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Exploiting Charge-Transfer States for Maximizing Intersystem Crossing Yields in Organic Photoredox Catalysts

Steven M. Sartor[†], Blaine G. McCarthy[‡], Ryan M. Pearson[‡], Garret M. Miyake[‡], and Niels H. Damrauer^{*,†}

[†]Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States

[‡]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

Abstract

A key feature of prominent transition-metal-containing photoredox catalysts (PCs) is high quantum yield access to long-lived excited states characterized by a change in spin multiplicity. For organic PCs, challenges emerge for promoting excited-state intersystem crossing (ISC), particularly when potent excited-state reductants are desired. Herein, we report a design exploiting orthogonal π -systems and an intermediate-energy charge-transfer excited state to maximize ISC yields (Φ_{ISC}) in a highly reducing ($E^{0*} = -1.7$ V vs SCE), visible-light-absorbing phenoxazine-based PC. Simple substitution of *N*-phenyl for *N*-naphthyl is shown to dramatically increase Φ_{ISC} from 0.11 to 0.91 without altering catalytically important properties, such as E^{0*} .

The recent resurgence of photoredox catalysis was facilitated by discrete photoredox catalysts (PCs) whose lowest energy excited states are formed in significant yields and are sufficiently long-lived to efficiently engage in outer-sphere electron transfer in competition with inner-sphere decay processes.¹ This property can confer distinct benefits for photoredox catalysis: making possible high conversion efficiencies, allowing for conditions employing small co-catalyst concentrations, making feasible catalysis via activated electron transfer, and decreasing catalyst loading.² Because long lifetimes are commonly enabled by spin interconversion in the excited state, initial PCs were chromophores incorporating transition metals (e.g., Ru or Ir) where Φ_{ISC} (where ISC refers to intersystem crossing) is approximately unity due to the heavy atom effect.³

The scarcity of Ru and Ir has motivated exploration of PCs built from abundant materials. Those incorporating first row transition metals similarly exploit the heavy-atom effect for

*Corresponding Author: niels.damrauer@colorado.edu.

Supporting Information

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Additional photophysical, computational, electrochemical, and data analysis details, including Figures S1–S18 and Tables S1–S9 (PDF)

ORCID

Garret M. Miyake: 0000-0003-2451-7090

Niels H. Damrauer: 0000-0001-8337-9375

Notes

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lifetime extension.⁴ Organic PCs (OPCs) are attractive by way of extending reaction scope⁵ and alleviate metal contamination concerns.⁶ However, unlike metal-containing PCs, optimization of Φ_{ISC} in OPCs must be tied to design. For excited-state oxidants, high Φ_{ISC} can be achieved using carbonyls⁵ or by incorporation of heavy halogens.⁷ Unfortunately, these strategies are often impractical for highly reducing chromophores^{6,8} due to the electron withdrawing character of these functional groups which can lessen the reducing power of the OPC or impact its chemical stability.^{2c,9}

Recently, we reported a highly reducing, phenoxazine-based OPC (**2**) which possesses a notably high $\Phi_{ISC} = 0.91$ and a triplet lifetime of 480 μs at room temperature (RT) in *N,N*-dimethylacetamide (DMAc).¹⁰ It was soon thereafter noted that high Φ_{ISC} is not shared by all structurally similar PCs. In particular, replacement of *N*-naphthyl with *N*-phenyl (**1**) results in $\Phi_{ISC} = 0.11$. This is surprising since the *N*-substituent does not impact the initial and final excited states in both compounds (vide infra), nor does it alter the reduction potential from the long-lived triplet, which has been reported as -1.70 and -1.72 V vs SCE for **1** and **2**.^{10,11} Notably, these reduction potentials are potent even by comparison to well-known Ir(III) complexes such as *fac*-Ir(ppy)₃ (-1.73 V vs SCE). The current work seeks to uncover the photophysical mechanism for this stark discrepancy in Φ_{ISC} , such that it may be exploited in comparable OPC systems.

