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Mechanistic Origin of Photoredox Catalysis Involving Iron(II) Polypyridyl Chromophores

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ABSTRACT: Photoredox catalysis employing ruthenium- and iridium-based chromophores have been the subject of considerable research. However, the natural abundance of these elements are among the lowest on the periodic table, a fact that has led to an interest in developing chromophores based on earth-abundant transition metals that can perform the same function. There have been reports of using Fe^{II}-based polypyridyl complexes as photocatalysts, but there is limited mechanistic information pertaining to the nature of their reactivity in the context of photoredox chemistry. Herein, we report the results of bimolecular quenching studies between $[Fe(tren(py)_3)]^{2+}$ (where tren(py)₃ = tris(2-pyridyl-methylimino-ethyl)amine) and a series of benzoquinoid acceptors. The data provide direct evidence of electron transfer involving the lowest-energy ligand-field excited state of the Fe(II)-based photosensitizer, definitively establishing that Fe(II) polypyridyl complexes can engage in photoinduced redox reactions but by a mechanism that is fundamentally different than the MLCT-based chemistry endemic to their second- and third-row congeners.

Photoredox catalysis is one of the most rapidly expanding fields in chemistry.¹ Driven by interest in developing new approaches to known chemistry as well as the discovery of previously unknown reactions, its transformational impact on both academic and industrial research is undeniable.² Central to this work has been the use of transition-metal-based compounds possessing excited states capable of engaging in electron and, more recently, energy transfer reactions with organic substrates. Notwithstanding efforts by a number of groups extending this reactivity motif to organic chromophores,³ photoredox catalysis has predominantly leveraged the well-documented and well-understood photoreactivity endemic to the charge-transfer excited states of second- and third-row transition metal polypyridyl complexes such as tris(2,2'bipyridine)ruthenium(II) ([Ru(bpy)₃]²⁺) and (fac-tris(2phenylpyridine)iridium(III) $(fac-Ir(ppy)_3)$ ⁴ The metal-toligand charge-transfer (MLCT) states accessed upon visible light excitation of these types of chromophores possess lifetimes on the order of microseconds and are capable of storing on the order of 2 V of energy,⁵ allowing them to engage in a wide range of chemical reactions reliant on electron and/ or energy transfer with a given substrate.

Despite all of the obvious advantages (and success) of ruthenium- and iridium-based photocatalysts, the fact that these elements are among the rarest in the earth's crust⁶ raises legitimate questions concerning cost and scalability of processes dependent upon such chromophores. These issues, coupled with the possibility of unlocking new chemistry, has motivated interest in exploring the possibility of replacing these compounds with chromophores based on earth-abundant transition metals that can carry out analogous excited-state reaction chemistry.⁷ Indeed, there have been multiple reports of copper,⁸ molybdenum,⁹ and chromium¹⁰ photocatalysts being used to sensitize photoredox reactions. There have also been reports of photoredox reactions utilizing iron(II)

polypyridyls as photocatalysts.¹¹ These latter compounds represent an interesting case insofar as they are isoelectronic with their ruthenium and iridium congeners, a fact that has led to an assumption that their mode of action will mirror the chemistry of their second- and third-row counterparts. However, important differences in excited-state electronic structure arise upon shifting to the first transition series, differences that should significantly impact the nature of their reactivity in the context of photoredox chemistry.¹² While the realization of a given chemical transformation can sometimes represent the desired end point of some studies, understanding the mechanism of photoredox reactions can lead to improvements in catalytic efficiency as well as widening and/or redefining the scope of a given reaction. We have therefore undertaken a study to probe the mechanism of a photoredox reaction involving a Fe(II) polypyridyl complex and a group of organic electron acceptors in an effort to define the mode of reactivity for this class of transition metal-based chromophores.

