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The Tandem Photoredox Catalysis Mechanism of [Ir(ppy)₂(dtb-bpy)]⁺ Enabling Access to Energy Demanding Organic Substrates

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ABSTRACT

We report the discovery of a tandem catalytic process to reduce energy demanding substrates, using the $[Ir(ppy)_2(dtb-bpy)]^+$ (1⁺) photocatalyst. The immediate products of photoinitiated electron transfer (PET) between 1⁺ and triethylamine (TEA) undergo subsequent reactions to generate a previously unknown, highly reducing species (2). Formation of 2 occurs *via* reduction and semi-saturation of the ancillary dtb-bpy ligand, where the TEA radical cation serves as an effective hydrogen atom donor, confirmed by nuclear magnetic resonance, mass spectrometry and deuterium labelling experiments. Steady-state and time-resolved luminescence and absorption studies reveal that upon irradiation, 2 undergoes electron transfer or proton-coupled electron transfer (PCET) with a representative acceptor (*N*-(diphenylmethylene)-1-phenylmethanamine; **S**). Turnover of this new photocatalytic cycle occurs along with the reformation of 1⁺. We rationalize our observations by proposing the first example of a mechanistic pathway where two distinct yet interconnected photoredox cycles provide access to an extended reduction potential window capable of engaging a wide range of energy demanding and synthetically relevant organic substrates including aryl halides.

INTRODUCTION

Transition metal complexes are central to recent strategies in chemical synthesis due to the breadth and ease of small molecule activation afforded under visible light irradiation.¹⁻⁹ The first examples¹⁰ and much of the recent resurgence was enabled by ruthenium(II) and iridium(III) complexes (Scheme 1a) possessing long-lived triplet excited states and tunable redox properties that allow the catalyst to be closely matched to substrate energy requirements.¹¹ In a representative photoredox cycle (Scheme 1b) using [Ir(ppy)₂(dtb-bpy)]⁺ (**1**⁺) as the catalyst, the reaction proceeds following absorption of visible light to generate the electronically excited state $\mathbf{1}^{+*}$ which is then reduced *via* electron transfer from a sacrificial donor (such as triethylamine (TEA)). This intermediate ([Ir(ppy)₂(dtb-bpy^{•-})]⁰, $\mathbf{1}^{0}$) reduces the substrate (**S**), thereby completing the cycle to re-generate the catalyst. An analogous cycle can be drawn for reactions in which the electronically excited state of the complex is first oxidized.¹

tBu



Scheme 1. Transition metal photoredox catalysis. (a) Examples of common photoredox catalysts and their relevant reduction potentials (quoted *vs* SCE; see ref. 1). ^aExcited state potentials of **1**⁺ were determined using $E_{0.0}$ values estimated from the low-temperature luminescence spectrum of **1**⁺; see Supporting Information. (b) Representative photoredox cycle involving: (i) photoexcitation of $[Ir(ppy)_2(dtb-bpy)]^+$, **1**⁺; (ii) reductive quenching of the electronically excited state **1**^{+*} by a sacrificial electron donor (TEA); and (iii) reduction of the substrate, **S**. (c) Examples of energy demanding substrates previously reported to engage in this mechanistic cycle.

The scope of any photocatalyst operating through these mechanisms is, therefore, fundamentally limited by the redox potentials of its ground and excited electronic states. Thus there is an ongoing challenge in organic chemistry to advance photocatalytic methodology beyond the inherent redox properties of the catalysts.¹² An elegant approach to extend the reduction potential of [Ru(bpy)₃]²⁺ through 'sensitization-initiated electron transfer' (senI-ET) enabled access to new substrates.¹³⁻¹⁴ Energy is transferred from the metal catalyst excited state to an intermediary species, such as pyrene, which then undergoes electron transfer with a substrate, although the exact nature of this process is

(a)

 vigorously debated.¹⁵⁻¹⁶ Reported systems where simple electron transfer between the catalyst and substrate proceeds efficiently despite being endergonic based on redox potentials are also poorly understood.¹² In substrates where hydrogen-bonding opportunities exist, this unexpected reactivity is often reconciled by concerted proton-coupled electron transfer (PCET).¹⁷⁻¹⁸ The thermochemistry of this hydrogen atom transfer process is governed by the bond dissociation free energy (BDFE), calculated using the pK_a and reduction potential. In a single reagent, these properties are often opposed, and it is not possible to alter the BDFE to match the substrate's energy requirements.¹⁹ Multisite PCET separates pK_a and reduction potential across two species, providing an effective BDFE that is now manipulatable. For example, an iridium photocatalyst acting as a reductant combined with a Brønsted acid provided access to aldehydes, ketones and imines with reduction potentials (E_p^{red}) extending beyond $-2.0 \text{ V } vs \text{ SCE}.^{20-21}$ Under conditions where hydrogen bonding is unlikely, such as the reduction of unactivated alkyl iodides ($E_p^{red} \leq -2.5 \text{ V } vs \text{ SCE}$) using photoredox catalyst 1⁺,²² the observed reactivity was tentatively ascribed to exciplex formation between the substrate and sacrificial electron donor.

We recently reported a chemoselective method for the photoredox mediated transfer hydrogenation of imines (Scheme 1b,c).²³ Stern-Volmer quenching experiments revealed the excited state of the catalyst 1⁺ is guenched by TEA and transient absorption measurements confirmed this interaction occurred via reductive quenching photoinitiated electron transfer (PET) to form the reduced complex 1⁰. The quenching of 1^{+*} by TEA was previously demonstrated in photocatalytic water reduction studies,²⁴⁻²⁵ and included in the postulated mechanisms of numerous synthetic transformations.²⁶⁻³² Subsequent oxidation of 1° back to 1^{+} was proposed to occur via electron transfer between the transition metal complex and the imine substrate,²³ despite a large difference between the formal potential of 1° ($E^{\circ'}(1^{+}/1^{\circ}) = -1.47 \text{ V vs SCE}$) and the peak potentials of the imines (e.g., $E_{p}^{\text{red}} = -2.18 \text{ V}$ vs SCE for N-(diphenylmethylene)-1-phenylmethanamine; Scheme 1c). Herein we reveal a heretofore unknown mechanistic cycle of the iridium photoredox catalyst 1^+ , in which the 1^0 intermediate is converted into a new complex characterized by a large negative shift in reduction potential. The product of this transformation is shown to undergo a dynamic PET interaction with imine substrates using both steady-state and time-resolved luminescence and absorption experiments. We propose a mechanism comprised of two distinct photoredox cycles operating in tandem and apply this system to engage energy demanding substrates. These findings have implications for the mechanistic understanding of iridium photoredox catalysis, as well as the design of new transition metal catalysts and synthetic methodology.