Figure 1 shows electronic absorption for **1** and **2** in DMAc. The spectra are highly similar, possessing comparable λ_{max} and molar extinction. These data were modeled using TD-DFT (see Supporting Information (SI)) which reveals that the prominent lowest-energy feature at 388 nm for both PCs is almost completely described as a single interorbital transition originating in a phenoxazine-localized HOMO. The acceptor orbitals (LUMO for **1** and LUMO+1 for **2**) are qualitatively the same and indicate wave function delocalization over the phenoxazine plus the adjacent rings of both biphenyl substituents (Figure S5). Neither involves the nearly perpendicular *N*-aryl substituent. We next consider the catalytically relevant lowest-energy excited states. Figure 2A,B shows selected nanosecond transient absorption (NSTA) spectra for **1** and **2**. The long and strongly oxygen sensitive lifetimes (1200 μs (**1**) and 480 μs (**2**)¹²) are highly suggestive that the lowest-energy excited state in these systems is a triplet.

Both compounds possess similar NSTA spectra, consisting of a prominent ground-state bleach and a largely unfeatured excited-state absorption (ESA). DFT calculations within the triplet manifold offer additional insight. Figure 2C shows the singly occupied molecular orbitals (SOMOs) determined for the geometry-optimized lowest-energy triplet of **2**. The SOMOs for **1** are highly similar (Figure S6). For both PCs, the lower SOMO is dominated by phenoxazine π character which strongly resembles the ground-state (GS) HOMO (Figure S5). In contrast, the higher SOMO (in both molecules) shows π character shifted asymmetrically, including one outer ring of the phenoxazine plus the adjacent ring from a single biphenyl substituent. This SOMO is suggestive of double-bond character between these two rings on one side of the PC, a point that is strongly supported by structural changes on that side of the molecule (shortening of the first inter-ring C–C bond concomitant with the decreasing of the inter-ring dihedral angle) noted in the comparison between the optimized triplet and GS geometries (see SI). With SOMOs in mind, the lowest

triplet of **1** and **2** is interpreted as charge transfer (CT), involving a shift of electron density from the phenoxazine toward one of the biphenyl substituents (denoted $T_{CT-Biph}$). We note that this symmetry-breaking CT is typical of acceptor–donor–acceptor complexes possessing relatively low quadrupolar moments, particularly in polar solvents (e.g., DMAc).¹³ Drawing on computational and NSTA results, **1** and **2** have highly similar lowest triplets. Notwithstanding, the measured Φ_{ISC} for **1** and **2** are highly divergent. Whereas Φ_{ISC} for **2** is 91%,¹⁰ this sharply contrasts with 11% reported here for **1**, as determined using a triplet–triplet energy-transfer method.¹⁰ These observations motivate a more extensive photophysical characterization.

Emission spectra (Figure 1) originate within the singlet manifold, an assignment supported by time-resolved measurements and their insensitivity to ambient oxygen (see SI). No triplet emission is observed for either compound. Both species exhibit a high degree of solvatochromism,^{10,11} indicating CT character in their emissive states. However, their spectral profiles are clearly distinct. Whereas that of **1** is unremarkable, that of **2** is broader and red-shifted with a shoulder at ~460 nm. Importantly, there are also substantial emission quantum yield differences: $\Phi_{em}(\mathbf{1}) = 80\%$ while $\Phi_{em}(\mathbf{2}) = 2.3\%$ (Table S1).

An initial effort to characterize dynamics involved time-correlated singlet photon counting (TCSPC). In addition to kinetic information, time evolution of spectral features can be assessed (see SI). **1** is again unremarkable. Under certain pump polarization conditions, a 350 ps rotational diffusion contribution is observed, but under no circumstances are profile changes seen (see Figures S9 and S11). The spectrum decays to baseline with a time constant of 2.87 ns, assigned to the lifetime of the S_1 (Table S1).

