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Communication

Improved Visible Light Absorption of Potent Iridium(III) Photo-oxidants for Excited-State Electron Transfer Chemistry

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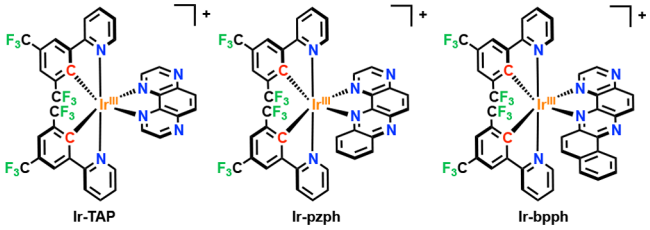
ABSTRACT: Three iridium photosensitizers, $[Ir(dCF_3ppy)_2(N{-}N)]^+$, where N−N is 1,4,5,8-tetraazaphenanthrene (TAP), pyrazino[2,3-*a*]phenazine (pzph), or benzo[*a*]pyrazino[2,3-*h*]phenazine (bpph) and dCF_3ppy is 2-(3,5-bis(trifluoromethyl-phenyl)pyridine), were found to be remarkably strong photo-oxidants with enhanced light absorption in the visible region. In particular, judicious ligand design provided access to **Ir-bpph**, with a molar absorption coefficient, ε = 9800 M^{-1} cm^{-1}, at 450 nm and an excited-state reduction potential, $E(Ir^{+*/0})$ = 1.76 V vs NHE. These complexes were successful in performing light-driven charge separation and energy storage, where all complexes photo-oxidized seven different electron donors with rate constants (0.089−3.06) × 10^{10} M^{-1} s^{-1}. A Marcus analysis provided a total reorganization energy of 0.7 ± 0.1 eV for excited-state electron transfer.

Since the early 2000s, cyclometalated iridium(III) complexes have emerged as powerful light-emitting materials, with exceptional photostability and highly tunable optoelectronic properties. They have found broad applications in lighting devices,[1−3] life sciences,[4−10] and photoredox chemistry;[11−16] however, their poor light harvesting in the visible region has largely precluded applications in solar energy conversion. Heteroleptic complexes with the architecture $[Ir(C{-}N)_2(N{-}N)]^+$ (C−N = cyclometalated ligand, N−N = diimine ligand) have been the focus of intense research because they possess spatially separated frontier orbitals.[17,18] This is a key advantage that enables the independent tuning of the C−N centered HOMO and N−N centered LUMO levels and hence the related reduction potentials, $E_{1/2}(Ir^{(n/n-1)})$. Potent (photo)oxidants with positive $E_{1/2}(Ir^{(IV/III)})$ or $E_{1/2}(Ir^{+*/0})$ are desired for applications such as water oxidation, hydrohalic acid oxidation, or photoredox catalysis.[19−26] Of particular interest is energetically demanding aqueous halide oxidation which occurs at $E_{1/2}(X^{\bullet/-})$ of 1.33, 1.93 and >2 V vs NHE for iodide, bromide, and chloride, respectively.[25] Unfortunately, due to limited visible light absorption and unsatisfactory thermodynamic properties, existing iridium(III) photosensitizers are of limited use. Efforts to circumvent their poor visible light harvesting include covalently linking additional chromophores,[27−29] engineering the HOMO−LUMO gap through ligand modifications[30−33] and changing the nature of the emissive excited states.[34,35] Here, we report access to iridium complexes (Chart 1 and Figure 1) that are strong photo-oxidants with a molar absorption coefficient suitable for visible-light-driven applications. Furthermore, excited-state electron transfer studies reported herein reveal a small reorganization energy, demonstrating that these new Ir complexes hold promise for visible-light-driven applications from both a kinetic and thermodynamic point of view.

Chart 1. Structures of Ir-TAP, Ir-pzph, and Ir-bpph



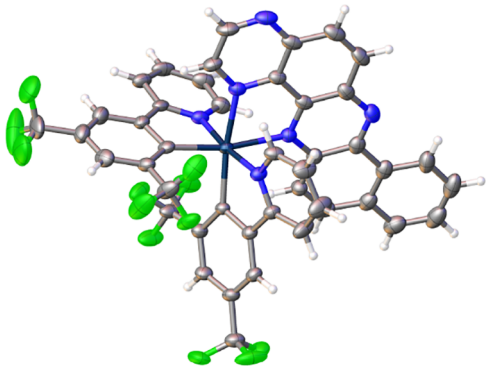


Figure 1. ORTEP diagram for **Ir-bpph** with the ellipsoids drawn at the 50% probability level. A PF_6^- counterion, as well as a diethyl ether molecule, were omitted for clarity.

