COBALT REDOX MEDIATORS FOR DYE-SENSITIZED SOLAR CELLS

By

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ABSTRACT

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Dye-sensitized solar cells have become an affordable alternative to conventional photovoltaics. Their efficiencies have become competitive by continued optimization of the semiconductor, dye, redox shuttle, and counter electrode. This thesis will evaluate low-spin Co(II) redox shuttles' ability to minimize photovoltage losses due to dye regeneration and recombination to semiconductor electrons. Their synthesis and properties will be described along with a comparison to typical high-spin Co(II) redox shuttles. The kinetic properties will be evaluated in terms of Marcus Theory with a particular focus being made on reorganization energy and free energy of electron transfer events. Chapter 1 will describe the motivation for dye-sensitized solar cells along with a description of their development and operation. Chapter 2 and 3 will describe the two extremes of redox potential of the redox shuttle. Chapter 4 demonstrates a system with a tunable potential inbetween. Chapter 5 will report other redox shuttle candidates and future directions to surpass 15% power conversion efficiency with low-spin Co(II) redox shuttles.

Copyright by AUSTIN L RAITHEL 2022 I dedicate this thesis to my parents (Daryl and Lori Raithel) and my wife Victoria Raithel. This work would not have been possible without your love and support. Thank you for being open to what I felt called to do.

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KEY TO ABBREVIATIONS

Α	Absorbance
A∞	Absorbance at last time infinity
A_1	Pre-exponential factor 1
A_2	Pre-exponential factor 2
A_0	Absorbance at time zero
a_1	radius 1
a_2	radius 2
ACN or MeCN	Acetonitrile
AgNO ₃	Silver nitrate
AgCl	Silver chloride
Ag ₂ O	Silver(I) Oxide
AgOTf	Silver Trifluoromethansulfonate
ALD	Atomic Layer Deposition
AM 1.5	Air mass coefficient of 1.5
α	Exponential electron trap distribution parameter
bpy	2,2'-Bipyridine
BF ₄	Tetrafluoroborate
С	Concentration
¹³ C	Carbon-13
СВ	Conduction band
CE	Counter electrode

CHN	Carbon, Hydrogen, Nitrogen	
CN	Cyanide	
CO ₂	Carbon dioxide	
Co ^{3+/2+}	Co(II/III) redox couple	
CoCl ₂ •6H ₂ O	Cobalt dichloride hexahydrate	
Co(OTf) ₂	Cobalt(II) Triflate	
C_{μ}	Chemical capacitance	
CV	Cyclic voltammetry	
D35cpdt or LEG4	3-{6-{4-[bis(2',4'-dibutyloxybiphenyl-4-yl)amino-]phenyl}-4,4-dihexy	
Dif	Redox shuttle diffusion	
DCM	Dichloromethane	
DMA	Dimethylamino	
DMP-CN	2,6-dimethylphenyl isocyanide	
DMSO	Dimethyl sulfoxide	
DPV	Differential pulse voltammetry	
DSSC	Dye-sensitized solar cell	
DTBP	2,6-Di-tert-butylpyridine	
ΔA_0	Change in absorbance at time zero	
Δd	Change in metal to ligand bond distance	
Δv	observed frequency shift	
3	Extinction coefficient	
ε_0	Dielectric constant	
E _{vac}	Vacuum permittivity	

Ε	Potential
<i>E</i> _{1/2}	Redox potential from half wave potential
Ec	Conduction band potential
E _F	Fermi level
EDOT	3,4-Ethylenedioxythiophene
eqv or eq	Equivalents
E_{sol}	Solution potential
eV	Electron volt
f_1	Bond force constant 1
f_2	Bond force constant 2
f_{12}	Non-linear correction term
$f_{e\!f\!f}$	Effective force constant
Fc ^{+/0}	Ferrocene/ferrocenium redox couple
FcMe2	Dimethyl ferrocene Fe(C ₅ H ₄ CH ₃) ₂
FcMe8	Octamethyl ferrocene Fe(C ₅ H(CH ₃) ₄) ₂
FcMe10	Decamethyl ferrocene Fe(C ₅ (CH ₃) ₅) ₂
FF	Fill factor
FT	Fourier transform
FTO	Fluorine doped tin oxide
¹⁹ F	Fluorine-19
GtC yr ⁻¹	Gigatons of carbon per year
ΔG_{inj}	Driving force for dye injection
ΔG_{rec}	Driving force for recombination to redox shuttle

ΔG_{reg}	Driving force for dye regeneration
¹ H	Hydrogen
HS	Hight-spin
НОМО	Highest occupied molecular orbital
IR	Infrared radiation
Inj	Dye injection
IPCE	Incident photon-to-electron conversion efficiency
I ⁻ /I ₃ ⁻	Iodide/triiodide
J	Current density and coupling constant
J_{sc}	Short-circuit current density
<i>k</i> ₁₁ or <i>k</i> ₂₂	Self-exchange rate constant
<i>k</i> ₁₂	Cross-exchange rate constant
<i>K</i> ₁₂	Equilibrium constant of cross-exchange
k _B	Boltzmann constant
<i>k</i> _{et}	Electron transfer rate constant
<i>k</i> _{ex}	Electron transfer self-exchange rate constant
KCN	Potassium cyanide
<i>k</i> _{obs}	Observed rate constant
K ₂ CO ₃	Potassium carbonate
λ	Reorganization energy
λ_{in}	Inner-sphere reorganization energy
λ_o	Outer-sphere reorganization energy
λ_{o,TiO_2}	Outer-sphere reorganization energy between TiO ₂ and redox shuttle

λ_{max}	Wavelength of maximum absorbance
$\lambda_{rec}~(\mathrm{eV})$	Reorganization energy of recombination to redox shuttle
L	Ligand
L	Film thickness
LiOTf	Lithium trifluoromethansulfonate
LiPF ₆	Lithium Hexafluorophosphate
LS	Low-spin
MLCT	Metal to ligand charge transfer
MgSO ₄	Magnesium Sulfate
NHE	Normal hydrogen electrode
NMBI	N-methylbenzimidazole
NMR	Nuclear magnetic resonance
N _t	Number of trap states below conduction band
n	Electron densitry
n_s	Density of conduction band electrons
n _{sol}	Refractive index of solution
Na ₂ CO ₃	Sodium carbonate
η	Power conversion efficiency
OCVD	Open-circuit voltage decay
OSRS	Outer-sphere redox shuttle
OTf	Trifluoromethanesulfonate
р	Porosity
PCE	Power conversion efficiency

PEDOT	Poly(3,4-ethylenedioxythiophene)
PEIS	Photoelectrochemical impedance spectroscopy
PF ₆	Hexafluorophosphate
PY3F	2,2'-(1-(6-fluoropyridin-2-yl)ethane-1,1-diyl)dipyridine
PY3FDMA1	2-(1-(6-fluoropyridin-2-yl)-1-(pyridin-2-yl)ethyl)-N,N-dimethylpyridin-4-amine
PY3FDMA2	2-(1-(4-(dimethylamino)pyridin-2-yl)-1-(pyridin-2-yl)ethyl)-6-fluoro-N,N-dimethylpyridin-4-amine
PY3Im	2,2'-(1-(6-(1H-imidazol-1-yl)pyridin-2-yl)ethane-1,1-diyl)dipyridine
PY3ImDMA1	2-(1-(6-(1H-imidazol-1-yl)pyridin-2-yl)-1-(pyridin-2-yl)ethyl)-N,N- dimethylpyridin-4-amine
PY3ImDMA2	2-(1-(4-(dimethylamino)pyridin-2-yl)-1-(pyridin-2-yl)ethyl)-6-(1H- imidazol-1-yl)-N,N-dimethylpyridin-4-amine
PY4Im	1,3-bis(di(pyridin-2-yl)methyl)-1H-imidazol-3-ium
PY5ImBr	1-(6-(1,1-di(pyridin-2-yl)ethyl)pyridin-2-yl)-3-(di(pyridin-2-yl)methyl)- 1H-imidazol-3-ium bromide
PY5ImDMA1Br	3-(di(pyridin-2-yl)methyl)-1-(6-(1-(5-(dimethylamino)pyridin-2-yl)-1- (pyridin-2-yl)ethyl)pyridin-2-yl)-1H-imidazol-3-ium bromide
PY5ImDMA2Br	3-(di(pyridin-2-yl)methyl)-1-(4-(dimethylamino)-6-(1-(5- (dimethylamino)pyridin-2-yl)-1-(pyridin-2-yl)ethyl)pyridin-2-yl)-1H- imidazol-3-ium bromide
PY5Me ₂	2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine
$arPhi_{reg}$	Regeneration efficiency
q	Charge of an electron
QTOF	Quadrapole time-of-flight
R	Center to center distance
R	Ideal gas constant or molecular radius

Rrec	Recombination resistance
Rec1	Recombination to oxidized dye
Rec2	Recombination to oxidized redox shuttle
Red	Redox shuttle reduction
Reg	Dye regeneration
RS	Redox shuttle
SDS	Sodium Dodecyl Sulphate
S/N	Signal to noise ratio
SPY	2-Mercaptopyridine
Т	Temperature
<i>t</i> _{1/2}	Time at half absorbance
<i>t</i> _{1/2rec}	Time at half absorbance for recombination
<i>t</i> _{1/2} <i>reg</i>	Time at half absorbance for regeneration
TAS	Transient absorption spectroscopy
TBAPF ₆	Tetrabutylammonium hexafluorophosphate
TBPAPF6	Tris(4-bromo-phenyl)amine hexafluorophosphate
TBP	4-tert-butylpyridine
terpy	2,2':6',2"-terpyridine
TFMP	4-(trifluoromethyl)pyridine
TiO ₂	Titanium dioxide
TiCl ₄	Titanium Tetrachloride
THF	Tetrahydrofuran
ttcn	1,4,7-Trithiacyclononane

Tl(OTf)	Thallium Triflate
TPA	Tris(2-pyridylmethyl)amine
τ	Electron lifetime
UV-Vis	Ultraviolet visible
$\mu_{e\!f\!f}$	Effective magnetic moment
μ_{so}	Spin-only magnetic moment
v_0	Spectrometer frequency
$\mathcal{V}(Co(II) - N)$	Symmetrical stretching frequency Co(II) to nitrogen
$\mathcal{V}(Co(\mathrm{III})-N)$	Symmetrical stretching frequency Co(III) to nitrogen
V _{oc}	Open-circuit voltage
<i>W</i> ₁₂	Electrostatic work term
WE	Working electrode
X _d	Diamagnetic susceptibility
X _d	Diamagnetic fraction
X _M	Molar susceptibility
X _p	Paramagnetic fraction
X_p	Paramagnetic susceptibility
ZnO	Zinc oxide

Chapter 1: Motivation and Dye-Sensitized Solar Cells

1.1 Climate Crises and Solar Energy Conversion

Current data reveals a steady increase in CO₂ emissions over recent decades. In the period of 2010 to 2019, CO₂ emissions have increased by 1.2 % yr⁻¹ (9.4 ± 0.5 GtC yr⁻¹) primarily due to fossil fuel consumption producing 81 % of the emissions.¹ With current emission mitigations and renewable energy adoption rates the Earth is likely to increase 3 °C by the year 2100 increasing the urgency for carbon neutral energy.² The most widely available and abundant renewable power source, solar (~114,000 TW), far exceeds current demand (~13 TW) and the potential output of wind (14-37 TW) and hydro (1.8 TW).^{3,4,5,6} Renewable and carbon neutral energy has steadily increased to 29 % of the world power in 2020 but more rapid adoption depends strongly on power generation cost and ease of fabrication.⁷ Solar cells are being installed increasingly and at a cheaper cost (\$0.94 per W) but further reductions will be required to be financially viable in more physical and economic environments.⁸ Reducing the fabrication cost of silicon solar cells has helped to drive cheaper solar energy but price reductions are becoming more difficult to achieve due to the rigorous fabrication conditions required.⁹ Larger reductions in solar energy is likely going to require solar cells with simpler fabrication methods, lower energy input and earth abundant materials. Alternative and cheap photovoltaics are being developed and one of the leading competitors is the dye-sensitized solar cell. Dye-sensitized solar cells have the capability to be very cheap based upon their ease of fabrication and earth abundant materials but further research into improving efficiencies and reducing materials cost is required for economic viability.¹⁰

1.2 Dye-Sensitized Solar Cells Origins

Dye-sensitized solar cells and other photovoltaics have a common origin in the work of Edmond Becquerel in 1839 when he observed current and voltage being produced after illuminating two platinum electrodes in contact with dissolved silver halides.¹¹ After a few decades, Vogel and Moser were independently studying the effects of "sensitization" by incorporating studying silver halides with dyes that absorbed in the visible region.^{12,13} Almost a century later Gerischer would describe the excited state of dissolved dyes injecting electrons into the conduction band of ZnO semiconductor crystals giving a clearer picture of the charge separation occuring.¹⁴ Much larger gains in current were made when ruthenium and guinone sensitizers were anchored to the surface, in 1979 and 1980 respectively, but they still were not practical current densities due to the planar electrodes being used allowing minimal light harvest by the sensitizers.^{15,16} In 1988, Grätzel and colleagues would increase the current several orders of magnitude by increasing the surface area with polycrystalline anatase TiO_2 films and incorporating the iodide/triodide redox shuttle to reduce the attached sensitizers. This allowed for nearly quantitative external quantum efficiencies where the sensitizer absorbed.¹⁷ In 1991, they would continue to improve the efficiency dramatically by using even higher surface area nanoparticle TiO₂ films and broadening the absorption spectrum to cover more of the solar spectrum.¹⁸ Just two years later a power conversion efficiency of 10 % would be achieved by further optimization of the TiO₂ electrode and expanding the light harvest sensitizers to collect nearly all visible light.¹⁹ This system of ruthenium dyes paired with the iodide/triodide redox couple would be studied for the next two decades with minimal improvements above 10 % PCE. It would not be until 2010 that iron, cobalt and copper based redox shuttles would begin to compete at greater than 5 % PCE.^{20,21,22} Then over the next decade organic sensitizers paired with outer-sphere redox shuttles improved power conversion efficiencies to 14 % but they have been limited to below 15% for the last five years.^{23,24,25,26} In the next section the fundamental processes that operate in the dye-sensitized solar cell will be expanded upon and then restraints that inhibit the devices from greater than 15 % PCE will also be discussed.

1.3 DSSC Operation and Kinetic Processes

Dye-sensitized solar cells are a photovoltaic that distributes charge separation and collection over several components unlike traditional crystalline semiconductor photovoltaics. In modern DSSCs, light is converted into separated charges by a dye or sensitizer anchored to a semiconductor nanoparticle (Figure 1.1a and 1.1b). The dye absorbs a photon of light which brings an electron into an excited state orbital of the dye. The electron in the excited state orbital is then at a sufficiently negative potential to have enough driving force (ΔG_{inj}) to inject an electron into the conduction band (injection) of the semiconductor nanoparticle. The semiconductor's role is to then transport these injected electrons (charge collection) to the FTO substrate (fluorine doped tin oxide). The dye then requires another electron to harvest more photons of light. A redox shuttle dissolved in the electrolyte then diffuses (diffusion) to the surface and donates an electron (regeneration) due to its redox potential being more negative than the HOMO of the dye to give it enough driving force for regeneration (ΔG_{reg}). The oxidized redox shuttle then diffuses to the counter electrode to accept an electron to complete the circuit. All going well, a DSSC can efficiently convert sunlight to electrical power. However, there are several limiting factors that limit the device performance. The dye in its excited state can decay to its ground state if injection is not orders of magnitude faster than the dyes decay or recombination with the TiO₂ electrons. To prevent the dye recombination with TiO₂ electrons the rate of dye regeneration should be much faster. Also, electrons in the TiO_2 can recombine to any

oxidized redox shuttles in solution before they are collected at the FTO if charge collection is not quick enough. The competition of these rates largely dictates the power conversion efficiency possible.



Figure 1.1 (a) Schematic of dye-sensitized solar cell showing redox shuttle (RS) diffusion (Dif), dye regeneration (Reg), dye injection (Inj), redox shuttle reduction (Red), recombination of TiO₂ electrons to the dye (Rec1) and recombination of TiO₂ electrons to the redox shuttle (Rec2). (**b**) The competing kinetic processes in the device and the driving force for dye regeneration (ΔG_{reg}), driving force for injection (ΔG_{inj}) and open circuit voltage (V_{oc}).

1.4 Limitations to Performance

DSSCs have been optimized for decades but still have several major energy losses or limitations. To quantitatively complete each electron transfer process within the device, overpotentials will be required to have each electron transfer process outcompete its negating process. One process that has been optimized thoroughly is the driving force for dye injection. Some of the best performing ruthenium organic dyes require only ~300 mV of driving force efficient injection to outcompete dye decay.^{27,28} The exact timescale of injection in these highly optimized dyes is quite variable (fs to ps) and likely covers a broad range due to multiple excited states participating in injection for some dyes.²⁹ However, excited state decay is several orders of magnitude slower (ns to µs) allowing for very efficient charge separation. The other primary loss in voltage is dye regeneration. Before outer-sphere redox shuttles became competitive one of the few redox shuttles with effective regeneration was the iodide/triodide redox shuttle. The redox shuttle benefitted strongly from its extremely slow recombination kinetics with TiO₂ electrons even when the TiO₂ surface was left exposed.³⁰ Its main drawback continued to be the large sacrifice in voltage needed for efficient dye regeneration (~0.7 V).³¹ It would not be until dyes or redox shuttles incorporated bulky alkyl groups to protect the TiO₂ surface that outer-sphere redox shuttles would not suffer from major recombination losses.^{32,21} Shortly afterward, due to the tunable nature of the ligands the V_{oc} was increased relative to the iodide/triodide redox shuttle resulting in the increases in efficiency up to 14 % mentioned in section 1.2. Even with these reductions there are still large voltage losses with outer-sphere redox shuttles either due to larger driving forces required for efficient regeneration or due to recombination to the redox shuttle moving the fermi level to more positive potentials. For most cobalt systems, recombination with TiO₂ electrons is straightforward to circumvent but larger driving forces for dye regeneration is

required (0.5 V) in the most optimized systems. Most cobalt complexes utilized in higher performing DSSCs have high-spin Co(II) to low-spin Co(III) electron self-exchanges. This results in a very slow electron self-exchange rate constant (10^{-1} to 10^{0} M⁻¹s⁻¹) which limits the losses due to recombination. For copper and iron redox shuttles, generally the *V_{oc}* observed is several hundred millivolts lower than the expected difference between the solution potential and the TiO₂ conduction band edge due to recombination losses or due to in situ base coordination.^{33,34} This is inherent to most the of these redox shuttles having faster electron-self exchanges (10^4 to 10^7 M⁻¹s⁻¹) giving a small barrier to recombination with the TiO₂.^{35,36,37} Based on these two electron self-exchange regimes there should be some optimal electron selfexchange rates between (10^0 to 10^4 M⁻¹s⁻¹) where the driving force for regeneration can be minimalized yet recombination does not ruin the performance with existing dye and TiO₂ architectures.

1.5 Low-Spin to Low-Spin Co(II/III) Redox Shuttles

The larger driving force for regeneration is mostly dictated by the large inner-sphere reorganization energy of high-spin Co(II) to low-spin Co(III) electron transfer which reduces the electron self-exchange rate.³⁸ To mitigate this large barrier several low-spin Co(II) to low-spin Co(III) redox shuttles have been synthesized with reduced inner-sphere reorganization energy and faster electron self-exchange rates as measured by stopped-flow spectroscopy (10^0 to 10^4 M⁻¹s⁻¹).^{39,40,41,42} These complexes have exhibited more efficient dye regeneration with reduced driving force when incorporated in a DSSC but exhibit problematic high recombination rates with TiO₂ electrons. The first complex [Co(ttcn)]^{3+/2+}, where ttcn is 1,4,7-Trithiacyclononane, had been studied previously in a DSSC. The redox shuttle had improved dye regeneration, due to its increased electron self-exchange rate constant of 9.1 × 10³ M⁻¹s⁻¹, compared to the best

performing redox shuttle $[Co(bpy)_3]^{3+/2+}$ (0.27 M⁻¹s⁻¹). Unfortunately, it suffered larger recombination losses due to its fast electron self-exchange rate and more positive redox potential $(0.11 \text{ V vs Fc}^{+/0})$ which reduced the open-circuit voltage expected. Chapter 2 of this thesis will discuss another low-spin Co(II) complex [Co(PY5Me₂)(CN)](OTf), where PY5Me₂ represents the pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine, that was synthesized and characterized. The complex also had a faster electron self-exchange rate constant of 20 M⁻¹s⁻¹ and resided at more negative redox potential (-0.38 V vs Fc^{+/0}). The [Co(PY5Me₂)(CN)](OTf) complex unfortunately formed a solvent bound complex, a dimer complex and a cluster complex in the presence of supporting electrolyte inhibiting full DSSC measurements. Recombination measurements with the stable [Co(PY5Me₂)(CN)](OTf)₂ were measured to show its increased recombination resistance to $[Co(bpy)_3]^{3+}$. In Chapter 3 the low-spin Co(II) $[Co(PY5Me_2)(DMP-$ CN](PF₆)₂ is reported where DMP-CN is 2,6-dimethylphenyl isocyanide. The complexes electron self-exchange could not be measured so the reorganization energy was estimated based on the single-crystal x-ray diffraction data of the Co(II) and (III) complexes. The estimated reorganization energy was approximately half that of $[Co(bpy)_3]^{3+/2+}$ and its redox potential was more positive (0.10 V vs $Fc^{+/0}$). In DSSCs the complex did have improved dye regeneration kinetics despite its reduced regeneration driving force but also suffered from recombination losses analogous to $[Co(ttcn)_2]^{3+/2+}$. In Chapter 4 three ligands PY5ImBr, PY5ImDMA1Br and PY5ImDMA2Br are reported and are coordinated to result in three low-spin Co(II) complexes. Their measured self-exchange rate constant was modestly improved to 2 to 4 M⁻¹s⁻¹ likely due to the complexes undergoing a 5-coordinate Co(II) to 6-coordinate Co(III) during the electron selfexchange. The ligand backbone allowed for tuning of the redox potential at more negative potentials ranging from -200 mV to -430 mV vs Fc^{+/0} of the Co(II/III) redox couples. All three

complexes in DSSCs had reduced recombination to TiO_2 electrons and nominally the same photocurrent to $[Co(bpy)_3]^{3+/2+}$ indicating that regeneration was not limiting the system. Chapter 5 will discuss other cobalt redox shuttles that were not fully characterized and future ligand designs that might circumvent issues the PY5ImBr series had. REFERENCES
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Chapter 2: Spin-Doctoring Cobalt Redox Shuttles for Dye-Sensitized Solar Cells

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2.1 Abstract

A new low spin (LS) cobalt(II) outer-sphere redox shuttle (OSRS) [Co(PY5Me₂)(CN)]⁺, where PY5Me₂ represents the pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine, has been synthesized and characterized for its potential application in dye-sensitized solar cells (DSSCs). Introduction of the strong field CN^{-} ligand into the open axial coordination site forced the cobalt(II) complex, $[Co(PY5Me_2)(CN)]^+$, to become LS based upon the complex's magnetic susceptibility $(1.91 \pm 0.02 \mu_B)$, determined by the Evans Method. Interestingly, dimerization and subsequent cobalt hexacyanide cluster formation of the [Co(PY5Me₂)(CN)]⁺ monomer was observed upon long-term solvent exposure or addition of a supporting electrolyte for electrochemical characterization. Although long-term stability of the [Co(PY5Me₂)(CN)]⁺ complex made it difficult to fabricate liquid electrolytes for DSSC applications, short-term stability in neat solvent afforded the opportunity to isolate the self-exchange kinetics of [Co(PY5Me₂)(CN)]^{2+/+} via stopped-flow spectroscopy. Use of Marcus theory provided a smaller than expected self-exchange rate constant of $20 \pm 5.5 \text{ M}^{-1}\text{s}^{-1}$ for $[\text{Co}(\text{PY5Me}_2)(\text{CN})]^{2+/+}$, which we attribute to a Jahn-Teller effect observed from the collected monomer crystallographic data. When compared side-by-side to cobalt tris(2,2)-bipyridine), $[Co(bpy)_3]^{3+}$, DSSCs employing

 $[Co(PY5Me_2)(CN)]^{2+}$ are expected to achieve superior charge collection, which result from a smaller rate constant, k_{et} , for recombination based upon simple dark *J-E* measurements of the two redox shuttles. Given the negative redox potential (0.254 V vs. NHE) of $[Co(PY5Me_2)(CN)]^{2+/+}$ and the slow recombination kinetics, $[Co(PY5Me_2)(CN)]^{2+/+}$ becomes an attractive OSRS to regenerate near IR absorbing sensitizers in solid state DSSC devices.

2.2 Introduction

Dye-sensitized solar cells, DSSCs, are a promising solar energy conversion technology due to their ability to achieve high power conversion efficiencies (PCEs) by way of low-cost processing. However, for well over a decade, efforts to push device efficiencies past 10% were stymied by the reliance on a single redox shuttle iodide/triiodide (I^{-}/I_{3}^{-}) paired with a small subset of ruthenium sensitizers.^{1,2} The major limitations of utilizing such dye-electrolyte combinations stems from the high overpotential (~0.7 eV) necessary for efficient regeneration, the fixed redox potential of iodide/triiodide, as well as the complicated kinetics associated with charge-transfer.¹⁻⁴ To avoid such problems, it has been of considerable interest to seek alternative redox shuttles that are better matched with the vast library of dyes that already exist. Outer-sphere redox shuttles (OSRSs) have arisen as a promising solution due to their tunable ligand framework and simple one-electron transfer mechanism.^{5–8} The mechanism for chargetransfer using OSRSs has been successfully modeled by the application of Marcus Theory and has already provided a better understanding of the regeneration and recombination pathways in DSSCs.^{9,10} With such kinetic predictability provided by Marcus Theory and the fine synthetic control over the properties of designing new OSRSs, new routes for optimization of device efficiencies are possible and more opportunities arise for DSSCs to be competitive with existing silicon PV technologies.

To date, the best performing DSSC has employed the OSRS cobalt tris(2,2'-bipyridine), $[Co(bpy)_3]^{3+/2+}$ (bpy = 2,2'-bipyridine) paired with a Zn-porphyrin sensitizer to produce a record PCE of over 13 %.¹¹ Although, DSSCs employing [Co(bpy)₃]^{3+/2+} have produced the highest efficiencies, the performance of these devices are still suboptimal which can be attributed to the spin change associated with the oxidation of the cobalt metal center. We have recently shown that the large inner-sphere reorganization energy associated with the loss of two anti-bonding electrons upon oxidation of high spin (HS) $[Co(bpy)_3]^{2+}$ to low spin (LS) $[Co(bpy)_3]^{3+}$ results in inefficient dye regeneration of the organic dye D35cpdt.^{9,12} Furthermore, our group and others have shown improved PCEs in DSSCs containing tandem electrolytes of a fast exchanging redox shuttle mixed with $[Co(bpy)_3]^{3+/2+}$ providing even more evidence that regeneration is suboptimal with electrolytes containing only $[Co(bpy)_3]^{3+/2+}$.¹²⁻¹⁴ Assuming regeneration can be modeled as a simple cross-exchange reaction between the dye and redox shuttle, Marcus Theory would suggest that redox shuttles with faster self-exchange kinetics should provide faster regeneration kinetics.³ This in fact is true and has been demonstrated in our lab through the use of a LS cobalt(II) OSRS $[Co(ttcn)_2]^{3+/2+}$, where ttcn represents 1,4,7-trithiacyclononane.⁹ Through external quantum yield measurements, it was determined that regeneration was nearly quantitative using $[Co(ttcn)_2]^{3+/2+}$ compared to $[Co(bpy)_3]^{3+/2+}$, despite only a ~60 mV smaller driving force to regenerate the sensitizer D35cpdt. Unfortunately, DSSCs employing $[Co(ttcn)_2]^{3+/2+}$ suffered from faster recombination compared to $[Co(bpy)_3]^{3+/2+}$ which diminished the charge collection efficiency. In principle, the charge collection can be improved by reducing the driving force, and thus the rate of recombination, without sacrificing advantageous regeneration kinetics. However, as the ligand framework of ttcn is comprised of sp³ carbons, there are no synthetic handles to tune the redox potential i.e. adding substituents onto the carbons

or increasing the number of carbon atoms on the ring system.^{15–17} We are unaware of any alternative LS cobalt(II) OSRS to $[Co(ttcn)_2]^{3+/2+}$, however, which has thwarted our effort to investigate regeneration and recombination reactions of LS cobalt (II) OSRS as a function of driving force.

We are therefore motivated to exploit alternative ligand systems and develop a new family of promising LS cobalt redox shuttles for DSSCs. Ideally, synthesis of new LS cobalt OSRSs would open up access to more negative redox potentials than the commonly used cobalt polypyridyl complexes in order to minimize the driving force for interfacial charge transfer i.e. slower recombination kinetics, while consequently maximizing the charge collection. With such negative redox potentials and fast exchange kinetics, efficient dye regeneration is expected at small overpotentials for sensitizers with smaller optical gaps. This in turn will provide a viable route for integrating new near IR absorbing sensitizers into DSSC devices. Inspiration for designing a family of OSRSs has come from the groups of Bach and Long where a pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine, PY5Me₂, was coordinated to a cobalt center to provide the parent complex, $[Co(PY5Me_2)(MeCN)]^{3+/2+}$, amenable to functionalization.^{18–21} It is expected that the variation of electron donating or withdrawing ligands in the axial site of these coordination complexes will provide a high degree of tunability with regards to formal potential and the spin-state of the cobalt metal center. Analogous studies done by Stack et al. has already demonstrated such tunability on a series of ferrous complexes with a structurally similar ligand, 2,6-(bis-(bis-2-pyridyl)methoxymethane)pyridine.²² In spanning the spectrochemical series via coordination of various axial ligands, each Fe(II) complex was highly susceptible to changes in spin-state and redox potential. Functionalization of the axial cobalt ligand via displacement of a weakly coordinated acetonitrile (MeCN) has already been done using common DSSC electrolyte

additives such as 4-*tert*-butylpyridine (TBP) and *N*-methylbenzimidazole (NMBI), however, use of such pyridine derivatives failed to significantly modulate the energetics of the resulting OSRSs or the spin–state of the cobalt metal center.²¹ To build on Stack and Bach's previous studies, we envisioned using a strong field ligand such as cyanide, CN^- , to obtain the desired results. Stack demonstrated that, as a strong donor and anionic ligand, cyanide can push the redox potential more negative than most ligands in the spectrochemical series. In addition, the strong field ligand induced a LS Fe(II). With this study in mind, we reasoned that introduction of the CN^- ligand to the sixth coordination site of the $[Co(PY5Me_2)(MeCN)]^{2+}$ complex would likewise result in a rare example of a LS Co(II) complex with a potential more negative of $[Co(ttcn)_2]^{3+/2+}$ and thus start a promising new class of OSRS.

In this work we have prepared and characterized the cobalt complexes, $[Co(PY5 Me_2)(CN)]^{2+/+}$. Through the use of Evans method studies, it was determined that coordination of a cyanide ligand to the parent $[Co(PY5Me_2)(MeCN)]^{2+}$ forced the Co(II), $[Co(PY5Me_2)(CN)]^+$, to become LS. Interestingly, addition of cyanide to $[Co(PY5Me_2)(MeCN)]^{2+}$ resulted in unexpected side reactions that were highly dependent on the reaction conditions imparted. Depending on the equivalents of cyanide, temperature and overall reaction time, dimerization and subsequent precipitation of a cobalt cluster complex were observed. The dimer complex was isolated and characterized; however, due to solubility issues, the cluster complex was only analyzed by X-ray crystallography. The instability of the pure $[Co(PY5Me_2)(CN)]^+$ complex was identified by ¹H NMR and electrochemistry studies. In neat acetonitrile, the complex remains stable for kinetic measurements using stopped-flow spectroscopy; however, dimerization results almost instantaneously upon addition of a supporting electrolyte. Although stability appears to be

an issue in liquid electrolytes, the short-term stability in neat solvent makes $[Co(PY5Me_2)(CN)]^{2+/+}$ an ideal candidate as a solid state hole conductor for DSSCs.



