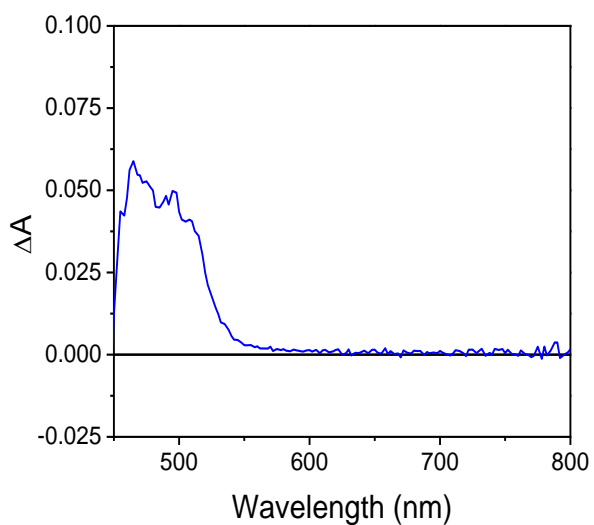


### VIII. Per-NMI-NDI nanosecond transient absorption



**Figure S12.** A.) Nanosecond transient absorption spectra of Per-NMI-NDI in dichloromethane. B.) Nanosecond transient absorption kinetics of Per-NMI-NDI in dichloromethane at 560 nm (black circles) and fit (red line).

### IX. $^3$ Per-NMI absorption spectrum



**Figure S13.** Per-NMI triplet spectrum in dichloromethane detected by nanosecond transient absorption spectroscopy after triplet energy transfer to Per-NMI from photogenerated triplet anthracene.

## X. Estimation of the diffusion limited charge recombination rate

As noted in the main text, the diffusion limited rate,  $k_D$ , for a bimolecular reaction between two charged chemical species A and B can be estimated using equation S30 below.<sup>8</sup>

$$k_D = 4\pi(D_A + D_B)\beta \quad (\text{S30})$$

$D_A$  and  $D_B$  are the diffusion coefficients of the oppositely charged reactants A and B and  $\beta$  is given by equation S31.<sup>8</sup>

$$\beta = \frac{-z_A z_B r_0}{1 - \exp\left(\frac{z_A z_B r_0}{R}\right)} \quad (\text{S31})$$

$z_A$  and  $z_B$  are the charges of the A and B reactants,  $R$  is the sum of the radii of A and B, and  $r_0$  is given by equation S32.<sup>8</sup>

$$r_0 = \frac{e^2}{\epsilon k_B T} \quad (\text{S32})$$

In equation S32,  $e$  is the charge of an electron and  $\epsilon$  is the dielectric constant of the solvent at temperature  $T$ . At 25 °C the dielectric constant of dichloromethane is 8.82,<sup>9</sup> and  $r_0 = 6.4$  nm. The values of  $D_A$  and  $D_B$  can be measured using cyclic voltammetry and equation S33 by determining the slope of the peak current versus the square root of the scan rate.

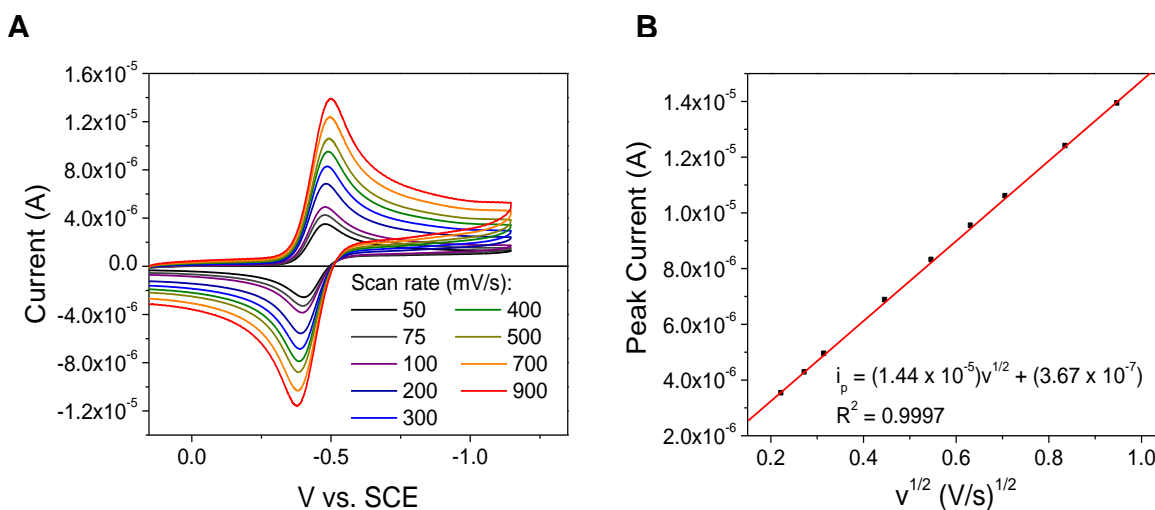
$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad (\text{S33})$$

