Engineering High-Potential Photo-Oxidants with Panchromatic Absorption

Ting Jiang, Nicholas F. Polizzi, Jeff Rawson, and Michael J. Therien*

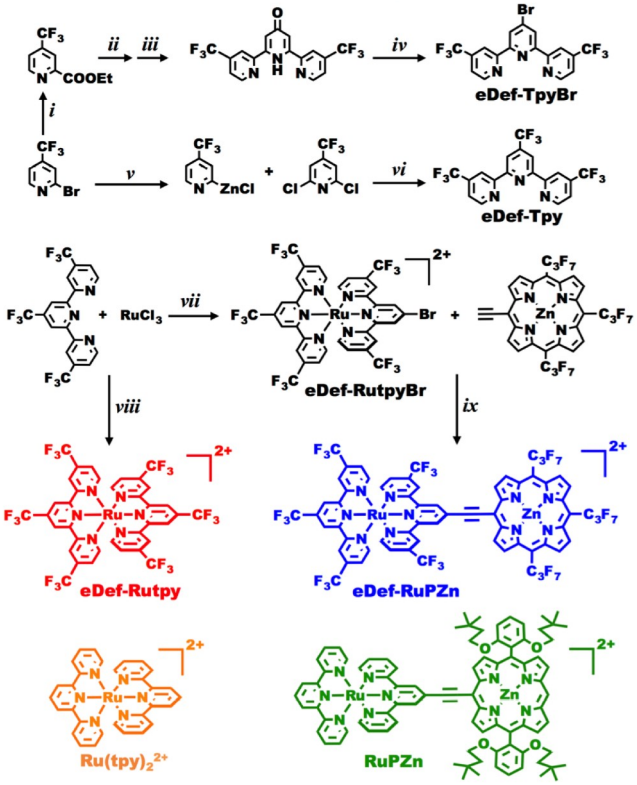
Department of Chemistry, Duke University, Durham, North Carolina, 27708, United States

Supporting Information Placeholder

ABSTRACT: Challenging photochemistry demands high-potential visible-light-absorbing photo-oxidants. We report (i) a highly electron-deficient Ru(II) complex (**eDef-Rutpy**) bearing an $E_{1/2}^{0/+}$ potential more than 300 mV more positive than that of any established Ru(II) bis(terpyridyl) derivative, and (ii) an ethyne-bridged **eDef-Rutpy**-(porphinato)Zn(II) (**eDef-RuPZn**) supermolecule that affords both panchromatic UV-vis spectral domain absorptivity and a high $E_{1/2}^{0/+}$ potential, comparable to that of $Ce(NH_4)_2(NO_3)_6$ [$E_{1/2}(Ce^{3+/4+})$ = 1.61 V *vs*. NHE], a strong and versatile ground-state oxidant commonly used in organic functional group transformations. **eDef-RuPZn** exhibits ~eight-fold greater absorptive oscillator strength over the 380-700 nm range relative to conventional Ru(II) polypyridyl complexes, and impressive excited-state reduction potentials ($^1E^{-/}$* = 1.59 V; $^3E^{-/}$* = 1.26 V). **eDef-RuPZn** manifests electronically excited singlet and triplet charge-transfer state lifetimes more than two orders of magnitude longer than those typical of conventional Ru(II) bis(terpyridyl) chromophores, suggesting new opportunities in light-driven oxidation reactions for energy conversion and photocatalysis.