RESULTS AND DISCUSSION

The fate of 1⁰. Formation of a new iridium complex

During the course of investigating the spectroscopic behavior of the iridium catalyst in the presence of electron donors, we noticed that prolonged irradiation of a de-oxygenated acetonitrile solution of 1^+ (0.1 mM) and TEA (50 mM) using blue light ($\lambda_{max} = 454$ nm) gave rise to a dramatic change in the luminescence of the solution from yellow to green (Figure 1a). This change is characterized by a new intense emission displaying a large hypsochromic spectral shift and a more structured spectral profile having maxima at 489 nm and 510 nm (Figure 1a), more consistent with emission from the higher energy triplet ligand-to-ligand and metal-to-ligand charge-transfer (³LLCT and ³MLCT_(ppy)) states of 1^{+*} .³³⁻³⁵ The absence of longer-wavelength yellow emission suggests that the rapid relaxation to the

lowest-energy excited state, ${}^{3}MLCT_{(dtb-bpy)}$, of $\mathbf{1}^{+}$ is inhibited in this new species. The new green emission has a longer lifetime ($\tau = 2.22 \ \mu$ s, Figure S1) than that of $\mathbf{1}^{+*}$ ($\tau = 0.57 \ \mu$ s), indicating the excited state is likely still of triplet character. Without irradiation, the intensity of the green emission was found to diminish over time, which occurred much more rapidly if oxygen was introduced (Supporting Information; Figure S2). The lack of significant change in the absorption spectrum of the solution after irradiation (Figure 1b), other than the loss of a shoulder at 300 nm, suggests the new green emission originates from a triplet excited state of an iridium-based complex closely related to $\mathbf{1}^{+}$, but possibly with a smaller contribution of ${}^{3}MLCT_{(dtb-bpy)}$ character as reflected by the decreased radiative decay rate and increased structure in the emission spectrum.



Figure 1. (a) Luminescence spectra of 1^+ (orange curve) and a solution of 1^+ (0.1 mM) and TEA (50 mM) measured at successive 46 s intervals upon irradiation with blue light (green curves). Inset: photographs of the emission colour before and after irradiation. (b) Absorption spectra of 1^+ and TEA before (orange curve) and after (green curve) irradiation, and 1^0 (black curve) produced by bulk electrochemical reduction. Inset: spectra highlighting

the MLCT absorption bands of 1^+ and 2. (c) Transient absorption spectra of 1^{+*} (orange curve) and 2^* prepared *in situ* (green curve), recorded 0.05 µs after excitation by a pump laser pulse at 355 nm.

Some organic photoredox catalysts have been proposed to undergo consecutive photo-induced electron transfer (conPET) events allowing access to new higher energy intermediates,³⁶⁻⁴² although a recent investigation has questioned this mechanism.⁴³ To explore the possibility that this emission originated from 1⁰* formed via conPET, spectroscopic measurements were conducted on solutions of 1⁰ produced by direct electrolytic reduction of 1⁺ (Figure S3). Upon reduction, the color of the solution changed from a weak yellow to an intense orange (Figure S4), characterized by intense absorption bands at 500 and 530 nm (Figure 1b), and a weaker, broad absorption band extending beyond 800 nm. These bands were not observed in the absorption spectrum of $\mathbf{1}^+$ in the presence of TEA before or after irradiation (Figure 1b). Importantly, no luminescence was detected from the solution of 1⁰ produced electrolytically (Figure S5). Time-dependent density functional theory (TDDFT) calculations on 1^+ and 1^0 (Figure S6) produced spectra displaying similar distributions to those observed experimentally (Figure 1b), but with higher absolute energies. Moreover, the spectra from TDDFT calculations for 1⁰, 1⁻, and 1²⁺ (Figures S6-S7, and Tables S1-S4; also see supporting information for molecular orbital (MO) calculations) all showed significantly lower energy absorption bands than those observed for 1⁺ before or after prolonged irradiation in the presence of TEA (Figure 1b). These results provide compelling evidence that the green phosphorescent species is not the triplet excited state 1⁰*, but rather a new iridium-based complex that will be designated as 2 in this work.

Elucidating the identity of iridium complex 2

Confident that the observed emission is not the result of the excited state 1^{0*} , we further probed the nature of this new iridium species. The transient absorption (TA) spectrum of the triplet excited state of the new species, 2^* , displays prominent absorption bands at 370 nm and 460 nm, a broad absorption band at wavelengths >650 nm, and overlaid on these, the phosphorescence signal centered at around 500 nm (Figure 1c). The equivalent rates of decay of the TA and phosphorescence signals (Figure S8) means that the same triplet excited state is responsible for both the transient absorption and luminescence signals. The TA spectrum of 2^* closely resembles that of the triplet excited state of 1^{+*} (Figure 1c), apart from the obvious hypsochromic shift of the peak at 390 nm in the spectrum 1^{+*} which was previously assigned to absorption by the radical anion dtb-bpy^{•-}.²³ The shift in this high energy TA band to 370 nm suggests the radical anion formed in the charge-transfer excited state of 2^* is instead localized on the ppy ligands,⁴⁴ indicating that the formation of 2 involves a chemical transformation of the dtb-bpy ligand.

