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Effects of Naphthyl Connectivity on the Photophysics of Compact Organic Charge-Transfer Photoredox Catalysts

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Abstract

Modular chromophoric systems with minimal electronic coupling between donor and acceptor moieties are well suited for establishing predictive relationships between molecular structure and excited-state properties. Here, we investigate the impact of naphthyl-based connectivity on the photophysics of phenoxazine-derived orthogonal donor–acceptor complexes. While compounds in this class are themselves interesting as potent organic photocatalysts useful for visible-light-driven organocatalyzed atom-transfer radical polymerization and small-molecule synthesis, many other systems (e.g., phenazine, phenothiazine, and acridinium) exploit charge-transfer excited states involving a naphthyl substituent. Therefore, aided by the facile tunability of the phenoxazine architecture, we aim to provide mechanistic insight into the effects of naphthyl connectivity that can help inform the understanding of other systems. We do so by employing time-resolved and steady-state spectroscopies, cyclic voltammetry, and temperature-dependent studies on two chemical series of phenoxazine compounds. In the first series (*N*-aryl 3,7-dibiphenyl phenoxazine), we find high sensitivity of photophysical behavior to naphthyl connectivity at its 1 versus 2 positions, including a drop in the intersystem-crossing yield (Φ_{ISC}) from 0.91 (*N*-1-naphthyl) to 0.54 (*N*-2-naphthyl), which we attribute to the establishment of an excited-state equilibrium in the singlet manifold. Drawing on the synthetic tunability afforded by phenoxazine, a modified series (*N*-aryl 3,7-diphenyl phenoxazine) is chosen to circumvent this equilibrium, thereby isolating the impact of naphthyl connectivity on charge-transfer energy and triplet formation. We conclude that donor–acceptor distance is a key design parameter that influences a host of excited-state and dynamical properties and can have an outsized impact on photochemical function.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b03286.

Synthetic procedures, photophysical methods, catalytic performance, cyclic voltammetry, emission of “monomer” analogue, fitting the steady-state emission, TCSPC kinetic traces, FSTA analysis, sensitivity analysis, and data analysis (Figures S1–S20 and Tables S1–S4) (PDF)

The authors declare no competing financial interest.

1. INTRODUCTION

In recent years, there has been extensive development and interrogation of organic donor–acceptor complexes, in part due to their utility in a wide variety of applications spanning photoredox catalysis,^{1–3} organic light-emitting diodes,^{4–6} organic photovoltaics,^{7–9} organic field-effect transistors,^{10,11} and molecular sensors.^{12–15} This effort is certainly motivated by a desire to replace existing costly rare-metal-based compounds and circumvent metal contamination concerns,^{16–19} but it is also driven by a recognition of the sophistication of the synthetic organic tool kit, which allows for tuning of functionality and control of structural complexity. In this context, a common approach toward the discovery of novel organic donor–acceptor complexes involves the synthesis of libraries of compounds followed by application-specific characterization.^{19–22} While effective, this method can be laborious and can translate poorly between areas of differing application. Ideally, one would possess a priori knowledge of the impact of a given synthetic modification,^{23,24} as this would significantly reduce the labor and cost of the discovery of new functional molecules. However, the current understanding in this regard, particularly in the context of photophysical and photochemical applications, remains incomplete.

Our labs have been investigating organic donor–acceptor complexes with an application toward photoredox catalysis involving challenging reductive chemistries for the synthesis of well-defined polymers and small molecules.^{18,25–28} In this vein, a variety of organic catalysts have been investigated, including chemical architectures built upon the easily oxidized phenoxazine core ($E^0(\text{phenoxazine}^{*+}/\text{phenoxazine}) = \sim 0.6 \text{ V}$ vs calomel reference electrode).^{20,26,29} This redox behavior of the phenoxazine motif engenders its catalytic activity and renders it particularly suitable for use in donor–acceptor molecules. Another key advantage of phenoxazine as a central chemical unit is the modularity it offers, inasmuch as there are multiple addressable substitution positions. The most readily functionalized sites are at the *N*-atom of the phenoxazine, as well as at the flanking 3 and 7 carbons (so-called

core substituents). While steric hindrance renders *N*-aryl substituents nearly orthogonal to the phenoxazine, flanking aryl core substituents are less restricted toward coplanarity and therefore have higher degrees of electronic coupling with the central phenoxazine moiety. As a result, these substituents play a large role in the absorption of light, and intramolecular charge-transfer (CT) states involving these substituents have the quality of charge sloshing where both donor (formally phenoxazine) and acceptor (formally aryl substituent) share common orbital space. In contrast, the *N*-aryl substituent is electronically distinct from the phenoxazine moiety and therefore plays a minimal role in the absorption of light. Further, this minimal electronic coupling allows for new CT states wherein electron transfer from phenoxazine to the *N*-aryl π^* acceptor is nearly complete. These electronic factors suggest that using the *N*-substituent to tune photophysical properties, rather than the flanking core substituents, is a potentially generalizable strategy applicable to systems beyond the phenoxazine motif.