For the analyte of interest,  $i_p$  (A) is the peak current of a redox couple,  $n$  is the number of electrons,  $A$  (cm<sup>2</sup>) is the surface area of the electrode,  $D$  (cm<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient,  $C$  (mol cm<sup>-3</sup>) is the concentration, and  $v$  (V/s) is the scan rate. Cyclic voltammograms at scan rates from 50 mV/s to 900 mV/s and corresponding plots of  $i_p$  versus  $v^{1/2}$  are shown in Figures S14 and S15 for the cobalt catalyst and Per-NMI in benzonitrile. The electrode area was 0.0314 cm<sup>2</sup>. The analyte concentration was 1.0 mM. Based on the slopes of linear fits the diffusion

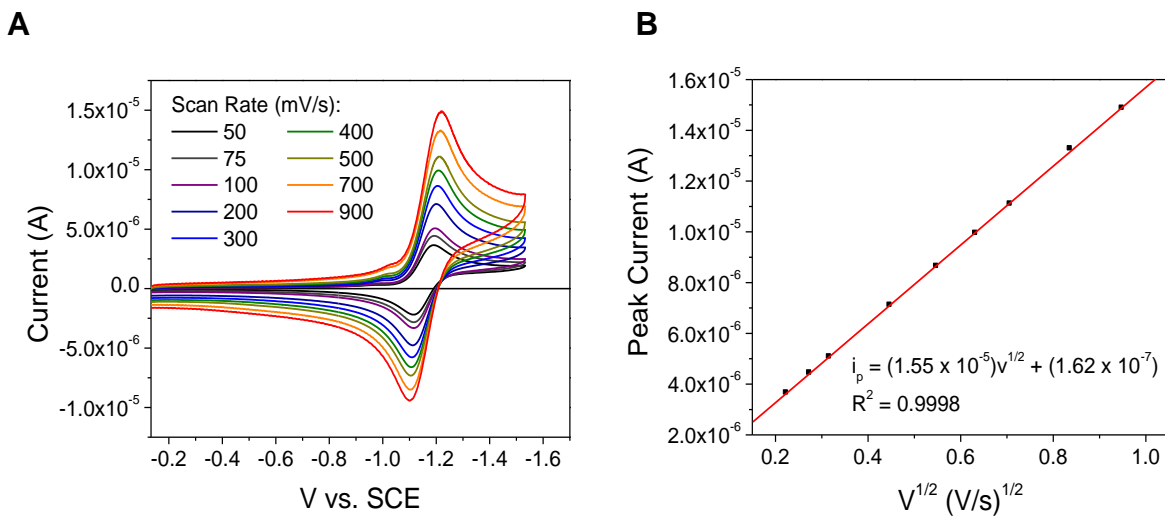
coefficients can be estimated to be  $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively, for the cobalt catalyst and Per-NMI in benzonitrile. Using the Einstein-Stokes relationship below, equation S34,<sup>8</sup> the diffusion coefficients in dichloromethane can be calculated based on the relative solvent viscosities,  $\eta$ , of benzonitrile and dichloromethane (1.267 mPa s for benzonitrile at 25 °C and 0.413 mPa s for dichloromethane at 25 °C)<sup>10</sup>.

$$D = \frac{k_B T}{6\pi r \eta} \quad (\text{S34})$$

In dichloromethane the diffusion coefficients are estimated to be  $8.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively, for the cobalt catalyst and Per-NMI. The sum of the radii,  $R$ , which is equal to 11 Å, can also be determined using equation S34, which gives the individual radii of the cobalt catalyst and Per-NMI. Substituting the appropriate values into equation S31 and then S30 gives a  $\beta$  value of 6.4 nm and an estimated  $k_D$  of  $9.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