Electrospray ionization-mass spectrometry (ESI-MS) of 1^+ revealed a single peak (m/z 769) with a diagnostic iridium isotope pattern (Figure 2a). In contrast, analysis of a solution containing **2** prepared *in situ* displayed two major iridium-containing cations at m/z 773 and 872. Tandem MS/MS experiments revealed that both peaks correspond to different ionization states of the same parent complex (772 a.m.u.) enabling their assignment as $[2+H]^+$ and $[2+IC]^+$, where IC is an iminium cation (formed following PET from TEA to 1^{+*} ; *vide infra*). High-resolution mass spectra support these peak assignments (Figure S9). The same $[Ir(ppy)_2]^+$ fragment (m/z 501) appears in the MS/MS pathways of 1^+ , $[2+H]^+$ and $[2+IC]^+$ and is consistent with spectroscopic observations that suggest structural changes to the ancillary ligand. The charge neutrality of the resulting metal complex, as evinced by competing ionization pathways, also supports conversion of the neutral dtb-bpy into a new mono-anionic ligand.



Figure 2. (a) Selected ESI mass spectra (top to bottom) of 1^+ and 2 prepared *in situ*, and MS/MS spectra of peaks at *m*/*z* 769, *m*/*z* 773, and *m*/*z* 872. (b) Partial ¹H NMR spectra (500 MHz, CD₃CN, 298 K) of the aromatic hydrogens adjacent to the C-Ir organometallic bond of the cyclometallating ligands, following cumulative irradiation of 1^+ and TEA. Orange highlighted regions are assigned to 1^+ and green highlighted regions to **2**. Spectra following irradiation have been scaled relative to 1^+ to account for loss of signal.

A solution comprising of 1^+ (5 mM) and TEA (50 mM) subjected to increasing irradiation times was characterized by ¹H NMR spectroscopy. A significant loss of signal intensity for peaks associated with 1^+ occurs over 20 minutes of irradiation, along with the evolution of a multitude of new peaks (Figures S10-S11). The absence of peak broadening confirmed that the products are diamagnetic, and that no radical-containing species are formed on a timescale measurable using NMR spectroscopy. Focusing on the diagnostic region of the ¹H spectrum at δ 5.80–6.30 ppm (Figure 2b), assigned to the aromatic hydrogens adjacent to the organometallic C–Ir bond of the cyclometallating ligands, a single major product is formed where the original signal in 1^+ (δ 6.28 ppm) gives rise to two new signals (δ 6.13 and 6.20 ppm). The resulting nonequivalence of the two cyclometallating ligands reveals that the original C_{2v} symmetry is lost and supports non-symmetric alteration of the ancillary ligand. Analysis of a reaction mixture by high performance liquid chromatography (HPLC) confirmed the presence of byproducts suggested by NMR (Figure S12). In addition to the major green emitting species there appears to be alternative iridium complexes that exhibit similar absorption spectra to 1^+ and 2, in addition to products derived from the radical oxidation products of TEA (Figure S13).

Attempts to isolate **2** from a preparative scale reaction yielded less convoluted NMR spectra (Figures S14-S17). Removal of excess TEA, as well as its photoproducts, revealed two non-equivalent peaks (δ 0.94 and 1.31 ppm) assigned to the *tert*-butyl groups of the ancillary ligand as well as several non-aromatic hydrogen environments not present in the original metal complex (Figure S15). The presence

of nonequivalent cyclometallating ligands is further supported by the ¹³C spectrum; many of the ¹³C signals assigned to the ppy ligands appear to split into two closely related peaks (Figure S16 and S17); the signal at δ 132.5 ppm in 1⁺, assigned to the carbon adjacent to the organometallic bond, splits into two nonequivalent peaks upon conversion to 2. Homo- and hetero-nuclear 2D experiments highlight the differences between the two *tert*-butyl groups. The downfield ¹H signal (δ 1.31 ppm) shows heteronuclear HMBC correlations that are very similar to that of 1^+ (δ 30.4, 36.3, 164.5 ppm vs δ 30.4, 36.4, 165.0 ppm, respectively) while the upfield peak (δ 0.94 ppm) substitutes its downfield correlation for a significantly less deshielded carbon (δ 26.8, 32.9 and 40.0 ppm; Figure S18). This carbon signal also shows a HSQC correlation to the new ¹H multiplet at δ 1.69 ppm, revealing that the previously quaternary sp² carbon is now a tertiary sp³ center (Figure S19). This ¹H multiplet also displays COSY cross-peaks with both an aromatic peak (δ 7.63 ppm) and many of the other nonaromatic hydrogen peaks that appear in the spectrum of 2 (Figure S20-S21). These correlations strongly suggest dearomatization of the pyridine heterocycle of the ancillary ligand evidenced by the appearance of methylene (CH_2) signals. Saturation of the *tert*-butyl functionalized carbon in one pyridine ring introduces at least one stereocenter to the ancillary ligand and the resulting diastereomers ($\mathbf{1}^+$ is a racemic mixture; Δ/Λ isomerism) likely account for the multiple 2D heteronuclear correlations of the tert-butyl carbons (Figures S18-S19).

Combining all the spectroscopic and structural evidence, the reaction $1^+ \rightarrow 2$ is assigned to a loss of aromaticity and semi-saturation of the dtb-bpy ligand following the initial PET between 1^{+*} and TEA (Scheme 2a). Select examples of bipyridine dearomatization in coordination complexes exist in the literature and all feature deprotonation of the nitrogen atom.⁴⁵⁻⁴⁹ Transformation of the ancillary ligand is likely to proceed through several steps whilst introducing new stereocenters, and formation of byproducts and diastereomers as observed by HPLC and NMR is not unexpected. Irrespective of either a concerted or stepwise hydrogen atom transfer, TEA can act as a source of electrons, protons or hydrogen atoms as required. The use of TEA as an electron donor for the photo-induced reduction of 1^{+*} generates the radical cation TEA⁺⁺, which initiates either hydrogen atom transfer or deprotonation, giving the strong reductant TEA[•] (Scheme 2b).⁵⁰ This neutral α -amino radical (indirectly observed via electrochemiluminescence experiments, vide infra) may be responsible for further electron transfer to give the corresponding iminium cation IC, which is observed by both ¹H NMR and ESI-MS. Coupling of electron transfer and proton transfer in photoredox catalysis is often invoked in substrate transformations¹⁷⁻¹⁸ and a cyclometalated iridium hydride complex formed following PET with triethanolamine proved capable of CO₂ reduction.⁵¹ Deuterium labelling confirmed that TEA was the hydrogen source in the formation of **2**. Substitution with d_{15} -TEA yielded a corresponding shift in the mass of the two major species identified by ESI-MS, although peak position and isotope pattern suggested deuteration was not quantitative (Figure S22). The diagnostic ¹H NMR signals assigned to the reduced heterocycle were absent when using d_{15} -TEA although the evolution of peaks in the aromatic region was similar (Figures S23-S24).



