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PCET-Based Ligand Limits Charge Recombination with an Ir(III) Photoredox Catalyst

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ABSTRACT: Upon photoinitiated electron transfer, charge recombination limits the quantum yield of photoredox reactions for which the rates for the forward reaction and back electron transfer are competitive. Taking inspiration from a proton-coupled electron transfer (PCET) process in Photosystem II, a benzimidazole-phenol (BIP) has been covalently attached to the 2,2'-bipyridyl ligand of [Ir(dF(CF₃)-ppy)₂(bpy)][PF₆] (dF(CF₃)ppy = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; bpy = 2,2'-bipyridyl). Excitation of the [Ir(dF(CF₃)ppy)₂(BIP-bpy)][PF₆] photocatalyst results in intramolecular PCET to form a charge-separated state with oxidized BIP. Subsequent reduction of methyl viologen dication (MV²⁺), a substrate surrogate, by the reducing moiety of the charge separated species demonstrates that



the inclusion of BIP significantly slows the charge recombination rate. The effect of \sim 24-fold slower charge recombination in a photocatalytic phthalimide ester reduction resulted in a greater than 2-fold increase in reaction quantum efficiency.

INTRODUCTION

Photosynthesis has transformed the Earth and has the potential to sustainably contribute to global energy resources. One step toward a sustainable chemical industry would be to develop solar energy sources for the myriad chemical processes that are essential to the global chemical enterprise.¹ Photoredox catalysis offers an opportunity to use solar energy to replace or augment thermal energy and provide the necessary potential to drive starting materials along their reaction coordinates to form the desired products. In a photoredox catalytic cycle, photoinduced electron transfer between photocatalyst excited state and the substrate promotes the catalytic generation of reactive radical intermediates under mild conditions. This has resulted in the widespread adaptation of photoredox protocols into a variety of catalytic contexts, enabling chemistry that is often unattainable using classical conditions and reagents.²

However, many transformations in contemporary photoredox catalysis are limited in either scope or quantum efficiency by charge recombination between the nascent radical (or radical ion) and the oxidized/reduced form of the photocatalyst.^{3,4} Charge recombination (CR) following excited state electron transfer in bimolecular processes often proceeds at a rate close to the diffusion limit (Figure 1A).^{5–7} Accordingly, the rate of the forward reaction must be sufficiently fast to be kinetically competitive for a substantial yield of product. One strategy to favor the product-forming pathway over recombination would be to introduce processes that slow recombination and therefore increase the lifetime of the substrate radical/radical ion. This principle was demonstrated in a spectroscopic study of a photoredox-catalyzed hydroamidation reaction.³ In this particular reaction, the joint action of the excited state of an Ir(III) polypyridyl photosensitizer and Brønsted base homolyzes the strong N-H bond of an N-aryl amide. Although the radical generation in this system was highly efficient (quenching yield of $\sim 90\%$), the overall quantum efficiency was limited by a majority of the amidyl radical intermediate undergoing a charge recombination process. It was then demonstrated that the addition of a disulfide additive led to the reversible trapping of the amidyl radical, disfavoring charge recombination pathways and resulting in a 4-fold improvement in the reaction quantum yield. The use of additives is an elegant solution to specific instances of poor quantum efficiency; however, a more general approach to increasing the lifetime of the reactive radical/ radical ion would be to introduce processes as part of the catalyst that would slow charge recombination with the oxidized/reduced photocatalyst. This strategy could expand the scope of numerous photocatalytic methods that are currently limited by charge recombination dynamics.

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Figure 1. (A) Charge recombination (CR) in photoredox catalysis can be competitive with the forward reaction to produce product B from substrate A. (B and C) Precedent bioinspired constructs bearing a benzimidazole-phenol (BIP) platform. (D) Structural modification of an iridium-based photocatalyst with BIP can limit charge recombination.