High-potential photo-oxidants that feature comprehensive absorptivity in the visible (vis) spectral domain and long-lived excited states are needed to resolve vexing photochemical challenges, such as light-driven water oxidation in dye-sensitized photoelectrosynthesis cells (DSPECs),[1-3] photoredox catalysis of organic transformations,[4,5] and photo-decomposition of heavily halogenated hydrocarbon wastes.[6,7] The literature is replete with studies utilizing (polypyridyl)metal complexes like $Ru(tpy)_2^{2+}$ and $Ru(bpy)_3^{2+}$ for these applications, yet relatively little progress has been made regarding the development of corresponding electron-deficient (eDef) high-potential chromophores capable of powering a broader range of light-driven oxidation reactions,[8-10] as eDef chromophores typically suffer from a combination of short excited-state lifetimes, limited vis-spectral domain absorptivity, or photochemical instability.[11-14] Here, we report the synthesis, electrochemistry, and photophysics of **eDef-Rutpy**, a chromophore having the highest $E^{0/+}$ value of any known Ru(II) bis(tridentate) complex, along with a corresponding ethyne-bridged **eDef-Rutpy**–(porphinato)Zn(II) (**eDef-RuPZn**) supermolecule, endowed with intense panchromatic absorptivity, a large magnitude excited-state reduction poten-

Scheme 1. Synthetic Route to eDef-Rutpy and eDef-RuPZn, Along with Structures of Corresponding Established Electron-Rich Analogues.



(i) n-BuLi, THF, -100 °C, ethyl formate, EtOH, K_2CO_3, I_2; (ii) NaH, acetone, DME, 90 °C; (iii) NH_4OAc, EtOH, reflux; (iv) PBr_5, $POBr_3$, 100 °C; (v) n-BuLi, THF, -100 °C, $ZnCl_2$; (vi) $Pd(PPh_3)_4$, THF, 70 °C; (vii) ethanol, reflux; **eDef-TpyBr**, ethylene glycol, 150 °C; (viii) ethylene glycol, reflux; 4,4',4''-pyrrolidinyl-2,2';6',2''-terpyridine, MeOH, reflux; (ix) $Pd_2(dba)_3$, $AsPh_3$, THF:MeCN:DIPA (5:5:1), 60 °C. All charged complexes feature PF_6^- as counter ions.

tial, and long-lived, highly oxidizing singlet and triplet charge-transfer (CT) excited states.

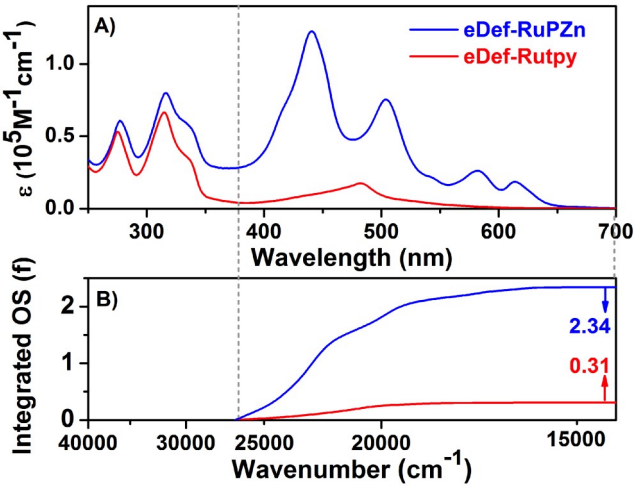


Figure 1. (A) Electronic absorption spectra of **eDef-Rutpy** and **eDef-RuPZn** in acetonitrile solvent; (B) Total integrated absorptive oscillator strengths calculated over the 26316 cm^{-1} (380 nm) to 14286 cm^{-1} (700 nm) spectral range. [15]

Given challenges commonly associated with cross-coupling reactions involving 2-pyridyl derivatives,[16] syntheses of **eDef-Tpy** and **eDef-TpyBr** precursor ligands defined key obstacles to the target **eDef-Rutpy** and **eDef-RuPZn** chromophores (**Scheme 1**); details describing these syntheses are contained in the Supporting Information (SI). **eDef-RuPZn** was constructed via Sonogashira cross-coupling of [5-ethynyl-10, 15, 20-tris(perfluoropropyl)porphinato]Zn(II) and **eDef-RutpyBr** fragments (SI), using a synthetic approach analogous to that developed for the **RuPZn** supermolecular chromophore.[17-19] Note that in contrast to perfluoroalkylated tris(bipyridyl)Ru(II) complexes,[11] **eDef-Rutpy** species enable panchromatic chromophore design strategies that can take advantage of the **RuPZn** design motif that optimally mixes porphyrin ligand π-π* and (polypyridyl)metal charge transfer states.[17-19]