Scheme 2. (a) Representation of the proposed dtb-bpy ancillary ligand transformation when **1**⁺ is irradiated in the presence of TEA to form the new iridium complex **2**. The generated stereocenters, leading to diastereomer formation, are labelled with *. [H] denotes formal addition of a hydrogen atom that may occur *via* one of three pathways; hydrogen atom abstraction, concerted proton and electron transfer, step-wise proton and electron transfer. (b) Triethylamine (TEA) enables all of these proposed hydrogen addition pathways following its oxidation to form the amine radical cation (TEA^{*+}).

Reductive quenchers capable of hydrogen atom transfer are necessary for the formation of **2**. Replacing TEA with closely related *N*,*N*-diisopropylethylamine and triisobutylamine resulted in the same loss of emission from **1**⁺ and growth of green emission, ascribed to **2**^{*} (Figure S25). Substitution for **1**,4-diazabicyclo[2.2.2]octane (DABCO) showed no change in emission color although quenching of the excited state **1**^{+*} was observed. The strained nitrogen bridgehead in DABCO⁺⁺ hinders both deprotonation and hydrogen abstraction therefore preventing formation of **2**. The absorption bands characteristic of the reduced photocatalyst **1**⁰ were similarly not observed, likely due to rapid back-electron transfer to the stable DABCO⁺⁺ radical (which persists for several seconds in acetonitrile).⁵² These findings indicated that an electron donor that rapidly decomposes after single-electron oxidation to products not capable of proton or H-atom transfer should result in the accumulation of **1**⁰, without generating **2**. The organic-soluble tetra-*N*-butylammonium oxalate (TBAOX),⁵³ with decomposition products of CO₂ and CO₂⁺⁻, should satisfy both of these criteria. To our delight, the irradiation of **1**⁺ and TBAOX produced significant concentrations of **1**⁰, with no conversion to **2** (Figure S26), thus providing clear evidence for the role of TEA in the formation of species **2** responsible for the green emission.

Electrochemical properties and excited state potentials

Cyclic voltammetry of $\mathbf{1}^+$ (Figure 3b, orange curve) shows reversible one-electron processes assigned to the oxidation of the iridium atom ($E^{0'}(\mathbf{1}^{2+}/\mathbf{1}^+) = 1.24 \text{ V}$ vs SCE) and reduction of the dtb-bpy ligand ($E^{0'}(\mathbf{1}^+/\mathbf{1}^0) = -1.47 \text{ V}$ vs SCE). Additional one-electron processes are observed following the first

 reduction (Figure 3b, dashed orange curve). Under cathodic potentials, 2 exhibits two distinct, quasireversible reductions at $E^{0'}(2/2^{-}) = -1.97$ V and $E^{0'}(2^{-}/2^{2^{-}}) = -2.21$ V vs SCE (Figure 3b, green curve). The position of the first peak is similar to the second reduction peak of 1⁺ (Figure 3b, dashed orange curve). The oxidation of 2 is obscured by the large excess of TEA in solution, and so an alternative approach exploiting the electrochemiluminescence (ECL) of the two complexes was devised. Essentially the reverse process to photoredox catalysis,⁵⁴ ECL is the emission of light from chemical reactions between species generated by an applied electrochemical potential.⁵⁵⁻⁵⁶ By positioning a photomultiplier tube at the flat transparent base of the electrochemical cell, we detected luminescence from a solution of 1^{+} and TEA during a potential sweep that was sufficient to oxidize both species (Figure 3c). In this case, TEA serves as a 'co-reactant', where its oxidation generates the highly reducing intermediate TEA[•] ($E^{\circ} = -1.6 \text{ V vs SCE}$,⁵⁷ Scheme 2b) capable of generating 1^{+*} upon reaction with the oxidized 1^{2+, 58-59} The onset voltage for ECL is in good agreement with the potential of 1⁺ determined by cyclic voltammetry (Figure 3b,c, orange curves). Applying the same potential sweep with 2, the onset of ECL was observed at 0.88 V vs SCE. The resultant electrochemical potential gap obtained for 2 (ΔE = 2.85 V) compared to 1⁺ (ΔE = 2.71 V) is reasonable, considering the large hypsochromic shift in emission (Figure 1a). Replacing the photomultiplier tube with a CCD spectrometer enabled the collection of ECL emission spectra, which confirmed 1⁺⁺ and 2⁺ as the source of emission in each reaction (Figure 3d).



Figure 3. Cyclic voltammograms of (a) *N*-(diphenylmethylene)-1-phenylmethanamine (**S**), (b) complexes 1^+ (orange curves) and **2** (green curve), prepared *in situ*. (c) The onset of ECL during a forward potential sweep for complexes 1^+ (orange curve) and **2** (green curve). (d) ECL emission spectra upon application of 1.4 V vs SCE for 20 s, for complexes 1^+ (orange curve) and **2** (green curve). Inset: photographs of the luminescence from the working electrode surface. The ECL spectrum of 1^+ was obtained from a solution containing 1^+ (0.2 mM) and TEA

(50 mM) prior to irradiation, and the ECL spectrum of **2** was obtained after irradiating the same solution for 20 minutes.