Our design strategy is inspired by photosynthesis, where nature employs a series of redox relays to transfer the oxidizing (h^+) and reducing (e^-) equivalents generated upon photo-excitation and charge separation to their respective catalytic sites. These redox relays are the essential components of a series of short-distance, fast redox-equivalent transfer steps that

effectively compete against charge recombination. They promote the efficient (high-yield) transport of redox equivalents over nanoscale distances by optimizing both the Marcus-type electronic coupling and thermodynamic factors so that the forward transfer of redox equivalents is favored over recombination at each step.^{8–10} An illustrative example of such

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a redox relay is the hydrogen-bonded tyrosine-histidine (Tyr_z-H190) pair located in Photosystem II (PSII).¹¹ Sunlight generates the excited state of the reaction-center (P_{680}^*) in PSII, which then reduces a nearby chlorophyll (Chl), forming an intermolecular charge-separated state, $P_{680}^{\bullet+}$ -Chl^{$\bullet-$}. This high energy state is responsible for the light-driven electron transfer reactions needed for water splitting, but it is simultaneously susceptible to charge recombination.^{12,13} To avoid recombination and to move the oxidizing equivalent closer to the site of water oxidation, Tyr_z , with its hydrogenbonded partner H190, rapidly fills the hole on $P_{680}^{\bullet+}$ using a proton-coupled electron transfer (PCET) process.

Inspired specifically by the function of the Tyr_z-H190 pair in PSII, model systems have been developed for charge transport, utilizing charge-separated states.^{14,15} These systems include a benzimidazole-phenol (BIP, see Figure 1B) platform which features PCET mimicking the Tyr_z-H190 pair.^{16–18} By incorporating the BIP as an electron transfer mediator, Zhao et al. have shown an improvement in the quantum yield for water splitting using dye-based systems, which is generally low because the charge recombination reaction is faster than the catalytic four-electron oxidation (Figure 1B).¹⁹

In the design of PSII mimics, the incorporation of a hydrogen-bonded, phenol-imidazole pair into the ligand framework of a heteroleptic Ru(II) photosensitizer was shown to similarly impede charge recombination (Figure 1C).²⁰ Emission from the ³MLCT state of Ru(II) complexes with coordinated imidazole-phenol pairs occurs at identical energies and with the same quantum yields as control complexes lacking the PCET ligand, indicating PCET does not occur in the excited state.²⁰ However, upon addition of methyl viologen dication (MV²⁺), electron transfer from the ³MLCT excited state of a similar Ru(II) complex to MV²⁺ generates an oxidized Ru(III) species.²¹ Rapid PCET from the coordinated imidazole-phenol pair fills the hole on Ru, effectively slowing charge recombination between Ru(III) and MV^{•+}.

However, these concepts and their attendant advantages are less explored in general photocatalytic organic synthesis, and we questioned whether BIP appended to an Ir(III) photosensitizer could play a similar role in h⁺ transfer, effectively delaying charge recombination and extending the lifetime of the substrate radical (Figure 1D). When compared to ruthenium photocatalysts, iridium photocatalysts offer greater stability and tunability of photophysical properties, due to larger ligand field splitting and the ease with which they support cyclometallating C-N ligands (such as 2-phenylpyridine, ppy).²² There are two possible mechanisms by which the appended BIP can slow charge recombination. If BIP oxidation is thermodynamically capable of quenching the Ircomplex ³MLCT state, intramolecular PCET will result in a charge-separated state (³CS), leaving a positive charge localized on BIP. On the other hand, BIP can be oxidized by Ir(IV), formed by electron transfer to the substrate from the ³MLCT, as is the case in the aforementioned Ru(II)complexes.

We report herein an Ir(III) complex (Figure 2, photocatalyst 2) inspired by the Tyr_z-H190 redox relay of PSII. Electrochemical, spectroscopic, and computational characterization demonstrates that excitation of 2 with blue light rapidly produces an intramolecular, triplet charge separated state (Figure 1D, middle). Characterization of charge recombination kinetics with MV^{2+} quencher illustrates that 2 slows charge

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Figure 2. Chemical structures of cyclometalated Ir(III) photocatalysts in this study.

recombination in the intermolecular charge separated state of oxidized photocatalyst 2^+ and $MV^{\bullet+}$, when compared to an Ir(III) photocatalyst without an appended BIP (photocatalyst 1). These results are then extended into preparative-scale photoredox catalysis, where quantum yield enhancement is observed with photocatalyst 2 in the reduction of redox-active *N*-hydroxyphthalimide esters (NHPI esters).