The structure and ground-state absorption spectrum of the photosensitizer—tris(2-pyridylmethyliminoethyl)amine iron-(II)—are shown in Chart 1 and Figure 1, respectively. This compound possesses a low-spin diamagnetic ground state; excitation in the visible produces a ¹MLCT state that converts to the lowest-energy excited state of the compound—a high-spin metal-centered ligand-field state (${}^{5}T_{2}$)—in ~200 fs that persists for 55 ns prior to ground-state recovery.¹³ The presence of this state is indicated by a loss of absorbance across

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Chart 1. Fe(II)-Based Photosensitizer ($[Fe(tren(py)_3)]^{2+}$) and the Series of Benzoquinones Used for the Bimolecular Quenching Experiments^{*a*}



^aDDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, DCBQ = 2,3-Dicyano-1,4-benzo-quinone, *o*-TCBQ = 3,4,5,6-Tetrachloro-1,2-benzoquinone, *o*-TBBQ = 3,4,5,6-Tetrabromo-1,2-benzoquinone, and *p*-TCBQ = 2,3,5,6-Tetrachloro-1,4-benzoquinone.



Figure 1. Electronic absorption spectrum of $[Fe(tren(py)_3)]^{2+}$ acquired in CH₃CN solution. The inset shows the compound's differential absorption spectrum following $^1A_1 \rightarrow \ ^1MLCT$ excitation at 580 nm and is characteristic of the lowest-energy ligand-field excited state of the compound.

the visible spectrum, as shown in the inset of Figure 1. Given the fact that this ligand-field excited state is formed on a time scale that is orders of magnitude faster than diffusion, the catalytically relevant excited state for any bimolecular photoredox chemistry exhibited by this compound will be this ${}^{5}T_{2}$ state.¹⁴

Unlike ruthenium(II) and iridium(III) polypyridyl complexes, the lowest-energy excited states of iron(II) polypyridyls are typically nonemissive due to a lack of radiative coupling between two electronic states that differ by two units of spin (i.e., S = 0 and S = 2 for the ${}^{1}A_{1}$ and ${}^{5}T_{2}$ ground and lowestenergy excited states of $[Fe(tren(py)_{3})]^{2+}$, respectively). Therefore, the zero-point energy (E_{00}) of the photoreactive excited state, which is typically obtained from an emission spectrum and is needed to determine the redox potential associated with the excited state based on the Rehm–Weller formalism,¹⁵ cannot be directly measured in these cases. We therefore chose a series of benzoquinones spanning a range of pubs.acs.org/JACS

reduction potentials to serve as electron acceptors in bimolecular quenching studies (Chart 1), using time-resolved absorption spectroscopy to probe the kinetics of the reaction shown in eq 1.

$$[Fe(tren(py)_3)]^{2+*} + A \to [Fe(tren(py)_3)]^{3+} + A^{-}$$
(1)

Data acquired in acetone solution using DDQ as an acceptor under pseudo-first-order conditions are shown in Figure 2a. It can be seen that the measured lifetime of the ${}^{5}T_{2}$ state of $[Fe(tren(py)_{3}]^{2+}$ systematically decreases with increasing concentration of DDQ₄ a clear indication of dynamic quenching of the ligand-field excited state of the iron(II) sensitizer. In contrast, analogous experiments using *p*-TCBQ, which has a significantly more negative reduction potential than DDQ₄ reveal an insensitivity of the ${}^{5}T_{2}$ -state lifetime to the presence of the quinone (Figure 2b), suggesting the absence of any reaction between the two compounds. Similar data acquired from studies on all five quinones shown in Chart 1 can be found in the Supporting Information and are summarized in the form of the Stern–Volmer plot shown in Figure 3.