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The synthetic approach to yield photo-oxidizing iridium complexes with increased visible light absorption relied on several factors. Two trifluoromethyl-substituted phenylpyridine ligands (dCF_3ppy) were chosen to decrease the Ir−C bond electron density and thus increase the photo-oxidizing character. The N−N ligand was systematically extended from the electron-deficient 1,4,5,8-tetraazaphenanthrene (TAP) backbone.[36,37] Conjugation of π-electron density was increased through the addition of one (pyrazino[2,3-*a*]phenazine, pzph) or two (benzo[*a*]pyrazino[2,3-*h*]phenazine, bpph) phenyl rings to TAP. Such annular modifications stabilized the LUMO level and hence increased visible light absorption independently of the excited-state reduction potential, $E_{1/2}(Ir^{+*/0})$. Moreover, the additional phenyl rings induced intraligand charge transfer (ILCT) bands between the phenyl donor groups and the electron-accepting pyrazine cores.[38]

The synthesis of the three planar ligands was achieved by condensation of 5,6-diamino-quinoxaline with the suitable dione (Figure S1). For pzph, this synthetic approach was an improvement compared to the previously published procedure.[39] For the newly reported bpph, this condensation yielded a mixture of regioisomers in 4:6 proportions, which were separated by chromatography on silica. Subsequently, each complex was formed by successive chelation of the cyclometalated ligands, as described by Nonoyama,[40] followed by addition of the N−N ligand. The three complexes were characterized by strong ligand-centered (LC) absorption bands from 200 to 350 nm while transitions at wavelengths >350 nm were attributed to mixed metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) charge transfer bands from the dCF_3ppy-Ir moiety to the N−N ligand (Figure 2).[8,41] For **Ir-pzph** and **Ir-bpph**, the greater electronic conjugation within the diimine ligand stabilized the Ir(III) LUMO and resulted in both a red shift of the lowest energy absorption feature as well as a significant increase in molar absorption coefficients which reached values of ε_{450} = 500, 1400, and 9800 M^{-1} cm^{-1} for **Ir-TAP**, **Ir-pzph**, and **Ir-bpph**, respectively.

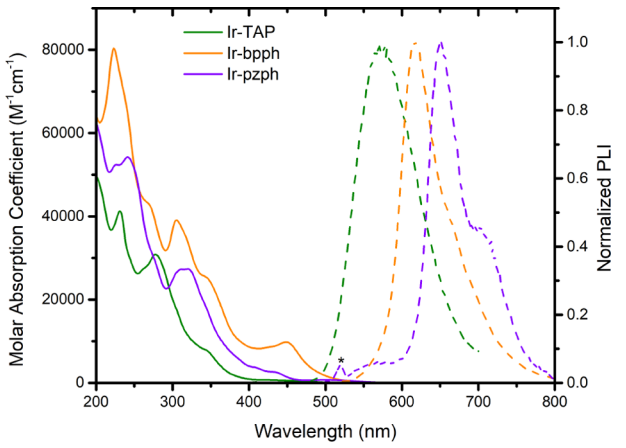

Figure 2. Absorption (solid) and steady-state photoluminescence (dash) spectra of the iridium complexes measured in acetonitrile at room temperature. An excitation wavelength between 400 and 470 nm was used, where the absorbance was below 0.1. *Raman peak of CH_3CN.

Time-dependent density functional theory indicated increased contribution from pzph or bpph intraligand charge transfer to these visible absorption bands (Figures S19−S24). These assignments were strengthened by vibronic structure evident in steady-state photoluminescence spectra (Figures 2 and S26 and S27), as well as their long excited-state lifetimes, τ, and their corresponding small radiative (k_r) and nonradiative (k_{nr}) rate constants (Table 1).

Reversible electrochemical reduction associated with the N−N ligands were determined by cyclic voltammetry in 0.1 M $TBAPF_6/CH_3CN$ electrolyte and reported vs NHE (Figure S25), $E_{1/2}(Ir^{(+/0)})$ = −0.41, −0.13, and −0.25 V for **Ir-TAP**, **Ir-pzph**, and **Ir-bpph**, respectively (Table 1). In all cases, $E_{1/2}(Ir^{(IV/III)})$ was >2.2 V. An excited-state reduction potential ($E_{1/2}(Ir^{+*/0})$) of *ca.* 1.77 V vs NHE was determined for all three complexes using the $Ir^{(+/0)}$ reduction potentials and E_{00} values determined through Franck−Condon line shape analysis of the photoluminescence spectra (Figures S26 and S27).[42−45]

Excited-state reactivity of **Ir-TAP**, **Ir-pzph**, and **Ir-bpph** was investigated by time-resolved photoluminescence quenching experiments with seven quenchers. In each case, excited-state quenching was solely dynamic in nature, as indicated by the initial amplitude of the time-resolved photoluminescence.[25,26,46] A representative example of **Ir-bpph** excited-state quenching with halides is shown in Figure 3. Quenching by all other complex/quencher combinations are presented in Figures S28−S34. The corresponding quenching rate constants (k_q) obtained through Stern−Volmer analysis ranged (0.089−3.06) × 10^{10} M^{-1} s^{-1} (Table 2).