RESULTS AND DISCUSSION

Synthesis. The Ir(III) photocatalysts 1 and 2 were synthesized in accordance with previous reports.^{23,24} We hypothesized that the electron-withdrawing ppy ligands were necessary for efficient oxidation of the BIP. The complete synthetic route, conditions, and structural characterization of the BIP-bipyridine ligand (**BIP-bpy L**) and photocatalysts 1 and 2 are described in the Supporting Information (SI 1.2).

Steady-State Absorption and Emission. The photophysics of photocatalyst 2 are intriguingly distinct from those of the reference photocatalyst 1. The electronic absorption and emission properties of photocatalysts 1 and 2 are summarized in Table 1. The absorption spectra of 1 and 2 feature $\pi\pi^*$

Table 1. Electronic Absorption and Emission of 1 and 2

photocatalyst	$\lambda_{\max}^{abs}/nm \ (\varepsilon/M^{-1} \text{ cm}^{-1})^a$	$\lambda^{\rm em}/{\rm nm}^{a,b}$	$\Phi^{\mathrm{em}a,b,c}$	$\lambda^{\rm em}/{\rm nm}^d$
1	380 (5100)	498	0.90	460
2	370 (18000)	515	0.0060	570
^{<i>a</i>} In CH ₃ CN at	room temperature. ^b Ir	n deoxygenate	d solvent.	^c Relative

to $Ir(ppy)_3$. ^{*d*}In 4:1 MeOH:EtOH glassy matrix at 77 K.

transitions in the UV and a lowest energy transition in the near-UV assigned as a mixed ligand centered (LC) (ppy $\pi \rightarrow \pi^*$) and Ir(d) \rightarrow ppy(π^*) transition (Figure S9).²⁵ The electronic absorption and emission spectra of 1 are consistent with literature reports.^{23,26} Emission quantum yields were determined relative to Ir(ppy)₃ ($\Phi = 0.97$ in MeTHF).²⁷ The emission quantum yield of 2 is approximately 2 orders of magnitude lower than that of 1, indicating quenching of the emissive excited state (Figure S10). Addition of 10 mM phenylphosphoric acid to 2 increases the emission quantum yield to 0.70 (Figure S11). Protonation of the imidazole proton acceptor in acidic solution prevents intramolecular PCET. The emission recovery upon acid addition suggests PCET quenches the emission of 2.

Electrochemistry. Cyclic voltammetry experiments were performed in degassed acetonitrile solution to gain insight into the electrochemical parameters of 2 compared with 1. Figure 3 displays cyclic voltammograms of 1 and 2 and Table 2 summarizes the most relevant electrochemical parameters. For

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Figure 3. Cyclic voltammograms of **2** (green trace) and the reference photocatalyst **1** (blue trace). Experimental conditions: 1 mM of the photocatalyst, 0.1 M nBu₄NPF₆ supporting electrolyte in dry CH₃CN. WE: glassy carbon. Pseudo RE: Ag wire (ferrocene as internal reference). CE: Pt wire. Scan rate, 100 mV s⁻¹.