Excited state potentials of $\mathbf{1}^{+*}$ ($E^{\circ}(\mathbf{1}^{2+}/\mathbf{1}^{+*}) = -1.15 (\pm 0.05)$ V and $E^{\circ}(\mathbf{1}^{+*}/\mathbf{1}^{0}) = 0.92 (\pm 0.05)$ V vs SCE) were estimated using the difference in energy between the zeroth vibrational levels of the ground and excited states (E_{0-0}), approximated from low-temperature emission spectra (Figure S27-S28). These values differ from commonly quoted excited state potentials of $\mathbf{1}^{+}$ that were estimated using emission spectra measured at ambient temperature (see Supporting Information for full derivation and comparison). In conjunction with the E_{0-0} of 2.58 eV, approximated from the low-temperature emission of $\mathbf{2}$ ($\lambda_{max} = 481$ nm; Figure S29), we estimate the potentials of the electronically excited $\mathbf{2}^{*}$ at $E^{\circ}(\mathbf{2}^{+}/\mathbf{2}^{*}) = -1.70$ V and $E^{\circ}(\mathbf{2}^{*}/\mathbf{2}^{-}) = 0.61$ V vs SCE. Moreover, the observation of ECL in these experiments confirms that TEA[•] is generated under the reaction conditions employed in photoredox catalysis (where TEA is oxidized by $\mathbf{1}^{+*}$ rather than electrochemically).

The tandem photoredox catalysis mechanism

Following elucidation of the electrochemical and optical properties of 2, we explored the role of this species in the photoredox mechanism of 1^+ . A flow system that rapidly circulated solution between a photoreaction chamber and a fluorescence cuvette (Figure S3) was used to continuously monitor the concentration of 1° (λ_{abs} = 530 nm) and 2 (λ_{em} = 465 nm) during irradiation of a deoxygenated solution containing 1⁺ (0.1 mM) and TEA (50 mM). Irradiation resulted in the rapid formation of 1⁰, followed by a slow exponential decay on a timescale of minutes, with a concomitant increase in the phosphorescence intensity from 2 (Figure 4a,b). The slight decrease in phosphorescence intensity at longer times suggests that 2 may be susceptible to decomposition upon prolonged irradiation of the reaction mixture. The maximum rate of formation of 2 exhibited a non-linear relationship with respect to light intensity (Figures S30-S31), suggesting that more than one photon is required for this transformation. Upon addition of the imine substrate (S), we observed a retardation of the growth of absorption by 1⁰ and the green emission from 2* (Figure 4a,b). Notably, the characteristic absorbance of 1⁰ persisted over the full experiment timescale and emission spectra collected at the conclusion of the experiment revealed a significant concentration of $\mathbf{1}^+$ remained in the reaction mixture (Figure 4c). Efficient reduction of S by 1° is not anticipated unless invoking a PCET pathway, due to the considerable difference in the formal potential of 1^+ ($E^{0'}(1^+/1^0) = -1.47$ V vs SCE; Figure 3b) and the peak potential of the imine ($E_p^{red} = -2.18 \text{ V vs SCE}$; Figure 3a). A comparison of the reductant/acid pairs of either 1° or 2^* with TEA⁺⁺ (pK_a ~14.7 in acetonitrile⁶⁰) reveals the green emitting complex has a lower effective BDFE, 26.6 kcal mol⁻¹, compared with 31.9 kcal mol⁻¹ for **1**⁰ (Table S6). Either iridium complex results in a PCET reagent pair that may facilitate iminyl N–H bond formation (28.7 kcal mol⁻ ¹). Nevertheless, the observed evolution of green emission over time excludes the efficient reduction of **S** by a conventional photocatalytic cycle utilizing only **1**⁺.

 (i)

(ii)

(iii)

(iii)

- (ii)



Figure 4. (a) Emission intensity of 2 (monitored at λ_{em} = 465 nm) and (b) absorbance intensity of 1⁰ (monitored at λ_{abs} = 530 nm) from replicate reactions of 1⁺ (0.2 mM) and TEA (50 mM) irradiated with blue light with the addition of (i) 0 mM, (ii) 10 mM, or (iii) 50 mM of imine S. (c) Normalized emission spectra of 1⁺ (orange curve), 2 prepared in situ (green curve), and the steady state emission spectrum (blue curve) recorded at the conclusion of (iii). Exponential fits of the profiles shown in Figure 4a(i) and 4b(i) are shown in Figure S32.

Experiments were then conducted to determine if the phosphorescence of 2, prepared in situ from a de-oxygenated solution containing 1^+ (0.1 mM) and TEA (50 mM), can be quenched in the presence of S. Steady-state and time-resolved luminescence measurements resulted in linear Stern-Volmer plots with calculated quenching rate constants of 1.2 ±0.6 × 10⁶ M⁻¹ s⁻¹ and 1.6 ±0.3 × 10⁶ M⁻¹ s⁻¹, respectively (Figure 5a). These rate constants are sufficiently similar to each other to conclude that the quenching reaction is a dynamic process involving solely the electronically excited 2* and S. Conversion of S also exhibited a non-linear dependence with respect to irradiation intensity (Figure S33).



Figure 5. (a) Stern-Volmer plot of the steady-state (red) and time-resolved (blue) emission quenching of **2**, prepared *in situ*, by the imine **S**. (b) TA spectra of **2** prepared *in situ* with the addition of **S** (50 mM) recorded at various times after excitation by a pump laser pulse at 355 nm.

Transient absorption (TA) spectroscopy was used to further probe the nature of this dynamic interaction. As mentioned above, the TA spectrum of 2^* prepared *in situ* (Figure 1c) displays absorption bands at 370 nm, 460 nm and >650 nm, along with phosphorescence centered at ~500 nm. Addition of **S** to this solution resulted in a very different TA spectrum (Figure 5b). The excited state decays rapidly, as observed by the absorption bands at 460 and >650 nm, but unlike the differential spectrum of **2** in the absence of **S** (Figure S8), much of the observed absorption does not fully decay over 10 µs, or even when the measurement time was increased to 250 µs (Figure S34). This is consistent with the quenching of 2^* via electron transfer (or PCET) with the imine substrate. Increasing the concentration of TEA did not increase the decay rate of the persistent absorption ascribed to the PET product of **2**. Once quenched, the absorption band at 370 nm shifts to 390 nm, and a new band at 540 nm (Figure 5b) emerges over the first 10-20 µs before remaining constant (Figure S34), irrespective of **S** concentration. These spectral features are remarkably similar to those of 1^0 , as measured by both time-resolved spectroscopy²³ and spectroelectrochemistry (Figure 1b). These findings, in addition to the persistence of $1^*/1^0$ observed in kinetic experiments, imply a mechanistic pathway in which 2^* is able to reform 1^* .