Transient absorption spectroscopy was performed with **Ir-TAP**, **Ir-pzph**, and **Ir-bpph** and tritolylamine (Me-TPA) in argon purged CH_3CN solutions (Figure S36). Pulsed light excitation of an Ir complex resulted in electron transfer from Me-TPA as evident through the observation of spectral features unambiguously attributed to the formation of $Me\text{-}TPA^+$, which also provided access to the spectra of the monoreduced iridium species (Figures S35 and S36).

Additional transient absorption spectroscopy experiments were performed using **Ir-bpph** with iodide, bromide, and chloride (Figure 3). With iodide and bromide, transient absorption changes were consistent with the formation of a monoreduced iridium complex and either $I_2^{\bullet-}$ or $Br_2^{\bullet-}$. UV−visible spectra before and after transient absorption experiments were superimposable, indicative of the high stability of these iridium complexes. In the case of chloride, excited-state quenching by transient absorption spectroscopy was evident only by a drastic decrease in the excited-state lifetime.

Table 1. Photophysical and Electrochemical Properties of the Ir(III) Complexes in Acetonitrile

complex	ε (M^{-1} cm^{-1})[a]	λ_{em} (nm)	Φ_{em}	k_r (s^{-1})	k_{nr} (s^{-1})	τ (μs)[b]	$Ir^{(+/0)}$ [c]	$Ir^{(+*/0)}$ [c]	E_{00} (eV)[d]
Ir-TAP	500	572	0.154[e]	1.1 × 10^5	6.0 × 10^5	1.4	−0.41	1.78	2.19
Ir-pzph	1400	651	0.028[f]	2.9 × 10^3	1.0 × 10^5	9.7	−0.13	1.77	1.90
Ir-bpph	9800	618	0.057[f]	1.2 × 10^3	2.0 × 10^4	47.0	−0.25	1.76	2.01

[a]At 450 nm. [b]Measured at a concentration of 10 μM. [c]V vs NHE. [d]Determined by Franck−Condon line shape analysis. [e]Measured vs quinine (Φ = 0.546).[47] [f]Measured vs $[Ru(bpy)_3]^{2+}$.[48]

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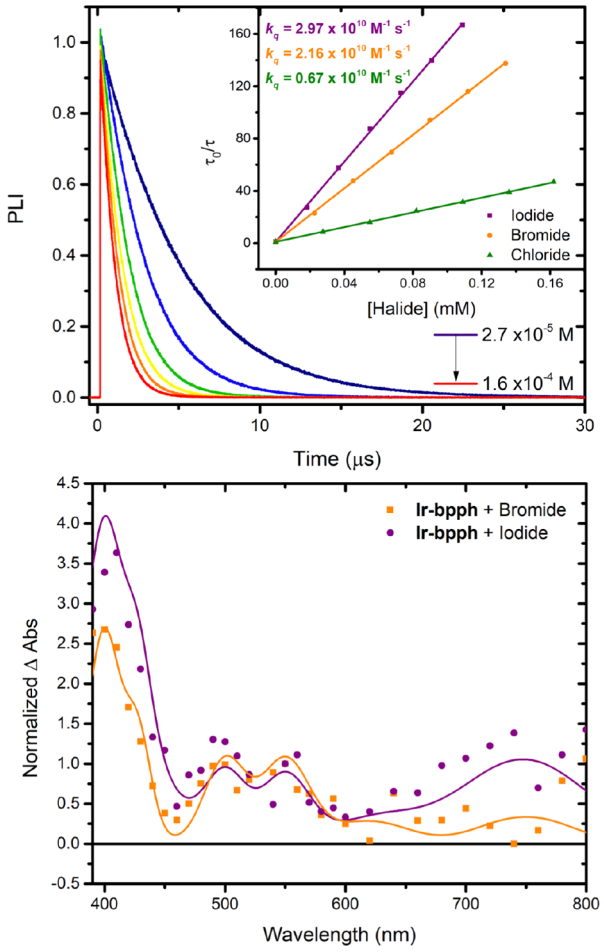

Figure 3. (Top) Time-resolved photoluminescence of **Ir-bpph** with increasing amount of TBACl in argon purged acetonitrile at room temperature. The inset represents the Stern–Volmer plots determined for the excited-state quenching of **Ir-bpph** by iodide (purple), bromide (orange) and chloride (green). (Bottom) Transient absorption spectroscopy of **Ir-bpph** in the presence of TBAI (purple) and TBABr (orange). Overlaid are results of spectral modeling based on spectra of $I_2^{\bullet-}$, $Br_2^{\bullet-}$, and monoreduced **Ir-bpph**.