Table 2. Electrochemical Potentials of Photocatalysts 1 and2 and Uncoordinated BIP-bpy L

photocatalyst	$\begin{array}{c} E_{1/2} [\mathrm{Ir}^{\mathrm{IV}} / \mathrm{Ir}^{\mathrm{III}}]^{a} \\ [\Delta E] \end{array}$	$\begin{array}{c} E_{1/2} [BIP^{\bullet +}/BIP]^{a} \\ [\Delta E] \end{array}$	$\begin{array}{c} E_{1/2} [\mathrm{bpy^0/bpy^-}]^a \\ [\Delta E] \end{array}$
1	1.35 [90 mV]	n/a	-1.64 [60 mV]
2	1.24 ^b	0.72 [60 mV]	-1.62 [60 mV]
BIP-bpy L ^c	n/a	0.71 [110 mV]	-1.99 [380 mV]
a_ •	h-		

^{*a*}Reported in V vs Fc⁺/Fc. ^{*b*}Reported potential for the anodic peak current of an irreversible oxidation. ^{*c*}Cyclic voltammogram shown in Figure S12.

2, a reversible one-electron reduction wave is observed ($E_{1/2}$ = -1.62 V vs Fc⁺/Fc, $\Delta E_{\rm p} = 60$ mV), which corresponds to adding an electron to a bipyridyl π^* orbital.^{26,28} This value is 20 mV more positive than 1 ($E_{1/2} = -1.64$ V vs Fc⁺/Fc, $\Delta E_p =$ 60 mV), suggesting that the covalent linkage of the BIP moiety on the periphery of the photocatalyst does not significantly affect the ligand-based bpy0/- redox couple. On the other hand, a reversible one-electron oxidation wave at 0.72 V vs Fc^+/Fc ($\Delta E_p = 60$ mV) is observed for 2 and is assigned as the phenoxyl radical/phenol couple of the attached BIP. This anodic couple of $\hat{2}$ occurs at a less positive potential than the value expected for the one-electron Ir^(IV/III) couple (removal of an electron from the Ir-based HOMO with mixed molecular orbital contributions from phenyl-pyridine π orbitals),^{26,28} which is observed for 1 at 1.35 V vs Fc⁺/Fc ($\Delta E_p = 90$ mV). In the case of 2, the phenol oxidation is coupled with proton transfer to the proximal nitrogen of the benzimidazole moiety through an intramolecular PCET process. The observed $E_{1/2}$ value for the phenoxyl radical/phenol couple in 2 is anodically shifted relative to the $E_{1/2}$ for the BIP model not covalently linked to a bipyridine $(E_{1/2} = 0.59 \text{ V vs Fc}^+/\text{Fc})$,²⁹ consistent with the electron withdrawing effect of bipyridine which makes the phenol moiety harder to oxidize. Moreover, an irreversible feature at ~1.24 V vs Fc^+/Fc was found (Figure S14); this oxidation process is assigned most likely to the metal center (Ir^(IV/III) couple).

Visible Transient Absorption Spectroscopy. The photophysics of 1 and 2 were examined with visible and mid-IR transient absorption spectroscopy. All transient

absorption experiments were performed in deoxygenated acetonitrile with $\lambda^{irr} = 400$ nm, and data were analyzed using Glotaran analysis.³⁰ The visible spectroelectrochemistry spectra of 1 and 2 are provided in Figure S15.

Excitation of 1 produces an excited state species with absorption at 476 nm and two decay components. The first component has a 1.5 ps lifetime, assigned as vibronic relaxation within the ³MLCT_{ppy} excited state (Figure 4A). A ppy(π^*) \rightarrow bpy(π^*) ligand-to-ligand charge transfer (LLCT) transition on the picosecond time scale has been reported for several cyclometalated Ir(III) complexes.^{31–33} However, a spectroscopic shift that would indicate a LLCT transition was not observed in the excited state absorption of 1. Transient absorption spectroscopy with the homoleptic complex Ir-(dFppy)₃ (dFppy = 2,4-difluorophenyl-2-pyridyl) reveals similar excited state absorption to that of 1 (Figure S25). The lowest energy excited state of 1 is thus assigned as the ³MLCT_{ppy} state (Figure 4C). The ³MLCT_{ppy} state of 1 has a 2.3 μ s lifetime in acetonitrile, coinciding with relaxation back to the ground state in close agreement with literature values.^{34,35}