As we have emphasized previously concerning mechanistic studies of photoredox reactions, ^{5a} a Stern–Volmer plot serves to establish that a reaction is occurring between the excited state of a sensitizer and a quencher, but it does not address the question of mechanism: energy transfer (both dipolar (i.e., Förster) and exchange (Dexter)) as well as electron transfer can all produce identical Stern–Volmer plots. Since [Fe(tren- $(py)_3$)]²⁺ is nonemissive, Förster transfer can be immediately ruled out. Dexter transfer does not require significant radiative coupling between the excited state of the sensitizer and its ground state; however, this mechanism can also be ruled out in the present case because coupling of the ⁵T₂ excited state of the quinone acceptor would not conserve angular momentum for the overall process and is therefore forbidden.¹⁶

An electron transfer quenching mechanism is best established via spectroscopic identification of the oxidized donor and/or the reduced acceptor. In the present case, overlapping features in the absorption profiles of the ${}^{5}T_{2}$ excited state of $[Fe(tren(py)_{3})]^{2+}$ (Figure 1, inset), [Fe(tren $(py)_{3})]^{3+}$, and the semiquinone forms of the quenchers (Figure S8) make it challenging to do this using electronic absorption spectroscopy. We argue that the exclusion of energy transfer as a viable mechanism combined with the clear correlation between quenching dynamics and the reduction potential of the quinones used in this study (Table 1) makes for a compelling case that electron transfer is the operative mechanism giving rise to the reaction dynamics reflected in Figure 3.

Given the difficulty with determining the zero-point energy of the ligand-field excited state alluded to above, we can look to the thermodynamic properties of the quinone acceptors, specifically, the cutoff potential for reactivity, as a means of estimating the effective redox potential for the reactive state of the iron complex.¹⁷ The data in Table 1 clearly show that quenching is suppressed in the case of *o*-TBBQ and *p*-TCBQ. Assuming this break corresponds to a transition from an exergonic to an endergonic reaction, we estimate an effective excited-state oxidation potential of the ${}^{5}T_{2}$ state of [Fe(tren-(py)₃)]²⁺ in acetone of ~ -0.35 ± 0.05 V versus the ferrocene/ferrocenium couple; corresponding data acquired in CH₃CN solution afford a value of ~ -0.25 ± 0.05 V and are

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Figure 2. (a) Single-wavelength kinetics of transient absorption quenching experiments between $[Fe(tren(py)_3)]^{2+}$ and DDQ in acetone solution with 0.1 M of TBAPF₆ as supporting electrolyte. The data were acquired at 560 nm following excitation at 580 nm and are probing the loss of the transient signal associated with the ${}^{5}T_{2}$ ligand-field excited state of $[Fe(tren(py)_3)]^{2+}$ illustrated in the inset of Figure 1. (b) Corresponding data from quenching experiments with $[Fe(tren(py)_3)]^{2+}$ and *p*-TCBQ₄ also in acetone solution with 0.1 M TBAPF₆. The invariance of the time constant indicates the absence of quenching of the ${}^{5}T_{2}$ excited state under these conditions.



Figure 3. Stern–Volmer plots of bimolecular quenching studies between $[Fe(tren(py)_3)]^{2+}$ and the quinones indicated (see Chart 1). All studies were carried out in acetone solution with 0.1 M TBAPF₆. The data were acquired via nanosecond time-resolved absorption measurements following ${}^{1}A_{1} \rightarrow {}^{1}MLCT$ excitation of the iron-based chromophore. Details concerning the analysis of the data, as well as corresponding measurements carried out in CH₃CN solution, can be found in the Supporting Information. Bimolecular quenching constants (k_{q}) calculated from the slopes of the lines shown are collected in Table 1.