Table 2. Excited-State Quenching Rate Constants (k_q) for the Ir(III) Complexes by Various Quenchers in CH_3CN

	$E(D^{n/n-1})$	k_q (× 10^{10} M^{-1} s^{-1})		
	V vs NHE	Ir-TAP	Ir-pzph	Ir-bpph
H_2Q	0.70[a]	0.84	0.67	0.65
MeO-TPA	0.72[b]	1.15	1.25	1.14
TPA	0.93[b]	1.17	1.34	1.21
I^-	1.23[c]	2.85	3.06	2.97
Br^-	1.35 ± 0.04[d]	1.89	2.29	2.16
Cl^-	1.46 ± 0.05[d]	0.82	1.04	0.67
^{t}Bu-phenol	1.50[e]	0.26	0.16	0.089

[a]From ref 49. [b]From ref 50. [c]From ref 51. [d]This work. [e]From ref 52.

Unfortunately, photoproducts resulting from electron transfer were not observed even when 100 mJ/pulse of 532 nm light was used.

Quenching rate constants, k_q, were then plotted as a function of the free energy change for the reactions between the quenchers and iridium complexes, $\Delta G^\circ = \{E_{1/2}(D^{n/n-1}) - E_{1/2}(Ir^{+*/0})\}F$ as shown in Figure 4A, when possible, as one-

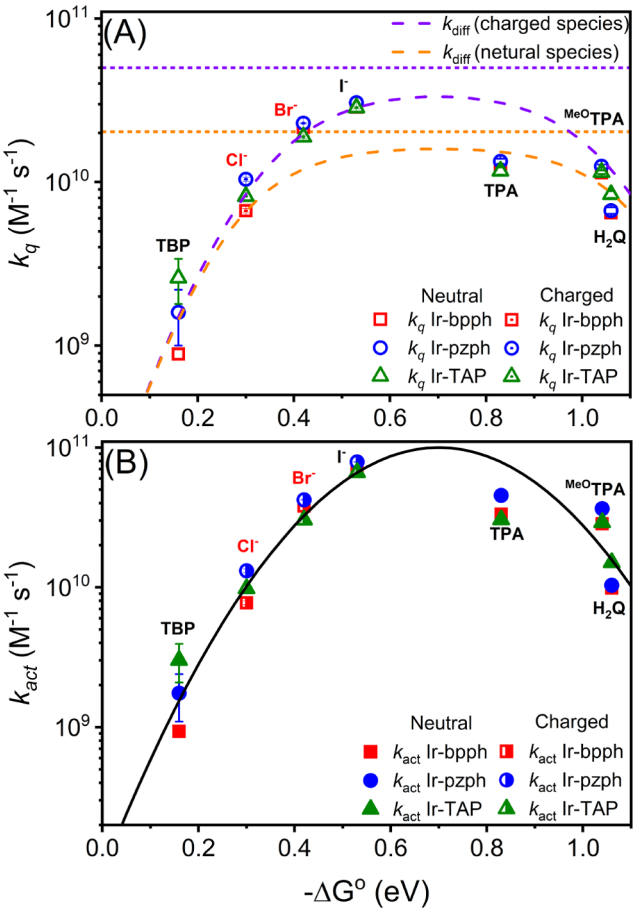

Figure 4. (Top) Experimentally determined k_q values for neutral (empty) and charged (dot-filled shape) species with three Ir^+ complexes as a function of driving force for electron transfer, $-\Delta G^\circ$. Horizontal dotted lines represent calculated diffusion limits for neutral (orange) and charged (purple) quenchers in CH_3CN solution. The dashed lines represent solutions to eq 1 using the determined values of k_{diff} and simulated values of k_{act}. (Bottom) Activated rate constants calculated by removing the influence of diffusion on experimentally determined k_q. The black solid line is a result from Marcus theory simulations using λ = 0.7 eV and $A' = 1 \times 10^{11}$ M^{-1} s^{-1}. k_{act} values used to determine ΔG° and $E_{1/2}(Br^{\bullet/-})$ and $E_{1/2}(Cl^{\bullet/-})$ through eqs 1 and 2 are indicated in red.

electron redox potentials for $Cl^{\bullet/-}$ and $Br^{\bullet/-}$ have not been previously reported in acetonitrile. Though the quenching species were not a homologous series and instead were composed of anionic inorganic and neutral organic donors, the driving force for quenching spanned nearly 1 eV and provided impetus to investigate electron transfer reactivity more closely.