Distinct excited state absorption features are observed upon excitation of photocatalyst 2. Excited state absorption features with maxima at 522 and 553 nm and broad absorption between 600 and 740 nm rise with $\tau_1 = 1.8$ ps (Figure 4B) and decay to the ground state with $\tau_2 = 220$ ns (Figure S27). The isosbestic point at 495 nm indicates a transition between two excited states and is assigned to the LLCT transition (Figure 4C). A similar spectrum with maximum absorption at 499 and 530 nm was reported upon photoreduction of 1 by benzothiophene in acetonitrile.³⁴ The red-shift between the excited state absorption of 2 and reduced 1 is expected with the increased aromatic conjugation provided by BIP covalently linked to bipyridine. Similar red shifts are observed upon increased aromatic conjugation of the polypyridyl ligand in other $[Ir(ppy)_2(NN)]^+$ complexes.³³ The similarity of the transient absorption spectra of 2 with the spectrum of reduced 1 indicates that the negative charge resides in the bpy(π^*) LUMO. A LLCT transition was detected in the complex [Ir(dF(CF3)ppy)2(deeb)][PF6] (deeb = 4,4'-diethylester-2,2'-bipyridyl) using time-resolved IR spectroscopy.²⁸ The extended conjugation of the bipyridyl ligand on 2 likely facilitates the LLCT. The excited state dynamics of 2 are summarized in Figure 4D.

Infrared Spectroelectrochemistry and Time-Resolved Infrared Spectroscopy. The previous section underlined the effect of linking the BIP moiety to the photocatalyst: ultrafast quenching of the ³MLCT_{ppy} excited state by BIP oxidation, resulting in a charge-separated state. Spectroscopic evidence of this charge separation, which ultimately leads to the benzimidazole protonation via intramolecular PCET, is also shown by time-resolved infrared (TRIR) spectroscopy and supported by infrared spectroelectrochemistry (IRSEC). Infrared spectroelectrochemistry (IRSEC) is valuable to follow the changes in the vibrational modes associated with both the reduced and oxidized forms of transition metal photocatalysts. The difference IR spectra taken under oxidative and reductive polarization as well as the recorded IR spectra collected stepwise in both electrochemical conditions for complexes 1 and 2 are shown in Figures S16 and S17, respectively. The difference IR spectra of oxidized and reduced forms are instrumental to the interpretation of the time-resolved infrared (TRIR) spectra (Figure 5); similar pattern in the band



Figure 4. (A) Evolution associated difference spectra obtained from global analysis fits of visible transient absorption spectra of 1 and (B) 2 in CH₃CN. λ^{irr} = 400 nm, 130 μ J/cm². (C) Jablonski diagrams depicting excited state dynamics of 1 and 2. (D) Summary of photophysical steps involved in the formation of the ${}^{3}CS_{bpv}$ state of 2.

evolution in the TRIR spectra is observed. Small differences between TRIR and IRSEC experiments are expected in the frequency and intensity of the bands, since certain transitions associated with the excited states cannot be replicated through electrochemical means.³⁶ Control IRSEC experiments performed with 1, without the pendant BIP moiety, show practically no changes in the region of interest (1550-1500 cm^{-1} , Figure 5A), in concordance with the featureless broad absorption observed in the TRIR spectra (Figure 5C). The ground state IR spectrum of 2 in CD₃CN (Figure S17A, black trace) resembles the ground state IR spectrum reported for an analogous Ir(III) complex, in which the only structural difference is the presence of ethyl ester groups at 4 and 4' positions of the bipyridine ligand instead of BIP.²⁸ In photocatalyst 2, distinguishing bands are present at the ring stretching region; the experimental frequencies together with their assignments are detailed in Table S1.

Upon electro-oxidation of 2, new bands appear consistent with formation of phenoxyl radical and protonation of benzimidazole nitrogen through intramolecular PCET. Among them, the band at 1556 cm⁻¹ is associated with the NH in-plane bending mode of the benzimidazolium ion, and the slight shift of the ν (C==N) of the benzimidazole to lower energy is expected upon protonation.³⁷ The bands located at 1622 and 1620 cm⁻¹ in the IRSEC difference spectra and TRIR spectra, respectively, are assigned to the imidazole C==N stretching mode and suggest proton transfer from the phenol.