On the basis of the accumulated evidence, we propose a mechanism comprising two interconnected photoredox cycles for the light-driven reduction of imine substrates using the catalyst/electron donor pair 1^+ and TEA. The initial PET (Scheme 3, steps (i,ii)) forms $1^0 (E^{0'}(1^+/1^0) = -1.47 \text{ V } vs \text{ SCE})$ and TEA⁺⁺. Readily reducible substrates may react with 1^0 (step (iii)) to complete a conventional photoredox cycle,

 which would prohibit the formation of **2** (step (iv)). In the case of less reducible substrates where electron transfer is thermodynamically unfavorable, hydrogen-atom transfer (either concerted or stepwise) from TEA⁺⁺ to the reduced (dtb-bpy)⁺⁻ ligand of **1**⁰ predominates to generate **2** (step (iv)). Previous examples of transition metal photoredox catalyst modification, such as the photo-initiated alkylation of homoleptic iridium complexes,⁶¹⁻⁶² typically result in complete loss of activity.

Absorption of light by 2 (step (v)) produces the excited state, 2*, which has a reduction potential $(E^{0'}(2^+/2^*) = -1.70 \vee vs$ SCE), well beyond those of 1^{+*} and 1⁰. The substrate S oxidizes 2*, *via* electron transfer or PCET process, to generate either S⁻ or SH[•] and 2⁺ (step (vi)), with 2⁺ presumably comprising iridium in the +4 oxidation state. When the imine is present, the small amount of 2 formed early in the reaction creates an effective photoredox cycle (steps (v-vii)) that continuously generates 2⁺. This oxidized intermediate ($E^{0'}(2^+/2) = 0.88 \vee vs$ SCE) reacts favorably with 1⁰ ($E^{0'}(1^+/1^0) = -1.47 \vee vs$ SCE) (step (vii)), to reform both 2 and 1⁺ in a single electron transfer (step (vii)) and results in a continuous flow of electrons between the two photoredox cycles. Although TEA is not a suitable electron donor to reduce 2⁺ (as observed by TA measurements), the concomitant reductive quenching of 1^{+*} by TEA generates 1⁰ and TEA[•] (*via* TEA^{•+}, Scheme 2b), both of which should reduce 2⁺ (step (vii)). We cannot rule out the possibility that 1⁺ is regenerated following hydrogen atom transfer from 2⁺ to acceptors such as S^{•-} or SH[•] (step (viii)). While PCET from metal complexes is a known phenomenon⁶³ it seems unlikely to occur from the semi-saturated heterocycle present in 2.



Scheme 3. Proposed interconnected photoredox mechanism: (i) Photoexcitation of $[Ir(ppy)_2(dtb-bpy)]^+$, **1**⁺; (ii) reductive quenching of the electronically excited catalyst by TEA; (iii) completion of a conventional photoredox cycle with a readily reduced substrate; (iv) generation of new catalyst, **2**, *via* (concerted or stepwise) hydrogen transfers from TEA⁺⁺ onto the dtb-bpy⁺⁻ ligand of **1**⁰; (v) photoexcitation of the new catalyst to form a more powerful reductant; (vi) reduction of substrate through oxidative quenching of the electronically excited catalyst; (vii) completion of the new catalytic cycle upon reaction with **1**⁰ (or TEA⁺); (viii) completion of the dual catalytic cycle *via* hydrogen abstraction from **2** by the reduced substrate; and finally (ix) product, **P**, formation. [H] denotes formal addition of a hydrogen atom that may occur *via* one of three pathways; hydrogen atom abstraction, concerted proton and electron transfer, step-wise proton and electron transfer. Reduction potentials for all species depicted in this scheme are compiled in Table S5.

Applicability to other energy demanding substrates

To gain further insight into the generality of the enhanced reactivity of 1^+ (*via* formation of 2), we examined the formation of aryl radicals from aryl halide precursors. Under photoredox conditions, these reactions are usually restricted to electron-poor substrates due to the limited reducing power of conventional catalysts.⁶⁴ The homoleptic Ir(ppy)₃ catalyst, for example, is known to reduce aryl iodides *via* an oxidative quenching cycle.⁶⁵⁻⁶⁶ Hydrodehalogenation and cyclization of alkyl iodides using catalyst 1^+ *via* a reductive quenching cycle using DIPEA as an electron donor has also been reported.^{22, 67} After a preliminary exploration of the mechanism, and noting the large difference in reduction potentials between various unactivated alkyl iodides ($E_p^{red} \leq -2.5 \vee vs$ SCE) and catalyst 1^+ ($E^{0'}(1^+/1^0) = -1.47 \vee vs$ SCE), the authors postulated a radical chain propagation process and exciplex formation between substrate and sacrificial amine (possibly accelerated by energy transfer from the catalyst), but they could not rule out the participation of alternative light-consuming events.

Applying our photocatalytic conditions to a range of aryl iodides, bromides and chlorides afforded the corresponding dehalogenated products in excellent yields (Table 1). The disubstituted 1-iodo-4bromobenzene was converted to the mono-substituted bromobenzene in a 93% yield, with a further 4% of the doubly reduced benzene product detected. Importantly, no product was detected in the absence of either photocatalyst 1^+ , light or TEA (Table S7). Although the irreversible reductive peak potentials of the substrates (Table S8) cannot be accurately compared to the reversible or quasireversible redox potentials of the metal complexes,⁶⁸⁻⁶⁹ we note that the excited state potential for 2*, estimated as $E^{0'}(2^+/2^*) = -1.7 \text{ V vs SCE}$, is similar to that of the well-known highly reductive photocatalyst $Ir(ppy)_3^*$ ($E^{0'}(Ir^+/Ir^*) = -1.73 \text{ V vs SCE}^1$ (Scheme 1a), so that the reductive scope of the tandem photoredox cycle (involving 1⁺ and 2; Scheme 3) extends at least to a potential similar to that of Ir(ppy)₃. We were surprised to observe excellent reactivity with highly deactivated substrates, E_p^{red} > -2.2 V vs SCE, and subsequent emission quenching experiments revealed an interaction between the excited state 2* and 4-bromoanisole ($E_p^{red} = -2.72$ V vs SCE; Figure S35). This may in part be rationalized by the fundamental error in referencing the cathodic peak potentials of organic substrate reductions compared to standard reduction potentials,⁷⁰ and the estimation of excited state potentials,⁷¹ but interactions that reduce the energy requirements of the PET cannot be ruled out.