Quenching rate constants were found to qualitatively increase with reaction exergonicity before appearing to saturate at intermediate driving forces. Much more interesting was that, beyond $-\Delta G^o > 0.8$ eV, k_q was found to decrease, suggestive of Marcus inverted behavior which is rarely observed in bimolecular reactions.[53] For Cl^- and Br^-, the expectation was that they should be more difficult to oxidize than I^-, which has a known one-electron reduction potential of 1.23 eV vs NHE.[25,26,51] This expectation was reflected in the Stern–Volmer analysis as smaller k_q values for Br^- and Cl^- were observed.

To develop a quantitative investigation into the kinetics of electron transfer, k_q was corrected for diffusional contributions,

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as it is related to the second-order activated rate constant, k_{act}, and the diffusion rate constant, k_{diff}, through eq 1.

$$\frac{1}{k_q} = \frac{1}{k_{act}} + \frac{1}{k_{diff}} \quad (1)$$

Diffusion limits for neutral and charged quenchers were calculated using the Stokes−Einstein equation, and included a Coulombic work term correction.[25,54,55] In agreement with literature values for diffusion of neutral species in acetonitrile, this was calculated as $k_{diff} = 1.9 \times 10^{10}$ M^{-1} s^{-1},[55] while the value for oppositely charged species, *i.e.*, a halide and Ir^+ complex, was estimated to be 5.0×10^{10} M^{-1} s^{-1}. Each series appeared to be near a diffusion limit, Figure 4A, and application of eq 1 allowed estimation of k_{act} for each complex/quencher combination (Table S7).

Activated rate constants were determined using k_{diff} for both halide and neutral quenchers and were similarly analyzed as a function of $-\Delta G°$, Figure 4B. Nonadiabatic Marcus theory, eq 2, was used to model k_{act} as a product of one prefactor, A', total reorganization energy, λ, and free energy change for the reaction, $\Delta G°$.

$$k_{act} = K_A k_{ET} = A'(\lambda) \exp\left(-\frac{(\Delta G° + \lambda)^2}{4\lambda k_B T}\right) \quad (2)$$

Two methods were used to examine the experimental data. First, a least-squares analysis of k_{act} with eq 2 provided $\lambda = 0.62$ eV and $A' = 8 \times 10^{10}$ M^{-1} s^{-1}, while excluding the quenching data for Cl^- and Br^-. A second method utilized values of $\lambda = 0.7$ eV and a transition state collision frequency of $A' = 1 \times 10^{11}$ M^{-1} s^{-1} commonly utilized for bimolecular electron transfer reactions.[56] From there, k_{act} was calculated over a 1.5 eV driving force range centered on $-\Delta G° = 0.7$ eV for both neutral and charged species, shown as the black solid line in Figure 4B, under an assumption that A' and λ were independent of the quencher identity. It was evident that a maximum in k_{act} alone revealed that oft-quoted magnitudes of $A' = 1 \times 10^{11}$ M^{-1} s^{-1} for bimolecular reactions were entirely appropriate.[56] Finally, an average k_{act} for Cl^- and Br^- and eq 1 were used to estimate the driving force for these electron transfer reactions, providing access to the one-electron reduction potentials given in Table 1.

In conclusion, the results highlight that, through rational ligand design, iridium complexes with $E_{1/2}(Ir^{(IV/III)}) > 2.2$ V, $E(Ir^{+*/0}) = 1.76$ V vs NHE and strong visible light harvesting ($\varepsilon = 9800$ M^{-1} cm^{-1} at 450 nm) can be realized and utilized for visible-light-driven chemistry. Nanosecond transient absorption spectroscopy revealed that the photosensitizer excited states were able to oxidize a variety of organic substrates and halides. Application of Marcus theory provided a small total reorganization energy of 0.7 eV implying small kinetic barriers for excited-state electron transfer. Hence the **Ir-bpph** complex combines enhanced visible light absorption, strong photo-oxidizing power, and low reorganization energy for rapid electron transfer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b12108.

Experimental section, Electrochemistry, X-ray crystallography, DFT calculations, Time-resolved photoluminescence quenching, Stern−Volmer plots, Transient absorption spectroscopy (PDF)

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Notes

The authors declare no competing financial interest.

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