The phenoxyl radical is characterized by the $\nu_{7a}(C-O)$ mode located at 1515 cm⁻¹, and it occurs at a similar frequency as that observed for other substituted phenoxyl radicals.^{38,39} In the TRIR spectra of 2 (Figure 5D), the frequency of this mode is found at $\sim 1521 \text{ cm}^{-1}$ and the upshift suggests a weaker hydrogen bond in the ³CS state. The bands at 1620 and 1521 cm⁻¹ signaling proton transfer and electron transfer, respectively, are evident in the TRIR spectra within 400 fs following excitation with a pulse centered at 400 nm. This spectrum is assigned to the radical cation of the BIP formed by an ultrafast PCET process (<400 fs) in which the transfer of an electron from the phenol to reduce Ir(IV) to Ir(III) is coupled to the transfer of the phenolic proton to yield the benzimidazolium cation. Intramolecular PCET quenches the ³MLCT_{ppy} excited state in less than 400 fs to yield the ³CS_{ppy} species observed in the TRIR spectrum at 400 fs (Figure 5D). Following the LLCT transition, the TRIR spectrum is similar to that observed by IRSEC (Figure 5B) and is assigned to the ³CS_{bpv} state. This species further cools to yield the spectrum taken at 7 ns.

Density Functional Theory Calculations. To gain further qualitative insight into the nature of the excited states of 1 and 2, density functional theory calculations were carried out using the Gaussian 16 software package.⁴⁰ Calculations were performed with either the unrestricted B3LYP, CAM-B3LYP, or wB97XD functional and with the 6-311G+(d,p)/



Figure 5. (A) Sum of IRSEC difference spectra upon positive and negative polarization of 1, (B) sum of IRSEC difference spectra upon positive and negative polarization of 2, (C) TRIR spectra of photocatalyst 1, and (D) TRIR spectra of photocatalyst 2 in CH₃CN, $\lambda^{irr} = 400$ nm, 3 μ J.

LanL2DZ (Ir) split basis set, in an acetonitrile polarizable continuum solvent model. The full details of these methods can be found in the SI. Across all three functionals, optimization of the lowest energy triplet stationary point of 2 shows that the photocatalyst has undergone intramolecular PCET, consistent with the ${}^{3}CS_{bpy}$ state (Figure S52). Visualization of the spin density and comparison of the change in charge on each atom between the two states using natural population analysis supports a structure where the phenol has been oxidized and the bipyridyl has been reduced. In contrast, calculations show that the lowest energy triplet stationary point of 1 has significant spin density on the ppy ligand (Figure S49), consistent with our assignment of the lowest energy excited state of 1 as the ${}^{3}MLCT_{ppy}$ state.

Limited Charge Recombination. The ability of the BIP ligand to limit charge recombination in 2 upon photoinitiated electron transfer to methyl viologen dication (MV^{2+}) was investigated with transient absorption spectroscopy. Solutions of 1 and 2 were absorbance-matched in a 3.3 mM stock solution of MV^{2+} . Photocatalysts 1 and 2 both undergo photoinitiated electron transfer to MV^{2+} upon $\lambda^{irr} = 400$ nm in CH₃CN. Formation of the characteristic $MV^{\bullet+}$ spectrum was observed on the nanosecond time scale (Figures S35 and S36). Charge recombination between the methyl viologen radical cation and the oxidized catalyst (1⁺ or 2⁺) was monitored as a function of 607 nm absorption ($\varepsilon = 13\,900\,M^{-1}\,cm^{-1}$),⁴¹ beginning at 1 μ s, after the decay of the excited state absorption. The second order rate constant for charge

recombination, k_{CR} , was determined to be 2.2 × 10¹⁰ M⁻¹ s⁻¹ with photocatalyst 1 and 2.9 × 10⁹ M⁻¹ s⁻¹ with photocatalyst 2, indicative of a 7.6-fold decrease (Figure 6).