Given the aforementioned fluorescence solvatochromism for **1**, we anticipate that the emitting state has symmetry-breaking CT character involving the phenoxazine and a single biphenyl substituent. This assignment is strongly supported by measurements of a chemical analogue possessing only one biphenyl substituent but is otherwise identical (called **1a**; see SI). Notably, while these compounds possess quite different absorption profiles,¹¹ the emission profiles of **1** and **1a** are remarkably similar (Figure S14), corroborating the symmetry-breaking CT assignment of the S_1 in **1**. We refer to it hereafter as $S_{CT-Biph}$.

In contrast to **1**, TCSPC data for **2** show marked spectral evolution. We have extracted 20 ps and 5.2 ns species-associated spectra (Figure 3). Interestingly, the early-time spectrum of **2** peaks at 460 nm, a value very similar to $\lambda_{max,em}$ for **1**. This is compelling evidence that **2** initially explores an emissive singlet similar to $S_{CT-Biph}$ in **1**. At later times, emission in **2** changes dramatically, culminating in the broad spectrum centered at 505 nm that is responsible for the red shift in Figure 1. Consideration of the only substitutional difference hints at participation by the *N*-naphthyl moiety.

Using Φ_{em} and TCSPC lifetimes, a radiative rate constant (k_r) can be quantified (see Table S1 for equations). **1** is straightforward, given only one emissive state. In **2**, early S_n emission (Figure 3) makes a minor contribution (~3.7%) and can be ignored. As seen in Table S1, k_r for **1** is a factor of 70 larger than in **2**. Further, using Φ_{ISC} along with the observed emission

lifetime, k_{ISC} can be isolated from other nonradiative pathways (k_{nr}). Notably, k_{ISC} for **2** is 4.5 times greater than for **1**.

These molecule-specific k_r and k_{ISC} values have a marked impact on catalytically important properties. To better understand their origins, femtosecond transient absorption (FSTA) experiments (400 nm pump) were conducted. In **1** (Figure 4A), the data reveal early processes that complete within ~ 10 ps. The remaining spectral features discussion) decay uniformly with a longer component (>2 ns) that cannot be fully resolved. This includes the 620 nm ESA, which is expected to involve $\pi^* \leftarrow \pi^*$ originating in excess charge density on the biphenyl. Given the TCSPC lifetime as well as spectral assignments (see SI), these latter TA features are assigned to $S_{CT-Biph}$.

We next turn to **2** (Figure 4B). At early times the spectrum is very similar to that of **1**, consistent with the GS absorption commonality. However, striking evolution follows, including the emergence of a broad ESA (~ 470 nm) over ~ 20 ps that then remains for the experiment duration. This evolution corroborates TCSPC evidence that **2** initially occupies a state analogous to $S_{CT-Biph}$ in **1** but then rapidly relaxes to an S_1 unique to **2**. Interestingly, beginnings of evolution on the nanosecond time scale are observable (Figure S15), corresponding to the emergence of features seen in longer time NSTA data (Figure 2). This is consistent with triplet-state formation.

The low degree of electronic coupling between the naphthyl substituent that is $\sim 90^\circ$ (GS geometry) relative to the phenoxazine enables assignment of this unique S_1 in **2** using absorption spectra of respective ions in a redox pair. The spectrum and molar extinction of the cation ($\sim 14\,400\text{ M}^{-1}\text{ cm}^{-1}$ at 490 nm) was determined by spectroelectrochemical bulk electrolysis of **2** (see SI). The anionic spectrum was produced by chemical reduction of naphthalene using sodium,¹⁵ and the molar extinction $\epsilon(\lambda)$ was estimated using relevant literature¹⁶ ($\sim 3500\text{ M}^{-1}\text{ cm}^{-1}$ at 465 nm) (see SI). The sum of these redox-derived data is used to simulate a FSTA spectrum, which is compared with a long-time FSTA spectrum of **2** in Figure 4C. These data agree well, particularly with respect to the ~ 475 nm ESA. The S_1 of **2** is thus assigned and denoted as $S_{CT-Naph}$.