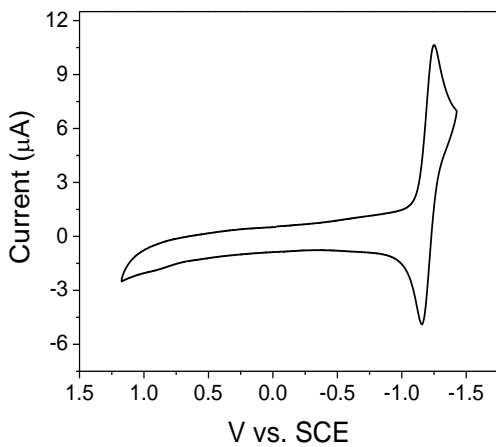


**Figure S14.** A.) Cyclic voltammograms of [Co(dmgbF<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] at scan rate from 50 mV/s to 900 mV/s. B.) Plot of the peak current,  $i_p$ , versus the square root of the scan rate,  $v^{1/2}$ .

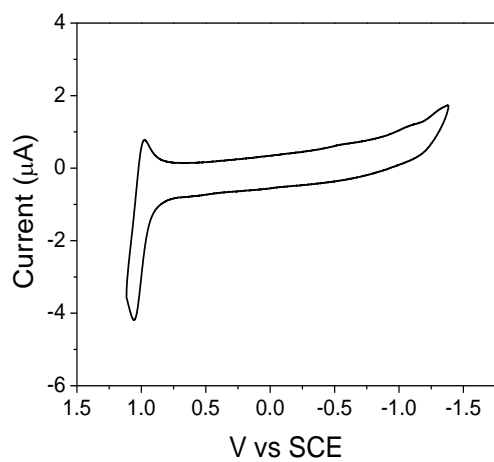


**Figure S15.** A.) Cyclic voltammograms of Per-NMI at scan rate from 50 mV/s to 900 mV/s. B.) Plot of the peak current,  $i_p$ , versus the square root of the scan rate,  $v^{1/2}$ .

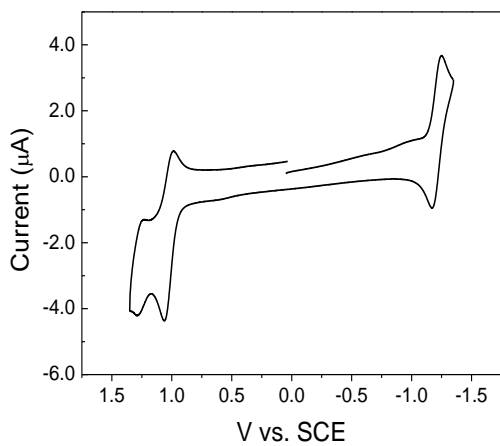
## XI. Cyclic voltammograms



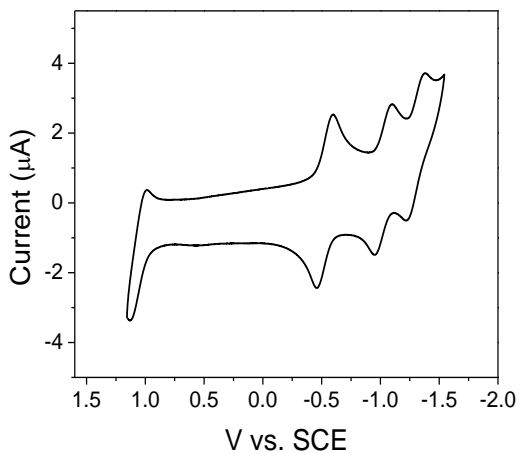
**Figure S16.** Cyclic voltammogram of NMI.



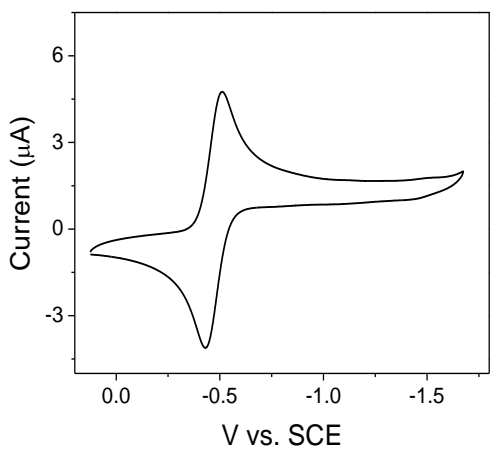
**Figure S17.** Cyclic voltammogram of Per.



**Figure S18.** Cyclic voltammogram of Per-NMI.



**Figure S19.** A) Cyclic voltammogram of Per-NMI-NDI.



**Figure S20.** Cyclic voltammogram of  $[\text{Co}(\text{dmgbF}_2)_2(\text{H}_2\text{O})_2]$ .

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