Figure 6. Second order kinetic plots with the inverse methyl viologen radical cation concentration determined from the decay of absorption at 607 nm with 1 or 2 absorbance-matched and 3.3 mM MV^{2+} in CH_3CN . $\lambda^{irr} = 400$ nm, 500 μ J/cm².

For photocatalyst 1^+ , the 1.80 V driving force for recombination is significantly greater than the 1.17 V driving force for charge recombination to 2^+ . The approximately order of magnitude difference in $k_{\rm CR}$ is likely due to the difference in driving force for charge recombination from MV^{•+} (MV^{2+/•+} = -0.85 V vs Fc⁺/Fc)⁴² to the oxidized photocatalyst and to the

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Figure 7. (A) Photoinduced electron transfer to *N*-hydroxyphthalimide ester **F** generates radical anion $\mathbf{F}^{\bullet-}$ that can either fragment to form product or undergo charge recombination with oxidized photocatalyst. (B) Comparison of reaction rate and quantum yield in the reduction of **F**, catalyzed by either photocatalyst **1** or **2**. Conditions: 0.3 mmol **F** (1.0 equiv, 0.1 M THF); photocatalyst OD_{440 nm} = 1.1; 1.0 equiv. thiophenol; 40 W, 440 nm Kessil lamp with attached 440 nm bandpass interference filter, fwhm of 10 nm; 25 °C. Product yield determined by GC-FID with an internal standard. Quantum yield calculated by average of two trials.

different recombination mechanisms, requiring ET with 1 and PCET with 2.

Encouraged by these results with MV²⁺ substrate surrogate, we sought to determine whether the slower second-order rate constants for charge recombination between MV⁺⁺ and 2⁺ relative to 1⁺ might also lead to improved quantum yields in preparative photoredox reactions. To this end, we designed a simple model system involving the reduction of a redox-active phthalimide ester (F, Figure 7A). N-Hydroxyphthalimide esters have enjoyed renewed interest in the field of organic synthesis as convenient precursors for alkyl radicals under reducing conditions.⁴³⁻⁵⁰ As illustrated in Figure 7A, an alkyl radical F• is generated via the loss of carbon dioxide and phthalimide anion following single-electron reduction of the phthalimide moiety. It has previously been suggested that the addition of a proton donor may accelerate the rate of fragmentation.^{43,51} However, without a proton donor in solution, we hypothesized that fragmentation may be in kinetic competition with charge recombination, and thus may serve as a platform to test our key hypothesis. Solutions of F containing either 1 or 2 in THF were absorbance-matched at 440 nm. Upon irradiation of these solutions with a 440 nm light source and in the presence of a thiophenol hydrogen-atom donor, we observed that the initial rate using photocatalyst 2 was more than twice as fast as an otherwise identical reaction using photocatalyst 1 (Figure 7B). The photon flux of the light source used for these reactions was determined using potassium ferrioxalate actinometry. The internal quantum yields are $(4.9 \pm 0.1) \times 10^{-3}$ for photocatalyst 2 and $(2.3 \pm$ 0.3) \times 10⁻³ for photocatalyst 1. A similar quantum yield increase was observed when reactions were irradiated with a 456 nm broadband light source, after adjusting for the

difference in extinction coefficients between the two photocatalysts (see SI for details).

Charge recombination from $F^{\bullet-}$ to oxidized photocatalyst is undoubtedly highly exergonic, with more driving force in the case of 1, but under standard cyclic voltammetry conditions the reduction of **F** is irreversible, making it impossible to assign a midpoint potential for the $F/F^{\bullet-}$ couple. For the improvement in reaction quantum yield to arise from a comparatively longer-lived $F^{\bullet-}$ intermediate, the decrease in charge recombination rate for 2 compared to 1 should result in a higher fraction of $F^{\bullet-}$ fragmenting to F^{\bullet} . To support this hypothesis, we ideally need to compare the rate constant of fragmentation with the two rate constants of charge recombination for the two photocatalysts. We estimated the first-order rate constant of $\overline{F^{\bullet-}}$ fragmentation using voltammetric methods (see the SI for details). By measuring the change in peak cathodic potential as a function of scan rate, the estimated rate constant of fragmentation was calculated to be $(8 \pm 5) \times 10^5$ s⁻¹. This range of values results from uncertainty in the half-wave potential for the reduction of F.