An energy level diagram is presented in Figure 5. In **1**, excitation to the Franck–Condon singlet (S_{FC}) is followed by solvent reorganization and inter-ring conformational relaxation as $S_{CT-Biph}$ is formed and thermalized on a <10 ps time scale. That state can undergo ISC, but ISC is in competition with efficient photoluminescence driven by a large k_r . The result is a high Φ_{em} concurrent with low Φ_{ISC} .

For **2** there is an important difference inasmuch as $S_{CT-Biph}$ is only transiently populated prior to formation of an intermediate $S_{CT-Naph}$. This has significant consequences that are, we believe, inherent to the geometry of $S_{CT-Naph}$ which resembles a radical pair. First, the perpendicular anion and cation π -systems significantly decrease k_r connecting $S_{CT-Naph}$ with the GS. This phenomenon is seen in compounds like 9,9-bianthryl.¹⁷ The second consequence concerns the overall reaction $S_{CT-Naph} \rightarrow T_{CT-Biph}$, which competes effectively against k_r and k_{nr} .

Here, there are two ISC pathways (denoted (A) and (B) in Figure 5) which cannot be definitely distinguished without further magnetic-field dependent measurements. For (A), the rate-limiting step is $S_{CT-Naph} \rightarrow T_{CT-Naph}$ ISC. These states should have comparable energies as the orthogonal orbital systems limit direct exchange interactions between the unpaired electrons. While spin-orbit coupling between $S_{CT-Naph}$ and $T_{CT-Biph}$ is not expected to be large given the common orbitals, the near-degeneracy could increase coupling via hyperfine interactions.¹⁸ In (B), ISC directly couples $S_{CT-Naph}$ with the long-lived $T_{CT-Biph}$. To understand why this might be fast, we draw on literature showing that CT states with perpendicular geometries have greatly enhanced k_{ISC} to a locally excited triplet¹⁹ because the large change in orbital angular momentum facilitates spin-orbit coupling between states. Due to the high degree of spatial separation of SOMOs generally required to facilitate ISC via (A),²⁰ (B) is considered to be the more likely pathway.

These findings show that the introduction of a CT state with perpendicular geometry at an appropriate energy can dramatically improve Φ_{ISC} for phenoxazine-based OPCs, and, importantly, this state has minimal impact on other photo-physical parameters key to photocatalysis.

Supplementary Material

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Acknowledgments

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Figure 1. Absorption (dashed)^{10,11} and emission (solid) of **1** (blue) and **2** (red) in deaerated RT DMAc.

Figure 2. Selected spectra from NSTA of **1** (A) and **2** (B)¹⁰ in deaerated RT DMAc. (C) Triplet SOMOs of **2** (cam-b3lyp/6-31g(d,p)/CPCM-DMA level of theory).

Figure 3. Species-associated emission spectra for **2** in deaerated RT DMAc generated by a globally fit biexponential model of the TCSPC data.¹⁴ See SI for details.

Figure 4.

Selected spectra for **1** (A) and **2** (B) from FSTA in deaerated RT DMAc. (C) Late-time TA spectrum of **2** (dashed, right axis) and simulated spectrum with relevant redox-derived data (solid, left axis).

Figure 5.

Energy level diagram with alternative ISC pathways (A) and (B) shown for **2**. Dashed lines reflect less likely pathways. Time constants (after formation of the lowest-energy singlet) are derived from coefficients tabulated in Table S1 using equations shown there. Generally, energies are derived from the absorption or emission λ_{max} . (see SI for $T_{CT-Naph}$ (gray) is not observed, and its energy is approximated. The y-axis * indicates energies determined computationally.