Figure 2.1 Molecular structures of various cobalt containing redox shuttles for DSSCs: cobalt tris(2,2'-bipyridine), [Co(bpy)3]3+/2+, cobalt bis(1,4,7-trithiacyclononane), [Co(ttcn)2]3+/2+, cobalt 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine acetonitrile, [Co(PY5Me2)(ACN)]3+/2+, and cobalt 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine cyanide [Co(PY5Me2)(CN)]2+/+.

2.3 Experimental

2.3.1 Materials

All reagents were obtained from commercial suppliers (Oakwood Chemical, Sigma Aldrich, Alfa Aesar or Strem Chemicals) and used as received unless otherwise stated. Solvents used in the synthesis, characterization and kinetics studies of all cobalt complexes were dried prior to being stored in a glovebox (MBRAUN Labmaster SP). Tetrahydrofuran (Fisher Chemical, Optima) and diethyl ether (Anhydrous, ACS Reagent, \geq 99.0%) were distilled over sodium/benzophenone. Methanol was dried by reacting magnesium turnings and iodine, then distilling under nitrogen and storing over 3Å molecular sieves. Acetonitrile (Fisher Chemical Certified ACS, \geq 99.5%) and dichloromethane (Macron Fine Chemicals AR ACS) were purified by being passed through an activated alumina column. The supporting electrolytes, tetrabutylammonium hexafluorophosphate (Sigma-Aldrich, 98%), TBAPF₆, and lithium triflate (Sigma-Aldrich, 99.995% trace metals basis), LiOTf, were stored in a glovebox under moisture free conditions prior to use. However, before storing in the glovebox, TBAPF₆ was recrystallized from ethanol/diethyl ether and dried under vacuum.

2.3.2 Instrumentation

CHN analysis was conducted at Michigan State University. UV-Vis spectra were measured with a Perkin-Elmer Lambda 35 UV-Vis spectrometer using 1 cm path length quartz cuvettes. High resolution mass spectra (HRMS) were obtained at the Michigan State University Mass Spectrometry Service Center using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI+). Infrared spectroscopy (IR) was obtained using a JASCO FT/IR-6600 spectrometer. Raman spectroscopy was collected using a Renishaw inVia Raman microscope employing a RL532C100 laser source. ¹H NMR spectra were measured at room temperature (25 °C) on an Agilent DirectDrive2 500 MHz spectrometer and referenced to residual solvent signals. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, m = multiplet). Cyclic voltammetry (CV) measurements were performed with a µAutolabIII/FRA2 potentiostat using a platinum disk working electrode, platinum mesh counter electrode and a homemade $Ag/AgNO_3$ (0.1 M TBAPF₆ acetonitrile) reference electrode. Ferrocene was used as an internal reference. The error associated with each redox shuttle's formal potential, E° , is based on the standard deviation of the formal potentials measured over three separate days. Reference conversion to NHE was done assuming the potential of Ferrocene in acetonitrile is 0.40 V vs SCE.⁴⁰ Dark J-E measurements were obtained for both $[Co(PY_5Me_2)(CN)]^{2+}$ and $[Co(bpy)_3]^{3+}$ in acetonitrile with 0.1M lithium triflate, LiOTf, using a three-electrode setup interfaced with the µAutolab mentioned above. The three electrode

setup contained a mesoporous thin film of TiO_2 nanoparticles attached to an FTO substrate (fabrication described below) which acted as a working electrode, a homemade Ag/AgNO₃ reference (described above) along with a high surface area platinum mesh counter electrode. Figure A2.16 gives a pictorial illustration of the setup.⁸

2.3.3 X-ray crystallography

Crystals were mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 173(2) K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXS (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of XL (Sheldrick, 2008) using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. There are two independent molecules in the asymmetric unit of the [Co(PY5 Me₂)(CN)](OTf) crystals. Structure and refinement data are summarized in Table A2.2 for [Co(PY5Me₂)(CN)](OTf), [Co(PY5Me₂)(CN)](OTf)₂, the dimer complex, the Cluster Complex and [Co(PY5Me₂)(F)](OTf)₂ can be found in the Appendix, Figures A2.1-A2.2.

2.3.4 [Co(PY5Me₂)(ACN)](OTf)₂

Unless otherwise noted, all synthesis procedures were performed under inert N₂ atmosphere using schlenk line or standard glovebox techniques. The ligand PY5Me₂ (2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) was synthesized according to a procedure previously reported in the literature.⁴¹ The synthesized ligand was characterized by ¹H NMR and the resulting chemical shifts were matched to the literature report: ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 8.45 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 4H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.52 (ddd, *J* = 8.1, 7.5, 1.9 Hz, 4H), 7.14 (ddd, *J* =

7.4, 4.8, 1.1 Hz, 4H), 7.04 (d, J = 7.9 Hz, 2H), 6.91 (dt, J = 8.1, 1.0 Hz, 4H), 2.13 (s, 6H). The $[Co(PY5Me_2)(ACN)](OTf)_2$ complex was synthesized using a modified literature procedure. First, $[Co(PY5Me_2)(I)]I$ was prepared, but only allowed to stir overnight (~12 hours) before being collected. Finally, metathesis of $[Co(PY5Me_2)(I)]I$ to yield $[Co(PY5Me_2)(ACN)](OTf)_2$ was done using thallium(I) triflate Tl(OTf) and allowed to stir overnight (~12 hours). Characterization of the parent $[Co(PY5Me_2)(ACN)](OTf)_2$ complex was carried out by way of elemental analysis, Table A2.1, mass spectrometry, and electrochemistry i.e. cyclic voltammetry (see Figure 2.6 above). During the mass spec measurements (M+), it was observed that each of the parent complexes lost their –ACN ligand. This resulted in intense peaks for $Co(PY5Me_2)^{2+}$ and $Co(PY5Me_2)(OTf)^+$ at 251.07 and 651.09. Elemental analysis: found (calcd) for $C_{33}H_{28}CoF_6N_6O_6S_2$: C, 45.33(47.09); H, 3.03(3.35); N, 8.56(9.99).

2.3.5 [Co(PY5Me₂)(CN)](OTf)

In a glovebox, [Co(PY5Me₂)(ACN)](OTf)₂ (0.178 mmol, 149.9 mg) was dissolved in (~5 mL) methanol and a separate methanolic solution (~3 mL) of KCN (0.264 mmol, 17.2 mg) was made before being pulled out and placed in an ice bath to cool. After allowing the mixtures to equilibrate to the temperature of the ice bath, the KCN solution was slowly charged to the stirring solution of [Co(PY5Me₂)(ACN)](OTf)₂, which immediately turned from bright yellow/orange to a dark reddish/brown. To avoid the accumulation of side-products the reaction mixture was only allowed to stir for one minute before being precipitated with dry diethyl ether. Dissolution of the crude [Co(PY5Me₂)(CN)](OTf) yielded a brown powder. The supernatant was decanted in the glovebox and the pure product was obtained after recrystallizing in dichloromethane and washing with diethyl ether (yield: 65.4%). (Note- insoluble particulate in dichloromethane was syringe filtered before being crashed with diethyl ether.) Crystals suitable

for single crystal X-ray diffraction analysis were obtained by slow vapor diffusion of ether into a concentrated acetonitrile solution of $[Co(PY5Me_2)(CN)](OTf)$ at room temperature. Mass spectrometry, elemental analysis and ¹H NMR were also used to characterize the $[Co(PY5Me_2)(CN)](OTf)$ complex, see SI. An intense peak for $[Co(PY5Me_2)(CN)]^+$ at 528.2 was observed in the mass spectra (M+), along with peaks for complexes that lost their exogenous CN ligand $([Co(PY5Me_2)]^{2+}$ at 251 and $[Co(PY5Me_2)(OTf)]^+$ at 651.1). Interestingly, even with pure material peaks for the oxidized complex were also observed ($[Co(PY5Me_2)(CN)]^{2+}$ at 264.1 and $[Co(PY5Me_2)(CN)](OTf)^+$ at 677.1). Elemental analysis: found (calcd) for $C_{31}H_{25}CoF_3N_6O_3S$: C, 54.47(54.95); H, 3.71(3.72); N, 11.90(12.40).

2.3.6 [Co(PY5Me₂)(CN)](OTf)₂.

[Co(PY5Me₂)(CN)](OTf) (0.133 mmol, 89.9 mg) was dissolved in a small amount (~5 mL) of acetonitrile. A second acetonitrile solution (~5 mL) of silver triflate, AgOTf, (0.132 mmol, 34.0 mg) was made and slowly added to the first. Fine gray silver particulate formed immediately after AgOTf addition and the reaction mixture turned from a dark reddish/brown to a light orange solution. The mixture was allowed to stir for 2 hours before the silver particulate was syringe filtered and the crude product was crashed with diethyl ether. The supernatant was decanted and the pure light orange product (yield: 52.8%) was isolated by washing with dichloromethane and ether. Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow vapor diffusion of ether into a concentrated acetonitrile solution of [Co(PY5Me₂)(CN)](OTf)₂ at room temperature. Mass spectroscopy, elemental analysis and ¹H NMR were also used to characterize the [Co(PY5Me₂)(CN)](OTf)₂ complex. Intense peaks for [Co(PY5Me₂)(CN)]²⁺ at 264.1 and [Co(PY5Me₂)(CN)](OTf)⁺ at 677.1 were observed by mass spectrometry (M+). However, it appeared even with pure material the mass spec also showed

peaks for the reduced complex: $[Co(PY5Me_2)]^{2+}$ at 251, $[Co(PY5Me_2)(OTf)]^+$ at 651.1 and $[Co(PY5Me_2)(CN)]^+$ at 528.1. ¹H NMR (500 MHz, acetonitrile-*d*₃) δ 9.91 (dd, *J* = 6.2, 1.4 Hz, 4H), 8.40 (dd, *J* = 8.7, 7.3 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 2H), 8.11 (ddd, *J* = 8.6, 7.3, 1.3 Hz, 4H), 8.04 (dd, *J* = 8.2, 1.7 Hz, 4H), 7.71 (ddd, *J* = 7.6, 6.2, 1.7 Hz, 4H), 2.81 (s, 6H). Elemental analysis: Found (Calcd) for C₃₂H₂₅CoF₆N₆O₆S₂: C, 45.67(46.50); H, 3.17(3.05); N, 9.59(10.17).

2.3.7 Synthesis of Cross-Exchange Redox Shuttles

OSRSs used in the stopped-flow studies were either purchased from commercial suppliers or synthesized from previous literature reports. Synthesis of the $[Co(terpy)_2]^{3+/2+}$ complexes, where terpy represents 2,2':6',2"-terpyridine, was carried out using a modified literature procedure.⁷ Briefly, the appropriate stoichiometric ratio (~2.1 equivalents) of the terpy (Alfa Aesar, 97%) ligand was reacted with (1 equivalent) cobalt dichloride hexahydrate (CoCl₂•6H₂O) in methanol. The reaction was brought to reflux and stirred in air for ~2 hours. Upon cooling, the reaction mixture was concentrated and an excess of TBAPF₆ (~6-8 equivalents) dissolved in methanol was added. A brownish/orange solid precipitated out of solution after sonication. The pure product was vacuum filtered and washed with copious amounts of methanol and diethyl ether before being collected and dried. The isolated paramagnetic $[Co(terpy)_2](PF_6)_2$ species was characterized by ¹H NMR containing chemical shifts up to ca. 100 ppm. Oxidation of the $[Co(terpy)_2](PF_6)_2$ complex was carried out using 1.1 equivalents of nitrosonium hexafluorophosphate (Strem Chemicals, min. 97%), NOPF₆, dissolved in a minimal amount of acetonitrile. The reaction was stirred in air overnight (~12 hrs.) to ensure the reaction reached completion. Isolation of the crude $[Co(terpy)_2](PF_6)_3$ product was carried out via precipitation from acetonitrile using diethyl ether. The solid was vacuum filtered and washed with dichloromethane, methanol and diethyl ether. Recrystallization in acetonitrile yielded the pure

[Co(terpy)₂](PF₆)₃ product confirmed via ¹H NMR. ¹H NMR (500 MHz, acetonitrile- d_3) δ 9.16 – 9.08 (m, 2H), 9.02 (d, J = 8.1 Hz, 4H), 8.61 (d, J = 7.8 Hz, 4H), 8.25 (t, J = 7.8 Hz, 4H), 7.44 (t, J = 6.8 Hz, 4H), 7.25 (d, J = 5.8 Hz, 4H). 1,1'-dimethylferrocene (Sigma Aldrich, 95%), [Fe(C₅H₅CH₃)₂], was used as received. Oxidation of [Fe(C₅H₅CH₃)₂] to obtain the ferrocenium salt, [Fe(C₅H₅CH₃)₂](BF₄), was carried out using a procedure reported in the literature.⁴¹

2.3.8 Cross-Exchange Kinetics

Stopped-flow measurements were performed using a similar methodology to that previously reported.^{9,12} Briefly, samples were measured using an Olis RSM 1000 DeSa rapid-scanning spectrophotometer with dual-beam UV-Vis recording to Olis SpectralWorks software. The instrument contained a quartz cell with a 1 cm path length. Scans were taken once every millisecond with 1 nm resolution. The 150 W Xenon arc lamp was controlled using an LPS-220B Lamp Power Supply and held to within 79-81 W during each measurement. The temperature was also held constant at 25 ± 0.1 °C using a NESLAB RTE-140 chiller/circulator. Two cross-exchange reactions were measured and described in detail below. All $[Co(PY5Me_2)(CN)](OTf)$, $[Co(terpy)_2](PF_6)_3$ and $[Fe(C_5H_5CH_3)_2]^{+/0}$ solutions were prepared neat using dry acetonitrile.

Pseudo-first order conditions were implemented in both cross-exchange reactions, which maintained at least a 10-fold excess of a single reactant species. In the case of the cross-reaction between $[Fe(C_5H_5CH_3)_2]$ and $[Co(terpy)_2](PF_6)_3$, however, a 10-fold excess of both a single reactant and product species was maintained since the reaction was expected to reach equilibrium. The concentrations of $[Co(PY5Me_2)(CN)](OTf)$ were varied and held in excess for the reactions with $[Co(terpy)_2](PF_6)_3$, however, both the concentrations of $[Fe(C_5H_5CH_3)_2]$ and $[Fe(C_5H_5CH_3)_2](BF_4)$ were held in excess while the $[Fe(C_5H_5CH_3)_2]$ concentration was varied

for the reactions with $[Co(terpy)_2](PF_6)_3$. In both cross-exchange reactions the spectral changes were monitored at 505 nm, following the growing absorbance of the $[Co(terpy)_2]^{2+}$ species. Scientific Data Analysis Software provided fits for the pseudo-first order rate constants, k_{obs} , using a nonlinear least-squares regression. Seven independent trials were averaged to provide the measured k_{obs} values. Absorbance plots for each pseudo-first order reaction were fit using: $A = A_{\infty} + (A_o - A_{\infty})e^{-k_{obs}t}$. The second-order rate constants were calculated from the slope of the k_{obs} versus the excess concentration of either $[Co(PY5Me_2)(CN)](OTf)$ or $[Fe(C_5H_5CH_3)_2]$ and each had a goodness of fit, $R^2 > 0.996$. The error associated with measured k_{obs} values were taken to be the standard deviation of the seven independent trials. The negligible error in concentration was propagated based on prepared stock solutions of each reaction mixture. It was assumed that uniform mixing led to minimal deviation in the reactants initial concentrations.

2.3.9 Semiconductor Anode Fabrication

High surface area thin films of titanium dioxide (TiO₂) on fluorine-doped tin oxide (FTO) glass substrates (TEC 15, Hartford), $12 \ \Omega \ cm^{-2}$, were made to conduct recombination studies to the oxidized redox shuttles: $[Co(PY5Me_2)(CN)]^{2+}$ and $[Co(bpy)_3]^{3+}$. The glass substrates were cleaned in an ultrasonic bath using (in order) soap water, deionized water, acetone and isopropyl alcohol. To burn off any organic residue the substrates were then baked at 400 °C for 30 minutes. After cooling, a blocking layer was deposited on the FTO substrates by way of atomic layer deposition (ALD). A Savannah 200 instrument (Cambridge Nanotech Inc) deposited 1000 cycles of titanium isopropxide (99.999% trace metals basis, Sigma-Aldrich) at 225 °C and water using reactant exposure times of 0.3 s and 0.015 s, respectively. Between each exposure, nitrogen was purged for 5 s. After ALD, a transparent thin film (~5-6 µm) of ~30 nm TiO₂ nanoparticles was prepared by doctor blading a commercial paste (DSL 30NR-D, DYESOL) on the FTO glass

substrates coated with the TiO₂ blocking layer. The doctor bladed films were allowed to relax for 10 minutes at room temperature on benchtop, then for another 15 minutes in the oven at 100 °C. The electrodes were annealed by heating in air to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes and 500 °C for 15 minutes. A post TiCl₄ treatment was completed after cooling the sintered TiO₂ anodes to ~70 °C. The post TiCl₄ treatment was carried out using ~40 mL of a 40 mM stock solution of TiCl₄ dissolved in Milli-Q water. The solution was heated to 70 °C for 10 minutes in an oven before the TiO₂ sintered films were immersed for 30 minutes. After 30 minutes, the films were rinsed with Milli-Q water and baked again at 500 °C for another 30 minutes. Upon cooling, electrical contact was made using copper wire leads coated in silver epoxy. Before deposition of the epoxy on the FTO substrates, part of the blocking layer was manually scraped off. As the epoxy dried gently on a hotplate, the TiO₂ films were covered to protect against any organic residue from diffusing into the mesopores.

2.4 Results and Analysis

2.4.1 Synthesis

Synthesis of the parent [Co(PY5Me₂)(ACN)](OTf)₂ was carried out following a modified literature procedure.¹⁸ Coordination of the neutral PY5Me₂ ligand to the acidic cobalt metal center yielded a stable halide product, [Co(PY5Me₂)I]I, using the proper metal salt and the robust solvato complex, [Co(PY5Me₂)(ACN)](OTf)₂, upon metathesis in a coordinating solvent such as acetonitrile. In principal, synthesis of the [Co(PY5Me₂)(CN)](OTf) complex from the parent [Co(PY5Me₂)(ACN)](OTf)₂ should be facile and clean via the addition of a cyanide source. Interestingly, however, the cyanide ligand was observed to be much more labile than anticipated. Careful control over the reaction conditions was necessary in order to mitigate dimerization and/or subsequent cluster formation of a cobalt hexacyanide complex.

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Isolation of the pure $[Co(PY5Me_2)(CN)](OTf)$ complex was obtained by ensuring the reaction between [Co(PY5Me₂)(MeCN)](OTf)₂ and CN⁻ was carried out using a slight excess $(\sim 1.2 - 1.5 \text{ eq.})$ of CN⁻, at low temperature (ice bath), under an inert atmosphere and in a noncompetitive solvent such as methanol. By visual inspection, the reaction was deemed complete within seconds as the solution changed from yellow to a dark reddish/brown upon cyanide addition. Single crystals were obtained via slow vapor diffusion of ether into a concentrated acetonitrile solution of [Co(PY5Me₂)(CN)](OTf) at room temperature, Figure 2.2a. ¹H NMR of the pure paramagnetic [Co(PY5Me₂)(CN)](OTf) indicated rather upfield chemical shifts that ranged from 4ppm to 20ppm with a single broad signal around 58ppm that was only identifiable at high concentrations, Figure A2.4. Oxidation of [Co(PY5Me₂)(CN)](OTf) to produce the stable Co(III) product, [Co(PY5Me₂)(CN)](OTf)₂, was obtained using silver triflate, AgOTf, in an acetonitrile solution. The short-term stability of [Co(PY5Me₂)(CN)](OTf) in neat acetonitrile coupled with the rapid reaction upon addition of Ag⁺ yielded a clean [Co(PY5Me₂)(CN)](OTf)₂ product via ¹H NMR, Figure A2.5. As expected, long-term stability is maintained for [Co(PY5Me₂)(CN)](OTf)₂ in neat solution as well as upon the addition of a supporting electrolyte, Figure A2.8. Single crystals suitable for X-Ray crystallography were again obtained via slow vapor diffusion of ether into a concentrated acetonitrile solution of $[Co(PY5Me_2)(CN)](OTf)_2$ at room temperature, Figure 2.2b. A full characterization of the structure, spin-state, optical and kinetic properties of both [Co(PY5Me₂)(CN)]^{2+/+} complexes were carried out and described in detail below.



Figure 2.2 Single crystal representations of a) $[Co(PY5Me_2)(CN)](OTf)$ and b) $[Co(PY5Me_2)(CN)](OTf)_2$ provided by Olex2 and structurally refined by ShelXT software. Note- the solvent and counter ions are excluded for clarity in each of the crystal structures above. Depicted ellipsoids are at the 50% probability level.

Dimerization was observed when the reaction conditions were modified such that only one or less equivalents (≤ 1 eq.) of CN⁻ are added to the [Co(PY5Me₂)(ACN)](OTf)₂ reaction mixture. Even at low temperature (ice bath) and under an inert atmosphere, the predominant product that was obtained was a dimer complex. Single crystals were readily grown by slow vapor diffusion of diethyl ether into a concentrated acetonitrile solution containing the dimer, Figure 2.3. Structural information and vibrational properties were measured from single crystals of the dimer complex. Due to the lability of the complex upon solvation and/or supporting electrolyte addition, Figures A2.6 and A2.12, solution measurements were avoided.

Interestingly, along with the dimer complex a second side product was observed. This came in the form of an insoluble precipitate that would crash out if the dimer solution or a [Co(PY5Me₂)(CN)](OTf) solution was allowed to sit for extended periods of time. The insoluble product was also readily obtained during the synthesis of the [Co(PY5Me₂)(CN)](OTf) complex if the reaction mixture was carried out at room temperature or allowed to stir for several minutes in a cold bath under conditions where excess cyanide (> 1.5 eq.) was present. The thermodynamically stable species was determined to be a cluster complex whose structure can be found in Figure A2.1 of the Appendix. Single crystals were difficult to isolate as the cluster complex was only soluble in DMSO; however, tiny single crystals were obtained from an attempt to grow [Co(PY5Me₂)(CN)](OTf) crystals over the course of several days.

2.4.2 X-ray Crystallography

The crystal structures of $[Co(PY5Me_2)(CN)](OTf)$ and $[Co(PY5Me_2)(CN)](OTf)_2$ are depicted in Figure 2.2. Refinement data for both complexes, as well as the dimer complex discussed below, are summarized in the SI, Table A2.2. The atom labeling is kept consistent for the $[Co(PY5Me_2)(CN)](OTf)$ and $[Co(PY5Me_2)(CN)](OTf)_2$ complexes in order to make sideby-side structural comparisons. Selected bond lengths and angles for each structure can be found in Table 2.1. Around the equatorial plane, nitrogen atoms N₂₋₅ of their respective pyridine subunits have been appropriately assigned with the nitrogen atom N₁ being associated with the pyridine unit axial to the exogenous cyanide ligand labeled C₃₀ and N₆.

Upon inspection of the $[Co(PY5Me_2)(CN)]^{2+/+}$ crystal structures, it appears that coordination of the exogenous cyanide to the sixth coordination site of the parent $[Co(PY5Me_2)(ACN)](OTf)_2$

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yields a distorted octahedral structure. In the case of the [Co(PY5Me₂)(CN)](OTf) complex, two independent molecules make up the asymmetric unit and are both represented above. Superposition of these two molecules leads to nearly indistinguishable structures with minor bond angle and/or bond length changes, Table 2.1. The cobalt (II) metal center resides slightly above the equatorial plane as each of the pyridine units (N₂-N₅) are slightly less (~1°) than 90° from the axial pyridine (N₁). Constrictive bond angles are observed for the pyridine units bound through the ethyl bridge and are rather acute for the cobalt (II) (81.6°–82.8°). Oxidation of the cobalt (II) leads to a contraction of the equatorial pyridines, which widens the N₂ – Co – N₃ bond angle creating a more symmetric complex. The average Co-N bond length change of the four pyridines in the equatorial plane is ~0.125 Å. A minor bond length change is observed for the axial pyridine unit upon oxidation. Also, as the axial pyridine (N₁) of the PY5Me₂ expands, the more electropositive Co(III) causes the Co-C bond length of the cyanide (C₃₀) to contract by nearly the same distance. Consequently, the shorter Co-C bond length causes the C-N triple bond to become slightly longer (~0.02 Å).

Table 2.1 Selected bond lengths and angles for $Co(PY5Me_2)(CN)](OTf)$ and $Co(PY5Me_2)(CN)](OTf)_2$. Note- bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis. Each of the N₁ - $Co - N_X (X = 2-5)$ bond angles are not listed since each value is nearly 90° (±1°-2°).

Bond			
Distances	[Co(PY5Me ₂)(CN)](OTf)	Co(PY5Me ₂)(CN)](OTf)	$C_{0}(\mathbf{PV5M}_{00})(\mathbf{CN}))(\mathbf{OTf})_{0}$
&	А	В	$CO(F I Sivie_2)(CIV) J(OII)_2$
Bond Angles			
$Co-N_1$	1.977(2)	1.964(3)	1.992(3)
$Co-N_2$	2.127(3)	2.074(3)	1.981(3)
$Co-N_3$	2.066(3)	2. 123(3)	1.981(3)
$Co-N_4$	2.138(3)	2.097(3)	1.980(3)
$Co-N_5$	2.088(3)	2.115(3)	1.973(3)
$Co-C_{30}$	1.913(3)	1.917(4)	1.891(3)
$C_{30} - N_6$	1.128(4)	1.133(4)	1.151(4)
N_2-Co-N_3	81.58(11)	82.77(11)	83.63(11)
N_2-Co-N_5	99.27(10)	95.64(11)	96.65(11)
$N_3-Co-N_4\\$	94.74(10)	98.31(11)	95.76(11)
$N_4-Co-N_5\\$	84.21(10)	83.15(11)	83.99(10)
N_2-Co-N_4	175.10(11)	177.23(11)	178.92(12)
$N_3-Co-N_5\\$	176.37(11)	176.54(11)	178.66(11)
$N_1 - Co - C_{30}$	178.38(13)	177.86(13)	179.68(14)
$N_6 - C_{30} - C_0$	177.7(3)	177.3(3)	178.9(3)

As mentioned in the synthesis section above, the labile CN^- ligand of the $[Co(PY5Me_2)(CN)](OTf)$ complex in acetonitrile leads to the formation of a dimer complex, Figure 2.3. Dark red crystals of this complex were readily obtained for single crystal X-ray analysis and the resulting bond lengths and bond angles for this complex are reported in the SI, Table A2.3. Each of the nitrogen atoms, N₁₋₅, bound to Co₁ are appropriately labeled to make side-by-side comparisons to the monomeric complex. Both of the axial bonds Co₁-N₁ and Co₁-C₃₀ appear to be longer than the monomer's by ~0.07 Å and ~0.05 Å, respectively. Around the equatorial plane the average Co-N₂₋₅ bond lengths are nearly identical between the two complexes, deviating only by ~0.009 Å. Interestingly, the average equatorial Co-N₈₋₁₁ bond length around the Co₂ is actually ~0.017 Å shorter than the average bond length for nitrogen's

bound to Co₁. Although the formal negative charge of the CN⁻ resides on the carbon atom, suggesting a tighter bond between Co₁ and C₃₀, the bond length between these two atoms is only ~0.024 Å shorter than the Co₂-N₆ bond. The delocalized charge throughout the cyanide bridge also causes the C₃₀-N₆ triple bond to weaken and expand. Both the Co₁-C₃₀-N₆ and Co₂- N₆-C₃₀ bond angles are measured to be the same (~177.6°), however, the N₁-Co₁-C₃₀ bond angle is slightly more acute (~0.8°) than the N₆-Co₂-N₇ bond angle. As with the monomeric complex, both cobalt metal centers lie slightly above the equatorial plane as each of the equatorial pyridines are less than 90° to the axial pyridines. Even though it is not shown in Figure 2.3, three triflates were found per dimer molecule, which would imply that each metal center is in its reduced state i.e. Co(II).



Figure 2.3 Single crystal representation of the dimer complex provided by Olex2 and structurally refined by ShelXT software. Note– the solvent and counter ions are excluded for clarity in the crystal structure above. Depicted ellipsoids are at the 50% probability level.

2.4.3 Magnetic properties

Magnetic susceptibility of the paramagnetic [Co(PY5Me₂)(CN)](OTf) complex was measured in acetonitrile-*d3* by ¹H NMR, Figure A2.9, using the Evans method.^{23,24} Measurements were collected using a regular NMR tube containing a known concentration of [Co(PY5Me₂)(CN)](OTf) dissolved in acetonitrile-*d3* along with a capillary insert filled with a saturated solution of Ferrocene (diamagnetic standard) also dissolved in acetonitrile-*d3*. The concentration of [Co(PY5 Me₂)(CN)](OTf) was varied at room temperature to provide the standard deviation in the calculated effective magnetic moment, μ_{eff} . The μ_{eff} for [Co(PY5Me₂)(CN)](OTf) was calculated using Equations 2.1 and 2.2, where χ_M is the molar susceptibility of the solute, Δv the observed frequency shift of the reference resonance (hertz), v_0 the spectrometer frequency (s⁻¹), *c* is the concentration of [Co(PY5Me₂)(CN)](OTf) (mol/L), χ_p is the paramagnetic contribution to the molar susceptibility of the solute, and *T* is the temperature

(K) of the sample.

$$\chi_M = \frac{3000\Delta v}{4\pi v_o c}$$
 E 2.1

$$\mu_{eff} = 2.828 \sqrt{\chi_p T}$$
 E 2.2

Given the diamagnetic contribution, χ_d , is generally small and negligible compared to the overall paramagnetic contribution, χ_p , the μ_{eff} was therefore determined directly from χ_M providing a $\mu_{eff} = 1.91 \pm 0.02 \ \mu_B.^{25}$ The spin-only magnetic moment, μ_{so} , for LS cobalt (II) complexes is calculated to be $\mu_{so} = 1.73 \ \mu_B$ suggesting that the experimentally determined value supports a LS cobalt (II) complex.

2.4.4 Vibrational Spectroscopy

Raman spectroscopy was used to further characterize the monomeric and dimer complexes, Figure 2.4. In both measurements single crystals of each complex were used. Of particular interest was to identify the CN vibrational frequencies for each complex. The dimer showed a single strong signal for the CN stretch at 2113 cm⁻¹ Figure 2.4b, which was slightly blue shifted from the primary CN vibrational signal of the Co(II) monomer at 2106 cm⁻¹. Oxidation of the Co(II) monomer also resulted in a blue shifted cyano stretch frequency at 2140 cm⁻¹. Looking at crystal structures of the monomeric complexes, it appears that the CN bond length elongates upon oxidation from Co(II) to Co(III). This may seem counter-intuitive to a general statement that the longer bond length would result in a lower vibrational frequency at the same bond order, however, previous investigations concluded that the CN vibrational frequency increase is due to the force constant increase of the bond.²⁸ Oxidation of the Co(II) metal center leads to a higher energy signal due to the decreased π backbonding ability of the metal center leading to less antibonding character on the cyanide ligand, Table 2.2.



Figure 2.4 Raman spectra using single crystals of a) $[Co(PY5Me_2)(CN)](OTf)$ (red line) and $Co(PY5Me_2)(CN)](OTf)_2$ (green line) as well as b) the dimer complex (blue line).