The electronic absorption spectrum (EAS) of **eDef-Rutpy** in acetonitrile solvent bears a close resemblance to that of $Ru(tpy)_2^{2+}$ (**Figure 1**). **eDef-Rutpy** evinces ligand-localized π-π* transitions over the 260-350 nm range (λ_{max} = 275 nm, ε = 53100 $M^{-1}cm^{-1}$; λ_{max} = 315 nm, ε = 66500 $M^{-1}cm^{-1}$), and a weaker MLCT manifold spanning the 400-600 nm spectral window (λ_{max} = 482 nm; ε = 17600 $M^{-1}cm^{-1}$), akin to those characteristic of $Ru(tpy)_2^{2+}$ [π-π* (λ_{max} = 271 nm, ε = 46800 $M^{-1}cm^{-1}$; λ_{max} = 307 nm, ε = 68700 $M^{-1}cm^{-1}$); MLCT (λ_{max}= 476 nm, ε = 17700 $M^{-1}cm^{-1}$)].[8] The similarities between the steady-state EAS of **eDef-Rutpy** and $Ru(tpy)_2^{2+}$ suggest that the six CF_3 groups of the former implement the electron-withdrawing effect through the ligand σ-bond network, without substantially perturbing the character of the π-electron system. In effect, the nature of the electronic transitions of **eDef-Rutpy** is unperturbed relative to $Ru(tpy)_2$, while **eDef-Rutpy** becomes uniformly more oxidizing (see below). However, the lack of significant oscillator strength in the visible remains a limitation of both $Ru(tpy)_2$ and **eDef-Rutpy** for light-driven reactions.

Directly addressing the issue of visible absorptivity, the EAS of **eDef-RuPZn** features almost eight times the oscillator strength as that of **eDef-Rutpy** in the 380-700 nm visible spectrum range, and displays spectral features similar to those evinced by **RuPZn** (**Figure 1**; see SI for EAS of chromophoric building blocks and **RuPZn**).[17-19] The porphyrin B-state derived transition centered at 441 nm manifests an absorption maximum that exceeds 1.2×10^5 $M^{-1}cm^{-1}$. The transition centered at 504 nm (ε = 75400 $M^{-1}cm^{-1}$) derives from the Ru(II) complex MLCT band and oscillator-strength mixing involving the porphyrin moiety.[17-19] Note that the weakest **eDef-RuPZn** absorption bands at 582 nm (ε = 26100 $M^{-1}cm^{-1}$) and 614 nm (ε = 18600 $M^{-1}cm^{-1}$) are more intense than the $Ru(tpy)_2^{2+}$ MLCT band.[8] These two low-energy bands derive from mixing of porphyrin Q-state transitions with the $Ru(tpy)_2^{2+}$ MLCT transition, enabled by head-to-tail transition dipole alignment of the (porphinato)metal and (terpyridyl)metal chromophoric components.[17-20]

Ultrafast transient absorption experiments demonstrate excited-state dynamics for **eDef-Rutpy** and **eDef-RuPZn** in acetonitrile solvent similar to those of their electron-rich counterparts (**Figure 2**).[18,19,21-24] Excitation of **eDef-Rutpy** at 480 nm generates the broad featureless transient absorption characteristic of the ^{3}MLCT state within the 200 fs time resolution of our instrument (**Figure 2A**). The 1 ns ^{3}MLCT state lifetime of **eDef-Rutpy** (**Figure S7**) is 4 times longer than the 250 ps lifetime of $Ru(tpy)_2^{2+}$, likely due to ^{3}MC state destabilization relative to the ^{3}MLCT state, resulting from -CF_3 substitu-

