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Engineering High-Potential Photo-oxidants with Panchromatic Absorption

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Supporting Information

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 ∼8-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 2 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 photodecomposition 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 potential, and long-lived, highly oxidizing singlet and triplet charge-transfer (CT) excited states.

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 $\pi-\pi^*$ and (polypyridyl)metal CT 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 $\pi-\pi^*$ transitions over the 260−350 nm range (λ_{max} = 275 nm, ε = 53 100 M^{-1} cm^{-1}; λ_{max} = 315 nm, ε = 66 500 M^{-1} cm^{-1}), and a weaker MLCT manifold spanning the 400−600 nm spectral window (λ_{max} = 482 nm; ε = 17 600 M^{-1} cm^{-1}), akin to those characteristic of $Ru(tpy)_2^{2+}$ [$\pi-\pi^*$ (λ_{max} = 271 nm, ε = 46 800 M^{-1} cm^{-1}; λ_{max} = 307 nm, ε = 68 700 M^{-1} cm^{-1}); MLCT (λ_{max} = 476 nm, ε = 17 700 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 $Ru(tpy)_2^{2+}$, while **eDef-Rutpy** becomes uniformly more oxidizing (see below). However, the lack of significant oscillator strength in the visible remains a limitation of both $Ru(tpy)_2^{2+}$ 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

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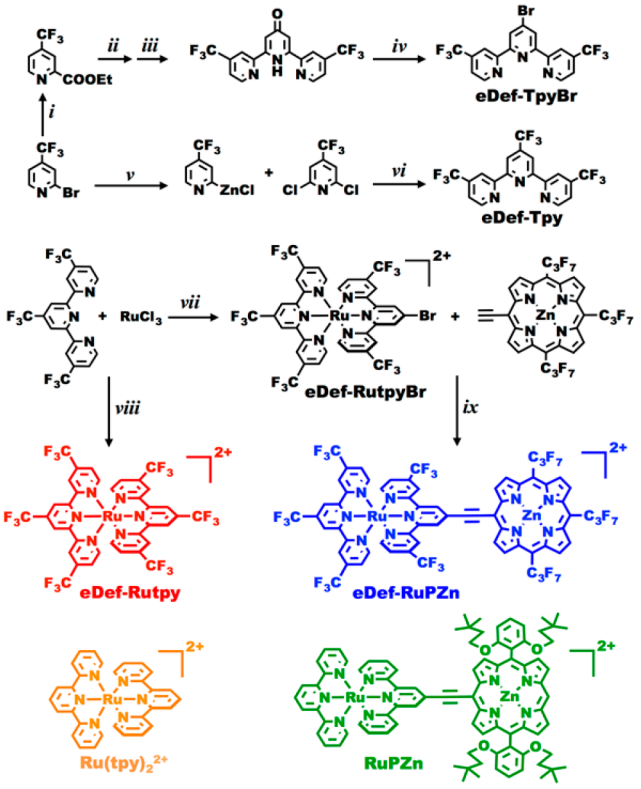
Scheme 1. Synthetic Route to eDef-Rutpy and eDef-RuPZn, Along with Structures of Corresponding Established Electron-Rich Analogues[a]



[a]Reagents and conditions: (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 counterion.

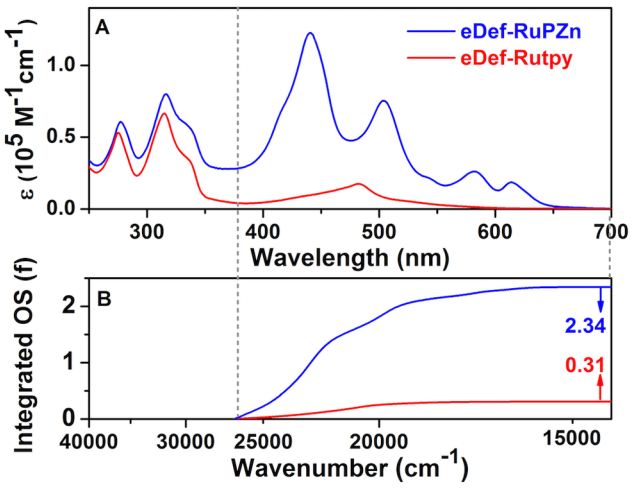


Figure 1. (A) Electronic absorption spectra of **eDef-Rutpy** and **eDef-RuPZn** in acetonitrile solvent. (B) Total integrated absorptive oscillator strengths calculated over the 26 316 cm^{-1} (380 nm) to 14 286 cm^{-1} (700 nm) spectral range.[15]

centered at 504 nm (ε = 75 400 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 = 26 100 M^{-1} cm^{-1}) and 614 nm (ε = 18 600 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