Two additional CN signals from the expected arise in the Raman for both monomeric complexes, Figure 2.4a. These CN signals, at 2254 cm⁻¹, can be attributed to trapped acetonitrile in the crystal lattice and agree well with the crystal structures which show one molecule of acetonitrile per molecule of monomeric complex. In the case of the [Co(PY5Me₂)(CN)](OTf)

complex, splitting of the cyanide signal is also observed. Given there are two independent molecules in the asymmetric unit of the [Co(PY5Me₂)(CN)](OTf) crystal, we speculate that the slight differences in localized environment i.e. solvent, counterions, bond distances or bond angles could change the polarizability of the CN bond, which result in the two distinct vibrational signals at very similar wavenumbers.

Table 2.2 Summary of cyano, CN, stretching frequencies using Raman spectroscopy and measuring single crystals of [Co(PY5Me₂)(CN)](OTf), [Co(PY5Me₂)(CN)](OTf) and the dimer complex.

Method	[Co(PY5Me ₂)(CN)](OTf)	[Co(PY5Me ₂)(CN)](OTf) ₂	Dimer Complex
	2106		
Raman (cm ⁻¹)	2114	2140	2113

2.4.5 UV-Vis Spectroscopy

The **UV-Vis** of $[Co(PY5Me_2)(CN)](OTf)$ the monomeric (red line) and [Co(PY5Me₂)(CN)](OTf)₂ (green line) complexes are shown in Figure 2.5. The cobalt (II) complex, [Co(PY5Me₂)(CN)](OTf), contains two metal-to-ligand charge transfer (MLCT) bands in acetonitrile between 300 - 400 nm ($\varepsilon > 2000$ M⁻¹ cm⁻¹). However, the only significant absorption feature of the [Co(PY5Me₂)(CN)](OTf)₂ UV-Vis is a weak multifeatured d-d transition band at ~442 nm, see Figure 2.5 inset. Presumably this band resides in the [Co(PY5Me₂)(CN)](OTf) UV-Vis spectrum, but is obscured by the onset of the MLCT band. In both spectra, below 300 nm a strong absorption band is present and is attributed to a metal independent ligand-based π - π^* transition.^{22,29} Such an assignment is made due to the absorption of the free PY5Me₂ ligand in acetonitrile, Figure A2.10, which has a λ_{max} at 263 nm and an $\varepsilon >$ 15000 M⁻¹ cm⁻¹.



Figure 2.5 UV-Vis spectra of $[Co(PY5Me_2)(CN)](OTf)$ (red line) and $[Co(PY5Me_2)(CN)](OTf)_2$ (green line) measured under air free conditions in acetonitrile. Inset–enhances the d-d transition of the $[Co(PY5Me_2)(CN)](OTf)_2$ complex.

2.4.6 Electrochemical Properties

Cyclic voltammetry (CV) was used to probe the redox behavior of each cobalt pentapyridine complex synthesized. To avoid degradation or potential oxidation, each CV was measured under an N₂ atmosphere. Similar to previous literature reports, $[Co(PY5Me_2)(ACN)](OTf)_2$ reveals a quasi-reversible redox wave at 0.822 V vs. NHE, Figure 2.6 (dark blue dashed line), corresponding to the cobalt (II)/(III) oxidation.²⁰ Interestingly however, a small shoulder is also observed in the $[Co(PY5Me_2)(ACN)](OTf)_2$ CV, though it is difficult to see in Figure 2.6 and never mentioned in prior reports. Previous electrochemical studies done on the free PY5Me₂ ligand reveal that the molecule is redox inactive, while the cobalt (I)/(II) transition is seen at -0.845 V vs. NHE, ruling out the possibility of these being the origin of the observed shoulder.^{19,20} Given the simplicity of the system, it is speculated that the shoulder could be attributed to a counterion coordinated complex, $[Co(PY5Me_2)(OTf)]^{2+/1+}$, or the five coordinate $[Co(PY5Me_2)]^{3+/2+}$ complex vacant of a species bound to the sixth coordination site.¹⁹



Figure 2.6 Cyclic Voltammograms (CVs) of $[Co(PY5Me_2)(CN)](OTf)$ (red line) and $[Co(PY5Me_2)(ACN)](OTf)_2$ (dark blue dashed line) measured in acetonitrile with 0.1 M TBAPF₆ using a platinum disk working electrode, a platinum mesh counter electrode and a homemade Ag/AgNO₃ (0.1 M TBAPF₆ acetonitrile) reference electrode.

Upon isolation of the $[Co(PY5Me_2)(CN)](OTf)$ complex, three quasi-reversible redox waves are observed when performing the electrochemistry in acetonitrile with 0.1M TBAPF₆, Figure 2.6 (red line). The largest and most negative wave at 0.254 V vs. NHE is assigned to the cobalt (II)/(III) redox potential of the $[Co(PY5Me_2)(CN)]^{2+/1+}$ complex. Even with the use of single crystals, it appears that, after solvation and addition of a supporting electrolyte, small amounts of the $[Co(PY5Me_2)(ACN)]^{2+}$ and what we speculate to be the counterion coordinated, [Co(PY $5Me_2)(OTf)]^+$, exist in solution. This phenomenon becomes more evident upon overlaying the two CVs as in Figure 2.6. The equilibrium of these two species is observed in the electrochemistry of the dimer complex as well, Figure A2.12. Although the cobalt (II)/(III) wave of the two metal centers is predominant and occurs successively between 0.2 - 0.4 V vs. NHE, upon further anodic sweeping the redox waves for both the $[Co(PY5Me_2)(ACN)]^{2+}$ and $[Co(PY5Me_2)(OTf)]^+$ also appear. Unlike $[Co(PY5Me_2)(CN)]^+$, measuring the initial CV of the $[Co(PY5Me_2)(CN)]^{2+}$ complex resulted in the observation of a single $[Co(PY5Me_2)(CN)]^{2+/+}$ redox process, indicating the stability of the oxidized monomer in supporting electrolyte. However, successive CVs of the $[Co(PY5Me_2)(CN)]^{2+}$ complex led to the observed side-product formation shown in Figure 2.6, as the concentration of $[Co(PY5Me_2)(CN)]^+$ built up in solution.

2.4.7 Cross-exchange Kinetics

Stopped-flow spectroscopy was used to determine the homogeneous electron-transfer selfexchange rate constant for $[Co(PY5Me_2)(CN)]^{2+/+}$. Although stability has been demonstrated to be an issue with $[Co(PY5Me_2)(CN)]^+$ while conducting electrochemical studies, short-term stability of the complex was confirmed in neat acetonitrile over the course of a day via ¹H NMR studies. By neglecting the use of a supporting electrolyte, ¹H NMR studies validated the reliability of carrying out stopped-flow studies over the course of a few hours in neat acetonitrile. To isolate the self-exchange rate constant for $[Co(PY5Me_2)(CN)]^{2+/+}$ using stopped-flow, a series of cross-exchange reactions between $[Co(PY5Me_2)(CN)]^+$ and cobalt bis(2,2':6',2''-terpyridine), $[Co(terpy)_2]^{3+}$, were performed, which provided the cross-exchange rate constant, k_{12} , for Reaction 2.1 below:

$$[Co(PY5Me_2)(CN)]^{+} + [Co(terpy)_2]^{3+} \xrightarrow{k_{12}} [Co(PY5Me_2)(CN)]^{2+} + [Co(terpy)_2]^{2+}$$
 E 2.3

Selection of $[Co(terpy)_2]^{3+}$ for the cross-exchange with $[Co(PY5Me_2)(CN)]^+$ was based on the complex's known outer-sphere one electron-transfer mechanism and slow electron-transfer kinetics.²⁹ Given the large potential difference between $[Co(terpy)_2]^{3+/2+}$ and $[Co(PY5Me_2)(CN)]^{2+/+}$, Table A2.4, the reaction was assumed to reach completion without an appreciable

back reaction. Although the large driving force facilitates faster electron-transfer kinetics, low concentrations of the reactants provided sufficient signal and observable decays on the time scale of stopped-flow, which was a result of the large extinction coefficient of the $[Co(terpy)_2]^{2+}$ species formed in solution, Figure A2.11.³¹ Figure 2.7a shows a single exponential fit, $A = A_{\infty} + (A_o - A_{\infty})e^{-k_{obs}t}$, to a plot of the absorbance at 505 nm vs. time, which corresponds to the growth of the $[Co(terpy)_2]^{2+}$ species due to the reduction of $[Co(terpy)_2]^{3+}$ by $[Co(PY5 Me_2)(CN)]^+$. In all reactions the $[Co(PY5Me_2)(CN)]^+$ species was held in excess of $[Co(terpy)_2]^{3+}$, which allowed the observed rate constants, k_{obs} , to be expressed by:

$$k_{obs} = k_{12} [Co(PY5Me_2)(CN)]^+$$
 E 2.3

Figure 2.7b shows a straight line fit of the k_{obs} values plotted as a function of the [Co(PY5 Me₂)(CN)]⁺ concentration and provided the value for the forward rate constant, k_{12} , from the slope, respectively. The initial concentrations for the [Co(PY5Me₂)(CN)]⁺ and [Co(terpy)₂]³⁺ reaction mixtures, as well as the observed pseudo-first order rate constants for each of these electron-transfer reactions can be found in Table A2.5.



Figure 2.7 a) Plot of absorbance at 505 nm vs. time, corresponding to the growth of the $[Co(terpy)_2]^{2+}$ species (red dots) and the resulting single exponential fit (black line) for the reduction of $[Co(terpy)_2]^{3+}$ (4.0 × 10⁻⁵ M) by $[Co(PY5Me_2)(CN)]^+$ (1.2 × 10⁻³ M). b) Pseudo-first

Figure 2.7 (cont'd)

order rate constants, k_{obs} , versus the excess concentration of $[Co(PY5Me_2)(CN)]^+$ for the reactions between $[Co(PY5Me_2)(CN)]^+$ and $[Co(terpy)_2]^{3+}$.

Using the experimentally determined cross-exchange rate constant, k_{12} , for Reaction 2.1 above, the Marcus cross-relation, Equation 2.4, was used to calculate the self-exchange rate constant, k_{11} , for [Co(PY5Me₂)(CN)]⁺:^{32,33}

$$k_{12} \cong \sqrt{k_{11}k_{22}K_{12}}$$
 E 2.4

Where k_{22} is the self-exchange rate constant of $[Co(terpy)_2]^{3+/2+}$, and K_{12} is the equilibrium constant for the electron-transfer reaction. The Marcus cross-relation shown above has been modified to neglect the non-linear correction term, f_{12} , and the electrostatic work term, W_{12} . Both terms are a function of the reaction mixture's ionic strength and given the stability issues of the $[Co(PY5Me_2)(CN)]^+$ complex related to the dissociation and appearance of the [Co(PY5 $Me_2)(ACN)]^{2+}$ and $[Co(PY5Me_2)(OTf)]^+$ complexes upon introduction of a supporting electrolyte, Figures 2.6 and A2.7, stopped-flow solutions were made neat, as mentioned above, and the f_{12} and W_{12} terms ignored. Without supporting electrolyte, however, it is expected that reduced coupling will result and an underestimate of the self-exchange rate constant, k_{11} , for $[Co(PY5Me_2)(CN)]^+$ will be made. The equilibrium constant, K_{12} , for the electron-transfer reaction can be determined based on the free-energy difference of Reaction 2.1 and can be described by Equation 2.5.

$$-nF\Delta E = -RT\ln K_{12} \qquad \qquad E 2.5$$

Where *n* is the number of electrons transferred (n = 1), *F* is Faraday's constant, ΔE is the formal potential difference between the oxidant and reductant in solution, *R* is the gas constant and *T* is the temperature. CVs shown in Figure A2.13 and summarized in Table A2.4 of the SI

indicate a 285 mV formal potential difference between [Co(PY5Me₂)(CN)]^{2+/+} and $[Co(terpy)_2]^{3+/2+}$. The calculated equilibrium constant for the cross-exchange Reaction 2.1 is therefore $(6.6 \pm 0.9) \times 10^4$. The self-exchange rate constant, k_{22} , for $[Co(terpy)_2]^{3+/2+}$ was measured independently by crossing the complex with 1,1'-dimethylferrocene [Fe(C₅H₄CH₃)], Reaction A2.1, under similar conditions i.e. neat acetonitrile. Details regarding the reaction mixtures, experimental design and the resulting equilibrium and kinetic rate constants can be found in the SI and the experimental below. Based on these stopped-flow studies, the selfexchange rate constant, k_{22} , for $[Co(terpy)_2]^{3+/2+}$ was calculated to be 41 ± 9.9 M⁻¹s⁻¹. Such a value matches well with prior literature reports.^{34,35} Using this experimentally determined selfexchange rate constant, k_{22} , for $[Co(terpy)_2]^{3+/2+}$ and the calculated equilibrium constant, K_{12} , the self-exchange rate constant for $[Co(PY5Me_2)(CN)]^{2+/+}$, k_{11} , was calculated to be $20 \pm 5.5 \text{ M}^{-1}\text{s}^{-1}$. This measured self-exchange value for $[Co(PY5Me_2)(CN)]^{2+/+}$ is surprisingly small. Isoelectronic cobalt (II) complexes such as $[Co(ttcn)_2]^{2+}$ sustain self-exchange rate constants several orders of magnitude large than [Co(PY5Me₂)(CN)]^{2+/+,9,36} A few explanations could reconcile the observed phenomenon and will be discussed in detail below. One explanation is that the slow self-exchange kinetics are due to a large inner-sphere reorganization that the complex undergoes upon oxidation. Looking at the crystal structures above, it appears that the equatorial pyridine units of the PY5Me₂ ligand significantly contract (~ 0.1 Å) when going from cobalt (II) to cobalt (III). The large structural change could inhibit the expected fast electron selfexchange, which results in a much smaller self-exchange rate constant.

2.4.8 Recombination Kinetics

To mimic the recombination reactions at a TiO_2 interface, as in operating DSSCs, half-cells were constructed as in Figure A2.16. The three-electrode set-up provided the opportunity to conduct dark recombination studies to better understand the kinetics of interfacial chargetransfer. As depicted, the three-electrode setup was constructed such that a thin mesoporous film of TiO₂, deposited onto an FTO substrate, acted as a working electrode, while a platinum mesh was used as a counter electrode and a homemade Ag/AgNO₃ electrode was used as a reference. Use of a reference electrode was important to these studies since it afforded a way to compare the current density, *J*, for each redox shuttle, at the same TiO₂ potential, regardless of any differences in solution potential there may have been. By directly measuring *J* the differences in recombination rate constants, k_{et} , to the dissolved acceptor, at any given applied potential, *E*, could be identified, assuming the density of conduction band electrons, n_s , at any given applied potential and the initial acceptor/redox shuttle concentrations, [*A*], were the same, Equation 2.6.³⁶

$$J(E) = -qk_{et}[A]n_s E 2.6$$

The measured current density plots as a function of applied potential, *J-E*, for the half-cells employing $[Co(PY5Me_2)(CN)](OTf)_2$ (green dots) and $[Co(bpy)_3](PF_6)_3$ (light blue dots) OSRSs can be found in Figure 2.8 below.



Figure 2.8 Current density (*J*) versus applied potential (*E*) plots for $[Co(PY5Me_2)(CN)](OTf)_2$ (green dots) and $[Co(bpy)_3](PF_6)_3$ (light blue dots) OSRSs measured using a mesoporous TiO₂ working electrode, a platinum mesh counter electrode and a homemade Ag/AgNO₃ (0.1M TBAPF₆) reference electrode in an acetonitrile solution with 0.1M LiOTf.

Selection of $[Co(bpy)_3]^{3+}$ has become the benchmark for our side-by-side comparisons of new OSRSs as it has emerged as the champion redox shuttle, along with the fact that it is expected to employ the same one electron-transfer mechanism as $[Co(PY5Me_2)(CN)]^{2+}$. To ensure accurate measurements were being acquired, CVs were measured before and after the dark recombination studies, which indicated the reference was stable and the redox shuttles were well behaved. We note that carrying out a single dark recombination measurement using $[Co(PY5Me_2)(CN)]^{2+}$ resulted in a negligible concentration of side-products as [Co(PY5Me₂)(CN)]⁺ was produced. However, successive CV scans, as mentioned above, resulted in an obvious evolution of sideproducts, similar to the phenomena observed in Figure 2.6. Based on the CVs, the formal potentials of $[Co(PY5Me_2)(CN)]^{2+/+}$ and $[Co(bpy)_3]^{3+/2+}$ were measured to be 0.254 V and 0.590 V vs. NHE, respectively. Given the dark J-E curve for $[Co(bpy)_3]^{3+/2+}$ was characteristic of that previously measured for $[Co(Me_2bpy)_3]^{3+/2+}$ DSSCs further validated the *J-E* behavior measured for [Co(PY5Me₂)(CN)]^{2+,8} Although rapid stirring was imparted during each measurement, the dark current density did deviated from ideal behavior at more negative potentials due to solution resistance. A comparison of both J-E curves indicates that the onset for recombination and the magnitude of dark current for $[Co(bpy)_3]^{3+}$ is more positive and significantly larger than $[Co(PY5Me_2)(CN)]^{2+}$. Since the current density is a direct measure of recombination, these measurements indicate that the kinetics for interfacial recombination is significantly faster for [Co(bpy)₃]³⁺ compared to [Co(PY5Me₂)(CN)]²⁺. Full DSSCs were fabricated and measured with both $[Co(PY5Me_2)(CN)]^{2+/+}$ and $[Co(bpy)_3]^{3+/2+}$ electrolytes. While the $[Co(PY5Me_2)(CN)]^{2+/+}$ cells outperformed the $[Co(bpy)_3]^{3+/2+}$ cells, the uncertainty in the solution potential, which changes with time, and concentrations of the various redox active species present at the TiO_2 surface, which also changes with time, prevented us from being confident in making solid conclusions; these data were therefore omitted.

2.5 Discussion

Rational design of new OSRSs is pivotal to the development of next generation DSSCs. Control over the coordination environment of cobalt OSRSs provides the ability to fine tune the charge-transfer kinetics of these complexes, which dictate the overall rates of regeneration and recombination in dye cells. Use of the pentadentate PY5Me₂ ligand affords a ligand periphery that enables the binding of a multitude of exogenous ligands, which can control the redox chemistry and spin-state of the cobalt metal center. In an effort to synthesize a new LS Co(II) OSRS that was expected to sustain fast electron-transfer kinetics and a more negative formal potential to inhibit recombination, cyanide, CN⁻, was chosen as the exogenous ligand.

[Co(PY5Me₂)(CN)](OTf) In the theory, synthesis of from the parent $[Co(PY5Me_2)(ACN)](OTf)_2$ was expected to be facile and clean via the addition of a cyanide source. To our surprise, however, the cyanide ligand was observed to be much more labile than anticipated. Careful control over the reaction conditions was necessary in order to mitigate dimerization and/or subsequent cluster formation of a cobalt hexacyanide complex. If the reaction between $[Co(PY5Me_2)(ACN)](OTf)_2$ and CN^- (> 1.5 eq.) was allowed to stir for an extended period of time in an ice bath or was attempted at room temperature, the thermodynamically stable cluster complex was observed to crash out of solution. Structural support of the complex came from X-Ray crystallography, Figure A2.1. Similar structures, referred to as "star-like clusters", have been reported in the literature by the Long group in an effort to study magnetic exchange.³⁷ Through the reaction of $[(PY5Me_2)V(ACN)]^{2+}$ with $[M(CN)_6]^{3-}$ (M = Cr, Mo), a cis cyano cluster $[(PY5Me_2)V_4M(CN)_6]^{5+}$ was obtained, which is
structurally equivalent to the $[(PY5Me_2)_4Co_4Co(CN)_6]^{4+}$ cluster complex that is isolated from our experiments. During ¹H NMR measurements, used to probe the stability of [Co(PY5Me₂)(CN)](OTf) over a couple day period, precipitation of what we expect to be free ligand and the cluster complex is observed, Figure A2.15, in neat acetonitrile and in acetonitrile electrolyte i.e. 0.1M TBAPF₆. Interestingly, with supporting decomposition of $[Co(PY5Me_2)(CN)](OTf)$ is facilitated more rapidly upon addition of the TBAPF₆ supporting electrolyte and after several days the ¹H NMR provides chemical shifts for the free PY5Me₂ ligand, the dimer complex, as well as the [Co(PY5Me₂)(CN)](OTf) complex originally being studied, Figure A2.7. Formation of the dimer complex indicates free cyanide being liberated into solution as well as the presence of the solvato complex, [Co(PY5Me₂)(ACN)]²⁺. Given the lability of Co(II) and the steric strain of the equatorial pyridines $(N_2 - Co - N_3)$, Table 2.1, the formation of $[Co(CN)_6]^{4-}$ seems feasible by way of excess cyanide displacing the PY5Me₂ ligand. Any available $[Co(PY5Me_2)(ACN)]^{2+}$ is then expected to coordinate via the accessible lone pair of the nitrogen Lewis base on the cyanide ligands of the $[Co(CN)_6]^{4-}$ complex formed in solution. This would provide an explanation for the observed precipitate and the lack of appreciable $[Co(PY5Me_2)(ACN)]^{2+}$ found in the ¹H NMR spectrum.

Modification of the reaction conditions such that only one or less equivalents (≤ 1 eq.) of CN⁻ are added to the [Co(PY5Me₂)(ACN)](OTf)₂ reaction mixture at low temperature, results in the predominant isolation of a dimer complex. Single crystals were easily grown and the structural integrity was confirmed via X-Ray crystallography, Figure 2.3. Vibrational studies of the dimer complex revealed a single sharp CN signal in the Raman spectrum that was slightly blue shifted from the monomeric Co(II) complex. ¹H NMR studies using single crystals of the dimer complex, Figure A2.6, provided unique a spectrum to that measured for

[Co(PY5Me₂)(ACN)](OTf), Figure A2.4. With chemical shifts as far downfield as 80ppm, we speculate that the dimer complex is HS, however, any attempt to measure the magnetic susceptibility via the Evans method would be difficult as there are clearly multiple species that form in solution upon solvation of the pure complex. When overlaid, the chemical shifts of both the [Co(PY5Me₂)(ACN)](OTf)₂ and [Co(PY5Me₂)(CN)](OTf), Figures A2.3 & A2.4, align well with the various chemical shifts found in the dimer spectrum, Figure A2.6. Electrochemical measurements of the dimer complex, Figure A2.12, rectify the phenomena observed by ¹H NMR. Though it is difficult to assess the abundance of $[Co(PY5Me_2)(CN)](OTf)$, as there are two successive redox waves atop the expected formal potential of $[Co(PY5Me_2)(CN)](OTf)$, it is clear that the $[Co(PY5Me_2)(ACN)](OTf)_2$ and what is speculated to be the [Co(PY5Me₂)(OTf)](OTf) complex are both present, which confirms the lability of the dimer complex in solution.

Isolation of the pure $[Co(PY5Me_2)(CN)](OTf)$ complex was achieved by ensuring the reaction between $[Co(PY5Me_2)(MeCN)](OTf)_2$ and CN^- was carried out using a slight excess of CN^- , at low temperature and in a non-competitive solvent. After complexation of the exogenous cyanide, the complex was determined to be stable for several hours in neat acetonitrile, which enabled magnetic susceptibility measurements to be carried out. However, introduction of any supporting electrolyte immediately induced the dissociation of cyanide, Figure 2.6, and the conversion to the dimer and/or cluster complex. Surprisingly, even the synthesis of the oxidized $[Co(PY5Me_2)(CN)](OTf)_2$ complex needed to be carefully completed. Initial attempts to oxidize the parent $[Co(PY5Me_2)(ACN)](OTf)_2$ complex with Ag^+ resulted in unwanted side products that readily formed purple crystals suitable for X-Ray crystallography, Figure A2.2. As was previously observed, oxidation of the parent $[Co(PY5Me_2)(ACN)](OTf)_2$ resulted in chemistry

occurring with the counterion in solution, which liberated fluoride to produce a $[Co(PY5Me_2)(F)](OTf)_2$ complex.²¹ Therefore, to obtain the pure $[Co(PY5Me_2)(CN)](OTf)_2$ complex, the synthesis was carried out by oxidizing $[Co(PY5Me_2)(CN)](OTf)$ with AgOTf. This yielded a clean product since any potential AgCN that precipitated out of solution was filtered off with the precipitated silver solid and any unreacted $[Co(PY5Me_2)(CN)](OTf)$ or $[Co(PY5Me_2)(MeCN)](OTf)_2$ could be neatly removed by washing the crude $[Co(PY5Me_2)(CN)](OTf)_2$ powder with dichloromethane.

An in-depth analysis of the $[Co(PY5Me_2)(CN)]^{2+/+}$ crystal structures appeared to suggest the changes in bond distances upon oxidation or reduction supported a LS Co(II) to LS Co(III) transition, which corroborate the data collected for magnetic susceptibility and ¹H NMR. The average bond length change of the Co-N bonds of the pyridine units is only ~0.104 Å, which is significantly smaller than those reported for well-known HS Co(II) redox shuttles such as $[Co(bpy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ that have known Co-N bond length changes of ~0.19 Å upon oxidation.^{16,38,39} Previously reported Co(II) redox shuttles with similar structures such as $[Co(PY5Me_2)(NMBI)]^{/2+}$, where NMBI represents *N*-methylbenzimiazole, also contained larger average Co-N bond length changes of ~0.150 Å.²¹ With such minor average Co-N bond length changes of the [Co(PY5Me₂)(CN)]^{2+/+} complex, one would expect intrinsically fast selfexchange kinetics, however, this doesn't appear to be the case. Using stopped-flow spectroscopy, the calculated self-exchange rate constant, k_{11} , for $[Co(PY5Me_2)(CN)]^{2+/+}$ was only determined to be 20 \pm 5.5 M⁻¹s⁻¹. This is orders of magnitude lower than the value (~1.1 × 10⁴ M⁻¹s⁻¹) determined for another isoelectronic LS Co(II) complex, $[Co(ttcn)_2]^{3+/2+}$, also measured using stopped-flow spectroscopy.^{9,16} Slower self-exchange kinetics were expected for the $[Co(PY5Me_2)(CN)]^{2+/+}$ cross-exchange reactions given the lack of supporting electrolyte.

However, such a drastic difference in self-exchange rates is unlikely to be strictly due to the increased work function associated with electron-transfer. Thus, we reasoned from the crystal structures and UV-Vis data that the slower observed kinetics were likely due to a Jahn-Teller distortion of the $[Co(PY5Me_2)(CN)]^+$ complex. As mentioned above, the equatorial pyridines go through a rather large contraction (~0.125 Å) upon oxidation, while the axial bonds change minimally, suggesting the complex undergoes a Jahn-Teller compression, Figure 2.9.

 $[Co(PY5Me_2)(CN)]^+$ complex.



Figure 2.9 Splitting of the d-orbitals based on the hypothesized Jahn-Teller compression of the $[Co(PY5Me_2)(CN)]^+$ complex.

It is difficult, however, to verify such phenomena using simple UV-Vis measurements of the $[Co(PY5Me_2)(CN)]^+$ species. The strong broad visible absorption coupled with the MLCT transitions between 300-400 nm masks any noticeable d-d transitions. Interestingly, even though LS Co(III) isn't supposed to Jahn-Teller distort, the multi-featured d-d transition, Figure 2.5 inset, implies non-degenerate d-orbitals with more than one electronic transition. This is expected to be more obvious in the $[Co(PY5Me_2)(CN)]^+$ UV-Vis, but again remains hidden by the broad visible absorption band. Aside from the complexes ability to go through a Jahn-Teller compression, another possible explanation for the smaller observed self-exchange rate constant

could be that the complex transfers charge via an inner-sphere mechanism rather than an outersphere mechanism. In all assumptions above, it is thought that the activation-complexes are two separate entities; however, it is difficult to rule out the possibility that $[Co(PY5Me_2)(CN)]^{2+/+}$ doesn't complex to transfer electrons. The accessible lone pair of the nitrogen Lewis base has been shown to dimerize in solution, which would suggest it could pair with the acidic cobalt metal center of the $[Co(terpy)_2]^{3+/2+}$ complex when carrying out the cross-exchange reaction.

Although the self-exchange kinetics of $[Co(PY5Me_2)(CN)]^{2+/+}$ are slower than expected, it still remains an interesting redox shuttle for regenerating IR absorbing sensitizers. Simple dark J-*E* measurements, Figure 2.8 above, comparing $[Co(PY5Me_2)(CN)]^{2+}$ to $[Co(bpy)_3]^{3+}$ qualitatively demonstrates that the recombination rates to $[Co(PY5Me_2)(CN)]^{2+}$ are much slower than to $[Co(bpy)_3]^{3+}$. According to Equation 2.6, the dark current that is measured for each shuttle is directly proportional to the rate constant for recombination, k_{et} , at any given applied bias of the TiO₂ electrode.³⁷ Thus, after comparing the dark currents between the two different redox shuttles at the same applied bias, it appears that at the formal potential of $[Co(PY5Me_2)(CN)]^{2+}$ (0.254 V vs. NHE), the recombination rate constant is over three orders of magnitude larger for [Co(bpy)₃]³⁺ than [Co(PY5Me₂)(CN)]²⁺. Additionally, nearly 0.380 V must be applied past the formal potential of $[Co(PY5Me_2)(CN)]^{2+}$, while only ~0.270 V must be applied past the formal potential of $[Co(bpy)_3]^{3+}$ in order to reach the same magnitude of dark current, -1 mA cm⁻². From these dark recombination measurements it seems clear that $[Co(bpy)_3]^{3+}$ is a much better acceptor than $[Co(PY5Me_2)(CN)]^{2+}$. Such a conclusion can be attributed to the reduced driving force for recombination of conduction band electrons and the intrinsically small self-exchange rate constant of [Co(PY5Me₂)(CN)]²⁺. Given the observed

kinetic behavior, if introduced into DSSCs, superior charge collection is expected for cells containing $[Co(PY5Me_2)(CN)]^{2+/+}$ coupled with the properly integrated IR absorbing sensitizer.

2.6 Conclusion

A new LS Co(II) redox shuttle has been synthesized and fully characterized for its potential application in DSSCs. The new class of cobalt redox shuttles shares the caveat that coordination of the pentapyridine ligand, PY5Me₂, affords the opportunity to functionalize the sixth site of the cobalt metal center with a variety of exogenous ligands that can not only modulate the redox potential of the shuttle, but also manipulate the spin-state of the complex. In an effort to force Co(II) to become LS, cyanide was chosen as the exogenous ligand. Magnetic susceptibility measurements were used to confirm the Co(II) complex, [Co(PY5Me₂)(CN)](OTf), was in fact LS upon isolating of the pure product. Interestingly, the cyanide ligand was much more labile than expected in a competitive coordinating solvent such as acetonitrile. Dissociation of the cyanide resulted in dimerization and the thermodynamically stable cluster complex. Without the use of a supporting electrolyte to help facilitate cyanide dissociation, the

 $[Co(PY5Me_2)(CN)](OTf)$ complex was stable enough in neat acetonitrile to collect kinetic measurements using stopped-flow spectroscopy. The unexpectedly slow self-exchange rate constant ($k_{11} = 20 \pm 5.5 \text{ M}^{-1}\text{s}^{-1}$) was hypothesized to arise from either a Jahn-Teller compression observed by collecting single crystals of the $[Co(PY5Me_2)(CN)]^{2+/+}$ complexes and/or a more complicated inner-sphere mechanism via complexation through the nitrogen lone pair of the exogenous cyanide ligand. Dark *J-E* measurements suggested that rates of recombination to the oxidized redox shuttle, $[Co(PY5Me_2)(CN)]^{2+}$ are actually slower than the champion redox shuttle, $[Co(bpy)_3]^{3+}$, when compared side-by-side. As a result, the $[Co(PY5Me_2)(CN)]^{2+/+}$ redox shuttle becomes an attractive candidate as a solid state hole conductor for DSSCs with the

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promise of achieving quantitative charge collection, while also having the ability to successfully regenerate near IR and/or IR absorbing sensitizers.