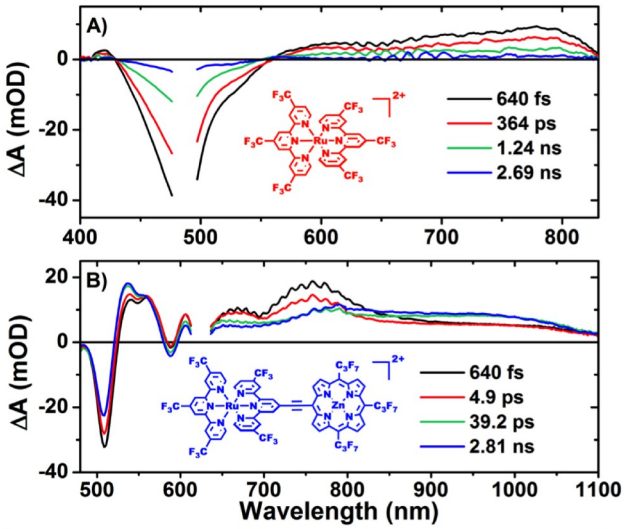


Figure 2. Representative ultra-fast transient absorption spectra recorded at several time delays for (A) **eDef-Rutpy** and (B) **eDef-RuPZn**. Experimental conditions: solvent = acetonitrile; temperature = 21 ° C; magic angle polarization; **eDef-Rupy**: λ_{ex} = 480 nm, P_{ex} = 1 ∝J/Pulse; **eDef-RuPZn**: λ_{ex} = 620 nm, P_{ex} = 870 nJ/pulse.

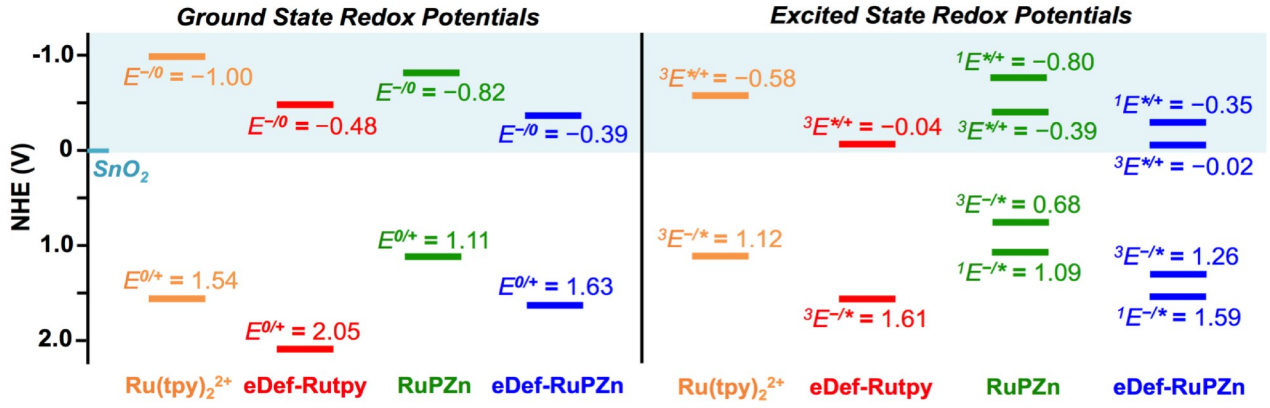


Figure 3. Left Panel: ground-state Ru(tpy)$_2^{2+}$, **eDef-Rutpy**, **RuPZn** and **eDef-RuPZn** potentiometric data. Right Panel: corresponding S_1- and T_1-state redox properties for these chromophores (see SI). Experimental conditions: 0.1 M $TBAPF_6$/acetonitrile electrolyte/solvent system; ambient temperature; potential *vs.* NHE; SnO_2 conduction band (cyan shadow, onset = 0 V) at neutral pH.

tion. Excitation of **eDef-RuPZn** at 620 nm generates an intense NIR transient absorption manifold that becomes more intense upon $S_1 \rightarrow T_1$ intersystem crossing (ISC) to the long-lived T_1 charge-transfer state (**Figure 2B**). For **eDef-RuPZn**, the 13.5 ps $S_1 \rightarrow T_1$ ISC time constant and the 93 μs T_1 excited-state lifetime (**Figures S8-S11**) are extended by at least two orders of magnitude relative to the sub-100 fs ISC time constants and ns-timescale T_1 lifetimes characteristic of Ru(tpy)$_2^{2+}$ and its derivatives.[25,26]