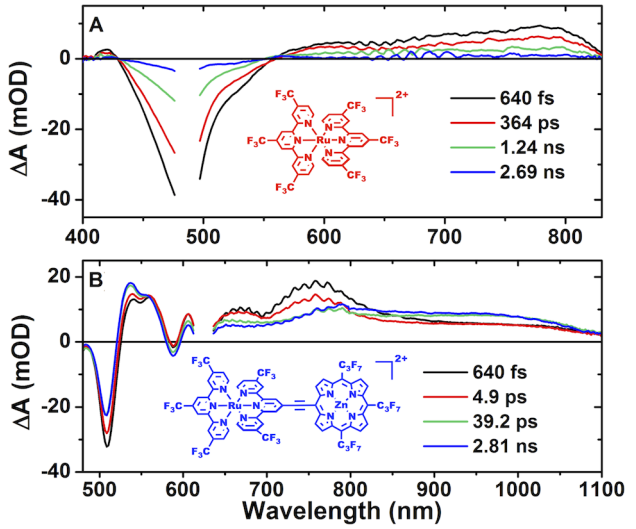


Figure 2. Representative ultrafast transient absorption spectra recorded at several time delays for (A) **eDef-Rutpy** and (B) **eDef-RuPZn**. Experimental conditions: solvent = acetonitrile; temperature = 21 °C; magic angle polarization. **eDef-Rupy**: λ_{ex} = 480 nm, P_{ex} = 1 μJ/pulse. **eDef-RuPZn**: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

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 S10) 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 $-CF_3$ substitution. 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 S11−S14) are extended by at least 2 orders of magnitude relative to the sub-100 fs ISC time constants and nanosecond time scale 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-picosecond time scale 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 semi-

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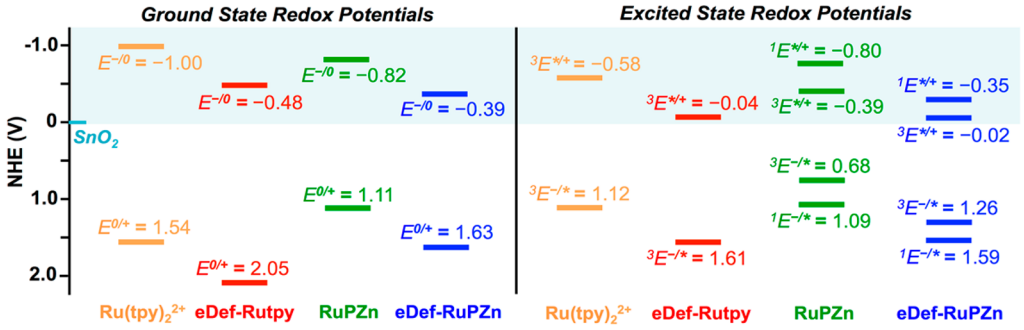

Figure 3. Left: ground-state $Ru(tpy)_2^{2+}$, **eDef-Rutpy**, RuPZn, and **eDef-RuPZn** potentiometric data. Right: corresponding S_1- and T_1-state redox properties for these chromophores (see SI). Experimental conditions: 0.1 M $TBAPF_6$/acetonitrile electrolyte/solvent system; ambient temperature;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

conductor 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 multidirectional 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 photoreduction 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 $Ru(CN\text{-}tpy)_2^{2+}$, which has the highest excited-state reduction potential among established tridentate Ru(II) complexes but much poorer absorptivity and an excited-state lifetime 2 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**, 2 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**)$^{\bullet+}$ 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 ∼8-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 visible-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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04400.

Synthetic details, compound characterization, and potentiometric and excited-state dynamical data (PDF)

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Notes

The authors declare no competing financial interest.

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