APPENDIX

Compound		Calculated			Found		
		C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
[Co(PY5Me ₂)(MeCN)](OTf) ₂	$C_{33}H_{28}CoF_6N_6O_6S_2$	47.09	3.35	9.99	45.33	3.03	8.56
[Co(PY5Me ₂)(CN)](OTf)	$C_{31}H_{25}CoF_3N_6O_3S$	54.95	3.72	12.40	54.47	3.71	11.90
[Co(PY5Me ₂)(CN)](OTf) ₂	$C_{32}H_{25}CoF_6N_6O_6S_2$	46.50	3.05	10.17	45.67	3.17	9.59

Table A2.1 Elemental analysis summary of the investigated cobalt complexes.

Table A2.2 Selected bond lengths and angles for the dimer complex, $C_{66}H_{56}Co_2F_9N_{13}O_9S_3$. Note– bond lengths are reported in angstroms (Å) and bond angles are in degrees (°). The standard deviations of each value are shown in parenthesis.

Bond Distances	Dimer Complex	Bond Angles	Dimer Complex
Co1 - N1	2.042(5)	N1 - Co1 - N2	87.6(3)
Co1 - N2	2.096(6)	N1 - Co1 - N3	88.2(3)
Co1 - N3	2.120(8)	N1 - Co1 - N4	86.6(3)
Co1 - N4	2.115(7)	N1 - Co1 - N5	88.8(2)
Col - N5	2.119(7)	N1 – Co1 –C30	178.2(3)
Co1 - C30	1.963(9)	N2 - Co1 - N3	82.4(3)
C30 - N6	1.16(1)	N2 - Co1 - N4	173.9(3)
Co2 - N6	1.987(9)	N2 - Co1 - N5	95.9(3)
Co2 - N7	2.066(5)	N2 - Co1 - C30	94.2(3)
Co2 - N8	2.085(8)	N3 - Co1 - N4	99.2(3)
Co2 - N9	2.138(6)	N3 - Co1 - N5	176.6(3)
Co2 - N10	2.095(8)	N3 - Co1 - C30	92.0(3)
Co2 - N11	2.147(6)	N4 - Co1 - N5	82.2(3)
-	-	N4 - Co1 - C30	91.6(3)
-	-	N5 - Co1 - C30	91.1(3)
-	-	N6 - C30 - Co1	177.7(7)
-	-	C30 - N6 - Co2	177.5(7)
-	-	N6 - Co2 - N7	179.0(3)
-	-	N6 - Co2 - N8	90.7(3)
-	-	N6 - Co2 - N9	93.5(3)
-	-	N6 - Co2 - N10	91.8(3)
-	-	N6 - Co2 - N11	93.6(3)
-	-	N7 - Co2 - N8	89.0(2)
-	-	N7 - Co2 - N9	87.5(2)
-	-	N7 - Co2 - N10	88.5(2)
-	-	N7 - Co2 - N11	85.4(2)
-	-	N8 - Co2 - N9	81.3(3)
-	-	N8 - Co2 - N10	176.8(3)
-	-	N8 - Co2 - N11	98.6(3)
-	-	N9 - Co2 - N10	96.6(3)
-	-	N9 - Co2 - N11	172.9(3)
-	-	N10 - Co2 - N11	83.2(3)



Figure A2.1 Single crystal representation of the Cluster complex, $C_{125}H_{112}C_{05}F_9N_{26}O_9S_3$, provided by Olex2 and structurally refined by ShelXT software. Note that protons and counterions are omitted for image clarity.



Figure A2.2 Single crystal representation of $[Co(PY5Me_2)(F)](OTf)_2$ provided by Olex2 and structurally refined by ShelXT software. Note that counter ions and solvent molecules are omitted for image clarity. Note- Similar structures to $[Co(PY5Me_2)(F)](OTf)_2$ (Complex 5 in Table A2.2 above) have been reported in prior literature.^{42,43}



Figure A2.3 ¹H NMR of [Co(PY5Me₂)(MeCN)](OTf)₂ in acetonitrile-d3.



Figure A2.4 ¹H NMR of [Co(PY5Me₂)(CN)](OTf) in acetonitrile-*d3*. Inset shows there is a broad downfield chemical shift around 58ppm, which is more obvious at higher concentrations.



Figure A2.5 ¹H NMR of $[Co(PY5Me_2)(CN)](OTf)_2$ in acetonitrile-*d3*. Inset shows the chemical shift and integration for the methyl groups of the PY₅Me₂ ligand.



Figure A2.6 ¹H NMR of the dimer complex, $C_{66}H_{56}Co_2F_9N_{13}O_9S_3$, in acetonitrile-*d3*. Inset is meant to demonstrate that there are no chemical shifts in the aromatic region for the $[Co(PY5Me_2)(CN)](OTf)_2$ and/or free PY5Me₂ ligand.



Figure A2.7 a) ¹H NMR indicating the stability of $[Co(PY5Me_2)(CN)](OTf)$ with 0.1M TBAPF₆ in acetonitrile-*d3* after several days and b) an enhancement of the aromatic region with the free PY5Me₂ ligand (purple) overlaid on the $[Co(PY5Me_2)(CN)](OTf)$ (red) spectrum. The inset of a) indicates the chemical shifts for the formation of the dimer complex. The inset of b) indicates the chemical shifts associated with the TBA.



Figure A2.8 a) & b) ¹H NMR indicating the stability of $[Co(PY5Me_2)(CN)](OTf)_2$ with 0.1M TBAPF₆ in acetonitrile-*d3* after several days. The inset of a) indicates the chemical shift for the methyl groups of the PY5Me₂ ligand. The inset of b) indicates the chemical shifts associated with the TBA. Note- $[Co(PY5Me_2)(CN)](OTf)_2$ is sparingly soluble in acetonitrile with 0.1M TBAPF₆ supporting electrolyte.



Figure A2.9 Magnetic susceptibility measurements in acetonitrile-*d3* using the Evans method and following the ¹H chemical shift of ferrocene, $[Fe(C_5H_5)_2]$, after additions of the paramagnetic $[Co(PY5Me_2)(CN)](OTf)$ complex.



Figure A2.10 UV-Vis spectrum of the PY5Me₂ ligand, where PY5Me₂ represents 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine, in acetonitrile.



Figure A2.11 UV-Vis spectra of the $[Co(terpy)_2](PF_6)_2$ (pink) and $[Co(terpy)_2](PF_6)_3$ (orange) complexes, where terpy represents 2,2':6',2''-terpyridine, in acetonitrile.



Figure A2.12 Normalized cyclic voltammogram (CV) of the Dimer Complex measured in acetonitrile with 0.1 M TBAPF₆ supporting electrolyte using a platinum disk working electrode, a platinum mesh counter electrode and a homemade $Ag/AgNO_3$ (0.1 M TBAPF₆ acetonitrile) reference electrode.



Figure A2.13 Normalized cyclic voltammograms (CVs) of $[Fe(C_5H_5)_2]$ (black line), $[Fe(C_5H_4CH_3)_2]$ (green line) and $[Co(terpy)_2](PF_6)_2$ (pink line) measured in acetonitrile with 0.1 M TBAPF₆ supporting electrolyte using a platinum disk working electrode, a platinum mesh counter electrode and a homemade Ag/AgNO₃ (0.1 M TBAPF₆ acetonitrile) reference electrode.

Table A2.3 Formal reduction potentials, E° , of $[Co(PY5Me_2)(X)]$ (X = MeCN or CN), $[Co(terpy)_2]^{3+/2+}$ and 1,1'-dimthylferrocene, $[Fe(C_4H_5CH_3)_2]^{+/0}$, redox shuttles measured via cyclic voltammetry (CV). Ferrocene, $[Fe(C_5H_5)_2]^{+/0}$, is also included as a point of reference in converting from Ag/AgNO₃ to NHE (ferrocene: 0.40V vs. SCE).⁴⁴ All formal potentials were measured in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate, TBAPF₆, supporting electrolyte using a platinum working electrode, platinum mesh counter electrode and a homemade Ag/AgNO₃ (0.1 M TBAPF₆ acetonitrile) reference electrode.

Redox Couple	E° (mV vs NHE)
$[Co(PY5Me_2)(MeCN)]^{3+/2+}$	822 ± 3
$[Co(PY5Me_2)(CN)]^{2+/+}$	254 ± 3
$\left[\text{Co}(\text{terpy})_2\right]^{3+/2+}$	539 ± 2
$[Fe(C_4H_5CH_3)_2]^{+/0}$	527 ± 5
$[Fe(C_5H_5)_2]^{+/0}$	641 ± 9

Table A2.4 Observed rate constants, k_{obs} , and the initial reaction mixtures for the cross-exchange reactions between [Co(PY5Me₂)(CN)](OTf) and [Co(terpy)₂](PF₆)₃, Reaction 2.1 of the main text, in neat acetonitrile at $25 \pm 0.1^{\circ}$ C.

$[Co(PY5Me_2)(CN)]^+ / M$	$\left[Co(terpy)_2\right]^{3+}/M$	k _{obs} / s ⁻¹
6.00×10^{-4}		4.5 ± 0.3
8.00×10^{-4}	4.00×10^{-5}	5.7 ± 0.2
1.00×10^{-3}		7.2 ± 0.2
1.20×10^{-3}		8.9 ± 0.5

$$[Fe(C_5H_4CH_3)_2] + [Co(terpy)_2]^{3+} \stackrel{k23}{\rightleftharpoons} [Fe(C_5H_4CH_3)_2]^{+} + [Co(terpy)_2]^{2+} \qquad \text{E A2.1}$$



Figure A 2.14 a) Plot of absorbance at 505 nm vs. time, corresponding to the growth of the $[Co(terpy)_2]^{2+}$ species (red dot) and the resulting fit (black line) for the reduction of $[Co(terpy)_2]^{3+}$ (3.0 × 10⁻⁵ M) by $[Fe(C_5H_4CH_3)]$ (6.0 × 10⁻⁴ M). b) Pseudo-first order rate constants, k_{obs} , versus the excess concentration of $[Fe(C_5H_4CH_3)]$ for the reactions between $[Fe(C_5H_4CH_3)]$ and $[Co(terpy)_2]^{3+}$.

Table A2.5 Observed rate constants, kobs, and the initial reaction mixtures for the cross-exchange between [Fe(C5H4CH3)] and [Co(terpy)2](PF6)3, Reaction (2) of the text, in neat acetonitrile at $25 \pm 0.1^{\circ}$ C.

$\left[Fe(C_5H_4CH_3)\right]/M$	$[Co(terpy)_2]^{3+} / M$	$[Fe(C_5H_4CH_3)]^+ / M$	$k_{\rm obs}$ / s ⁻¹
3.00×10^{-4}			7.6 ± 0.2
$4.00 imes 10^{-4}$			10.3 ± 0.4
$5.00 imes10^{-4}$	$3.00\times 10^{\text{-5}}$	3.00×10^{-4}	12.4 ± 0.2
$6.00 imes10^{-4}$			14.4 ± 0.3
$7.00 imes10^{-4}$			17.2 ± 0.5

Table A2.6 Kinetic summary of the cross-exchange rate constants, k_{23} and k_{32} , and the measured equilibrium constants for the forward reaction, K_{23} , for Reaction 2.2 between [Fe(C₅H₄CH₃)] and [Co(terpy)₂](PF₆)₃ in neat acetonitrile at 25 ± 0.1°C.

Kinetic Parameter	Cross-exchange values
K_{23} (Nernst)	1.6 ± 0.3
$K_{23} (k_{23} / k_{32})$	9.8 ± 5.9
$k_{23} / (\mathrm{M}^{-1}\mathrm{s}^{-1})$	$(2.3\pm0.8)\times10^4$
$k_{32} / (\mathbf{M}^{-1}\mathbf{s}^{-1})$	$(2.4 \pm 1.4) \times 10^3$



Figure A2.15 NMR tubes displaying $[Co(PY5Me_2)(CN)]$ degradation (precipitate) in neat acetonitrile-*d3* (right) and in acetonitrile-*d3* with 0.1 M TBAPF₆ supporting electrolyte (left).



Figure A2.16 Experimental three-electrode setup used to measure the recombination kinetics of $[Co(PY5Me_2)(CN)](OTf)_2$ and $[Co(bpy)_3](PF_6)_3$.⁴⁵ Depicted is a mesoporous TiO₂ film sintered to an FTO substrate (working electrode) clamped to a cuvette cutout and exposed to 2mL of an acetonitrile containing 20mM of the oxidized redox shuttle and 0.1M LiOTf. A high surface area platinum (Pt) mesh was used as a counter electrode and a homemade Ag/AgNO₃ (0.1M TBAPF₆) was used as a reference electrode as well. CVs were taken with a Pt wire working electrode before and after the dark recombination studies in order to check that the redox potentials of $[Co(PY5Me_2)(CN)](OTf)_2$ and $[Co(bpy)_3](PF_6)_3$ were stable and/or side products weren't forming.

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Chapter 3: Low-Spin Co(II) Redox Shuttle by Isocyanide Coordination

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3.1 Abstract

Coordination of the strong-field ligand 2,6-dimethylphenyl isocyanide (DMP-CN) to the $Co(PY5Me_2)$ framework, where PY5Me_2 represents the pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine, has resulted in a new low-spin Co(II) complex with a relatively low reorganization energy and fast electron-transfer kinetics compared to the prototypical cobalt trisbipyridine redox shuttle, $[Co(bpy)_3]^{3+/2+}$, where bpy represents 2,2'-bipyridine. Despite nearly 160 mV reduced regeneration driving force, the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ redox shuttle displayed an increased regeneration efficiency relative to $[Co(bpy)_3]^{3+/2+}$, however recombination losses hinder the performance as evidenced by a reduced recombination resistance. Future directions point to low-spin Co(II) redox shuttles with more negative redox potentials to be paired with a dye or dye mixture that absorbs into the near infrared region.

3.2 Introduction

Dye-sensitized solar cells, DSSC's, remain a promising solar energy conversion technology. Through continued optimization of the photoanode, dye, redox shuttle and counter electrode, DSSC's have recently reached power conversion efficiencies greater than 13 % under AM 1.5 illumination and 32 % under 1000 lux illumination.^{1,2,3,4} The first major successes came from a small class of ruthenium sensitizers with long excited state lifetimes and broad absorbance across the visible spectrum.^{5,6} These systems performed well when paired with the iodide/triiodide electrolyte but had several inherent drawbacks. Primarily, a large overpotential was required to efficiently regenerate these dyes due to the multi-electron transfer pathway of the redox shuttle.^{7,8} In order to reduce the voltage loss of the devices, one electron outer-sphere redox couples have been used to efficiently reduce the oxidized sensitizers. The most successful of these redox couples have been cobalt and copper based redox shuttles that have displayed near unity dye regeneration with less required driving force than iodide.^{9,10} By tuning the ligand scaffold of these complexes; the redox potentials have been optimized to supply the maximum photovoltage while still efficiently regenerating the sensitizers. The reorganization energy is a key parameter that should allow for further optimization of the charge-transfer kinetics in a DSSC. It has been shown previously that cobalt redox couples typically have a large innersphere reorganization energy due to the structural changes associated with the high-spin Co(II) to low-spin Co(III) electronic configuration change during electron transfer.¹¹ In order to reduce the electron transfer barrier, we have investigated use of strong-field ligands to induce a low-spin electronic configuration of Co(II) metal centers.¹² For example, [Co(ttcn)]^{3+/2+} displayed improved dye regeneration kinetics over the high performing redox couple $[Co(bpy)_3]^{3+/2+}$ despite 50 mV less driving force for regeneration.¹³ However, the redox couple suffered from greater recombination losses due to the smaller inner-sphere reorganization energy which resulted nominally the same power conversion efficiency. While the $[Co(ttcn)]^{3+/2+}$ redox shuttle has some promising attributes, it is limited by not being amenable to manipulation of redox potential through modification of the ligand framework. There are very few other reported examples of low-spin Co(II) complexes which are viable alternative redox shuttles for DSSCs.

In order to develop a new family of low-spin Co(II) complexes, where the redox potential can be tuned, we turned to the PY5Me₂ ligand, where PY5Me₂ represents the pentadentate ligand 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine.¹⁴ Some $[Co(PY5Me_2)(L)]^{3+/2+}$ redox couples have been used previously in dye-sensitized solar cells, but these works involved relatively small perturbations in the redox potential by coordination of bases commonly used in the electrolyte, and no examples of low-spin Co(II) complexes.¹⁵ Our group attempted to develop a new lowspin Co(II) redox shuttle by cyanide coordination to the PY5Me₂ framework.¹⁶ Unfortunately, the cyanide ligand acted as a bridging unit to form dimer and cluster complexes in solution which prohibited the redox shuttle from being used in full devices. In this work, the strong-field ligand 2,6-dimethyphenyl isocyanide (DMP-CN) was coordinated to the $[Co(PY5Me_2)(L)]^{3+/2+}$ couple to result in a new low-spin Co(II) redox shuttle. This allowed for further study between the balance of redox potential and reorganization energy and their effects on the kinetics of electron transfer in the DSSCs.

3.3 Experimental

3.3.1 Materials

All chemicals were either purchased from commercial suppliers or synthesized from commercially available reagents. 2-ethyl pyridine, 2-fluoropyridine, and 2,6-difluoropyridine were purchased from oakwood chemical and used as received. Acetonitrile-d3, EDOT, and

sodium dodecyl sulfate were purchased from MilliporeSigma. Tert-butyl alcohol was purchased from Alfa Aesar and used as received. PY5Me₂ (2,6-bis(1,1-bis(2-pyridyl)-ethyl)pyridine) was synthesized as reported previously.¹⁴ Tris(4-bromo-phenyl)amine was purchased from TCI America and used as received. Tris(4-bromo-phenyl)amine hexafluorophosphate [TBPA](PF₆) was synthesized by modifying a previous preparation as described below.¹⁷ Dimethyl phenyl isocyanide was synthesized as previously described but purified further by recrystallizing twice from hot hexanes and cooling in a freezer.¹⁸ Thallium hexafluorophosphate was obtained from STREM chemical and used as received. Nitrosonium hexafluorophosphate was purchased from Fisher Scientific and used as received. D35cpdt was purchased from Dyenamo and used as received. Chenodeoxycholic acid and 25 μ m surlyn were purchased from Solaronix and used as received. [Co(bpy)₃](PF₆)₂ and [Co(bpy)₃](PF₆)₃ were synthesized using previously established procedures.¹² [Co(PY5Me₂)(I)]I and [Co(PY5Me₂)(ACN)](PF₆)₂ were synthesized as listed previously except the reaction time was shortened to 16 hours for both complexes.¹⁹ All [Co(PY5Me₂)(L)] complexes were synthesized in a nitrogen filled glovebox.

3.3.2 [Co(PY5Me₂)(ACN)](PF₆)₃

 $[Co(PY5Me_2)(ACN)](PF_6)_2$ (0.12 mmol 0.100 g) was weighed into a 20-mL vial. [TBPA](PF_6) (0.12 mmol 0.075 g) was weighed into a separate 20-mL vial then quantitatively transferred with 3 x 1 mL portions of dry acetonitrile. The solution immediately turned dark red with a white precipitate. After stirring for two hours 18 mL of dry dichloromethane was added to solvate the white solid and precipitate the red-brown solid product. The solvent was decanted and the solid was washed with 3 x 1 mL portions of dry DCM (Yield: 0.107 g, 91.3 %). 1H NMR (500 MHz, Acetonitrile-d3) δ 9.53 (d, J = 6.3 Hz, 4H), 8.38 – 8.31 (m, 1H), 8.29 – 8.22 (m, 8H), 8.17 (dd, J = 8.1, 1.5 Hz, 4H), 7.89 – 7.82 (m, 4H) 2.87 (s, 6H) Elemental analysis: found (calculated) for Co(PY5Me₂)(ACN)(PF₆)₃, C₃₁H₂₈CoF₁₈N₆P₃: C, 37.89(38.05); H, 3.04(2.88); N, 7.79(8.59).

3.3.3 [Co(PY5Me₂)(DMP-CN)](PF₆)₂

 $[Co(PY5Me_2)(ACN)](PF_6)_2$ (0.88 mmol, 0.734 g) was weighed into a 20-mL vial. Dimethyl phenyl isocyanide (1.3 mmol, 0.173 g) was weighed into a separate 20-mL vial. The DMP-CN was quantitatively transferred with 3 x 1 mL portions of dry DCM into the vial containing the $[Co(PY5Me_2)(ACN)(PF_6)_2$ complex. Another 10 mL of dry DCM was added, and the mixture was stirred for 24 hours. The solvent was then removed by roto-evaporation outside the glovebox. The product was brought back into the glovebox and was washed with 3 x 2 mL portions of dry diethyl ether (Yield: 0.782 g, 88.0 %). Elemental analysis: found (calculated) for $Co(PY5Me_2)(DMP-CN)(PF_6)_2 \cdot CH_2Cl_2$, $C_{39}H_{36}Cl_2CoF_{12}N_6P_2$: C, 46.64(46.45); H, 3.47(3.60); N, 8.47(8.33).

3.3.4 [Co(PY5Me₂)(DMP-CN)](PF₆)₃

 $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ (0.54 mmol, 0.500 g) was weighed into a 20-mL vial. [TBPA](PF_6) (0.54 mmol, 0.339 g) was weighed into a separate 20-mL vial. The [TBPA](PF_6) was quantitatively transferred with 3 x 2 mL portions of dry dichloromethane into the vial with $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$. The dark red solution was then stirred resulting in the precipitation of a yellow solid. After stirring for 2 hours the mixture was centrifuged at 3000 rpm for 5 minutes outside the glovebox. The solvent was then decanted and the solid was washed with 3 x 2 mL portions of dichloromethane with centrifugation between each wash at 3000 rpm for 5 minutes (Yield: 0.354 g, 61.2 %). 1H NMR (500 MHz, Acetonitrile-d3, 0.2 M DMP-CN) δ 9.77 – 9.65 (d, J = 6.23 4H), 8.48 (dd, J = 8.6, 7.3 Hz, 1H), 8.39 (d, J = 7.9 Hz, 2H), 8.30 – 8.21 (m, 8H), 7.78 (td, J = 6.4, 2.6 Hz, 4H), 7.58 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 7.7 Hz, 2H), 2.94 (s, 6H), 2.25 (s, 6H). Elemental analysis: found (calculated) for C₃₈H₃₄CoF₁₈N₆P₃: C, 41.34(42.71); H, 3.14(3.21); N, 7.51(7.86).

3.3.5 DSSC Fabrication

TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 min followed by manual scrubbing of the FTO with Kimwipes. The pieces were then sonicated in DI water for 10 minutes, rinsed with acetone and sonicated in isopropanol for 10 min. The pieces were dried in room air and were immersed in an aqueous 40 mM solution TiCl₄ solution for 30 min at 70 °C. The pieces were immediately rinsed with 18 MΩ water and were annealed by heating from room temperature to 500 °C and then holding at 500 °C for 30 minutes. A 0.36 cm² area was doctor bladed with commercial 30 nm TiO₂ nanoparticle paste (DSL 30NRD) diluted with equal masses of α -terpinol and 10 % ethyl cellulose by weight in ethanol. The transparent films were left to rest for 10 minutes and were then placed in a 100 °C oven for 15 min. The oven was then ramped to 325 °C for 5 min, 375 °C for 5 min, 450 °C for 5 min, and 500 °C for 15 min. After cooling to room temperature, a scattering layer was applied (PST-400C, JGC Catalysts) and annealed by the same method as the transparent layer. The 30 nm film thickness was measured to be 1 µm and with scattering layer deposited on top 6.5 µm total. After cooling to room temperature, a second TiCl₄ treatment was performed as described above. When the anodes had cooled to 80 °C they were soaked in a dye solution of 0.1 mM D35cpdt with 0.1 mM chenodeoxycholic acid in 1:1 acetonitrile: tert-butanol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen. The PEDOT counter electrodes were prepared by electropolymerization in a solution of 0.01 M EDOT in 0.1 M SDS in 18 MΩ water.²⁰ A constant current of 8.3 mA for 300 seconds was applied to a 54 cm² piece of TEC 15 FTO with predrilled holes using an equal size

piece of FTO as the counter electrode. The PEDOT electrode was then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 2.0 cm pieces. The working and counter electrodes were sandwiched together with 25 μ m surlyn films by placing them on a 140 °C hotplate and applying pressure with a hot iron. Contact to the TiO₂ electrode was made by scratching the edge of the electrode gently with sandpaper and applying silver epoxy and copper wire. The counter electrode was connected directly with silver epoxy and copper wire. The silver epoxy was dried in a 60 °C vacuum oven for 90 minutes and then the cells were filled with electrolyte through one of the two predrilled holes and were sealed with 25 μ m surlyn backed by a glass coverslip and applied heat to seal. The electrolyte consisted of 0.15 M Co(II), 0.01 M Co(III) and 0.1 M LiPF₆ in dry acetonitrile. 0.2 M dimethyl phenyl isocyanide was also solvated in the [Co(PY5Me₂)(DMP-CN)]^{3+/2+} electrolyte. Cells were measured approximately 18 hours after fabrication where they rested in ambient lighting. Ten dye-sensitized solar cells were measured for each electrolyte condition.

3.3.6 Instrumentation

ATIR spectra were collected in a JASCO FT/IR-6600 spectrometer under ambient air with 64 scans and 2 cm⁻¹ resolution. NMR spectra were collected at room temperature on an Agilent DirectDrive2 500 MHz spectrometer and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, m = multiplet). Cyclic voltammograms were collected using a μ AutolabIII potentiostat using a BASi glassy carbon working electrode, a fabricated platinum mesh counter electrode, and a fabricated 0.01 M AgNO₃, 0.1 M TBAPF₆ in acetonitrile Ag/AgNO₃ reference electrode.

All measurements were also internally referenced to the Ferrocenium/Ferrocene couple by addition of ferrocene to the solution after measurements or measured in a separate solution of the same solvent and supporting electrolyte. Cyclic voltammograms under illumination (Light JV's) were performed with a potentiostat (Autolab PGSTAT 128N) used with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻², and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A 400 nm long-pass filter was used to prevent direct excitation of the TiO₂ in all light measurements. A black mask with an open area of 0.12 cm^2 was applied on top of the cell active area. The solution potential of the devices was determined by immersing a platinum wire and the Ag/AgNO3 electrode into the electrolyte used to fill the devices and measuring the potential between the electrodes. A monochromator (Horiba Jobin Yyon MicroHR) attached to the 450 W xenon arc light source was used for monochromatic light for IPCE measurements. The photon flux of the light incident on the samples was measured with a laser power meter (Nova II Ophir). IPCE measurements were made at 20 nm intervals between 400 and 800 nm at short circuit current. EIS measurements were measured with an Autolab PGSTAT 128N/FRA2 potentiostat/frequency response analyzer and all data plots were simulated with ZView software. Open circuit voltage decays were measured by leaving the cells in the dark until the potential stabilized and then switching on 100 mW cm⁻² illumination for one second with a light shutter (Thorlabs) and then the shutter closing automatically after 1 second and monitoring the decay. Variable light intensity EIS measurements were made by using optical filters from Thorlabs (NEK01). Equivalent circuits used for EIS fitting can be found in the supporting information (Figure A3.11: Equivalent circuit used to fit full dye-sensitized solar cells.). UV-vis spectra were measured with a PerkinElmer Lambda 35 UV-vis spectrometer using 1 cm path length quartz cuvettes at 480 nm min⁻¹. CHN analysis were obtained at Midwest Microlab. For single crystal x-ray diffraction, single crystals were mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystals were kept at T = 173(2) K during data collection. Using Olex2 (Dolomanov et al., 2009), the structures were solved with the ShelXS (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of XL (Sheldrick, 2008) using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

3.3.7 Transient Absorption Spectroscopy

Transient absorption measurements were performed using a Vibrant 355 Nd:YAG/OPO (OPOTEK) tunable laser system ($\lambda_ex=550$ nm). A probe pulse generated by a LP980 laser flash photolysis system (Edinburgh Instruments) monitored the decay of the oxidized dye population ($\lambda_pr=700$ nm). Pulses were generated at a frequency of 1 Hz. A linear polarizer (Thorlabs) was used to limit the energy density to of the pump pulse to 0.3 mJ/cm². Samples were positioned at a 45° angle to both light sources using a homemade sample clamp fastened to a stationary stage. Raw signal was collected alongside fluorescence and probe background scans which were applied to the raw signal as corrections using LP900 software program (Edinburgh Instruments). The corrected scans were averaged 50 times for each run to improve S/N. 6 devices were fabricated for each of the four electrolyte conditions studied and the results obtained from fitting each individual spectrum were averaged. The data was fit using a bi-exponential using the Logger Pro software package. Samples were prepped by cutting glass slides into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 min followed by manual scrubbing of the glass with Kimwipes. The pieces were then dried in room air and the active rea of 0.49 cm² was
doctor bladed with commercial 30 nm TiO₂ nanoparticle paste (DSL 30NRD). The transparent films were left to rest for 10 minutes and were then placed in a 100 °C oven for 15 min. The oven was then ramped to 325 °C for 5 min, 375 °C for 5 min, 450 °C for 5 min, and 500 °C for 15 min. The film thickness was measured to be 6 µm. After cooling to room temperature, a TiCl₄ treatment was performed at 40 mM for 30 min at 70 °C. The samples were immediately rinsed with 18 MΩ water and were then placed in an oven to heat from room temperature to 500 °C and then held for 30 minutes. When the anodes had cooled to 80 °C they were soaked in a dye solution of 0.1 mM D35cpdt with 0.1 mM chenodeoxycholic acid in 1:1 acetonitrile: tert-butanol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen. The samples were sandwiched to another piece of glass slide with two predrilled holes using 25 µm surlyn films by placing them on a 140 °C hotplate and applying pressure. Electrolyte was injected into one of the pre-drilled holes and then 25 µm surlyn was used to seal the back with a glass coverslip but the surlyn was cut to not cover the active area. Heat was used to seal the surlyn to result in devices without leaks for at least several weeks. The devices were allowed to rest for 24 hours before being measured to allow for the devices to equilibrate. The inert electrolyte consisted of 0.1 M LiPF₆ in acetonitrile and the cobalt electrolytes consisted of 0.15 M Co(II), 0.10 M Co(III), and 0.1 M LiPF₆ in acetonitrile. The $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$ electrolyte also had 0.2 M DMP-CN present.

3.4 Results and Discussion

The $[Co(PY5Me_2)(I)]I$ and $[Co(PY5Me_2)(ACN)](PF_6)_2$ complexes were synthesized as reported previously.¹⁹ The bound acetonitrile of $[Co(PY5Me_2)(ACN)](PF_6)_2$ was readily substituted with 2,6-dimethylphenyl isocyanide (DMP-CN) using a moderate excess (1.5 equivalents) in the non-coordinating solvent dichloromethane. Oxidation of

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[Co(PY5Me₂)(ACN)](PF₆)₂ and [Co(PY5Me₂)(DMP-CN)](PF₆)₂ resulted in coordination of fluoride ions or nitrosonium biproducts when silver(I) hexafluorophosphate or nitrosonium hexafluorophosphate were used, respectively. The outer-sphere oxidant 4-bromotriphenylamine hexafluorophosphate [TBPA](PF₆) was then used. The [TBPA]⁺ oxidant was synthesized in dichloromethane from 1.00 equivalent of 4-bromotriphenylamine and 0.95 equivalents of nitrosonium hexafluorophosphate to insure nitrosonium was not present when using [TBPA](PF₆) in the subsequent oxidation.²¹ The oxidation of the Co(II) complexes occurred immediately upon addition of [TBPA](PF₆) as indicated by the color change of the solution from dark blue to dark red. Both Co(III) complexes were readily purified of the oxidant by washing with dichloromethane to remove both oxidation states of the triphenylamine present.

obtained $[Co(PY5Me_2)(DMP-CN)](PF_6)_2,$ Crystal structures were for the [Co(PY5Me₂)(DMP-CN)](PF₆)₃, [Co(PY5Me₂)(ACN)](PF₆)₂, and [Co(PY5Me₂)(ACN)](PF₆)₃ complexes. The $[Co(PY5Me_2)(DMP-CN)]^{2+}$ complex has shorter axial bonds between the Co(II) and the isocyanide ligand and central pyridine ligand, resulting in a distorted octahedral structure, compared to the $[Co(PY5Me_2)(ACN)]^{2+}$ complex. The reduction in the degeneracy of the bonding and antibonding orbitals for the [Co(PY5Me₂)(DMP-CN)](PF₆)₂ complex is a result of being a low-spin Co(II) complex, which was confirmed by the Evan's method to measure the effective magnetic moment (μ_{eff}). This asymmetry is also present for the low-spin Co(II) reported previously.^{16,22} complexes $[Co(PY5Me_2)(CN)](OTf)$ and $[Co(ttcn)_2](BF_4)_2$ Coordination of the strong-field isocyanide ligand to cobalt metal centers also results in a significant reduction of the metal to ligand bond distance changes upon oxidation compared to the acetonitrile bound complex. The average metal to ligand bond change for the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple is 0.082 Å which is close to half the change for the

 $[Co(PY5Me_2)(ACN)]^{3+/2+}$ couple at 0.156 Å. The reduction of the metal to ligand bond distance change upon oxidation significantly impacts the inner-sphere reorganization energy of the isocyanide redox couple.