Table 1. Reduction Potentials and Quenching Rate	
Constants for Quenchers in Acetone with 0.1 M TBAPF ₆ ^{<i>a</i>,}	5

Quencher	$E_{\rm red}~({\rm V})$	$k_{\rm q}~({\rm M}^{-1}~{\rm s}^{-1})$	ΔG (V)
DDQ	0.07	2.7×10^{5}	-0.41
DCBQ	-0.15	2.6×10^{5}	-0.19
o-TCBQ	-0.33	2.1×10^{5}	-0.01
o-TBBQ	-0.35	-	0.01
p-TCBQ	-0.42	_	0.08

^{*a*}Potentials are relative to the ferrocene/ferrocenium couple. ^{*b*}The Fe(II)/Fe(III) couple sits at +0.51 V and +0.55 V in acetone and acetonitrile solutions, respectively (see Figures S4 and S7).

provided in the Supporting Information. The ca. 0.1 V shift in the effective driving force for the reaction in response to the change in solvent is yet another indication that electron transfer is the operative reaction mechanism in this chemistry, as energy transfer processes are far less sensitive to variations in solvent dielectric.

In summary, with this report we have provided the first direct evidence supporting an electron transfer mechanism in a photoredox reaction involving an iron(II)-based polypyridyl chromophore. Based on the well-documented electronic structure and dynamics of the iron complex used, this study definitively establishes that the electron transfer chemistry involves a metal-centered ligand-field excited state of the chromophore. This makes it fundamentally different from the charge transfer-based photoredox chemistry associated with chromophores of the second and third transition series more commonly employed in the photoredox catalysis community. We believe this mechanistic distinction is important insofar as the types of chemical modifications needed in order to alter the

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catalysts' photoreactivity are fundamentally different depending on whether the excited state involved is charge-transfer or ligand-field in nature. More detailed mechanistic studies, including a wider range of spectroscopic probes as well as additional iron(II)-based sensitizers designed to expand the scope of this chemistry, are currently underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08389.

Synthesis, characterization, cyclic voltammetry, spectroelectrochemistry, ground-state absorption, and transient absorption single wavelength data (PDF)

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Notes

The authors declare no competing financial interest.

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(14) It should be noted that the electronic structures and dynamics of $[Fe(tren(py)_3)]^{2+}$ and compounds such as $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ —the latter two having been employed as photoredox catalysts by several researchers (cf. ref 11)—are identical with regard to the ultrafast nature of MLCT-state deactivation (~100 fs), the identity of the ligand-field excited states that lie below the initially formed MLCT state, as well as their relative energies. The only significant difference is that the weaker ligand-field excited states. This will attenuate the redox potential associated with the ${}^{5}T_{2}$ state and thereby affect the types of reactions the photocatalyst can engage in, but not its innate reactivity. The increase in lifetime (55 ns versus ~1 ns for the ${}^{5}T_{2}$ state of $[Fe(bpy)_{3}]^{2+}$ in CH₃CN) has the added benefit of facilitating its study using the nanosecond time-scale methods employed here.

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(16) The excited state of $[Fe(tren(py)_3)]^{2+}$ is a quintet (i.e., S = 2). Since the ground states of the quinone and $[Fe(tren(py)_3)]^{2+}$ are both diamagnetic (S = 0), only an excited state of the quinone having S = 2 could engage in energy transfer and yield a process for which $\Delta S = 0$. For additional details concerning the issue of angular momentum conservation in energy transfer, see: Guo, D.; Knight, T. E.; McCusker, J. K. Angular Momentum Conservation in Dipolar Energy Transfer. *Science* **2011**, 334, 1684–1687.

(17) The quenching dynamics depend upon the thermodynamics of the reactant pair but are also a reflection of the kinetics. The latter are affected by both the driving force of the reaction and the associated reorganization energy. Conversion of high-spin Fe(II) to low-spin Fe(III), which is the process that accompanies the quenching process in question, involves a substantial change in the geometry of the sensitizer (in an electrochemical sense, this can be equated to a large overpotential for the reaction). Absent an independent measurement of one of these two parameters, we can only estimate what we consider to be an "effective" driving force. Since the same sensitizer is being used for all of the reactions, and the reorganization energy associated with reduction of the quinones should be similar, the trend in $k_{\rm q}$ will nevertheless reflect the change in the thermodynamics of the reaction.