CONCLUSIONS

Transition metal photoredox catalysts (particularly d^6 iridium(III) and ruthenium(II) complexes) have long been considered purely as electron shuttles between organic substrates. The present work reveals that this is not always the case. Irradiation of the iridium complex 1^+ , a common photoredox catalyst, in the presence of TEA leads to its chemical transformation into a new iridium-based analogue, , *via* the PET product 1^0 . The structure of 2 is distinguished by the semi-saturation of the dtb-bpy ancillary ligand, with hydrogens sourced from the trialkylamine. This new complex is capable of reducing more deactivated substrates than 1^+ , and helps explain the previously observed reactivity of substrates that possess reduction potentials inaccessible by any redox state of 1^+ . Luminescence quenching and TA spectroscopy experiments revealed that a representative imine substrate interacts solely with the excited state 2^* *via* an electron transfer process, with subsequent steps leading to the regeneration of 1^+ .

The combined evidence supports the existence of two distinct but inextricably linked photoredox cycles, allowing the engagement of substrates with a wide range of energy requirements. This is the first known example of dual oxidative and reductive photoredox cycles operating in tandem, and the utility of this pathway was further demonstrated through the efficient reduction of aryl and alkyl halides that would otherwise have been considered thermodynamically unfeasible based solely on a single cycle involving 1⁺. This work extends the understanding of the mechanism of iridium-based photoredox processes and its application in the design and development of new catalysts and synthetic methodology is currently the subject of further investigation.



Table 1. Application of 1⁺ and TEA for the reductive dehalogenation of selected aryl and alkyl halides.

EXPERIMENTAL SECTION

General. Unless otherwise stated, reagents and solvents were purchased from commercial sources and used without further purification. $[Ir(ppy)_2(dtb-bpy)]PF_6$ and *N*-(diphenylmethylene)-1-phenylmethanamine (**S**) were prepared as previously reported.²³ The organic soluble tetra-*N*-butylammonium oxalate salt was prepared as previously reported.⁷²⁻⁷⁴ Acetonitrile was distilled over calcium hydride under a nitrogen atmosphere and collected as needed. Triethylamine (TEA) was distilled over potassium hydroxide pellets under a nitrogen atmosphere and stored under nitrogen in an amber bottle.

¹H NMR spectra were recorded using a Bruker 400 Ultrashield (400 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm) and referenced to internal solvent peaks. Electrospray

ionisation-mass spectrometry (ESI-MS) experiments were performed using a Thermo Scientific Q Exactive mass spectrometer fitted with a HESI-II ion source. Positive ion electrospray mass spectra were recorded in an appropriate mass range set for 140,000 mass resolution. Samples were introduced by direct infusion using a syringe pump set at 5 μ L min⁻¹ as acetonitrile solutions. The nitrogen nebulizing/desolvation gas used was heated to 250°C, the sheath gas flow rate was set to 5 and the auxiliary gas flow rate to 0 (both arbitrary units). The spray voltage was 4.50 kV and the capillary temperature was 260°C. MS/MS experiments were performed by selecting the precursor ion and subjecting it to a normalized collision energy of 35 eV in a higher-energy collisional dissociation (HCD) cell.

UV-Vis absorbance spectroscopy. Absorption spectra were measured using a Perkin Elmer Lambda 1050 spectrometer or a Cary 300 Bio UV/Vis spectrophotometer. Transient absorption spectra were recorded using an Edinburgh Instruments LP900 spectrometer coupled with a nanosecond pulsed Nd³⁺-YAG laser (Quantel, Brio), operating at 355 nm and 10 Hz repetition rate as the excitation source.

Photoluminescence spectroscopy. Steady-state spectra were measured using a Cary Eclipse spectrofluorometer (5 nm band pass, 1 nm data interval, PMT voltage: 600 V). Spectra were corrected for the change in instrument sensitivity across the wavelength range, using a correction factor established using a quartz halogen tungsten lamp of standard spectral irradiance. Low temperature spectra were obtained using a Cary Eclipse spectrofluorometer and an OptistatDN Variable Temperature Liquid Nitrogen Cryostat (Oxford Instruments) with custom-made quartz sample holder.⁷⁵ Spectra were corrected as described above. Spectra were collected at 85 K to avoid damage to the spectroscopic cuvettes near 77 K.⁷⁶⁻⁷⁷ No difference was observed in the λ_{max} at 77 K and 85 K for complexes such as [Ru(bpy)₃]²⁺ and Ir(ppy)₃ under our instrumental conditions.⁷⁵ Additional steady-state spectra and time-resolved emission spectra were measured using an Edinburgh Instruments FLSP920 spectrometer equipped with a 378 nm pulsed diode laser excitation source. The value obtained for the lifetime of **1**⁺ in de-oxygenated acetonitrile in the present work of 0.57 µs is consistent with other reported values: 0.62 µs,⁷⁸ 0.56 µs,⁷⁹ and 0.55 µs.⁸⁰

Electrochemistry and electrochemiluminescence (ECL). The cell comprised a cylindrical glass vessel with a flat base and custom-built Teflon lid⁸¹ with holes to fit the electrodes (glassy carbon working (CH Instruments), platinum wire counter and either silver wire or 'leakless' Ag/AgCl (eDAQ) reference). The cell was housed in a light-tight Faraday cage. Potentials were applied using an Autolab PGSTAT204 potentiostat, and referenced *in situ* to the ferrocenium/ferrocene (Fc^{+/0}) couple, and converted to the reported reference (SCE) using Fc^{+/0} = +0.4 V.⁸² Freshly distilled acetonitrile with 0.1 M TBAPF₆ supporting electrolyte was used as the solvent. Electrodes were cleaned/polished prior to each experiment. The working electrodes were polished using 0.05 µm alumina powder on a felt pad with deionized water. All electrodes were rinsed with deionized water, ethanol and acetone. The solvent was degassed with nitrogen or argon for 5 minutes. Additional electrochemical experiments were conducted using the flow system described in the Supporting Information.