Figure3.1.Structuresof[Co(PY5Me2)(ACN)](PF6)2(right).

 $[Co(PY5Me2)(DMP\text{-}CN)](PF6)2 \qquad (left) \qquad and \qquad$

Bond Distances (Å)	[Co(PY5Me ₂)(DMP- CN)] ²⁺	$[Co(PY5Me_2)(DMP-CN)]^{3+}$	[Co(PY5Me ₂)(A CN)] ²⁺	[Co(PY5Me ₂)(ACN)] ³⁺
Co-N1	1.969(4)	1.960(3)	2.094(3)	1.959(7)
Co-N2	2.123(5)	1.996(3)	2.137(3)	1.996(7)
Co-N3	2.060(5)	1.990(3)	2.133(3)	1.973(7)
Co-N4	2.138(5)	1.980(3)	2.130(3)	1.984(7)
Co-N5	2.078(4)	1.960(3)	2.121(3)	1.982(7)
Co-C30	1.884(6)	1.878(4)		
C30-N6	1.162(7)	1.135(5)	1.134(5)	1.116(10)
Co-N6			2.132(4)	1.917(6)

Table 3.1 Bond distances from single crystal x-ray diffraction data. $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ bond lengths are from structure A of the data set and $[Co(PY5Me_2)(ACN)](PF_6)_2$ bond lengths are from structure 1 of the data set.

In order to estimate the effect of the spin state on the inherent electron transfer barrier; the inner-sphere (λ_{in}), outer-sphere (λ_o) and total reorganization (λ) energies were calculated for each complex. Using symmetrical stretching frequencies of $v_{(Co(II)-N)} = 266$ cm⁻¹ from [Co(bpy)₃](ClO₄)₂ and $v_{(Co(III)-N)} = 378$ cm⁻¹ from [Co(phen)₃](ClO₄)₃ the force constants for each complex were estimated.^{23,24} The effective force constant (*f_{eff}*) was then calculated and used with the change in each metal to ligand bond distance (Δd) of each complex's crystal structure to obtain the inner-sphere reorganization energy.²⁵

$$f_1 = 4\pi^2 v_{Co(II)-N}^2 \mu_{eff}$$
 E 3.1

$$f_{eff} = \frac{2f_1 f_2}{f_1 + f_2}$$
 E 3.2

$$\lambda_{in} = \frac{1}{2} \sum f_{eff} \Delta d^2 \qquad \qquad E \ 3.3$$

The calculated inner-sphere reorganization energy of 2.76 eV for $[Co(bpy)_3]^{3+/2+}$ is in good agreement with the value of 2.63 eV derived from the self-exchange rate constant.¹³ The $[Co(PY5Me_2)(ACN)]^{3+/2+} \lambda_{in}$ is reduced significantly to 1.74 eV despite also being a high-spin Co(II) complex. Similar redox couples [Co(PY5Me₂)(NMBI)]^{3+/2+} and [Co(PY5Me₂)(TBP)]^{3+/2+} displayed similar average changes in bond length ($\Delta d = 0.15$ Å) which was attributed to the constrained of the PY5Me₂ ligand absorbing structural changes.¹⁵ The nature $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple displays even larger reductions in the inner-sphere reorganization energy to 0.77 eV. The [Co(PY5Me₂)(DMP-CN)](PF₆)₂ complex has a low-spin d⁷ electronic structure which reduces the electronic rearrangement, with a loss of only one electron from an anti-bonding $d_{x^2-y^2}$ orbital during the oxidation, compared to removal of one electron and pairing of another for high-spin d⁷ complexes. We note that one bond of each of the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ complexes are Co-C bonds, and the force constants are taken from Co-N bond frequencies, for the analysis above. This assumption does not affect the result of the calculation since the Co(II)-C bond and the Co(III)-C bond are statistically the same, and thus Δd = 0 in the calculation for those bonds.²⁶

The outer-sphere reorganization energy was also determined from the crystal-structure data. The radius was averaged for each cobalt to exterior hydrogen, of the ligands, of the $[Co(PY5Me_2)(ACN)](PF_6)_{3/2}$ and the $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$ couples. Using the dielectric constant ($\varepsilon_0 = 36.64 \text{ F cm}^{-1}$) and refractive index of acetonitrile ($n_{sol} = 1.3442$), the radius of each reactant (a_1 and a_2) and center to center distance (R); the outer-sphere reorganization energy was calculated.^{27,28}

$$\lambda_o = \frac{\Delta e^2}{4\pi\varepsilon_{vac}} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right) \left(\frac{1}{n_{sol}^2} - \frac{1}{\varepsilon_0}\right)$$
 E 3.4

Comparing the outer-sphere reorganization energies, the largest radius $[Co(bpy)_3]^{3+/2+}$ has the smallest outer-sphere reorganization energy and increases marginally as the radius decreases for $[Co(PY5Me_2)(ACN)]^{3+/2+}$ and $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$. From the sum of the outer-sphere and inner-sphere reorganization energies, the total reorganization energy was calculated for each complex. The total reorganization energy is dominated by the inner-sphere reorganization energy for each complex due to the large ligand to metal bond distance changes upon electron transfer. For the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple, both the coordination of the PY5Me₂ and DMP-CN ligand results in the largest reduction in reorganization energy. Comparing the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple to $[Co(bpy)_3]^{3+/2+}$, the total reorganization energy is almost 2 eV lower; 1.42 eV compared to 3.37 eV. According to Marcus Theory, the $[CoPY5Me_2)(DMP-CN)]^{3+/2+}$ couple will have a lower barrier for both regeneration and recombination compared to $[Co(bpy)_3]^{3+/2+}$ and $[Co(PY5Me_2)(ACN)]^{3+/2+}$.

Table 3.2 Redox potential, effective magnetic moment for Co(II) complexes, complex radius, average bond distance change, inner-sphere, outer-sphere, and total reorganization energy.

Co ^{3+/2+} Couple	$E_{1/2}$ vs Fc ⁺ /Fc	$\mu_{e\!f\!f}~(\mu_b)$	<i>R</i> (Å)	Δd (Å)	$\lambda_{in}(\mathrm{eV})$	$\lambda_o(\mathrm{eV})$	$\lambda(eV)$
	(V)						
$[Co(bpy)_3]^{3+/2+}$	-0.066	~ 4.6 ²⁹	6.5 ³⁰	0.198 31,32	2.76	0.62	3.37
[Co(PY5Me ₂)(0.165	4.25 ± 0.01	5.6	0.156	1.74	0.71	2.45
ACN)] ^{3+/2+}							
[Co(PY5Me ₂)(0.098	2.08 ± 0.02	6.1	0.082	0.77	0.66	1.42
DMP-CN)] ^{3+/2+}							

For both oxidation states of the [Co(PY5Me₂)(DMP-CN)]^{3+/2+} complexes, the bound DMP-CN was found to be labile in neat acetonitrile. When the $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ complex is introduced into deuterated acetonitrile for ¹H NMR studies, immediately after solvation, the spectrum consists of a mixture of [Co(PY5Me₂)(ACN)](PF₆)₂ and [Co(PY5Me₂)(DMP-CN)](PF₆)₂ indicating rapid ligand dissociation without the excess isocyanide (Figure 3.2a). As the DMP-CN concentration is increased the downfield signals between 25 ppm to 95 ppm associated with the $[Co(PY5Me_2)(ACN)(PF_6)_2 \text{ complex decrease}]$ while the peaks lower than 30 ppm increase which is assigned to the [Co(PY5Me₂)(DMP-CN](PF₆)₂ complex. To confirm the peaks assigned to the [Co(PY5Me₂)(DMP-CN)](PF₆)₂ complex, ¹H NMR was also matched in the non-coordinating solvent deuterated dichloromethane to insure no ligand displacement. Therefore, to maintain the [Co(PY5Me₂)(DMP-CN)1^{3+/2+} couple, 0.2 M DMP-CN was used to eliminate any significant contributions of the $[Co(PY5Me_2)(ACN)]^{3+/2+}$ couple for all measurements in acetonitrile.

The effect of substitution of DMP-CN by ACN was also measured by differential pulse voltammetry. In the differential pulse voltammetry experiments, the [Co(PY5Me₂)(DMP-

CN)]^{3+/2+} couple has a broad peak when dissolved in ACN with supporting electrolyte. This is likely due to the solution having a mixture of both the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ and the $[Co(PY5Me_2)(ACN)]^{3+/2+}$ couple present. Upon addition of DMP-CN to the electrolyte the peak maximum shifts negative until approximately 0.1 M of DMP-CN ligand was added and then the potential remains constant (Figure 3.2b). Comparing the redox potentials obtained by cyclic voltammetry, the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple is shifted 67 mV negative of the precursor $[Co(PY5Me_2)(ACN)]^{3+/2+}$ couple due to the donating nature of the DMP-CN ligand and lies 164 mV positive of the $[Co(bpy)_3]^{3+/2+}$ couple. The $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ complex was found to be reversible at a glassy carbon electrode and from the scan rate dependence a diffusion coefficient of $2.8 \pm 0.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, was obtained which is similar to that determined previously for $[Co(bpy)_3]^{2+,33,34}$



Figure 3.2 (a) ¹H NMR of 15 mM [Co(PY5Me₂)(DMP-CN)(PF₆)₂ in acetonitrile with increasing concentrations of DMP-CN. [Co(PY5Me₂)(ACN)](PF₆)₂ complex for reference (violet), 0.00 M DMP-CN (blue), 0.10 M DMP-CN (green), 0.15 M DMP-CN (yellow), and 0.20 M DMPCN (red). (b) Differential pulse voltammetry of 5 mM [Co(PY5Me₂)(DMP-CN)](PF₆)₂ in acetonitrile with 100 mM TBAPF₆ and increasing concentrations of DMP-CN.

were fabricated using $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$. Dye-sensitized solar cells $[Co(bpy)_3]^{3+/2+}$ and $[Co(PY5Me_2)(ACN)]^{3+/2+}$ as redox shuttles. The $[Co(bpy)]^{3+/2+}$ and $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ redox shuttles produce nominally the same current density (J) vs. applied voltage (V) behavior under simulated AM 1.5 illumination and therefore power conversion efficiencies, despite the large differences in reorganization energy (Table 3.3). Interestingly, the $[Co(PY5Me_2)(ACN)]^{3+/2+}$ shuttle performed significantly worse than either $[Co(bpy)]^{3+/2+}$ or $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ despite a reorganization energy value in between the two. Some of the J-V behavior must therefore be attributed to differences in solution potential (E_{sol}) which determines the driving forces for the forward (dye regeneration) and reverse (recombination) reactions. The $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple has a larger driving force for recombination and a smaller driving force for regeneration compared to the $[Co(bpy)]^{3+/2+}$ couple. Therefore, dye regeneration and recombination kinetics were investigated in detail below as a function of redox shuttle. We note the photocurrents obtained by integrating IPCE curves substantiate the short circuit photocurrent density, J_{sc} , determined by the J-V curves.



Figure 3.3 (a) Plots of current density vs applied voltage curves under 100 mW cm⁻² illumination for the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ (green), $[Co(bpy)_3]^{3+/2+}$ (blue), and $[Co(PY5Me_2)(ACN)]^{3+/2+}$ (red) electrolytes. (b) Incident photon-to-current conversion efficiency (diamonds) of $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ (green), of $[Co(bpy)_3]^{3+/2+}$ (blue) and of $[Co(PY5Me_2)(ACN)]^{3+/2+}$ (red) electrolytes using monochromatic light and the integrated J_{sc} (circles).

In order to compare the kinetics and efficiency of dye regeneration reaction as a function of redox shuttle, nano-second transient absorption spectroscopy (TAS) measurements were performed. The D35cpdt dye was excited by a pump beam at 550 nm and after the approximately pico-second time scale associated with electron injection to the TiO₂, the oxidized dye was monitored at 700 nm.³⁵ Due to the complex nature of the kinetic traces the data could not be fit to a single stretched exponential so a bi-exponential was used to obtain each time constant of the decay in accord with prior analyses.^{36,37}



$$\Delta A(t) = \Delta A_0 + A_1 \exp^{-tk_1} + A_2 \exp^{-tk_2}$$
 E 3.5

Figure 3.4 Transient absorption traces observed at 700 nm of the oxidized sensitizer with $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ (green), $[Co(byy)_3]^{3+/2+}$ (blue), $[Co(PY5Me_2)(ACN)]^{3+/2+}$ (red) and inert (black) with fits as solid lines. Electrolytes were the same composition as full DSSC electrolytes. Inert consisted of 0.1 M LiPF₆ in acetonitrile.

In the equation 3.5, ΔA_0 is the change and absorbance at time zero, A_1 and A_2 are the preexponential factors for the contribution of each process and k_1 and k_2 are the observed rate constants of each process. From the results of fitting equation 3.5 to the decay curves displayed in Figure 3.4, the regeneration efficiency can be estimated by solving for the time at $\Delta A = 0.5$, to obtain the $t_{1/2}$ for both recombination and regeneration. The recombination halftime ($t_{1/2rec}$) was obtained without the presence of a redox couple and the regeneration halftimes $(t_{1/2reg})$ were obtained in the presence of each redox couple. The $t_{1/2rec}$ was found to be 344 ± 57 ns which is somewhat faster than values found within the literature.^{36,38} It has been previously shown that the time-scale of recombination to the D35cpdt dye is influenced strongly by the pump light intensity (i.e. initial TiO₂ electron concentration).³⁹ It was found that the $t_{1/2rec}$ spanned three orders of magnitude by varying the pump light intensity; therefore it's absolute value is dependent on the experimental conditions of the device and the transient absorption setup. However, the redox couple's $t_{1/2reg}$ is less dependent on light intensity which allows for a sound comparison of the relative ability of each redox shuttle to regenerate the D35cpdt dye. From the ratio of the $t_{1/2rec}$ and the $t_{1/2reg}$ the regeneration efficiency (Φ_{reg}) can be estimated for each redox shuttle according to:⁴⁰

$$\Phi_{reg} = \frac{k_{reg}}{k_{reg} + k_{rec}} = 1 - \frac{t_{1/2reg}}{t_{1/2rec}}$$
 E 3.6

Introduction of each redox couple accelerates the decay of the oxidized sensitizer as expected. The $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ shuttle displays the fastest regeneration kinetics and associated regeneration efficiency (Table 3.3). Specifically, the D35cpdt regeneration is twice as fast with $[Co(PY5Me_2)(DMP-CN)]^{2+}$ compared to $[Co(bpy)_3]^{2+}$ despite a 160 mV smaller driving force for the reaction. The faster regeneration can be attributed to the reduced inner-sphere reorganization energy.^{41,40} We note that the regeneration efficiency is lower than typically reported for the $[Co(bpy)_3]^{3+/2+}$ couple, which is partly due to using a lower concentration of the Co(II) complexes due to solubility limitation of the $[Co(PY5Me_2)]^{3+/2+}$ couples; 0.15 M relative to 0.20-0.25 M seen in the literature.^{37,40,42} In addition, as noted above, the efficiency is determined by the recombination kinetics which is highly variable by system and laser power intensity, which makes the trend, or relative values, more meaningful than the absolute efficiencies determined. The $[Co(PY5Me_2)(ACN)]^{3+/2+}$ couple has an even smaller driving force for regeneration than $[Co(PY5Me_2)(DMP-CN)]^{2+}$ and larger reorganization energy, which explains the slow kinetics, poor regeneration efficiency and photocurrent density measured with the redox shuttle.

To illustrate a clearer description of the influence of the reorganization energy and driving force on regeneration process, the dye regeneration ($k_{et,reg}$) can be modeled and compared using Marcus theory where²⁸

$$k_{et,reg} = k_{et,max} e^{-(\Delta G_{reg} + \lambda_{reg})^2 / 4\lambda_{reg} k_B T}$$
 E 3.7

Since the pre-exponential term (e.g. coupling) is expected to be nominally constant for the redox couple-dye pairs, relative rate constants can be estimated through comparisons of the nuclear terms. The driving force of regeneration (ΔG_{reg}) is taken from the difference of the redox potential of the redox shuttles and the redox potential of the dye d35cpdt (0.45 V vs Fc⁺/Fc) measured previously on TiO₂.¹³ The reorganization energy of the regeneration event (λ_{reg}) is the average of each redox couple's reorganization energy with the sensitizer's reorganization energy. We are not aware of the reorganization energy being measured previously for d35cdpt but similar triarylamine sensitizer's reorganization energies have been estimated computationally which provides a value of 0.95 eV which we use here.⁴³ From the calculations of the exponential

term of the Marcus equation, the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ couple is expected to have the fastest regeneration kinetics while $[Co(bpy)_3]^{3+/2+}$ and $[Co(PY5Me_2)(ACN)]^{3+/2+}$ have nominally the same rate of regeneration. The regeneration efficiencies compared with the regeneration terms have a discrepancy between $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ where there is only a two-fold difference in regeneration halftime and a three order of magnitude difference in the calculated exponential term. This is likely due to an overestimation of the reorganization energy of $[Co(bpy)_3]^{3+/2+}$ when comparing the reorganization energy determined from the crystal structures compared to that measured by self-exchange previously.^{13,30} This would also explain Marcus theory's prediction of $[Co(bpy)_3]^{3+/2+}$ having a slower regeneration rate than $[Co(PY5Me_2)(ACN)]^{3+/2+}$ while the halftime for $[Co(bpy)_3]^{3+/2+}$ regeneration is faster. If the total reorganization energy values from the self-exchange rate constant of 2.64 eV and 3.21 eV were used to calculate the exponential term, the term would increase to 1.4×10^{-4} and 1.1×10^{-5} respectively making for greater agreement of the halftimes of regeneration and Marcus theory.

Electrolyte	$[Co(bpy)_3]^{3+/2+}$	[Co(PY5Me ₂)(DMP-	[Co(PY5Me ₂)(ACN)]	
		$CN]^{3+/2+}$	3+/2+	
E_{sol} vs Fc ⁺ /Fc (V) ^a	-0.156	0.044	0.084	
Voc (V)	0.66 ± 0.03	0.67 ± 0.02	0.64 ± 0.02	
$Jsc (mA cm^{-2})$	6.6 ± 0.5	7.2 ± 0.5	4.3 ± 0.3	
IPCE (mA cm ⁻²)	6.63	6.31	4.11	
FF	0.68 ± 0.03	0.69 ± 0.03	0.65 ± 0.02	
η (%)	3.0 ± 0.2	3.4 ± 0.2	1.8 ± 0.2	
$t_{1/2reg}$ (ns)	152 ± 30	86 ± 22	248 ± 40	
$\Phi_{ m reg}$	0.57 ± 0.09	0.75 ± 0.06	0.28 ± 0.11	
$\Delta G_{reg}(eV)$	0.52	0.35	0.29	
$\lambda_{reg} (\mathrm{eV})$	2.16	1.19	1.72	
$e^{-\left(\Delta G_{reg}+\lambda_{reg}\right)^2/4\lambda_{reg}k_BT}$	$5.04 imes 10^{-6}$	3.3×10^{-3}	$8.2 imes 10^{-6}$	

Table 3.3 Summarized average of each performance parameter for $[Co(bpy)_3]^{3+/2+}$, $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$, and $[Co(PY5Me_2)(ACN)]^{3+/2+}$ electrolytes used in dye-sensitized solar cells.

^{*a*} Solution potential of electrolytes used to fill devices were measured with a platinum wire working electrode, platinum mesh counter electrode and fabricated Ag/AgNO₃ reference electrode measured to be -0.077 V vs Fc⁺/Fc.

Since the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ shuttle produces similar *J-V* behavior as the $[Co(bpy)_3]^{3+/2+}$ shuttle, despite more efficient dye regeneration and more positive solution potential enabling a larger V_{oc} , the recombination to $[Co(PY5Me_2)(DMP-CN)]^{3+}$ must be faster to offset these advantages. To evaluate recombination at the photoanode/electrolyte interface, photoelectrochemical impedance spectroscopy (PEIS) measurements were performed to compare electron recombination resistances, which are inversely proportional to recombination rates, at a given electron occupance.⁴⁴ Measurements were performed at open circuit to maintain constant

Fermi levels (E_F) throughout the TiO₂ film, and the light intensity was varied to control the electron population, which is reflected in the chemical capacitance (C_μ) obtained from fitting the data to an equivalent circuit (Figure A3.10, Figure A3.11). Since the solution potentials are different for each electrolyte, and the V_{oc} is the difference between solution (reference) potential and the E_F of TiO₂, a correction needs to be introduced to compare recombination at the same $E_{F,n}$. The chemical capacitance provides quantitative information about the electron occupancy of TiO₂ at a given E_F , assuming a fixed conduction band potential, E_c , ⁴⁵ according to

$$C_{\mu} = L(1-p)\alpha \frac{q^2 N_t}{k_B T} \exp \exp\left(\alpha \frac{(E_{sol} - E_c)}{k_B T}\right) \exp \exp\left(\alpha \frac{q V_{oc}}{k_B T}\right)$$
 E 3.8

where *L* is the film thickness, *p* is the porosity of TiO₂ film, *q* is the electron charge, $k_{\rm B}$ is Boltzmann's constant, *T* is the temperature, $N_{\rm t}$ is the total number of trap states below the conduction band, and α is the exponential electron trap distribution parameters.⁴⁶

We note that the base DMP-CN has been added to the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ electrolyte, which can affect the band edge potential and lead to problems in comparing recombination rates. Inspection of the chemical capacitance as a function of the applied potential (corrected for differences in solution potential), snows that the trend is not affected by the electrolyte indicating that there is no detectable shift in band position for each electrolyte composition.



Figure 3.5 R_{rec} as a function of C_{μ} to compare at the same electron density (*n*) from results of the PEIS analysis of DSSCs at various light intensity conditions (100, 80, 50, 25, and 10 mW cm⁻²) with $[\text{Co}(\text{PY5Me2})(\text{DMP-CN})]^{3+/2+}$ (green diamonds), $[\text{Co}(\text{bpy})_3]^{3+/2+}$ (blue circles) and $[\text{Co}(\text{PY5Me2})(\text{ACN})]^{3+/2+}$ (red triangles).

Figure 3.5 shows the extracted recombination resistance (R_{rec}) with respect to the capacitance by modulation of the light intensity, for the $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$, $[Co(bpy)_3]^{3+/2+}$ and $[Co(PY5Me_2)(ACN)]^{3+/2+}$ redox shuttles. increases in The $R_{\rm rec}$ the order of $[Co(PY5Me_2)(ACN)]^{3+/2+}$, $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$, and $[Co(bpy)_3]^{3+/2+}$ at a given C_{μ} which means the recombination rate constants decrease in the same order. Given the potential of the TiO_2 conduction band measured previously in acetonitrile with lithium supporting electrolyte (0.8 V vs Ag/AgCl) and the redox potentials of each redox couple, the driving force for recombination (ΔG_{rec}) can be estimated for each couple.⁴⁷ The outer-sphere reorganization energy can also be calculated for the TiO₂ (λ_{o,TiO_2}) and redox couple electron transfer as

described previously.¹³ Values are provided in Table 3.4 Relative to the other redox couples, $[Co(bpv)_3]^{3+/2+}$ has the slowest rate of recombination which matches predictions made by Marcus theory given the largest reorganization energy and smallest driving force for recombination and being well within the Marcus normal region. However, comparisons of the $[Co(PY5Me_2)(ACN)]^{3+/2+}$ and $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ redox shuttles are not as straightforward. While [Co(PY5Me₂)(DMP-CN)]^{3+/2+} has a smaller reorganization energy and driving force for recombination relative to [Co(PY5Me₂)(ACN)]^{3+/2+}, they are both close to optimal exoergicity; [Co(PY5Me₂)(ACN)]^{3+/2+} is expected to be in the normal region and $[Co(PY5Me_2)(DMP-CN)]^{3+/2+}$ is expected to be in the inverted region, and thus have similar rate constants for electron transfer from the conduction band. This analysis ignores contributions from sub-bandgap states, however, which may be significant and different for the two redox shuttles.⁴⁷ Another possible reason for the discrepancy between the recombination resistance measured and the trend expected from Marcus theory may be the excess DMP-CN ligand which is present in the [Co(PY5Me₂)(DMP-CN)]^{3+/2+} electrolyte. The excess DMP-CN ligand may block recombination by coupling to TiO₂ states or sterically hindering charge transfer, analogous to 4-tert-butylpyridine.48,49

Table 3.4 Outer-sphere reorganization energy of TiO₂ and electrolyte interface λ_{o,TiO_2} , total reorganization energy of recombination event λ_{ET} , and driving force for recombination from TiO₂ band to redox couple ΔG_{rec} .

Redox Couple	$[Co(bpy)_3]^{+3/+2}$	$[Co(PY5Me_2)(DMP-CN]^{+3/+2}$	$[Co(PY5Me_2)(ACN)]^{+3/+2}$
λ_{o,TiO_2} (eV)	0.531	0.561	0.608
$\lambda_{rec}~(\mathrm{eV})$	1.909	0.947	1.504
$\Delta G_{rec} \left(eV \right)$	1.091	1.255	1.322

3.5 Conclusions

Utilizing the strong-field ligand 2,6-dimethylphenyl isocyanide in combination with the Co(PY5Me₂) framework has resulted in a low-spin Co(II) redox couple with improved regeneration kinetics over $[Co(bpy)_3]^{2+}$ while utilizing 160 mV less driving force. Utilizing this redox couple with a more positive potential should have resulted in a larger open-circuit voltage, however the recombination rate also increased for [Co(PY5Me₂)(DMP-CN)]³⁺ compared to [Co(bpy)₃]³⁺ which offset the possible gains. The [Co(PY5Me₂)(DMP-CN)]^{3+/2+} did display promising performance with a power conversion efficiency similar to $[Co(bpy)_3]^{3+/2+}$ but the performance has limited gains with the large recombination losses present. These results and analysis agree with our previous reports using the redox couple $[Co(ttcn)_2]^{3+/2+}$. Such attempts to make gains by lowering the reorganization energy, and thus reduce the energy penalty required to achieve efficient dye regeneration, has minimal benefits with large driving forces for TiO₂/Electrolyte recombination ($\geq 1 \text{ eV}$).¹³ The significant advantage of [Co(PY5Me₂)(DMP-(CN)]^{3+/2+} compared to $[Co(ttcn)_2]^{3+/2+}$, however, is that in principle the ligand can be modified with electron donating/withdrawing groups to modulate the redox potential (thus relative driving forces) and thereby fully optimize devices with such low-spin cobalt redox systems. In order to capitalize on these low-spin cobalt redox shuttles, more negative redox potentials are needed.

Although a sacrifice in V_{oc} will be made, this will be compensated by reduced recombination and broader light absorption with sensitizers that absorb deeper into the red.⁵⁰ Work is in progress in our lab to test this hypothesis.

APPENDIX



Figure A3.1 ¹H 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 A3.2 ¹H NMR of 15 mM Co(PY5Me₂)(DMP-CN)(PF₆)₃ in deuterated acetonitrile with 0.2 M DMP-CN in CD₃CN. 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 A3.3 ¹H NMR of 10 mM $[Co(PY5Me_2)(ACN)](PF_6)_3$ complex in deuterated CD₃CN. Peak at 5.5 ppm is residual dichloromethane from the synthesis.



Figure A3.4 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_6.



Figure A3.5 Peak anodic current (green) and peak cathodic (violet) as a function of the square root of scan rate for [Co(PY5Me₂)(DMP-CN)](PF₆)₂.



Figure A3.6 ¹H 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 A3.7 ¹H 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 A3.8 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 \equiv N stretching modes were analyzed by an infrared spectroscopy using an attenuated total reflection set up 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⁻¹ for the isocyanide stretch of the complex which is shifted from the signal of the free DMP-CN ligand (2118 cm⁻¹), (Figure A3.8 ATIR spectrum of the Co(PY5Me2)(DMP-CN)(PF6)₂ complex (green) and of the Co(PY5Me2)(DMP-CN)(PF6)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 π 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 wavenumber signal at 2211 cm⁻¹ 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.⁵¹ The increase in bond strength from Cobalt (II) to Cobalt (III) is rationalized by the reduced π backdonation into the π^* -antibonding orbital increasing the bond order of the C=N bond of the Cobalt (III) complex.



Figure A3.9 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.

Electrolyte	ΔA_0	A_1	$k_1(10^{-3})$ (ns ⁻¹)	A_2	$k_2 (10^{-3}) (\text{ns}^{-1})$	\mathbb{R}^2
Inert	0.12 ±	0.35 ±	1.2 ± 2.1	0.45±	5.4 ± 3.5	0.89 ±
	0.02	0.02		0.06		0.07
$[Co(bpy)_3]^{3+/2+}$	$0.09 \pm$	$0.35 \pm$	2.5 ± 5.1	0.45 ±	7.9 ± 4.7	$0.90 \pm$
	0.03	0.06		0.05		0.03
[Co(PY5Me ₂)(-0.04 \pm	$0.40 \pm$	2.7 ± 4.1	$0.50 \pm$	11.9 ± 10.2	$0.7 \pm$
DMP-CN)] ^{+3/+2}	0.02	0.09		0.08		0.1
[Co(PY5Me ₂)($0.06 \pm$	$0.42 \pm$	2.0 ± 2.5	0.43 ±	5.2 ± 3.9	$0.93 \pm$
ACN)] ^{3+/2+}	0.02	0.04		0.04		0.02

Table A3.1 Fitting parameters from TA measurements from bi-exponential equation. Results are average and error of 6 devices of each electrolyte.



Figure A3.10 Example Nyquist plots of full DSSCs at 100 mW cm⁻² fitted to the equivalent circuit.



Figure A3.11 Equivalent circuit used to fit full dye-sensitized solar cells.



Figure A3.12 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 A3.13 Light JV's as a function of light intensity for the $[Co(PY5Me_2)(DMP-CN)(PF_6)_{3/2}]$ electrolyte.



Figure A3.14 Light JV's of $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$ and $[Co(bpy)_3](PF_6)_{3/2}$ with unmodified 30 nm TiO₂ nanoparticle film at 6.5 µm film thickness with no scattering layer. Electrolyte consisted of 0.15 M Co(II), 0.015 M Co(III), 0.1 M LiPF₆ 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 A3.2 Summarized performance of devices measured for Figure X (5 devices measured for each electrolyte).