Transient absorption experiments with 1 or 2 and F (0.1 M) were conducted to determine charge recombination rate constants (Figure S42 and S43). However, recombination rate constants were not obtained because neither the photocatalyst ground state bleach nor $F^{\bullet-}$ absorption are discernible in the visible spectrum. The ³MLCT excited state lifetime of 1 is 2.2 μ s in THF and is quenched to 1.3 μ s in the presence of F (Figure S44). The ³CS state lifetime of 2 is 296 ns in THF and is reduced to 279 ns with F (Figure S44). The lifetime differences with and without F were used to calculate observed rate coefficients, k_{obs} , for photoinitiated electron transfer; $3.15 \times 10^5 \text{ s}^{-1}$ with 1 and $2.06 \times 10^5 \text{ s}^{-1}$ with 2 (SI page S39). Using the measured quantum yields of final

fraction of $\mathbf{F}^{\bullet-}$ to successfully fragment. An additional consideration for accurate comparison of the two reaction quantum yields is that fragmentation of F must be the turnover-limiting step whether photocatalyst 1 or 2 is used. In this regard, initial rates for the reactions of both photocatalysts were found to exhibit a zero-order kinetic dependence on the concentration of the thiophenol reductant. suggesting that the HAT and photocatalyst turnover steps are not kinetically relevant (Figure S67). Furthermore, we observed an insignificant difference in the measured solvent kinetic isotope effect between reactions with either 1 or 2 $(k_{\text{THF}}/k_{\text{d8-THF}} = 1.2)$, indicating that the solvent (THF) does not play a key kinetic role in these reactions (SI page S86). Finally, the measured reaction rate was found to be linear with respect to light intensity for both photocatalysts, suggesting that two-photon processes are not operative in this reaction (SI page S89). These observations are all consistent with fragmentation being the turnover-limiting step in the process, and with the notion that competition between fragmentation and charge recombination is likely a key determinant in the overall quantum efficiency. Accordingly, we hypothesize that the improved performance of 2 is a direct result of its slower charge recombination kinetics, which leads to more productive fragmentation from a comparatively long-lived F^{•-} intermediate.

recombination rate occurred, allowing a significantly larger

CONCLUSIONS

The strategy described here is a general method for the improvement of photoredox reaction quantum efficiency. By introducing a bioinspired PCET-based process as an intrinsic component of photocatalyst 2, the dynamics of the yieldlimiting charge recombination process in the catalytic cycle are altered via the formation of a well-characterized triplet chargeseparated state. The modified charge recombination process resulted in a 10-fold reduction in the second-order rate constant for charge recombination between reduced methyl viologen and oxidized photocatalyst, as well as doubling the quantum yield of a preparative-scale photoredox reaction. This observed improvement in photocatalyst performance is particularly remarkable, given the shorter lifetime of the triplet charge-separated state (2^*) compared to the standard photocatalyst (1^*) , and the charge recombination rate in the preparative-scale reaction is slowed ~24-fold using 2. Studies are ongoing to further understand the nature of the charge separation and charge recombination processes on photocatalyst 2, as well as to further improve the performance of 2 and the BIP-based platform in preparative scale reactions. These results provide further evidence that PCET is a useful blueprint for improving intermolecular charge-separated state lifetimes, and we anticipate that this approach can be extended to other reactions involving both reductive and oxidative excited-state quenching, increasing the scope and quantum efficiency for a broad spectrum of photoredox processes.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c01701.

Comprehensive information regarding synthesis, electrochemistry, spectroscopic studies, computational methods, and reaction characterization (PDF)

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Notes

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