Long excited-state lifetimes of photo-oxidants are crucial for achieving high yields of desired photoreactions. For instance, sub-ps timescale electron injection from the short-lived ^{1}MLCT states of Ru(II) polypyridyl complexes into TiO_2 semiconductor interfaces cannot typically proceed with unit quantum yield; hence, a substantial degree of electron injection occurs from the energetically lower ^{3}MLCT states over the 10-100 ps time domain.[3,9] Given the magnitudes of the respective **eDef-RuPZn** S_1- (13.5 ps) and T_1-state (93 μs) lifetimes, it is clear that this chromophore design offers not only new opportunities to achieve high-yield charge injection at semiconductor interfaces, but the possibility to engineer energy conversion systems that realize substantial electron transfer quenching of the ^{1}**eDef-RuPZn*** state, before energy-wasting ^{1}MLCT → ^{3}MLCT ISC can occur.

Potentiometric data acquired for **eDef-Rutpy** and **eDef-RuPZn** reveal that perfluoroalkyl substitution raises the $E^{0/+}$ values of these chromophore motifs by ~0.5 V relative to their respective chromophoric benchmarks (**Figure 3**). Note that the measured $E_{1/2}(Ru^{2+/3+})$ value for **eDef-Rutpy** (2.05 V) is ~300 mV higher than the $Ru^{2+/3+}$ potentials realized for electron-poor Ru(tpy)$_2^{2+}$ derivatives that feature extensive -CN/-NO$_2$ substitution,[27,28] and ~200 mV higher than that reported for Ru(dqxp)$_2^{2+}$, a chromophore having the highest $E_{1/2}(Ru^{2+/3+})$ potential yet established for tridentate Ru(II) complexes.[26] Similarly, the $E_{1/2}$(**eDef-RuPZn**)$^{0/+}$ potential (1.63 V) is more than 0.5 V larger than that determined for **RuPZn** (**Figure 3**).[17,19] Note that the **eDef-RuPZn** $E^{0/+}$ value is remarkably high for a large π-conjugated system. While π-conjugation expansion is a common approach by which panchromatic absorptivity may be realized, it comes at the expense of a destabilized HOMO level that diminishes $E_{1/2}^{0/+}$: here broad high-oscillator strength vis domain spectral absorptivity derives from the multi-directional CT nature of low-lying **eDef-RuPZn** excited states,[17-20] preserving a substantial $E_{1/2}^{0/+}$.

Excited-state redox potentials ($E^{-/*}$ and $E^{*/+}$) of **eDef-Rutpy** and **eDef-RuPZn** determine thermodynamic driving forces (ΔG) for photo-reduction and photo-oxidation reactions (**Figure 3** and SI). The S_1-state reduction potential ($^1E^{-/*}$ = 1.59 V) of **eDef-RuPZn** is impressive, even slightly higher than that of Ru(CN-tpy)$_2^{2+}$, which has the highest excited-state reduction potential among established tridentate Ru(II) complexes but much poorer absorptivity and an excited state lifetime two orders of magnitude shorter.[28] In the context of DSPEC architectures, comparison of the chromophore $E^{*/+}$ values with the conduction band onsets of semiconductor electrodes evaluates the feasibility of photoinduced electron injection to generate (chromophore)$^+$ species that may perform desired oxidative chemistry. The S_1 state $E^{*/+}$ value of **eDef-RuPZn** is −0.35 *V*, indicating an exergonic ΔG for electron injection into SnO_2, a popular semiconductor electrode material with a low conduction band onset of 0 V (*vs.* NHE) at neutral pH.[29] The 13.5 ps S_1-state lifetime of **eDef-RuPZn**, two orders of magnitude longer than those of conventional Ru(II) terpyridyl derivatives, suggests opportunities to realize high quantum yield S_1 state electron injection; it is also important to underscore that in circumstances where **eDef-RuPZn** ISC dynamics prevail over electron injection from the S_1 state, electron injection remains thermodynamically viable from the long-lived (93 μs) T_1 state (**Figure 3**). The potential of the (**eDef-RuPZn**)$^+$ hole (1.63 V *vs.* NHE) is comparable with the reduction

potential of the strong chemical oxidant $Ce(NH_4)_2(NO_3)_6$,[30] suggesting the breadth of chemistry that could be driven by DSPECs incorporating this high-potential panchromatic chromophore.