Electrolyte	$V_{OC}(V)$	J_{sc} (mA cm ⁻²)	FF	η
[Co(PY5Me ₂)(DMP-CN)](PF ₆) _{3/2}	0.58 ± 0.01	7.7 ± 0.2	0.54 ± 0.02	2.4 ± 0.2
$[Co(bpy)_3](PF_6)_{3/2}$	0.48 ± 0.01	9.2 ± 0.4	0.44 ± 0.04	1.9 ± 0.1

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Chapter 4: Molecular Switch Cobalt Redox Shuttle with a Tunable Hexadentate Ligand

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4.1 Abstract

A strong-field and hexadentate ligand series has been synthesized and coordinated to cobalt to result in three new low-spin to low-spin Co(II/III) redox couples. The ligand back bone has been modified with dimethyl amine groups to result in redox potential tuning from -200 mV to -430 mV vs Fc^{+/0} of the Co(II/III) redox couples. The complexes exhibit modestly improved electron self-exchange rate constants of 2.2 to 4.2 M⁻¹ s⁻¹ compared to the high-spin to low-spin redox couple $[Co(bpy)_3]^{3+/2+}$ at 0.27 M⁻¹ s⁻¹. The complexes were utilized in dye-sensitized solar cells with the sensitizer LEG4 and exhibited orders of magnitude lower recombination measured by impedance spectroscopy and open-circuit voltage decays. The series obtained nominally the same photocurrent as $[Co(bpy)_3]^{3+/2+}$ indicating regeneration was not limiting the devices despite an increase in regeneration driving force up to 360 mV. Future directions point towards pairing the low-spin to low-spin Co(II/III) tunable series to dyes with significantly more negative HOMO potentials that absorb into the near-IR where outer sphere redox shuttles have failed to produce efficient dye regeneration.

4.2 Introduction

Dye-sensitized solar cells (DSSC) remain a promising power generation technology that can be produced at minimal cost with great tunability. The ability to replace the photoanode, dye, redox shuttle and counter electrode of the devices have allowed for gradual improvement of devices with time. Efficiencies up to 14 % PCE, power conversion efficiency, have been

demonstrated with various dye and redox shuttle systems but the highest efficiencies have used either cobalt or copper based redox systems as their electrolyte.^{1,2,3,4} Due to the adjustable electron donation of the ligands to the metal centers, the redox potential has been optimized to reduce the driving force for dye regeneration enabling high PCE devices. Unfortunately, the best performing devices have had little improvement in recent years from those records. The DSSCs of the copper and cobalt systems have primarily focused on harvesting light between 300 to 800 nm leaving a large section of the solar spectrum unharvested and limiting the maximal efficiency attainable. Harvesting deeper into the near-infrared (800-1100 nm) has been left solely to the iodide/triiodide redox couple but with limited efficiencies ≈10% PCE due to either large photovoltage losses or poor dye regeneration.^{5,6,7} To enable these near-infrared dyes to be used effectively, redox shuttles need to be tuned to more negative redox potentials while still minimizing the dye regeneration driving force needed to maximize the open-circuit voltage. $[Co(bpy)_3]^{3+/2+}$ is currently the champion redox shuttle but it still requires large driving forces for efficient dye regeneration $\approx 0.5 \text{ V}$.^{8,9} This voltage loss is largely dictated by the large inner-sphere reorganization energy of the complex undergoing a high-spin Co(II) to low-spin Co(III) transition upon oxidation reducing the dye regeneration rate.¹⁰ Our group has attempted to minimize the driving force by changing the spin state of cobalt redox shuttles by inducing lowspin Co(II) complexes. By inducing a low-spin Co(II) to low-spin Co(III) electron transfer process, the inner-sphere reorganization energy is decreased which reduces the needed driving force for dye regeneration.^{11,12} Two of the redox shuttles $[Co(ttcn)]^{3+/2+}$ and $[Co(PY5Me_2)(DMP-$ CN)]^{3+/2+} showed efficient dye regeneration but still resided at redox potentials too positive for near-infrared sensitizers. One low spin Co(II) redox couple, [Co(PY5Me₂)(CN)]^{2+/1+}, was at suitable redox potentials but suffered from instability issues and the formation of dimer and cluster complexes in solution.¹³ We therefore sought to synthesize a system with increased stability, redox potential tunability and a strong-field ligand framework for low-spin Co(II) redox couples. Inspiration for a similar system came from the PY4Im ligand developed by Smith and Long.¹⁴ The ligand induced a low-spin Co(II) complex and a more negative redox potential due to the strong sigma donation of the incorporated *N*-heterocyclic carbene (NHC). To have increased stability we report a new hexadentate ligand that also allows for incorporation of dimethylamine (DMA) functional groups to adjust the redox potential. This has resulted in a new series of low-spin to low-spin cobalt(II/III) redox shuttles to be paired with near-infrared sensitizers at more negative potentials.

4.3 Experimental

4.3.1 Materials

All chemicals and materials were obtained from commercial suppliers unless otherwise noted (MiliporeSigma, Oakwood Chemical, Alfa Aesar, Solaronix, Cambridge Isotopes and Dyenamo). All solvents used for the synthesis of compounds **1-3,10a-12b** and all measurements with the cobalt complexes were dried over activated 3A molecular sieves for two days and were then degassed by Schlenk line before being stored in a nitrogen filled glove box for use. Potassium carbonate was dried for 24 hours under vacuum at 100 °C before synthesis of **10a-12b**. 4-dimethylamino-2-fluoropyridine and 4-dimethylamino-2,6-difluoropyridine were synthesized with previously established procedures.¹⁵ Bromobis(2-pyridyl)methane was synthesized from synthesized 2-(2-Pyridylmethyl)pyridine, both following reported procedures.^{16,17} [Fc](OTf) [FcMe2](OTf), [FcMe8](OTf) and [FcMe10](OTf) were synthesized following a reported method except in a nitrogen filled glove box.¹⁸

4.3.2 PY3F (1)

A 500 mL 2 neck flask, with attached reflux condenser, was dried and then replaced with a nitrogen atmosphere. 200 mL of dry and degassed THF was then added by canula transfer and the flask cooled to -78 °C on a dry ice ethanol bath. 2-ethyl pyridine was degassed by nitrogen bubbling for 15 minutes and was added to the flask (15 mL 131 mM). The solution was allowed to cool for 30 minutes then (45.0 mL, 113 mM) 2.5 M n-butyllithium in hexanes was added by canula transfer over a period of 15 minutes. The solution was stirred for 30 minutes then the flask was warmed to -20 °C by adding water slowly to the dry ice bath. After 10 minutes (4.9 mL, 57 mM) degassed 2-fluoropyridine was added by syringe to the flask and the flask was placed on an oil bath to heat to reflux. After 1 hour of reflux, the flask was cooled to room temperature and (2.6 mL, 29 mM) degassed 2,6-difluoropyridine was added by syringe to the flask. The solution was heated to reflux for 1 hour then cooled to room temperature. The reaction was quenched with 100 mL of deionized water. After 15 minutes of stirring the organic layer was separated and the aqueous layer was extracted 3 times with 50 mL of diethyl ether. The organic layers were combined and dried over MgSO₄ for 20 minutes and then filtered. The solvent was removed by rotary evaporation and the product was purified by column chromatography with silica gel. The product was loaded onto the column with dichloromethane and then 500 mL of dichloromethane was used to wash the product. The product was then eluted with acetonitrile and dried to an oil by rotary evaporation. The product was dried under vacuum as an off white solid (Yield: 4.22 g, 52.8%). NMR: ¹H NMR (500 MHz, Chloroform-d) δ 8.58 (ddd, J = 4.8, 1.9, 0.9 Hz, 2H), 7.67 (td, J = 8.3, 7.6 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.13 (ddd, J = 7.4, 4.8, 1.1 Hz, 2H), 7.08 (dt, J = 8.0, 1.0 Hz, 2H), 6.96 (ddd, J = 7.6, 2.7, 0.7 Hz, 1H), 6.76 (ddd, J = 8.1, 3.2, 0.7 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 165.19,

164.83 (d, J = 12.4 Hz), 162.49 (d, J = 237.9 Hz), 148.86, 140.87 (d, J = 7.3 Hz), 136.15, 123.36, 121.43, 120.96 (d, J = 4.3 Hz), 107.00 (d, J = 37.6 Hz), 59.70, 27.02. ¹⁹F NMR (470 MHz, Chloroform-*d*) δ -66.85 (d, J = 8.3 Hz). Elemental analysis: found (calculated) for C₁₇H₁₄FN₃: C, 72.88 (73.10); H, 5.09 (5.05); N, 14.96 (15.04).

4.3.3 PY3FDMA1 (2)

A 500 mL 2 neck flask, with attached reflux condenser, was dried and then replaced with a nitrogen atmosphere. 200 mL of dry and degassed THF was then added by canula transfer and the flask cooled to -78 °C on a dry ice ethanol bath. 2-ethyl pyridine was degassed by nitrogen bubbling for 15 minutes and was added to the flask (15 mL 131 mM). The solution was allowed to cool for 30 minutes then (45.0 mL, 113 mM) 2.5 M n-butyllithium in hexanes was added by canula transfer over a period of 15 minutes. The solution was stirred for 30 minutes then the flask was warmed to -20 °C by adding water slowly to the dry ice bath. After 10 minutes (7.93 g, 57 mM) 4-dimethylamino-2-fluoropyridine dissolved in 15 mL of dry and degassed THF was added by syringe to the flask and the flask was placed on an oil bath to heat to reflux. After 1 hour of reflux, the flask was cooled to room temperature and (2.6 mL, 29 mM) degassed 2,6difluoropyridine was added by syringe to the flask. The solution was heated to reflux for 1 hour then cooled to room temperature. The reaction was quenched with 100 mL of deionized water. After 15 minutes of stirring the organic layer was separated and the aqueous layer was extracted 3 times with 50 mL of diethyl ether. The organic layers were combined and dried over MgSO₄ for 20 minutes and then filtered. The solvent was removed by rotary evaporation and the product was purified by column chromatography with silica gel. The product was loaded onto the column with dichloromethane and then 500 mL of dichloromethane was used to wash the product. The product was then eluted with acetonitrile and dried to an oil by rotary evaporation. The product

was dried under vacuum as an off white solid (Yield: 2.28 g, 24.7%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.57 (ddt, J = 4.8, 1.8, 0.9 Hz, 1H), 8.21 (d, J = 5.9 Hz, 1H), 7.64 (q, J = 8.0 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.14 – 7.07 (m, 2H), 6.98 (dd, J = 7.6, 2.5 Hz, 1H), 6.76 – 6.70 (m, 1H), 6.36 (dd, J = 5.9, 2.5 Hz, 1H), 6.29 (d, J = 2.6 Hz, 1H), 2.88 (d, J = 1.0 Hz, 6H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.72, 165.35 (d, J = 12.3 Hz), 164.84, 162.45 (d, J = 237.4 Hz), 154.61, 148.90, 148.70, 140.68 (d, J = 7.5 Hz), 136.00, 123.55, 121.23 (m), 106.69 (d, J = 37.7 Hz), 106.23, 104.62, 59.67, 39.02, 26.93. ¹⁹F NMR (470 MHz, Chloroform-*d*) δ - 67.28 (d, J = 8.3 Hz). Elemental analysis: found (calculated) for C₁₉H₁₉FN₄: C, 70.70 (70.79); H, 6.40 (5.94); N, 17.33 (17.38).

4.3.4 PY3FDMA2 (3)

A 250 mL 2 neck flask, with attached reflux condenser, was dried and then replaced with a nitrogen atmosphere. 100 mL of dry and degassed THF was then added by canula transfer and the flask cooled to -78 °C on a dry ice ethanol bath. 2-ethyl pyridine was degassed by nitrogen bubbling for 15 minutes and was added to the flask (8.4 mL 73 mM). The solution was allowed to cool for 30 minutes then (25.1 mL, 63 mM) 2.5 M n-butyllithium in hexanes was added by canula transfer over a period of 15 minutes. The solution was stirred for 30 minutes then the flask was warmed to -20 °C by adding water slowly to the dry ice bath. After 10 minutes (4.43 g, 31 mM) 4-dimethylamino-2-fluoropyridine dissolved in 15 mL of dry and degassed THF was added by syringe to the flask and the flask was placed on an oil bath to heat to reflux. After 1 hour of reflux, the flask was cooled to room temperature and (2.50 g, 16 mM) 4-dimethylamino-2,6-difluoropyridine was dissolved in 10 mL of dry and degassed THF was added by syringe to the flask. The solution was heated to reflux for 1 hour then cooled to room temperature. The reaction was quenched with 50 mL of deionized water. After 15 minutes of stirring the organic

layer was separated and the aqueous layer was extracted 3 times with 50 mL of diethyl ether. The organic layers were combined and dried over MgSO₄ for 20 minutes and then filtered. The solvent was removed by rotary evaporation and the product was purified by column chromatography with silica gel. The product was loaded onto the column with dichloromethane and then 500 mL of dichloromethane was used to wash the product. The product was then eluted with acetonitrile and dried to an oil by rotary evaporation. The product was dried under vacuum as an off white solid (Yield: 4.58 g, 83.4%). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.57 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.22 (d, *J* = 5.6 Hz, 1H), 7.54 (td, *J* = 7.8, 1.9 Hz, 1H), 7.17 – 7.03 (m, 2H), 6.35 (m, *J* = 5.8 Hz, 2H), 6.24 (t, *J* = 1.9 Hz, 1H), 5.86 (d, *J* = 1.9 Hz, 1H), 2.87 (s 12H), 2.24 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 166.29, 165.56, 165.40, 164.03 (d, *J* = 17.1 Hz), 163.75, 158.32 (d, *J* = 11.8 Hz), 154.54, 148.81, 148.57, 135.81, 123.77, 121.00, 105.5 (d, *J* = 247.2 Hz) 105.19 (d, *J* = 2.6 Hz), 87.57 (d, *J* = 44.3 Hz), 59.70, 39.39, 39.03, 26.97. ¹⁹F NMR (470 MHz, Chloroform-*d*) δ -69.93. Elemental analysis: found (calculated) for C₂₁H₂₄FN₅: C, 69.04 (69.02); H, 7.05 (6.62); N, 19.16 (19.16).

4.3.5 PY3Im (4)

PY3F (3.71 g, 13 mM), K_2CO_3 (3.67 g, 27 mM) and imidazole (2.71 g, 40 mM) were combined in a dried 100 mL round bottom flask with attached reflux condenser. The system was then degassed by 3 cycles of 5 minutes of vacuum followed by nitrogen filling. The reaction was then heated to 180 °C for 24 hours. The reaction was then cooled to room temperature and 40 mL of chloroform and 40 ml of water were added to the flask. The mixture was sonicated until all material was dissolved and then the two layers were separated. The aqueous layer was extracted 3 times with 50 mL of chloroform. The organic layers were washed 3 times with 50 mL of saturated Na₂CO_{3(aq)}. The organic layers were dried over MgSO₄ and the solvent removed by rotary evaporation to result in a sticky white solid. 50 mL of diethyl ether was added and the product sonicated. The solid was filtered and a second crop of material was obtained by placing the diethyl ether in a freezer at -30 °C overnight. The second crop was filtered and combined with the first as white crystals. (Yield: 4.20 g, 96.5 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (dd, J = 4.8, 1.9 Hz, 2H), 8.18 (s, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.61 (td, J = 7.8, 1.9 Hz, 2H), 7.50 (d, J = 1.5 Hz, 1H), 7.22 – 7.09 (m, 7H), 2.36 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.75, 165.34, 148.83, 147.59, 138.93, 136.05, 134.95, 130.42, 123.45, 121.90, 121.46, 115.90, 109.30, 60.06, 27.04. Elemental analysis: found (calculated) for C₂₀H₁₇N₅: C, 73.60 (73.37); H, 5.29 (5.23); N, 21.04 (21.39).

4.3.6 PY3ImDMA1 (5)

PY3FDMA1 (1.96 g, 6.0 mM), K₂CO₃ (1.67 g, 12 mM) and imidazole (1.23 g, 18 mM) were combined in a dried 100 mL round bottom flask with attached reflux condenser. The system was then degassed by 3 cycles of 5 minutes of vacuum followed by nitrogen filling. The reaction was then heated to 180 °C for 24 hours. The reaction was then cooled to room temperature and 40 mL of chloroform and 40 ml of water were added to the flask. The mixture was sonicated until all material was dissolved and then the two layers were separated. The aqueous layer was extracted 3 times with 50 mL of chloroform. The organic layers were washed 3 times with 50 mL of saturated Na₂CO_{3(aq)}. The organic layers were dried over MgSO₄ and the solvent removed by rotary evaporation to result in a sticky white solid. 50 mL of diethyl ether was added and the product sonicated. The solid was filtered and a second crop of material was obtained by placing the diethyl ether in a freezer at -30 °C overnight. The second crop was filtered and combined with the first as white crystals. The combined solids were dried under vacuum overnight. (Yield: 2.10 g, 93.6 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.58 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 8.25

-8.19 (m, 2H), 7.71 (t, J = 7.9 Hz, 1H), 7.59 (td, J = 7.7, 1.9 Hz, 1H), 7.51 (t, J = 1.4 Hz, 1H), 7.18 -7.09 (m, 5H), 6.38 (dd, J = 6.0, 2.5 Hz, 1H), 6.33 (d, J = 2.5 Hz, 1H), 2.90 (s, 6H), 2.33 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 166.17, 165.84, 165.05, 154.56, 148.91, 148.61, 147.45, 138.66, 135.89, 134.96, 130.25, 123.66, 122.28, 121.26, 115.96, 109.12, 106.15, 104.66, 77.30, 77.05, 76.79, 60.03, 39.04, 27.00. Elemental analysis: found (calculated) for C₂₂H₂₂N₆: C, 70.35 (71.33); H, 6.17 (5.99); N, 21.61 (22.69).

4.3.7 PY3ImDMA2 (6)

PY3FDMA2 (4.00 g, 10.9 mM), K₂CO₃ (3.02 g, 21.8 mM) and imidazole (2.23 g, 32.8 mM) were combined in a dried 100 mL round bottom flask with attached reflux condenser. The system was then degassed by 3 cycles of 5 minutes of vacuum followed by nitrogen filling. The reaction was then heated to 180 °C for 24 hours. The reaction was then cooled to room temperature and 40 mL of chloroform and 40 ml of water were added to the flask. The mixture was sonicated until all material was dissolved and then the two layers were separated. The aqueous layer was extracted 3 times with 50 mL of chloroform. The organic layers were washed 3 times with 50 mL of saturated Na₂CO_{3(aq)}. The organic layers were dried over MgSO₄ and the solvent removed by rotary evaporation to result in a sticky white solid. 50 mL of diethyl ether was added and the product sonicated. The solid was filtered and a second crop of material was obtained by placing the diethyl ether in a freezer at -30 °C overnight. The second crop was filtered and combined with the first as a white powder. The combined solids were dried under vacuum overnight. (Yield: 3.36 g, 74.3 %). ¹H NMR (500 MHz, Chloroform-d) δ 8.58 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 8.24 (d, J = 5.9 Hz, 1H), 8.16 (d, J = 1.2 Hz, 1H), 7.55 (td, J = 7.8, 2.0 Hz, 1H), 7.47 (t, J = 1.4 Hz, 1H), 7.15 (dt, J = 8.1, 1.1 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.44 (d, J = 2.0Hz, 1H), 6.40 (d, J = 2.5 Hz, 1H), 6.36 (dd, J = 5.9, 2.5 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 2.96 (s, 6H), 2.87 (s, 6H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 166.57, 165.69, 165.34, 156.61, 154.44, 148.80, 148.77, 148.45, 135.60, 135.22, 129.74, 123.90, 120.97, 116.23, 106.50, 105.39, 104.53, 92.00, 59.99, 39.48, 39.05, 26.97. Elemental analysis: found (calculated) for C₂₄H₂₇N₇: C, 69.64 (69.71); H, 6.75 (6.58); N, 23.63 (23.71).

4.3.8 PY5ImBr (7)

PY3Im (5.20 g, 15.9 mM) and bromobis(2-pyridyl)methane (3.95 g, 15.9 mM) were dissolved in 20 mL of acetonitrile in a 100 mL round bottom flask with attached reflux condenser. The solution was brought to reflux for 24 hours and was then cooled to room temperature. The product was precipitated with 70 mL of diethyl ether and was collected by filtration. More product was obtained by placing the filtrate in a freezer at -30 °C for 18 hours. The second crop was filtered and combined with the first crop resulting in a light red solid. The combined solids were dried under vacuum for 24 hours. (Yield: 5.63 g, 61.4 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 11.70 (t, *J* = 1.6 Hz, 1H), 8.56 (dddd, *J* = 21.9, 4.9, 1.8, 0.9 Hz, 4H), 8.36 (s, 1H), 8.21 (dd, J = 2.1, 1.4 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.90 (t, J = 8.0 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.78 (dt, J = 7.9, 1.1 Hz, 2H), 7.73 (td, J = 7.7, 1.8 Hz, 2H), 7.63 (td, J = 7.8, 1.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.18 (ddd, J = 7.5, 4.8, 1.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 166.16, 164.50, 154.67, 149.57, 148.81, 144.61, 140.19, 137.52, 136.49, 135.56, 125.35, 124.69, 123.79, 123.77, 123.31, 121.76, 116.91, 111.64, 66.38, 59.93, 27.01. Elemental analysis: found (calculated) for C₃₁H₂₆BrN₇: C, 64.13 (64.59); H, 4.44 (4.55); N, 16.72 (17.01).

4.3.9 PY5ImDMA1Br (8)

PY3ImDMA1 (1.00 g, 2.7 mM) and bromobis(2-pyridyl)methane (0.67 g, 2.7 mM) were dissolved in 20 mL of acetonitrile in a 100 mL round bottom flask with attached reflux

condenser. The solution was brought to reflux for 18 hours and was then cooled to room temperature. The product was precipitated with 70 mL of diethyl ether and was collected by filtration. More product was obtained by placing the filtrate in a freezer at -30 °C for 18 hours. The second crop was filtered and combined with the first crop resulting in a light pink solid. The combined solids were dried under vacuum for 24 hours. (Yield: 1.28 g, 76.7 %) ¹H NMR (500 MHz, Acetonitrile-d3) δ 10.07 (s, 1H), 8.58 (ddd, J = 4.8, 1.9, 0.9 Hz, 2H), 8.50 (ddd, J = 4.8, 1.9, 1.0 Hz, 1H), 8.14 – 8.03 (m, 2H), 8.01 – 7.92 (m, 2H), 7.87 (td, J = 7.7, 1.8 Hz, 2H), 7.69 (ddd, J = 15.6, 7.9, 1.7 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.46 – 7.35 (m, 3H), 7.27 – 7.12 (m, 2H), 6.50 (dd, J = 6.0, 2.5 Hz, 1H), 6.43 (d, J = 2.5 Hz, 1H), 2.90 (s, 6H), 2.29 (s, 3H). ¹³C NMR (126 MHz, cdcl₃) δ 166.33, 164.81, 154.92, 154.67, 149.74, 149.58, 148.79, 144.57, 139.98, 137.51, 136.24, 135.41, 125.65, 124.67, 124.64, 123.78, 123.49, 121.63, 117.17, 111.56, 105.96, 104.76, 66.38, 59.78, 39.22, 26.95. Elemental analysis: found (calculated) for C₂₀H₁₇N₅: C, 62.54 (63.97); H, 5.69 (5.04); N, 16.34 (18.09).

4.3.10 PY5ImDMA2Br (9)

PY3ImDMA2 (1.00 g, 2.4 mM) and bromobis(2-pyridyl)methane (0.60 g, 2.4 mM) were dissolved in 20 mL of acetonitrile in a 100 mL round bottom flask with attached reflux condenser. The solution was brought to reflux for 18 hours and was then cooled to room temperature. The product was precipitated with 70 mL of diethyl ether and was collected by filtration. More product was obtained by placing the filtrate in a freezer at -30 °C for 18 hours. The second crop was filtered and combined with the first crop resulting in a light brown solid. The combined solids were dried under vacuum for 24 hours. (Yield: 1.25 g, 78.4 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 11.86 (t, J = 1.6 Hz, 1H), 8.57 (ddq, J = 15.7, 4.8, 1.1 Hz, 3H), 8.24 (d, J = 5.9 Hz, 1H), 8.07 (s, 1H), 8.04 – 7.98 (m, 1H), 7.88 (s, 1H), 7.75 – 7.68 (m, 4H), 7.56 (td,

J = 7.8, 1.9 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.21 (d, J = 2.0 Hz, 1H), 7.11 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 7.07 (dt, J = 8.0, 1.1 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 6.37 (dd, J = 6.0, 2.5 Hz, 1H), 6.25 (d, J = 2.5 Hz, 1H), 3.05 (s, 6H), 2.89 (s, 6H), 2.28 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 165.70, 165.01, 164.68, 156.99, 154.77, 154.70, 149.62, 148.60, 148.33, 146.01, 137.48, 135.85, 135.35, 124.54, 123.78, 123.77, 122.69, 121.27, 117.73, 107.40, 106.18, 104.55, 94.13, 66.61, 59.79, 40.01, 39.15, 26.94. Elemental analysis: found (calculated) for C₂₀H₁₇N₅: C, 61.72 (63.44); H, 5.48 (5.48); N, 18.54 (19.02).

4.3.11 [Co(PY5Im)](OTf)₂ (10a)

PY5ImBr (2.00 g, 3.5 mM), Co(OTf)₂ (1.23 g, 3.5 mM), K₂CO₃ (1.44 g, 10.4 mM) and Tl(OTf) (1.23 g, 3.5 mM) were combined in a 100 mL round bottom flask in a nitrogen filled glove box. A stir bar and 15 mL of acetonitrile were added and the reaction was stirred for 18 hours. The mixture was then syringe filtered (0.45 μ m) and precipitated with 70 mL of diethyl ether. The solvent was decanted and then washed with 10 mL of diethyl ether. The product was then redissolved in 20 mL of dichloromethane and syringe filtered (0.45 μ m) and precipitated with 70 mL of diethyl ether. The solvent was decanted and then washed with 10 mL of diethyl ether. The product was then redissolved in 20 mL of dichloromethane and syringe filtered (0.45 μ m) and precipitated with 70 mL of diethyl ether. The solvent was decanted and the product dried under vacuum to yield a green-brown solid. (Yield: 1.93 g, 65.4 %). Elemental analysis: found (calculated) for C₃₃H₂₅CoF₆N₇O₆S₂: C, 46.42 (46.49); H, 2.82 (2.96); N, 11.28 (11.50).

4.3.12 [Co(PY5ImDMA1)](OTf)₂ (11a)

PY5ImDMA1Br (0.500 g, 0.80 mM), Co(OTf)₂ (0.288 g, 0.80 mM), K₂CO₃ (0.335 g, 2.42 mM) and Tl(OTf) (0.285 g, 0.80 mM) were combined in a 20 mL vial in a nitrogen filled glove box. A stir bar and 4 mL of acetonitrile were added and the reaction was stirred for 18 hours. The mixture was then syringe filtered (0.45 μ m) and precipitated with 15 mL of diethyl ether. The solvent was decanted and then washed with 3 mL of diethyl ether. The product was then

redissolved in 6 mL of dichloromethane and syringe filtered again (0.45 μ m) and precipitated again with 13 mL of diethyl ether. The solvent was decanted and the product dried under vacuum to yield a green-brown solid. (Yield: 0.659 g, 91.2 %). Elemental analysis: found (calculated) for C₃₅H₃₀CoF₆N₈O₆S₂: C, 46.85 (46.93); H, 3.70 (3.38); N, 12.27 (12.51).

4.3.13 [Co(PY5ImDMA2)](OTf)2(12a)

PY5ImDMA2Br (1.00 g, 1.5 mM), Co(OTf)₂ (0.536 g, 1.5 mM), K₂CO₃ (0.622 g, 4.5 mM) and Tl(OTf) (0.530 g, 1.5 mM) were combined in a 20 mL vial in a nitrogen filled glove box. A stir bar and 8 mL of acetonitrile were added and the reaction was stirred for 18 hours. The mixture was then syringe filtered (0.45 μ m) and precipitated with 25 mL of diethyl ether. The solvent was decanted and then washed with 5 mL of diethyl ether. The product was then redissolved in 10 mL of dichloromethane and syringe filtered again (0.45 μ m) and precipitated again with 20 mL of diethyl ether. The solvent was decanted and the product dried under vacuum to yield a brown solid. (Yield: 0.942 g, 66.9 %). Elemental analysis: found (calculated) for C₃₇H₃₅CoF₆N₉O₆S₂: C, 46.98 (47.34); H, 4.00 (3.76); N, 13.43 (13.43).

4.3.14 [Co(PY5Im)](OTf)₃(10b)

 $[Co(PY5Im)](OTf)_2$ (0.200 g, 0.24 mM) and [Fc](OTf) (0.079 g, 0.24 mM) were combined in a 20 mL vial with 5 mL of dichloromethane. The mixture was allowed to stir for 2 hours then the solvent was decanted. The solid was washed 3 times with 2 mL dichloromethane. The solid was dried under vacuum to yield a yellow solid. (Yield: 0.199 g, 84.8 %). ¹H NMR (500 MHz, Acetonitrile-*d*₃) δ 8.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.66 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.55 – 8.47 (m, 3H), 8.41 (d, *J* = 2.1 Hz, 1H), 8.32 (d, *J* = 2.1 Hz, 1H), 8.29 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.12 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.10 – 7.98 (m, 5H), 7.76 (ddd, *J* = 5.4, 3.5, 1.3 Hz, 2H), 7.72 – 7.66 (m, 1H), 7.60 (dddd, *J* = 10.3, 7.3, 5.9, 1.4 Hz, 2H), 7.20 (td, *J* = 6.1, 2.7 Hz, 1H), 7.06 (ddd, *J* = 7.5, 5.9, 1.5 Hz, 1H), 6.99 (dd, J = 6.0, 1.3 Hz, 1H), 3.02 (s, 3H). ¹³C NMR (126 MHz, Acetonitrile- d_3) δ 159.32, 157.33, 156.47, 156.42, 156.17, 155.30, 155.27, 153.90, 153.42, 152.13, 145.98, 144.05, 143.40, 143.32, 142.68, 130.50, 129.42, 128.98, 127.50, 127.46, 127.11, 127.06, 126.33, 126.18, 125.62, 124.43, 115.16, 69.56, 59.08, 19.67. ¹⁹F NMR (470 MHz, Acetonitrile- d_3) δ -79.11. Elemental analysis: found (calculated) for C₃₄H₂₅CoF₉N₇O₉S₃: C, 40.42 (40.77); H, 2.89 (2.52); N, 9.44 (9.79).

4.3.15 [Co(PY5ImDMA1)](OTf)₃(11b)

[Co(PY5ImDMA1)](OTf)₂ (0.200 g, 0.24 mM) and [Fc](OTf) (0.075 g, 0.24 mM) were combined in a 20 mL vial with 5 mL of dichloromethane. The mixture was allowed to stir for 2 hours then the solvent was decanted. The solid was washed 3 times with 2 mL dichloromethane. The solid was dried under vacuum to yield an orange-red solid as a mixture of isomers. (Yield: 0.179 g, 73.1 %). ¹H NMR (500 MHz, Acetonitrile- d_3) δ 8.62 (ddd, J = 9.7, 8.2, 1.5 Hz, 1.6H), 8.54 - 8.42 (m, 2.4H), 8.37 (t, J = 2.4 Hz, 0.9H), 8.28 (dd, J = 6.7, 2.1 Hz, 0.9H), 8.23 (td, J = 6.7, 2.1 Hz, 0.9H), 8.238.2, 0.9 Hz, 1.1H), 8.13 – 7.96 (m, 4.6H), 7.81 (ddd, J = 8.7, 5.9, 1.3 Hz, 1.1H), 7.70 (dd, J = 8.7, 5.9, 1.3 Hz, 5.8, 1.5 Hz, 0.6H), 7.67 - 7.52 (m, 2.4H), 7.17 (ddd, J = 7.4, 5.9, 1.6 Hz, 0.5H) 7.09 (ddd, J = 7.4, 5.9, 1.6 H 7.4,5.9, 1.6 Hz, 0.5 H) 7.05 (dt, J = 6.1, 1.3 Hz, 0.7H), 7.02 (td, J = 5.9, 5.5, 1.6 Hz, 0.7H), 6.99 -6.96 (m, 0.9H), 6.82 (d, J = 7.2 Hz, 0.6H), 6.60 (dd, J = 7.1, 2.8 Hz, 0.5H), 6.25 (dd, J = 7.3, 2.9 Hz, 0.6H), 3.25 (s, 2.7H), 3.05 (s, 3.2H), 2.94 (d, J = 5.3 Hz, 3H). ¹³C NMR (126 MHz, Acetonitrile- d_3) δ 160.18, 160.01, 158.10, 157.02, 156.93, 156.46, 156.40, 156.32, 156.22, 155.27, 155.22, 155.19, 154.92, 154.19, 153.66, 153.36, 153.30, 152.55, 152.24, 152.10, 151.07, 145.78, 145.68, 143.80, 143.71, 143.15, 143.07, 142.94, 142.47, 130.39, 130.25, 129.10, 129.01, 128.78, 128.67, 127.26, 127.20, 127.17, 126.88, 126.83, 125.99, 125.86, 125.22, 124.07, 123.84, 114.85, 114.82, 109.48, 108.52, 108.37, 106.66, 69.50, 69.46, 65.28, 58.97, 58.60, 39.33, 19.54, 19.49, 14.65. ¹⁹F NMR (470 MHz, Acetonitrile- d_3) δ -79.26. Elemental analysis: found (calculated) for C₃₆H₃₀CoF₉N₈O₉S₃: C, 41.19 (41.39); H, 3.55 (2.89); N, 10.83 (10.73).