The intensity of light emanating from electronically excited species formed in reactions between intermediates generated at the working electrode surface were measured by positioning a photomultiplier tube (PMT) below the flat transparent base of the electrochemical cell described above. ECL spectra were measured by replacing the PMT with a collimating lens (Ocean Optics 74-UV, 200–2000 nm) vertically aligned with the face of the working electrode and fitted to an optical fiber (1.0 m length, 1.0 mm core diameter) to transfer light to an Ocean Optics QEpro CCD spectrometer. Acquisition was triggered using a HR 4000 Break-Out box in conjunction with the potentiostat. Under the configuration employed, the effective spectral resolution was 30 nm (FWHM).⁷⁶ The color of the ECL was recorded by instead positioning a Canon EOS 6D DSLR camera fitted with a Tonika AT-X PRO MACRO 100 mm f/2.8 D lens below the base of the electrochemical cell, within the purpose-built light-

tight Faraday cage. The camera shutter activation was controlled by the potentiostat *via* the configurable DIO port, using a simple transistor switch and relay to electronically control the remote shutter release.

Kinetics Measurements. Using a peristaltic pump (Gilson Minipuls 3), reaction solutions were aspirated from a photoredox chamber *via* two flow-through quartz cuvettes and returned the chamber (Figure S2). The cuvettes had three windows to enable either absorbance or photoluminescence measurements, obtained using the spectrometers above. The distance of tubing (0.8 mm i.d. PTFE) from the reaction chamber to the cuvette was 0.4 m and flow rate was 3.5 mL min⁻¹, such that solution was moved to the cuvette in 6 s. For the electrochemical reduction, a bulk electrolysis cell kit (BASi) was used. The chamber was fitted with three electrodes: a reticulated vitreous carbon working, a Pt wire counter in a fritted cell containing 0.1 M TBAPF₆ in acetonitrile, and a 'leakless' Ag/AgCl reference. To reduce 1^+ to 1^0 , a potential of -1.8 V vs SCE was applied at the working electrode.

Imine conversion as a function of light intensity was measured using a Kessil PR160 lamp (467 nm, 40 W) operated at different power settings. Reagents were combined in acetonitrile in a septum capped sample vial, degassed for three minutes and then irradiated for 15 minutes. Substrate conversion was determined by ¹H NMR spectroscopy. Reported values are the average of duplicate runs.

Photoredox catalysis screening. Reactions were performed using a custom-built blue LED photoreactor. The reactor was comprised of a rectangular metal frame (100 mm × 110 mm) with 14 blue LEDs (2 × SP-02-V4 LED assembly, each consisting of 7 LXML-PR02-A900 RoyalBlue LUXEON Rebel ES LEDs; the spectral output of the LEDs spans the 400–500 nm range with a maximum intensity at 447 nm. www.luxeonstar.com). The photoreactor was fitted with PC cooling fans and heat sinks for temperature control (internal temperature of the reactor typically reaches 27±5°C overnight). The power of the light source can be varied using an intensity control. The emission output of the light source used was measured using a Princeton Instruments PIXIS 1024BR CCD Detector. The measurement was conducted by shining the LED light indirectly into the aperture of the detector. The dependence of product formation as a function of light intensity was performed using a standard PR-160-456 Kessil® lamp with four levels of intensity control (www.kessil.com). Additional photoredox catalysis experiments were conducted using the flow system described in the Supporting Information.

General method for reductive dehalogenation of organohalides. The appropriate aryl or alkyl halide (0.1 mmol) and [Ir(ppy)₂(dtb-bpy)]PF₆ (1.5 mol %) were placed in a 4 mL pressure relief vial and dissolved in deuterated acetonitrile (1 mL). Triethylamine (1.0 mmol) was added, and the reaction mixture sparged with N₂ for 10 min at 0°C to avoid evaporation of volatile materials. The cap was wrapped with Teflon tape and parafilm, and the reaction mixture stirred at room temperature for 16 hours, whilst being irradiated with 40 W blue LED light. Sulfolene (0.1 mmol) was added as an internal standard and the reaction mixture analysed directly by ¹H NMR spectroscopy (see supporting information for representative spectra). Control experiments were prepared according to the same procedure without the inclusion of the appropriate reagent (photocatalyst, amine or light). These reaction mixtures were analysed directly by ¹H NMR spectroscopy using 2,5-dimethylfuran (0.1 mmol) as an internal standard (*see* Figures S36-S37).

Computational approach. DFT calculations were carried out within the Gaussian 16 suite of programs.⁸³ Ground state singlet and triplet geometries as well as redox states were optimized in the presence of solvent with the mPW1PW91 functional⁸⁴ in conjunction with the def2-SVP basis set and associated core potential.⁸⁵ Frequency calculations were performed at the same level of theory and confirmed that all structures are minima with no imaginary frequencies. The polarizable continuum model (PCM)⁸⁶ self-consistent reaction field (SCRF) was used to model solvent effects with Truhlar's SMD solvent model,⁸⁷ with a solvent of acetonitrile for consistency with the experimental system.

Molecular orbitals were calculated with BP86⁸⁸⁻⁸⁹ and a def2-TZVP basis set (Tables S9-S11 and Figure S38), which has been shown to produce reliable results.^{76,90} Molecular orbital analysis was carried out with the QMForge program.⁹¹ TD-DFT calculations were performed with the long-range corrected method ω B97XD⁹² in conjunction with the def2-SVP basis set.

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SUPPORTING INFORMATION

Description of equipment, extra experimental data and numerical calculations

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Table of Contents Image