Established photo-oxidants such as porphyrin derivatives, perylene diimides, and metal complexes all exhibit limited visible spectral coverage.[1,8,12,14] Enhancement of long-wavelength oscillator strength by extending π-conjugation typically comes at the expense of a lower $E^{0/+}$ value (HOMO destabilization), thus diminishing the ΔG for oxidative chemistry. This work realizes a high-potential (terpyridyl)metal-based chromophore having panchromatic UV-vis spectral domain absorptivity, with an integrated visible oscillator strength ~eight fold greater than those of typical Ru(II) terpyridyl complexes. **eDef-RuPZn** is a panchromatic chromophore with a $E_{1/2}^{0/+}$ potential comparable to that of $Ce(NH_4)_2(NO_3)_6$, [$E_{1/2}(Ce^{3+/4+})$ = 1.61 V *vs*. NHE],[30] which affords **eDef-RuPZn** with an uncommonly large excited-state reduction potential ($^1E^{-/}$* = 1.59 V; $^3E^{-/}$* = 1.26 V). The combination of a vis-light triggered photoexcited state having high electrochemical potential, with long S_1-(13.5 ps) and T_1-state (93 μs) lifetimes, suggests new opportunities to drive challenging photo-oxidation reactions for applications such as energy conversion and photocatalysis.

ASSOCIATED CONTENT

Supporting Information.
Synthetic details, compound characterization, potentiometric, and excited-state dynamical data. It is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
michael.therien@duke.edu

Note
The authors declare no competing financial interest.

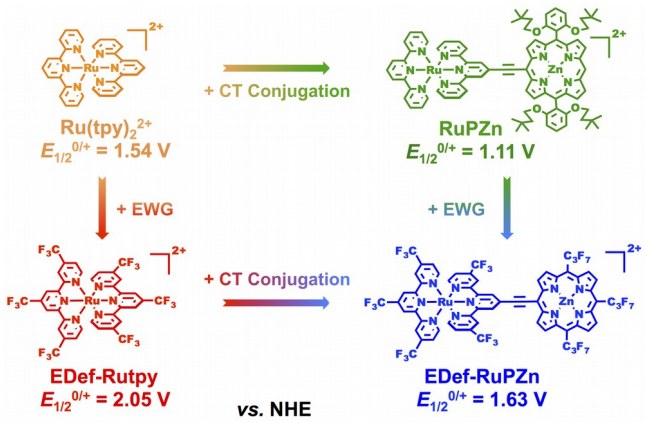
ACKNOWLEDGMENT

The authors gratefully acknowledge research support from the National Science Foundation through Grant CHE-1413333**.**