4.3.16 [Co(PY5ImDMA2)](OTf)₃(12b)

[Co(PY5ImDMA2)](OTf)₂ (0.200 g, 0.21 mM) and [Fc](OTf) (0.071 g, 0.21 mM) were combined in a 20 mL vial with 5 mL of dichloromethane. The mixture was allowed to stir for 2 hours then the solvent was decanted. The solid was washed 3 times with 2 mL dichloromethane. The solid was dried under vacuum to yield a red solid. (Yield: 0.191 g, 82.4 %). ¹H NMR (500 MHz, Acetonitrile- d_3) δ 8.58 (dd, J = 7.8, 1.5 Hz, 1H), 8.45 (td, J = 7.7, 1.4 Hz, 1H), 8.25 (d, J = 2.1 Hz, 1H), 8.21 (d, J = 2.1 Hz, 1H), 8.09 – 7.95 (m, 4H), 7.90 (s, 1H), 7.81 (dd, J = 5.9, 1.3 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.49 (d, J = 2.8 Hz, 1H), 7.19 – 7.08 (m, 4H), 7.06 (dd, J = 5.8, 1.3 Hz, 1H), 7.01 (d, J = 7.1 Hz, 1H), 6.60 (dd, J = 7.1, 2.8 Hz, 1H), 3.41 – 3.12 (m, 12H), 2.86 (s, 3H). ¹³C NMR (126 MHz, Acetonitrile- d_3) δ 159.16, 158.75, 157.01, 156.36, 156.11, 155.77, 154.73, 154.56, 153.81, 153.71, 152.48, 151.16, 143.51, 142.69, 142.27, 130.21, 128.88, 128.54, 126.96, 126.41, 126.21, 125.68, 125.31, 109.31, 106.82, 106.44, 96.37, 69.21, 58.23, 40.11, 39.28, 19.53. Elemental analysis: found (calculated) for C₃₆H₃₀CoF₉N₈O₉S₃: C, 41.30 (41.96); H, 3.28 (3.24); N, 11.61 (11.59).

4.3.17 DSSC Fabrication

TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 minutes, followed by manual scrubbing of the FTO with Kimwipes. The FTO pieces were then sonicated in DI water for 10 minutes, rinsed with acetone and sonicated in isopropanol for 10 minutes. The FTO pieces were dried in room air then immersed in an aqueous 40 mM solution TiCl4 solution for 60 minutes at 70 °C. The water used in the for the TiCl₄ treatment was preheated to 70 °C prior to adding 2 M TiCl₄ to the water. The 40 mM solution was

immediately poured onto the samples and placed in a 70 °C oven for the 60 minute deposition. The FTO pieces were immediately rinsed with 18 M Ω water followed by isopropanol and were annealed by heating from room temperature to 500 °C, holding at 500 °C for 30 minutes. A 0.36 cm² area was doctor bladed with commercial 30 nm TiO2 nanoparticle paste (DSL 30NRD) that was diluted with equal masses of a-terpinol and 10% ethyl cellulose by weight in ethanol. The diluted paste was allowed to stir for 2 days before being used for doctor blading. The transparent films were left to rest for 10 minutes and were then placed in a 125 °C oven for 30 minutes. After cooling to room temperature, a scattering layer was applied (PST-400C, JGC Catalysts). The samples were annealed in an oven that was ramped to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes, and 500 °C for 15 minutes. The 30 nm nanoparticle film thickness was 3.5 µm, and a total thickness of 7.5 µm with the addition of the scattering layer. After cooling to room temperature, a second TiCl₄ treatment was performed as described above. When the anodes had cooled to 80 °C, they were soaked in a dye solution of 0.2 mM D35cpdt (LEG4) in 1 : 1 acetonitrile : tert-butyl alcohol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen.

The PEDOT counter electrodes were prepared by electropolymerization in a solution of 0.01 M EDOT and 0.1 M LiClO₄ in 0.1 M SDS in 18 M Ω water.¹⁹ A constant current of 8.3 mA for 250 seconds was applied to a 54 cm² piece of TEC 8 FTO with predrilled holes using an equal size piece of FTO as the counter electrode. The PEDOT electrodes were then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 2.0 cm pieces. The working and counter electrodes were sandwiched together with 25 µm surlyn films by placing them on a 140 °C hotplate and applying pressure. The cells were then filled in a nitrogen filled glove box with electrolyte through one of the two predrilled holes and were sealed

with 25 µm surlyn backed by a glass coverslip and applied heat to seal with a soldering iron. The electrolyte consisted of 0.16 M Co(II), 0.04 M Co(III), 0.1 M Li(OTf), 0.2 M 4- (trifluoromethyl)pyridine in acetonitrile. Contact to the TiO₂ electrode was made by scratching the edge of the electrode gently with sandpaper and applying silver epoxy and copper wire. The counter electrode was connected directly with silver epoxy and copper wire. The silver epoxy was dried in a fume hood for 18 hours. Cells were measured approximately 18 hours after fabrication where they rested in ambient lighting. At least ten dye-sensitized solar cells were measured for each electrolyte condition and the average and standard deviation is given.

4.3.18 Instrumentation

NMR spectra were collected at room temperature on an Agilent DirectDrive2 500 MHz spectrometer and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. All coupling constants are apparent *J* values measured at the indicated field strengths in hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, m = multiplet). Cyclic voltammograms were collected using a μ AutolabIII potentiostat using a BASi glassy carbon working electrode, a fabricated platinum mesh counter electrode, and a fabricated 0.01 M AgNO3, 0.1 M TBAPF6 in acetonitrile Ag/AgNO3 reference electrode. All measurements were also internally referenced to the ferrocenium/ferrocene couple by addition of ferrocene to the solution after measurements or measured in a separate solution of the same solvent and supporting electrolyte. Photoelectrochemical measurements were performed with a potentiostat (Autolab PGSTAT 128N) in combination with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻², and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A black mask with an open

area of 0.07 cm⁻² was applied on top of the cell active area. The solution potential of the devices was determined by immersing a platinum wire and the Ag/AgNO₃ electrode into the electrolyte used to fill the devices and measuring the potential between the electrodes. The reference electrode was then referenced to Fc^{+/0} by measuring cyclic voltammograms in ACN with 0.1 M LiOTf immediately after. A monochromator (Horiba Jobin Yvon MicroHR) attached to the 450 W xenon arc light source was used for monochromatic light for IPCE measurements. The photon flux of the light incident on the samples was measured with a laser power meter (Nova II Ophir). IPCE measurements were made at 20 nm intervals between 340 and 800 nm at short circuit current. EIS measurements were measured with an Autolab PGSTAT 128N/FRA2 potentiostat/frequency response analyzer and all data plots were simulated with ZView software. Variable light intensity EIS measurements were made by using optical filters from Thorlabs (NEK01). Equivalent circuits used for EIS fitting can be found in the supporting information (Figure A4.14). UV-vis spectra were measured with a PerkinElmer Lambda 35 UV-vis spectrometer using 1 cm path length quartz cuvettes at 480 nm min⁻¹. CHN analysis were obtained at Midwest Microlab. Magnetic susceptibility of the paramagnetic complexes was measured in acetonitrile-d₃ by ¹H NMR using the Evans method.²⁰ Measurements were collected using a NMR tube containing a capillary insert filled with a saturated solution of ferrocene also dissolved in acetonitrile- d_3 (diamagnetic standard). The ¹H signal of ferrocene was used and the signal was monitored as the paramagnetic complex concentration was varied. The effective magnetic moment μ_{eff} was determined directly from the molar magnetic susceptibility assuming the diamagnetic contribution was small.²¹

4.4 Results and Discussion

The hexadentate ligands PY5ImBr, PY5ImDMA1Br and PY5ImDMA2Br were synthesized in three steps (**Figure 4.1**). First one pot syntheses of PY3FDMA1 and PY3FDMA2 were developed which took inspiration from the previously reported synthesis of PY3F.²² By introducing dimethyl amine groups in the *para* positions of the pyridine precursors, the tris(pyridyl) unit could have three variations in donating ability. The three pyridine units were coupled together by lithiation of excess ethyl pyridine to the 2-fluoropyridine derivatives followed by the addition of 2,6-difluoropyridine derivatives. The second step was the nucleophilic substitution of fluorine with imidazole following a previously developed synthesis method for similar multidentate ligands to introduce the NHC unit.²³ The resulting compounds PY3Im, PY3ImDMA1, and PY3ImDMA2 were then reacted with bromobis(2-pyridyl)methane to give the cationic hexadentate ligand products, in a similar method to the synthesis of PY4Im, in good yields (61-78 %).¹⁴



Figure 4.1 (Top reaction) Stepwise reaction of 2-ethyl pyridine, n-butyllithium, 2-fluoropyridine derivative and 2,6-difluorpyridine derivative to form compounds **1-3**. (Middle reaction) Reaction of **1-3** with imidazole to form compounds **4-6**. (Top reaction) Reaction of **4-6** with bis(2-pyridyl)bromomethane to form the ligand series compounds **7-9**.

Transmetallation with Ag_2O was attempted to coordinate the PY5Im ligand to cobalt metal centers following the procedure reported for the analogous PY4Im ligand. While coordination to the silver ion was found to occur, coordination attempts to $Co(OTf)_2$ with the silver bound ligand resulted in mixtures of Co(II) and Co(III) ligand bound complexes and other impurities. We therefore attempted deprotonation with an excess of the mild base K₂CO₃, which resulted in successful coordination to the Co(II) center with the carbene and pyridine units without partial oxidation to Co(III). The bromide ion was removed with thallium(I) triflate resulting in the Co(II) complexes [Co(PY5Im)](OTf)₂, [Co(PY5ImDMA1)](OTf)₂, and [Co(PY5ImDMA2)](OTf)₂ (**Figure 4.2**). The Co(II) complexes were then oxidized in the presence of ferrocenium triflate to result in the Co(III) complexes [Co(PY5Im)](OTf)₃, [Co(PY5ImDMA1)](OTf)₃, and [Co(PY5ImDMA2)](OTf)₃.



Figure 4.2 (Top reaction) Coordination of the hexadentate ligand to Co(II)triflate. (Bottom reaction) Oxidation of the Co(II) complexes to Co(III) with ferrocenium triflate.

Crystals of 10a, 10b, 11a, 11b, 12a and 12b were grown and analyzed single crystal x-ray diffraction. Interestingly, the structures showed that all three Co(II) complexes were 5-coordinate despite the ligand being hexadentate (**Figure 4.3**)(**Table 4.1**). Each Co(II) complex has a pseudo square pyramidal geometry but with large distortions from the ideal geometry. The geometry distortion is likely due to a strong Jahn-Teller distortion due the low-spin d7 electronic configuration of all the Co(II) complexes as confirmed by the Evan's method (**Table 4.2**). These large distortions from ideal geometries have also been seen for the [Co(PY5Me₂)(CN)](OTf), [Co(PY5Me₂DMP-CN)](PF₆)₂ and [Co(ttcn)](BF₄)₂ complexes we have studied previously but those examples were all 6-coordinate.^{13,12,24} There are other examples of both 5-coordinate and 6 coordinate low-spin Co(II) complexes and a cursory observation is that the ligand systems with more flexibility are typically 6-coordinate due to their ability to accommodate the Jahn-Teller

distortion.^{25,26} When the ligand environment is more rigid, there are examples of other 5coordinate pseudo square pyramidal low-spin Co(II) complexes. One example of a complex with four low-spin Co(II) metal centers demonstrates two metal centers being 6-coordinate while two are 5-coordinate. However, the same ligand coordinated to four Fe(III) metal centers is octahedral.²⁷ In both complexes the bond angles of the coordinating atoms with the metal are distorted indicating significant strain. Likely in the case of low-spin Co(II) complexes the energy difference between an octahedral geometry and square pyramidal are close enough that ligand strain is more of a contributing factor than in the case for the octahedral geometry Fe(III) cluster. The Co(II) to ligand bond distances and angles are nearly identical for all the complexes measured, indicating the DMA additions have little impact. Upon oxidation, each complex coordinates the pendant pyridine moiety to form a distorted octahedral geometry. The Co(III) complexes have nearly identical coordination environments indicating the reorganization energies should be very similar for all three Co(III/II) couples.



Figure 4.3 Crystal structures of $[Co(PY5Im)](OTf)_2$ (top left), $[Co(PY5ImDMA1)](OTf)_2$ (top middle), $[Co(PY5ImDMA2)](OTf)_2$ (top right), $[Co(PY5Im)](OTf)_3$ (bottom left), $[Co(PY5ImDMA1)](OTf)_3$ (bottom middle) and $[Co(PY5ImDMA2)](OTf)_3$ (bottom right) complexes.

Complex	Co-N ₁	Co-N ₂	Co-N ₃	Co-N ₄	Co-N ₅	Co-C ₁
[Co(PY5Im)] ²⁺	1.926(3)	1.998(3)	2.086(3)	1.973(3)		1.847(4)
$[Co(PY5Im)]^{3+}$	1.990(3)	1.958(3)	1.959(3)	1.952(3)	1.974(3)	1.865(3)
[Co(PY5ImDMA1)] ²⁺	1.9557(2)	1.9256(2)	2.073(2)	1.959(2)		1.830(2)
[Co(PY5ImDMA1)] ³⁺	1.953(2)	1.923(3)	1.938(2)	1.979(2)	1.935(3)	1.863(3)
[Co(PY5ImDMA2)] ²⁺	1.9359(2)	1.9608(2)	2.1056(2)	1.9511(2)		1.830(2)
[Co(PY5ImDMA2)] ³⁺	1.923(5)	1.960(5)	1.930(6)	1.974(5)	1.950(5)	1.853(7)

Table 4.1 Metal to ligand bond distances (Å) from single crystal X-ray diffraction data.

Cyclic voltammograms were collected for each complex in acetonitrile (**Figure 4.4**). Both the Co(III/I) and Co(II/I) waves were visible and found to be reversible from the scan rate dependence despite the coordination number change of the complexes (**Figure A4.4-A4.6**). A 4-coordinate Co(III) complex has been reported with similar behavior.²⁸ Upon oxidation the complex rearranges to a 6-coordinate complex and displays reversible electron transfers by cyclic voltammetry. In both the reported complex and these complexes, the change in coordination results in a rearrangement in the ligand environment around the metal but with no new ligands in the inner coordination sphere. The change in coordination number will affect the inner-sphere reorganization energy but it seems to not affect the reversibility in both cases analogously to complexes that undergo large metal to ligand bond distance changes upon electron transfer without a change in coordination number. The diffusion coefficient for the [Co(PY5Im)](OTf)_{3/2}, [Co(PY5ImDMA1)](OTf)_{3/2} and [Co(PY5ImDMA2)](OTf)_{3/2} (**Table 4.2**). Introduction of the NHC carbene unit into the ligand framework did result in a 140 mV negative

redox potential compared to $[Co(bpy)_3]^{3+/2+}$. The addition of the dimethyl amine groups to the ligand resulted in even larger shifts in redox potential of approximately 100 mV for each group relative to the parent complex $[Co(PY5Im)]^{3+/2+}$.



Figure 4.4 Cyclic Voltammograms of 2 mM of [Co(PY5Im)](OTf)₂ (red), [Co(PY5Im)](OTf)₂ (green) and [Co(PY5ImDMA2)](OTf)₂ (blue) in 0.1 M LiOTf in acetonitrile at scan rate of 100 mV s⁻¹.

Stopped-flow experiments were performed to determine the electron transfer self-exchange rate constant for each complex by cross-exchange reactions. The ferrocene derivatives FcMe₂, FcMe₈, and FcMe₁₀ were used as standards due to their well-defined self-exchange rate constants and their close redox potentials to the cobalt complexes to slow down the observed cross exchange rates to the instrument's time scale. Each ferrocene derivatives self-exchange rate constant was measured by the NMR line broadening method in deuterated acetonitrile with

lithium triflate supporting electrolyte to imitate conditions in the DSSC and to confirm their rate (**Figure A4.10-A4.12**).²⁹ The self-exchange rate constants were found to be $6.8 \pm 0.8 \times 10^6$, $2.0 \pm 0.4 \times 10^7$, and $3.8 \pm 0.7 \times 10^7$ for [FcMe2](OTf)_{1/0}, [FcMe8](OTf)_{1/0} and [FcMe10](OTf)_{1/0} respectively, in good agreement with previous reports.^{30,31} Knowing the self-exchange rate constant and redox potential of each ferrocene derivative, cross-exchange experiments were performed to determine the electron-self exchange rate constant of each cobalt complex. Pseudo-first-order conditions were utilized where the ferrocene complexes were prepared at 10-fold excess. One ferrocene derivative's concentration was then increased to change the observed rate constant of the reaction. The data were fit to single stretch exponential function to extract the observed rate constant for each concentration (**Table A4.1-A4.3**) (**Equation 4.1**).

$$A = A_{\infty} + (A_0 - A_{\infty})e^{-k_{obs}t}$$
 E 4.1

For each Co(II) complex, a MLCT absorbance feature is seen at the edge of the visible spectrum giving strong signal to observe at 400 nm for the experiments (**Figure A4.1-A4.3**). In the case of $[Co(PY5Im)](OTf)_{3/2}$, the $[Co(PY5Im)](OTf)_2$ complex was oxidized by $[FcMe_2](OTf)$ resulting in a decrease in the signal at 400 nm as seen in **Figure 4.4a**. Fitting each exponential increase, the k_{obs} was obtained for each $[FcMe_2](OTf)$ concentration. From the slope of k_{obs} vs $[FcMe_2](OTf)$, the cross exchange rate constant k_{12} was obtained (**Figure 4.4b**). Then using the equilibrium constant K_{12} determined from the difference in redox potentials and the measured self-exchange rate constant of the $[FcMe_2](OTf)_{1/0}$, the electron self-exchange rate constant k_{11} was determined from the simplified Marcus cross-relation for the $[Co(PY5Im)](OTf)_{3/2}$ couple (**Table 4.2**) (**Table A4.7**).^{32,33}

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}}$$
 E 4.2

For $[Co(PY5Im)](OTf)_{3/2}$, the self-exchange rate constant was approximately an order of magnitude larger than $[Co(bpy)_3](PF_6)_{3/2}$ determined previously. As seen with the other low-spin Co(II) complexes mentioned earlier, the low-spin to low-spin Co(III/II) self-exchange process has a reduced internal electron transfer barrier despite large distortion from idealized geometries. It appears, however, that the increase in self-exchange rate constant is modest when compared to $[Co(ttcn)]^{3+/2+}$ and $[Co(PY5Me_2)(CN)]^{2+/1+}$.^{11,13} This is likely due to the large structural changes resulting from the 5-coordinate Co(II) to 6-coordinate Co(III) adjustments offsetting some of the inner-sphere reorganization energy. $[Co(PY5ImDMA1)](OTf)_{3/2}$ was then crossed with $[FcMe_8](OTf)_{1/0}$ and $[Co(PY5ImDMA2)](OTf)_{3/2}$ was crossed with $[FcMe_{10}](OTf)_{1/0}$. The resulting electron self-exchange rate constants of the three redox shuttles fall within close agreement suggesting adjustments by the dimethyl amine groups have little to no effect on the reorganization energy.



Figure 4.5 (a) Cross-exchange reaction between 0.015 mM $[Co(PY5Im)](OTf)_2$ with 0.25 mM $[FcMe_2](OTf)$ observing the decay of the $[Co(PY5Im)](OTf)_2$ signal at 400 nm. (b) Pseudo-first-order rate constants, k_{obs} , versus the concentration of $[FcMe_2](OTf)$ for the reactions between $[Co(PY5Im)](OTf)_2$ and $[FcMe_2](OTf)$.

Table 4.2 Effective magnetic moment, redox potential vs Fc^+/Fc , diffusion coefficient and electron self-exchange rate constants for Co(II/III) redox couples.

Co(II) Complex	$\mu_{\mathrm{eff}}(\mu_{\mathrm{b}})$	$E_{1/2} vs Fc^{+}/Fc$ (V)	$D (cm^2 s^{-1})$	$k_{11} (\mathrm{M}^{-1}\mathrm{s}^{-1})$
$[Co(bpy)_3](PF_6)_2$	4.6 ³⁴	-0.066	$8.7 \pm 0.4 \times 10^{-6.35}$	0.27 11
[Co(PY5Im)](OTf) ₂	1.81 ± 0.02	-0.205 ± 0.003	$6.6\pm0.5\times10^{\text{-}6}$	4.2 ± 0.3
[Co(PY5ImDMA1)](OTf) ₂	2.02 ± 0.06	-0.299 ± 0.003	$8.2\pm0.9\times10^{\text{-6}}$	2.4 ± 0.1
[Co(PY5ImDMA2)](OTf) ₂	1.72 ± 0.05	$\textbf{-0.426} \pm 0.001$	$9.7\pm0.8 imes10^{-6}$	2.2 ± 0.1

Dye-sensitized solar cells were prepared to evaluate the redox shuttles performance compared to the standard redox shuttle $[Co(bpy)_3]^{3+/2+}$ along with sensitizer LEG4 (D35cpdt). All the Co(II) concentrations were limited to 0.16 M due to solubility limitations of the [Co(PY5ImDMA2)](OTf)₂ complex. We found that the common base additive 4-tertbutylpyridine (TBP) coordinates to the open site of the [Co(PY5Im)](OTf)₂ complex. Upon addition of TBP to the electrolyte, as well as other common coordinating bases, the solution potential shifts negatively by approximately 200 mV, which complicates analysis and diminishes performance. Several alternative bases were investigated and the electron withdrawing base TFMP and the sterically hindered based 2,6-Di-tert-butylpyridine (DTBP) were found to be compatible with the cobalt complexes; no significant shifts in solution potential were observed (Table A4.8). Therefore, 4-(Trifluoromethyl)pyridine (TFMP) was used as a base additive in order to improve the voltage output of cells. The electrolyte of each system consisted of 0.16 M Co(II), 0.04 M Co(III), 0.1 M Li(OTf) and 0.2 M TFMP. Comparing the current density (J) vs. applied voltage (V) behavior under simulated AM 1.5 illumination, each redox shuttle produces similar current densities, with the exception of $[Co(PY5Im)]^{3+/2+}$ being slightly larger (Figure 4.5a) (Table 4.3). If dye regeneration is limiting the photocurrent, more negative solution

potentials of the redox couple would increase the driving force for dye regeneration and thereby increase the photocurrent. That trend is not observed here which suggests dye regeneration rate is not limiting the performance. Inspection of the incident photon-to-current efficiency (IPCE) increase is seen for $[Co(PY5Im)]^{3+/2+}$ and the spectral an shape of spectra, $[Co(PY5ImDMA1)]^{3+/2+}$ and $[Co(PY5ImDMA2)]^{3+/2+}$ broaden relative to $[Co(bpy)_3]^{3+/2+}$ (Figure **4.5b**). The integrated current densities found from IPCE align well with those from the J-Vmeasurements. This seems to indicate that diffusion of the redox shuttles through the TiO₂ is not a major issue since the current density from AM 1.5 spectrum matches well with the IPCE integrated current density which is measured at a lower light intensity.³⁶ The broadening of the spectra indicates increased charge collection efficiency at wavelengths where the dye, LEG4, has a lower extinction coefficient. This observation is suggests a decreasing recombination with more negative potential redox shuttles.³⁷

Surprisingly, the V_{oc} of each new cobalt redox shuttle are within error of each other as well despite over 200 mV difference in solution potential. All else being equal, a more negative solution potential should decrease the open circuit voltage. A constant V_{oc} , however, indicates the fermi level shifts with the solution potential which may be attributed to decreased recombination. We note that ideally a 200 mV shift if fermi level would result from 3-4 orders of magnitude reduction in recombination, which is much larger than expected. Alternatively, the conduction band edge can shift which – or some combination of the two factors – which can likewise affect the voltage.



Figure 4.6 (a) Current density vs. voltage curves under 100 mW cm⁻² illumination for $[Co(PY5Im)](OTf)_{3/2}$ (red), $[Co(PY5ImDMA1)](OTf)_{3/2}$ (green), $[Co(PY5ImDMA2)](OTf)_{3/2}$ (blue) and $[Co(bpy)_3](PF_6)_{3/2}$ (black). (b) The incident photon-to-current conversion efficiency (diamonds) of each redox couple and the integrated J_{sc} from the IPCE spectra (squares).

 Table 4.3 DSSC summarized performance under 100 mW cm⁻² illumination.

Electrolyte	E _{sol} (V) ^a	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η
$[Co(bpy)_3]^{3+/2+}$	-0.107	-0.585 ± 0.005	9.8 ± 0.3	0.55 ± 0.05	3.1 ± 0.3
$[Co(PY5Im)]^{3+/2+}$	-0.274	-0.47 ± 0.02	11.6 ± 0.5	0.42 ± 0.02	2.3 ± 0.2
[Co(PY5ImDMA1)] ^{3+/2+}	-0.352	$\textbf{-0.45} \pm 0.02$	9.9 ± 0.7	0.42 ± 0.03	1.9 ± 0.2
[Co(PY5ImDMA2)] ^{3+/2+}	-0.460	$\textbf{-0.47} \pm 0.01$	10.3 ± 0.4	0.45 ± 0.03	2.2 ± 0.2

 $^{\rm a}$ The solution potential of each electrolyte measured vs Fc^+/ Fc prior to injection into the devices.



Figure 4.7 (a) Fermi level vs chemical capacitance. (b) Lifetime vs Fermi level from opencircuit voltage decays (lines) and from impedance spectroscopy (symbols). Potentials were corrected by adding the solution potentials measured against Fc^+/Fc to the measured voltage. [Co(PY5Im)](OTf)_{3/2} (red circles), [Co(PY5ImDMA1)](OTf)_{3/2} (green upward triangles), [Co(PY5ImDMA2)](OTf)_{3/2} (blue downward triangles) and [Co(bpy)₃](PF₆)_{3/2} (black squares).

The relative recombination rates of each redox shuttle were directly compared with opencircuit voltage decay (OCVD) and impedance spectroscopy (IS) measurements carried out for each redox shuttle. For open-circuit voltage decays and impedance spectroscopy, the potentials were corrected to Fc^{+/0} to account for differences in solution potentials between the four different electrolytes (Table 4.3). IS was measured for DSSCs at open-circuit conditions over various light intensities (1-100 mW cm⁻²) to induce different pseudo-Fermi energy levels of the TiO₂ (E_F) vs Fc^{+/0}. Using a diffusion-recombination equivalent circuit model, the C_{μ} and R_{rec} were extracted from the Nyquist plots, and they are plotted as a function of $E_{\rm F}$ vs Fc^{+/0} (Figure 4.6a, Figure A4.13, Figure A4.14).³⁸ Comparing each redox shuttle at the same potential there is a positive shift in the TiO₂ conduction band edge in the order of $[Co(bpy)_3]^{3+/2+}$ < $[Co(PY5ImDMA2)]^{3+/2+} < [Co(PY5ImDMA1)]^{3+/2+} < [Co(PY5Im)]^{3+/2+}$ according to the relations, $\ln(C_{\mu}) \propto E_{CB}$. Normally it is assumed that there is a minimal variation in the conduction band edge upon changing the redox mediator.³⁹ Large shifts in the band edge are typically observed when different bases are used such as TBP, but each electrolyte contains the same base TFMP.⁴⁰ An interesting possible explanation is an interaction of the redox mediator with the TiO₂ since this is the only changing factor. The Co(II) complexes of this series all contain a hanging pyridine arm that could behave analogously to bases added to the electrolyte by interacting with the TiO₂ surface. The trend observed is that the most electron rich redox shuttle, $[Co(PY5ImDMA2)]^{3+/2+}$ has the most negatively shifted conduction and the other redox shuttle's TiO_2 band edges move more positive with the redox shuttle's potential. The conduction band shift could also affect the J_{SC} of DSSCs by adjusting the driving force difference for the electron injection which could explain the increased photocurrent of $[Co(PY5Im)]^{3+/2+}$ if dve regeneration is not the limiting process as we found above. The electron lifetime (τ_n) with
respect to the $E_{\rm F}$ of the TiO₂ calculated by the equation, $\tau_{\rm n}^{\rm EIS} = C_{\mu}R_{\rm rec}$ from the IS results to compare relative recombination rates. In the lifetime vs E_F data for each redox shuttle, the lifetime increases at the same measured potential as the redox couple's solution potential becomes more negative (Figure 4.6a). The results of the electron lifetime determined from open circuit voltage decay (OCVD) also showed good agreements with τ_n^{EIS} . The increasing lifetime with more negative solution potential aligns well with the prediction of Marcus theory that the recombination rate should decrease exponentially with decreasing recombination driving force. The shift in the conduction band edge does complicate determining more accurate recombination further than the relative ordering of $[Co(bpy)_3]^{3+/2+} > [Co(PY5Im)]^{3+/2+} >$ rates $[Co(PY5ImDMA1)]^{3+/2+} > [Co(PY5ImDMA2)]^{3+/2+}$ due to the different electron concentrations at the same recombination driving force as illustrated in **Figure 4.7**. This would suggest, based upon the lifetime vs potential data and the light J-V measurements, that the fermi level of the TiO₂ shifts more negative due to the decreased recombination rates to result in the same opencircuit voltage for the newly reported redox shuttles. As a result, little to no voltage loss results from increasing the regeneration driving force by over 200 mV for this dye and redox shuttle system due to the concomitant increased lifetimes that raise the fermi level of TiO2 more negative when comparing $[Co(PY5Im)]^{3+/2+}$ to $[Co(PY5ImDMA2)]^{3+/2+}$.



Figure 4.8 Scheme of the TiO₂/dye/electrolyte interface in the device illustrating the band edge and fermi level shift resulting from each redox shuttle under 100 mW cm⁻² illumination. The voltage difference from the fermi level (E_F) and the redox shuttle is taken from the V_{oc} . The driving force for regeneration was taken by subtracting the redox potential of each redox shuttle from that of LEG4 determined previously (0.45 V vs Fc⁺/Fc).¹¹

4.5 Conclusions

A new hexadentate ligand and redox system has been prepared that has resulted in three new Co(III/II) redox shuttles. The carbene and the addition of dimethyl amine groups has resulted in a tunable framework at significantly negative redox potentials. Introduction of the strong-field NHC carbene induced low-spin Co(II) complexes which increased the electron self-exchange rate constant. The self-exchange rate was modestly improved relative to other low-spin Co(II) redox couples measured previously due to the 5-coordinate to the 6-coordinate rearrangement. Likely the driving force for dye regeneration could be minimized further if the distortions of low-spin Co(II) redox shuttles were minimized to increase the self-exchange rate. By moving to more negative potentials each redox shuttle has largely reduced recombination when compared to $[Co(bpy)_3]^{3+/2+}$ resulting in smaller voltage losses. Unfortunately, the Co(II) complexes suffered from coordination effects from more donating pyridine bases that prevented increasing

the open-circuit voltage further by adding them to electrolyte. The lower self-exchange and instability to bases could possibly be fixed by a more flexible strong-field ligand system like ttcn that can absorb the structural distortions. The series performed worse when comparing the power conversion efficiencies but maintained the same or higher photocurrent. The series seems well suited for dye or dye systems with more negative HOMO levels than that of LEG4 where $[Co(bpy)_3]^{3+/2+}$ would suffer from poor dye regeneration rates. The system is positioned to replace dye or dye system where outer-sphere redox shuttles or iodide/triodide have failed to give efficient dye regeneration. Future work points to integrating this redox series with dyes that absorb more into the infrared which would enable single devices or tandem DSSCs that could harvest 300-1200 nm analogous to silicon photovoltaics.

APPENDIX



Figure A4.1 UV-visible spectrum of $[Co(PY5Im)](OTf)_2$ (red) and $[Co(PY5Im)](OTf)_3$ (burgundy).



Figure A4.2 UV-visible spectrum of $[Co(PY5ImDMA1)](OTf)_2$ (green) and $[Co(PY5ImDMA1)](OTf)_3$ (olive).



Figure A4.3 UV-visible spectrum of $[Co(PY5ImDMA2)](OTf)_2$ (blue) and $[Co(PY5ImDMA2)](OTf)_3$ (navy).



Figure A4.4 Scan rate dependence of cyclic voltammograms for 2 mM $[Co(PY5Im)](OTf)_2$ in 0.1 M LiOTf with glassy carbon working electrode, platinum mesh counter electrode and Ag/AgNO₃ reference electrode calibrated to Fc⁺/Fc.



Figure A4.5 Scan rate dependence of cyclic voltammograms for 2 mM $[Co(PY5ImDMA1)](OTf)_2$ in 0.1 M LiOTf with glassy carbon working electrode, platinum mesh counter electrode and Ag/AgNO₃ reference electrode calibrated to Fc⁺/Fc.



Figure A4.6 Scan rate dependence of cyclic voltammograms for 2 mM $[Co(PY5ImDMA2)](OTf)_2$ in 0.1 M LiOTf with glassy carbon working electrode, platinum mesh counter electrode and Ag/AgNO₃ reference electrode calibrated to Fc⁺/Fc.



Figure A 4.7 ¹H NMR of [Co(PY5Im)](OTf)₂ in CD₃CN. Residual dichloromethane and diethyl either are visible at 5.47 ppm (DCM), 3.44 and 1.44 ppm (ether).



Figure A4.8 ¹H NMR of [Co(PY5ImDMA1)](OTf)₂ in CD₃CN. Residual dichloromethane and diethyl either are visible at 5.47 ppm (DCM), 3.44 and 1.44 ppm (ether).



Figure A4.9 ¹H NMR of [Co(PY5ImDMA2)](OTf)₂ in CD₃CN. Residual dichloromethane and diethyl either are visible at 5.47 ppm (DCM), 3.44 and 1.44 ppm (ether).



Figure A4.10 1H NMR for Evan's Method, (Top) of ferrocene proton signal (red) as a function of the concentration of [Co(PY5Im)](OTf)₂ 5.4 mM (gold), 9.8 mM (green), 13.3 mM (blue), and 16.2 mM (purple). Measured in deuterated acetonitrile. (Bottom) Signals of [Co(PY5Im)](OTf)₂.



Figure A4.11 1H NMR for Evan's Method, of ferrocene proton signal (red) as a function of the concentration of [Co(PY5ImDMA1)](OTf)₂ 5.6 mM (gold), 10.0 mM (green), 13.7 mM (blue), and 16.7 mM (purple). Measured in deuterated acetonitrile. The signal of [Co(PY5ImDMA1)](OTf)₂ is visible at 3.78 ppm.



.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 Chemical shift / ppm

Figure A4.12 1H NMR for Evan's Method, of ferrocene proton signal (purple) as a function of the concentration of $[Co(PY5ImDMA2)](OTf)_2$ 5.6 mM (blue), 10.1 mM (green), 13.7 mM (gold), and 16.8 mM (red). Measured in deuterated acetonitrile. The signals of $[Co(PY5ImDMA2)](OTf)_2$ are visible at 3.88 ppm and 3.76 ppm.

Table A4.1 Concentrations of reactants after mixing for the cross-exchange reaction between $[Co(PY5Im)](OTf)_{3/2}$ and $[FcMe2](OTf)_{1/0}$ and the resulting observed rate constant k_{obs} obtained from fitting.

$[Co(PY5Im)](OTf)_2(mM)$	[FcMe2](OTf) (mM)	[FcMe2] (mM)	$k_{\rm obs}~({\rm s}^{-1})$
	0.15		3.01 ± 0.09
	0.20		4.41 ± 0.07
0.015	0.25	0.15	5.8 ± 0.2
	0.30		7.3 ± 0.1
	0.35		9.5 ± 0.2

Table A4.2 Concentrations of reactants after mixing for the cross-exchange reaction between [Co(PY5ImDMA1)](OTf)3/2 and [FcMe8](OTf)1/0 and the resulting observed rate constant k_{obs} obtained from fitting.

[Co(PY5ImDMA1)](OTf) ₃ (mM)	[FcMe8] (mM)	[FcMe8](OTf) (mM)	$k_{\rm obs}~({\rm s}^{-1})$	
	0.15		8.1 ± 0.7	-
	0.20		11.1 ± 0.5	
0.015	0.25	0.15	14.1 ± 0.7	
	0.30		15.9 ± 0.9	
	0.35		18.2 ± 0.7	

Table A4.3 Concentrations of reactants after mixing for the cross-exchange reaction between $[Co(PY5ImDMA2)](OTf)_{3/2}$ and $[FcMe10](OTf)_{1/0}$ and the resulting observed rate constant k_{obs} obtained from fitting.

[Co(PY5ImDMA2)](OTf) ₃ (mM)	[FcMe10] (mM)	[FcMe10](OTf) (mM)	$k_{\rm obs}~({\rm s}^{-1})$
	0.15		4.9 ± 0.3
	0.20		7.2 ± 0.3
0.015	0.25	0.15	8.7 ± 0.3
	0.30		10.2 ± 0.4
	0.35		12.4 ± 0.4

Table A4.4 Electron self-exchange measurements of $[FcMe2](OTf)_{1/0}$ determined by NMR line broadening measurements. X_d and X_p are the mole fraction of FcMe2 and [FcMe2](OTf) respectively. Chemical shift is the location of the peak fitted, width is the line width at half height and k_{ex} is the determined electron self-exchange rate constant for each mixture. k_{22} was determined from the average of samples 3 through 7.

Sample Number	Xd	Хр	Chemical Shift (hz)	Width (hz)	$k_{\rm ex} ({ m M}^{-1} { m s}^{-1})$
1	1.00	00	985.4	1.9	
2	0	1.00	-4938.5	137.01	
3	0.80	0.20	-288.9	881.38	5.52E+06
4	0.65	0.35	-1241.2	1074.34	6.52E+06
5	0.50	0.50	-2235.7	1068.5	7.36E+06
6	0.35	0.65	-3152.85	1013.67	7.24E+06
7	0.20	0.80	-3916.3	756.87	7.27E+06

Table A4.5 Electron self-exchange measurements of $[FcMe8](OTf)_{1/0}$ determined by NMR line broadening measurements. X_d and X_p are the mole fraction of FcMe8 and [FcMe8](OTf) respectively. Chemical shift is the location of the peak fitted, width is the line width at half height and k_{ex} is the determined electron self-exchange rate constant for each mixture. k_{22} was determined from the average of samples 3 through 7.

Sample Number	Xd	Хр	Chemical Shift (hz)	Width (hz)	$k_{\rm ex} ({ m M}^{-1} { m s}^{-1})$
1	1.00	0	985.4	1.9	
2	0	1.00	-4938.5	137.01	
3	0.80	0.20	-288.9	881.38	1.758E+07
4	0.65	0.35	-1241.2	1074.34	2.675E+07
5	0.50	0.50	-2235.7	1068.5	2.148E+07
6	0.35	0.65	-3152.85	1013.67	1.874E+07
7	0.20	0.80	-3916.3	756.87	1.614E+07

Table A4.6 Electron self-exchange measurements of $[FcMe10](OTf)_{1/0}$ determined by NMR line broadening measurements. X_d and X_p are the mole fraction of FcMe10 and [FcMe10](OTf) respectively. Chemical shift is the location of the peak fitted, width is the line width at half height and k_{ex} is the determined electron self-exchange rate constant for each mixture. k_{22} was determined from the average of samples 3 through 7.

Sample Number	Xd	Хр	Chemical Shift (hz)	Width (hz)	$k_{\rm ex} ({\rm M}^{-1}~{\rm s}^{-1})$
1	1.00	0	761.55	72.6	
2	0	1.00	-18736	324.6	
3	0.80	0.20	-2627.1	2254.9	3.585E+07
4	0.65	0.35	-5593.05	2840.8	4.055E+07
5	0.50	0.50	-8819.4	2577.3	5.021E+07
6	0.35	0.65	-12210.9	3611.3	3.220E+07
7	0.20	0.80	-14907.15	2595.9	3.292E+07

Table A4.7 Cross exchange parameters used to determine the electron self-exchange rate constants of each redox couple. K_{12} was determined from the difference in redox potential of the redox couple and the reference couple, k_{12} is the slope determined from k_{obs} vs reference couple concentration and k_{22} is the electron self-exchange rate constant of the reference couple determined by NMR line broadening measurements.

Redox Couple	K ₁₂	$k_{12} (M^{-1} s^{-1})$	Reference Couple	$k_{22} (\mathrm{M}^{-1} \mathrm{s}^{-1})$
[Co(PY5Im)](OTf) _{3/2}	34.6	31440	[FcMe2](OTf) _{1/0}	$6.8 \pm 0.8 \times$
				10 ⁶
[Co(PY5ImDMA1)](OTf) _{3/2}	51.1	49846	[FcMe8](OTf) _{1/0}	$2.0 \pm 0.4 \times$
				10 ⁷
[Co(PY5ImDMA2)](OTf) _{3/2}	15.3	35829	[FcMe10](OTf) _{1/0}	$3.8 \pm 0.7 \times$
				10 ⁷

Table A4.8 Solution potentials (E_{sol}) of electrolytes measured against Fc⁺/Fc with 0.2 M [Co(PY5Im)](OTf)₂, 0.02 M [Co(PY5Im)](OTf)₃, 0.1 M Li(OTf) and 0.5 M of each base to replicate composition used in the device.

Lewis Base	E _{sol} vs Fc ⁺ /Fc (V)
No Base	-0.264
Pyridine	-0.470
4-tert-butylpyridine	-0.508
2-Methylpyridine	-0.456
4-(Trifluoromethyl)pyridine	-0.282
2,6-di-tert-butylpyridine	-0.287
2,6-dimethylpyridine	-0.443
2-propylpyridine	-0.411
2-pentylpyridine	-0.414
2-isopropylpyridine	-0.397



Figure A4.13 Nyquist plot of PEDOT symmetrical sandwich cells of each electrolyte for $[Co(PY5Im)](OTf)_{3/2}$ (red), $[Co(PY5ImDMA1)](OTf)_{3/2}$ (green), $[Co(PY5ImDMA2)](OTf)_{3/2}$ (blue) and $[Co(bpy)_3](PF_6)_{3/2}$ (black).



Figure A4.14 Impedance Spectroscopy (IS) for DSSCs with cobalt redox shuttles. (a) a diffusion-recombination equivalent circuit model including the Warburg impedance for the diffusion of redox shuttles. (b-f) Nyquist plots for the DSSCs with cobalt redox shuttles at various illumination conditions, (b) 1, (c) 0.5, (d) 0.25, (e) 0.1, and (f) 0.01 suns.



Figure A4.15 Recombination resistance (R_{rec}) of DSSCs with cobalt redox shuttles as a function of ${}_{n}E_{\rm F}$ of TiO₂ with respect to the Fc/Fc⁺ measured by impedance spectroscopy (IS) at various illumination conditions (1 to 0.01 suns).

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Chapter 5: Alternative Cobalt Redox Shuttles

I would like to acknowledge Richard Staples for the collecting and fitting of the single crystal xray data.

5.1 Introduction

Several other cobalt redox shuttles were designed to obtain the desired properties of inducing low-spin Co(II) complexes with increased self-exchange rate constants. The redox shuttles in this chapter either had severe drawbacks, were not low-spin Co(II) or did not have the desired properties in DSSCs. The first is a variation of the $[Co(PY5Me_2)(DMP-CN)](PF_6)_{3/2}$ redox shuttle where tert-butyl isocyanide was used to form the [Co(PY5Me₂)(T-BuCN)](PF₆)_{3/2} using the PY5Me₂ ligand.^{1,2} The Co(III) complex could not be stabilized with excess isocyanide in acetonitrile due to the isocyanide displacing the PY5Me₂ ligand so it was not pursued further. To increase stability of the strong-field ligand the ligand TPA (Tris(2-pyridylmethyl)amine) was used that allowed for the strong-field ligand to be bidentate.³ Unfortunately the bidentate ligand chosen SPY (2-mercaptopyridine), was found not to induce low-spin Co(II). The PY4Im ligand developed by Smith and Long was then coordinated and characterized.⁴ The ligand had many desirable properties of low-spin Co(II) complexes and more negative redox potentials but the potential range it could be tuned to was quite limited. The last section will discuss future ligand systems that could result in low-spin Co(II) redox shuttles with increased stability, increased electron self-exchange rate constants, and more negative potentials for near-IR sensitizers.

5.2 Experimental

5.2.1 Materials

All chemicals and materials were obtained from commercial suppliers unless otherwise noted (MiliporeSigma, Oakwood Chemical, Alfa Aesar, Solaronix, Cambridge Isotopes and Dyenamo). All solvents used for synthesis and measurements with the cobalt complexes were dried over activated 3A molecular sieves for two days and were then degassed by Schlenk line before being stored in a nitrogen filled glove box for use. PY5Me₂ and PY4ImBr were prepared as reported previously.^{1,4} TPA and SPY were obtained from MiliporeSigma without further purification.

5.2.2 Instrumentation

ATIR spectra were collected in a JASCO FT/IR-6600 spectrometer under ambient air with 64 scans and 2 cm⁻¹ resolution. NMR spectra were collected at room temperature on an Agilent DirectDrive2 500 MHz spectrometer and referenced to residual solvent signals. All NMR spectra were evaluated using the MestReNova software package features. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t =triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, m = multiplet). Cyclic voltammograms were collected using a μ AutolabIII potentiostat using a BASi glassy carbon working electrode, a fabricated platinum mesh counter electrode, and a fabricated 0.01 M AgNO₃, 0.1 M TBAPF₆ in acetonitrile Ag/AgNO₃ reference electrode. All measurements were also internally referenced to the Ferrocenium/Ferrocene couple by addition of ferrocene to the solution after measurements or measured in a separate solution of the same solvent and supporting electrolyte. Cyclic voltammograms under illumination (Light JV's) were performed with a potentiostat (Autolab PGSTAT 128N) used with a xenon arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm⁻², and the light intensity was calibrated with a certified reference cell system (Oriel Reference Solar Cell & Meter). A 400 nm long-pass filter was used to prevent direct excitation of the TiO₂ in all light measurements. A black mask with an open area of 0.12 cm² was applied on top of the cell active area. Open circuit

voltage decays were measured by leaving the cells in the dark until the potential stabilized and then switching on 100 mW cm⁻² illumination for one second with a light shutter (Thorlabs) and then the shutter closing automatically after 1 second and monitoring the decay. For single crystal x-ray diffraction, single crystals were mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystals were kept at T = 173(2) K during data collection. Using Olex2 (Dolomanov et al., 2009), the structures were solved with the ShelXS (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/6 of XL (Sheldrick, 2008) using Least Squares minimization. All nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Magnetic susceptibility of the paramagnetic complexes was measured in acetonitrile-d₃ by ¹H NMR using the Evans method.⁵ Measurements were collected using a NMR tube containing a capillary insert filled with a saturated solution of ferrocene also dissolved in acetonitrile- d_3 (diamagnetic standard). The ¹H signal of ferrocene was used and the signal was monitored as the paramagnetic complex concentration was varied. The effective magnetic moment μ_{eff} was determined directly from the molar magnetic susceptibility assuming the diamagnetic contribution was small.⁶

5.2.3 DSSC Fabrication

TEC 15 FTO was cut into 1.5 cm by 2 cm pieces which were sonicated in soapy DI water for 15 min followed by manual scrubbing of the FTO with Kimwipes. The pieces were then sonicated in DI water for 10 minutes, rinsed with acetone and sonicated in isopropanol for 10 min. The pieces were dried in room air and were immersed in an aqueous 40 mM solution TiCl₄ solution for 30 min at 70 °C. The pieces were immediately rinsed with 18 M Ω water and were annealed by heating from room temperature to 500 °C and then holding at 500 °C for 30

minutes. A 0.36 cm² area was doctor bladed with commercial 30 nm TiO₂ nanoparticle paste (DSL 30NRD). The transparent films were left to rest for 10 minutes and were then placed in a 100 °C oven for 15 min. The oven was then ramped to 325 °C for 5 min, 375 °C for 5 min, 450 °C for 5 min, and 500 °C for 15 min. After cooling to room temperature, a scattering layer was applied (PST-400C, JGC Catalysts) and annealed by the same method as the transparent layer. The 30 nm film thickness was measured to be 6.5 μ m and with scattering layer deposited on top 10.0 μ m total. After cooling to room temperature, a second TiCl₄ treatment was performed as described above. When the anodes had cooled to 80 °C they were soaked in a dye solution of 0.1 mM D35cpdt with 0.1 mM chenodeoxycholic acid in 1:1 acetonitrile: tert-butanol for 18 hours. After soaking, the anodes were rinsed with acetonitrile and were dried gently under a stream of nitrogen.

The PEDOT counter electrodes were prepared by electropolymerization in a solution of 0.01 M EDOT in 0.1 M SDS in 18 M Ω water.⁷ A constant current of 8.3 mA for 300 seconds was applied to a 54 cm² piece of TEC 15 FTO with predrilled holes using an equal size piece of FTO as the counter electrode. The PEDOT electrode was then washed with DI water and acetonitrile before being dried under a gentle stream of nitrogen and cut into 1.5 cm by 2.0 cm pieces. The working and counter electrodes were sandwiched together with 25 µm surlyn films by placing them on a 140 °C hotplate and applying pressure with a hot iron. Contact to the TiO₂ electrode was made by scratching the edge of the electrode was connected directly with silver epoxy and copper wire. The counter electrode was connected directly with silver epoxy and copper wire. The silver epoxy was dried in a 60 °C vacuum oven for 90 minutes and then the cells were filled with electrolyte through one of the two predrilled holes and were sealed with 25 µm surlyn backed by a glass coverslip and applied heat to seal. The electrolyte consisted of 0.2

M Co(II), 0.02 M Co(III) and 0.1 M LiPF₆ in dry acetonitrile. Cells were measured approximately 18 hours after fabrication where they rested in ambient lighting.

5.2.4 [Co(PY5Me₂)(T-BuCN)](PF₆)₂ Synthesis

[Co(PY5Me2)(I)](I) (0.066 mmol, 0.050 g) was suspended in dichloromethane (~5 mL). Tl(PF6) (0.132 mmol, 0.046 g) was suspended in a separate dichloromethane solution (~5 mL) and then combined with the solution containing [Co(PY5Me2)(I)](I). Tert-butyl isocyanide (0.912 mmol, 0.130 g) was then immediately added to the solution mixture. The mixture was allowed to stir for 18 hours and the thallium iodide was removed by filtration of the suspension. The dark brown solution was then precipitated with diethyl ether (~25 mL) to result in a brown powder. After allowing the solid to settle the solvent was decanted leaving the brown powder behind (Yield: 0.0268 g, 46.3%).

5.2.5 [Co(TPA)(SPY)](PF₆) Synthesis

 $[Co(TPA)(ACN)(PF_6)_2 (0.073 \text{ mmol}, 0.0500 \text{ g}) \text{ and } 2\text{-mercaptopyridine } (0.081 \text{ mmol}, 0.0090 \text{ g}) were weighed into a 20 mL vial. Triethylamine (0.23 mmol , 0.0230 g) was dissolved in 5 mL of dichloromethane and was added to the 20 mL vial. The reaction was stirred for 4 hours and the product was then precipitate by adding 15 mL of diethyl ether. After decanting the solvent, red crystalline product was collected. (Yield: 0.0325 g, 72.5%)$

5.2.6 [Co(PY4Im)(ACN)](PF6)2 Synthesis

PY4ImAgBr (1.7 mmol ,1.0 g), CoI₂ (1.7 mmol, 0.528 g) and Tl(PF₆) (3.4 mmol, 1.179 g) were combined in 10 mL of acetonitrile. The reaction was stirred for 24 hours and was then syringe filtered. The filtrate was then precipitated with 30 ml of diethyl ether. The solvent was decanted, leaving a brown powder that was collected (Yield: 0.872 g, 68.9%)

5.2.7 [Co(PY4Im)(ACN)](PF6)3 Synthesis

 $[Co(PY4Im)(ACN)](PF_6)_2$ (0.20 mmol, 0.150 g) and TBPA(PF_6) (0.20 mmol, 0.125 g) were combined in a 20 mL vial with 15 mL of dichloromethane. After stirring for 18 hours, the solvent was decanted and the product washed 3 times with 2 mL of dichloromethane. The product was then collected as a red solid (Yield: 0.134 g, 74.9 %).

5.3 [Co(PY5Me₂)(T-BuCN)](PF₆)_{3/2} Complex

In chapter 2 the [Co(PY5Me₂)(DMP-CN)](PF₆)_{3/2} couple was studied but another isocyanide complex was studied as a potential redox shuttle in a DSSC. The ligand *tert*-butyl isocyanide (T-BuCN) was coordinated to the PY5Me₂ framework which resulted in another low-spin Co(II) complex as confirmed by Evan's Method 2.31 \pm 0.05 (Figure A5.1). The T-BuCN ligand was also found to labile as was found for the DMP-CN ligand. The Co(II) complex could be studied in noncoordinating solvent dichloromethane without solvent coordination but an excess of 0.1 M T-BuCN or greater was required in acetonitrile which was the desirable solvent for DSSCs. In acetonitrile the strong sigma donation of the isocyanide ligand resulted in a 100 mV shift negative in redox potential (-0.004 V vs Fc^{+/0}) compared to the DMP-CN bound complex.



Figure 5.1 Cyclic voltammogram in acetonitrile with 0.1 M TBAPF₆ where black is the $[Co(PY5Me_2)(T-BuCN)](PF_6)_2$ complex and red is with 0.2 M T-BuCN added. The electrodes consist of a glassy carbon working electrode, Pt mesh counter electrode and Ag/AgNO₃ reference electrode calibrated to the Fc^{+/0} redox couple.

A FTIR spectrum was also collected to confirm that tert-butyl isocyanide was bound. $[Co(PY5Me_2)(T-BuCN)](PF_6)_2$ complex displays a medium strength signal at 2185 cm⁻¹ which is shifted to a higher wavenumber signal from the free t-butyl-CN ligand (2136 cm⁻¹)(Figure 5.2). The shift in frequencies from free isocyanide ligand to a higher frequency is likely due to the piback bonding interaction with cobalt decreasing the anti-bonding character of the isocyanide ligand.



Figure 5.2 FTIR spectra of [Co(PY5Me₂)(T-BuCN)](PF₆)₂ (red).

Single crystal x-ray diffraction data was collected for the complex it was found to also have a distorted structure from octahedral geometry likely due to a strong Jahn-Teller distortion analogous to $[Co(PY5Me_2)(DMP-CN)](PF_6)_2$ (Figure 5.2). Unfortunately after further study the $[Co(PY5Me_2)(T-BuCN)](PF_6)_3$ was found to be unstable with time with excess T-BuCN present. A species with a redox potential of -0.25 V vs Fc^{+/0} was formed when taking cyclic voltammograms in acetonitrile presumably due to PY5Me_2 ligand displacement. Due to the Co(III) complex being unstable the complex was not pursued further.



Figure 5.3 Single crystal x-ray diffraction structure of the $[Co(PY5Me_2)(T-BuCN)](PF_6)_2$ complex with atoms labeled.

5.4 [Co(TPA)(SPY)](PF6) Complex

Due to the instable nature of monodentate ligands with the PY5Me₂ framework, the TPA ligand (Tris(2-pyridylmethyl)amine) was utilized allowing for coordination of strong-field bidentate ligands to adjust the redox potential. 2-mercaptopyridine (SPY) was studied as the bidentate ligand due to its strong sigma donating nature to move the redox potential more negative. The SPY ligand was coordinated to the [Co(TPA)(ACN)]²⁺ complex reported previously by deprotonation of the sulfur by excess triethylamine.⁸ A single crystal structure of the complex was collected and found to have a distorted structure from octahedral geometry due to the strain of the SPY and the TPA ligands (Figure 5.3).



Figure 5.4 Single crystal structure of the [Co(TPA)(SPY)](PF₆) complex.

Cyclic voltammograms were collected for the complex in acetonitrile and the redox potential was found to be -0.403 V vs Fc^{+/0}. The redox potential is likely so negative due to the strong sigma donation of the anionic sulfur bound to the complex. However, with continued scans new redox features were visible in the cyclic voltammogram. The redox features matched well to that of the free TPA ligand. It is possible the Co(III) complex underwent ligand exchange to bind more of the SPY ligands due to the anionic ligand having a strong columbic attraction to the Co(III) metal center. Unfortunately when effective magnetic moment was measured by Evan's method the complex was found to be closer to a high-spin Co(II) complex ($3.56 \pm 0.01 \mu_{b}$.) Though sulfur bound ligands typically have strong sigma donation to increase the ligand field, the anionic character of the deprotonated sulfur resulted in too much pi-bonding to reduce the ligand field analogous to halide ligands. Based upon the instability in the cyclic voltammograms and the Co(II) complex being high-spin, the complex was not studied further.



Figure 5.5 The cyclic voltammogram of $[Co(TPA)(SPY)](PF_6)$ in acetonitrile with 0.1 M TBAPF₆.

5.5 [Co(PY4Im)(X)](PF6)3/2 Complexes

As mentioned in Chapter 4, the PY4Im ligand was developed by Smith and Long and coordinated to several first-row transition metals. They showed that the Co(II) complex was low-spin Co(II) and the Co(III/II) redox couple resided at -0.19 V vs $Fc^{+/0}$. We hoped to use the complex analogously to the $[Co(PY5Me_2)(X)]^{3+/2+}$ redox couples mentioned earlier except the chelating PY4Im would induce low-spin Co(II) complexes and move the redox potential more negative. The redox potential could then be tuned by various monodentate ligands from the more negative starting point.⁹

The synthesis was modified to start with the PY4ImAgBr being coordinated to cobalt(II) iodide instead of cobalt(II) triflouromethanesulfonate as was reported to avoid coordination to the Co(III) complexes synthesized. The complex was oxidized in the presence of TBPA(PF₆)

analogously to the synthesis of the $[Co(PY5Me_2)(DMP-CN)](PF_6)_3$ mentioned in Chapter 3. Measuring cyclic voltammetry of the $[Co(PY4Im)(ACN)](PF_6)_2$ complex in acetonitrile, the redox potential was found to be more positive at -0.13 V vs Fc^{+/0} compared to the -0.19 V vs Fc^{+/0} reported for the $[Co(PY4Im)(ACN)](OTf)_2$ complex. The acetonitrile ligand was found to be labile and could be replaced with bases commonly used in DSSCs to shift the redox potential of the complex when taking cyclic voltammograms.

Table 5.1 Redox potentials of $[Co(PY4Im)(ACN)](PF_6)_2$ complex in acetonitrile with and without excess bases. NMBI and MeIm were prepared at 0.5 M.

$E_{1/2}$ (V) vs Fc ⁺ /Fc
-0.13
-0.18
-0.23

The $[Co(PY4Im)(ACN)](PF_6)_{3/2}$ redox couple was used in DSSCs with the dye LEG4 and was compared against the standard redox shuttle $[Co(bpy)_3](PF_6)_{3/2}$. Surprisingly the performance was practically the same for both redox shuttles. Despite increasing the regeneration driving force by approximately 100 mV the photocurrents were the same. Open-circuit voltage decays were then measured to determine if recombination was an issue. Upon inspection of, lifetime vs potential the lifetimes were very similar as well. It would be expected that by moving the redox potential more negative for $[Co(PY4Im)(ACN)](PF_6)_{3/2}$ the rate of recombination would decrease to increase the lifetime. However the likely increased self-exchange could reduce the internal barrier to recombination from TiO₂ electrons. Since the system minimally shifted the balance between regeneration and recombination, the tunable system discussed in chapter 4 was developed.



Figure 5.6 (a) Current density vs applied voltage curves under 100 mW cm⁻² illumination. (b) Lifetime as a function of measured potential from open-circuit voltage decay. $[Co(bpy)_3]^{3+/2+}$ with no base (navy) and $[Co(PY4Im)(ACN)]^{3+/2+}$ no base (red).

5.6 Alternative Ligand Systems for Low-Spin Co(II) Complexes

The PY5ImBr series had many promising features but it did not fully capitalize on the increased electron self-exchange rate constant of being low-spin Co(II) and it was negatively

affected by coordinating bases that can be used to boost the DSSC efficiency. To make a lowspin Co(II) redox shuttle with an increased self-exchange like $[Co(ttcn)_2]^{3+/2+}$, a more electron donating and flexible ligand system is required to increase stability and move to more negative potentials to decrease recombination. Two suggested ligands would likely produced a low-spin Co(II) at more negative potentials.



Figure 5.7 Structure of PY2ImBr and PY4ImDMA2Br ligands to be coordinated to cobalt.

The first PY2ImBr would behave analogously to ttcn by closing the coordination sphere with two flexible tridentate ligands. The ligand has been coordinated previously to copper by O'Hearn and Singer where they described the ligand to be unaffected by moisture and oxygen. The strongly sigma donating NHC central unit would then induce low-spin Co(II) while pushing the redox potential to more negative potentials as desired.¹⁰

The second ligand PY4ImDMA2Br ligand would behave similarly to PY4ImBr ligand mentioned previously but would likely reside at more negative potentials due to the incorporation of DMA groups. As mentioned in the previous section the [Co(PY4Im)(X)]^{3+/2+} system had good performance in DSSCs even when strongly coordinating bases were used like TBP. The system did suffer from significant recombination losses which could be mitigated by pushing the potential more negative. Small modulations at more negative potentials could then
be induced by choice of the base added to the DSSC electrolyte as shown for PY4Im in the previous section. This would allow for efficient regeneration of the sensitizer, low recombination rates at more negative potentials and full utilization of the open-circuit potential boost that strongly coordinating bases induce.¹¹ This would allow the system to be integrated with near-IR dye systems where iodide/triodide has large voltage losses to drive dye regeneration.^{12,13}

APPENDIX



Figure A5.1 ¹H NMR of ferrocene signal as a function of $[Co(PY5Me_2)(T-BuCN)](PF_6)_2$ red (0 mM), yellow (5.5 mM), green (10.0 mM), blue (13.6 mM), and violet (16.6 mM). 0.2 M T-BuCN was present to maintain the complex.



Figure A5.2 ¹H NMR of $[Co(TPA)(SPY)](PF_6)$ in CD₃CN. Dichloromethane (5.4 ppm) and diethyl ether (3.4 and 1.2 ppm) are residual from the synthesis.



Figure A5.3 ¹H NMR of $[Co(PY4Im)(ACN)](PF_6)_2$ in CD₃CN. Dichloromethane (5.4 ppm) and diethyl ether (3.4 and 1..2 ppm) are residual from the synthesis.



Figure A 5.4 ¹H NMR of $[Co(PY5Im)(ACN)](PF_6)_3$ in CD₃CN. Dichloromethane (5.4 ppm) is residual from the synthesis.

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