REFERENCES

(1) Vagnini, M. T.; Smeigh, A. L.; Blakemore, J. D.; Eaton, S. W.; Schley, N. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W.; Co, D. T.; Wasielewski, M. R. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15651.
(2) Alibabaei, L.; Luo, H.; House, R. L.; Hoertz, P. G.; Lopez, R.; Meyer, T. J. *J. Mater. Chem. A* **2013**, *1*, 4133.
(3) Ashford, D. L.; Gish, M. K.; Vannucci, A. K.; Brennaman, M. K.; Templeton, J. L.; Papanikolas, J. M.; Meyer, T. J. *Chem. Rev.* **2015**, *115*, 13006.
(4) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat Chem* **2010**, *2*, 527.
(5) Schultz, D. M.; Yoon, T. P. *Science* **2014**, *343*, 985.
(6) Sarakha, M.; Bolte, M.; Burrows, H. D. *The Journal of Physical Chemistry A* **2000**, *104*, 3142.
(7) Silva, M. I.; Burrows, H. D.; Formosinho, S. J.; Alves, L.; Godinho, A.; Antunes, M. J.; Ferreira, D. *Environ. Chem. Lett.* **2007**, *5*, 143.
(8) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
(9) Kuciauskas, D.; Monat, J. E.; Villahermosa, R.; Gray, H. B.; Lewis, N. S.; McCusker, J. K. *J. Phys. Chem. B* **2002**, *106*, 9347.
(10) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802.
(11) Furue, M.; Maruyama, K.; Oguni, T.; Naiki, M.; Kamachi, M. *Inorg. Chem.* **1992**, *31*, 3792.
(12) Goll, J. G.; Moore, K. T.; Ghosh, A.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 8344.
(13) Wang, L.; Mirmohades, M.; Brown, A.; Duan, L.; Li, F.; Daniel, Q.; Lomoth, R.; Sun, L.; Hammarstrom, L. *Inorg. Chem.* **2015**, *54*, 2742.
(14) Jiang, J.; Swierk, J. R.; Materna, K. L.; Hedström, S.; Lee, S. H.; Crabtree, R. H.; Schmuttenmaer, C. A.; Batista, V. S.; Brudvig, G. W. *J. Phys. Chem. C* **2016**, *120*, 28971.
(15) Turro, N. J. *Principles of Modern Molecular Photochemistry*; University Science Books: Sausolito, CA, 2009.
(16) Dick, G. R.; Woerly, E. M.; Burke, M. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 2667.
(17) Uyeda, H. T.; Zhao, Y. X.; Wostyn, K.; Asselberghs, I.; Clays, K.; Persoons, A.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 13806.
(18) Duncan, T. V.; Rubtsov, I. V.; Uyeda, H. T.; Therien, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9474.
(19) Duncan, T. V.; Ishizuka, T.; Therien, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 9691.
(20) Hu, X. Q.; Xiao, D. Q.; Keinan, S.; Asselberghs, I.; Therien, M. J.; Clays, K.; Yang, W. T.; Beratan, D. N. *J. Phys. Chem. C* **2010**, *114*, 2349.
(21) Singh-Rachford, T. N.; Nayak, A.; Muro-Small, M. L.; Goeb, S.; Therien, M. J.; Castellano, F. N. *J. Am. Chem. Soc.* **2010**, *132*, 14203.
(22) Ishizuka, T.; Sinks, L. E.; Song, K.; Hung, S. T.; Nayak, A.; Clays, K.; Therien, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 2884.
(23) Olivier, J. H.; Bai, Y. S.; Uh, H.; Yoo, H.; Therien, M. J.; Castellano, F. N. *J. Phys. Chem. A* **2015**, *119*, 5642.
(24) Nayak, A.; Park, J.; De Mey, K.; Hu, X.; Duncan, T. V.; Beratan, D. N.; Clays, K.; Therien, M. J. *ACS Cent. Sci.* **2016**, *2*, 954.
(25) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.
(26) Pal, A. K.; Hanan, G. S. *Chem. Soc. Rev.* **2014**, *43*, 6184.
(27) Fallahpour, R. A.; Neuburger, M.; Zehnder, M. *New J. Chem.* **1999**, *23*, 53.
(28) Wang, J. H.; Fang, Y. Q.; Hanan, G. S.; Loiseau, F.; Campagna, S. *Inorg. Chem.* **2005**, *44*, 5.
(29) Knauf, R. R.; Brennaman, M. K.; Alibabaei, L.; Norris, M. R.; Dempsey, J. L. *J. Phys. Chem. C* **2013**, *117*, 25259.
(30) Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 16017.

TOC Figure


Ru(tpy)2 2+
E1/2 0/+ = 1.54 V
+ CT Conjugation
RuPZn
E1/2 0/+ = 1.11 V
+ EWG
+ EWG
+ CT Conjugation
EDef-Rutpy
E1/2 0/+ = 2.05 V
vs. NHE
EDef-RuPZn
E1/2 0/+ = 1.63 V