Previously, we demonstrated the significant role that the *N*-aryl substituent plays in determining photophysical properties for phenoxazine-based photocatalysts.²⁹ We found that the use of an *N*-naphthyl substituent (**2** in Figure 1), as compared to that of an *N*-phenyl substituent (**1**), allows for the population of an energetically accessible orthogonal CT state during excited-state evolution. This state, which is formed in the first tens of picoseconds, is critical for function as it minimizes radiative losses while giving rise to favorable geometric and electronic conditions for a high yield of intersystem crossing (Φ_{ISC}) to the long-lived triplet state. However, there exist two inequivalent naphthyl carbon positions (1 and 2) through which to attach to the *N*-atom of the phenoxazine, and it is unclear what photophysical consequences will result upon exchanging one connectivity for the other. One might reason at the outset that attachment in the 2-position reduces steric hindrance toward coplanarity with phenoxazine, which can be expected to increase the electronic coupling between the phenoxazine donor and the naphthyl acceptor, with impacts on facilitating intramolecular electron-transfer dynamics in the excited-state manifold. However, as a 90° dihedral angle between the donor and acceptor is known to increase spin-orbit coupling,^{30,31} the less sterically confined 2-naphthyl connectivity may actually lead to less efficient ISC that accompanies electron transfer. Currently, it is far from certain how the various effects of naphthyl connectivity will play out in the photophysical dynamics. As such, in the absence of stronger evidence informing impacts, one must somewhat arbitrarily choose one arrangement over the other or simply construct both. Previously, this has been done, and naphthyl connectivity has been found to impact catalytic performance. Photocatalyst **2** and its *N*-2-naphthyl analogue (**3**) have been synthesized and investigated as catalysts for organocatalyzed atom-transfer radical polymerization (O-ATRP)^{20,26} and were found to exhibit discrepancies in their performance under the same synthetic conditions, suggesting differences in their photoinduced properties (see the Supporting Information (SI) for more details).

We therefore set out here to characterize the impact of naphthyl connectivity. It is noted that while this investigation solely relies on the phenoxazine architecture, efforts are made to conduct studies such that results can help inform other systems (e.g., phenazine,^{27,32} phenothiazine,^{33–35} flavin,³⁶ acridinium,^{37–39} xanthene,⁴⁰ and BODIPY^{41,42}) with different

applications. That said, phenoxazine derivatives are themselves increasingly important in the field of organic photoredox catalysis, and a significant secondary aim of the current work is to refine our understanding of this architecture and how excited-state processes can be controlled. In this context, we take advantage of the system's synthetic modularity and resultant tunability to uncover structure–function relationships. For example, early in this study, we find that the replacement of the *N*-1-naphthyl substituent (**2**) with an *N*-2-naphthyl substituent (**3**) results in an excited-state equilibrium between two distinct CT states, one of which involves the *N*-naphthyl substituent and the other involves a core biphenyl substituent. As this equilibrium of states is potentially problematic for our investigation, synthetic modularity enables us to exchange the core substituents to raise the energy of the core-substituent-localized CT state while minimally perturbing the CT state involving the *N*-naphthyl substituent.

2. RESULTS AND DISCUSSION

2.1. Initial Dibiphenyl System.

Figure 2 shows the electronic absorption data for **1**, **2**, and **3** at room temperature (RT) in *N,N*-dimethylacetamide (DMAc). All three compounds possess similar absorption spectra with comparable wavelengths of maximum absorption and molar absorptivities. The similarity suggests that the *N*-substituent does not participate significantly in the absorption of light in the near-UV region, i.e., that all three compounds access a similar Franck–Condon excited state (S_{FC}) when excited in the vicinity of 400 nm. Previously reported time-dependent density functional theory (DFT) calculations²⁹ have demonstrated that the lowest-energy electronic transition of **1** and **2** is dominated by a single interorbital transition composed of electronic movement from the phenoxazine-localized highest occupied molecular orbital to a higher-lying molecular orbital, which is delocalized over the phenoxazine and both biphenyl substituents. Due to the spectral and structural similarity of the three molecules, the absorption of **3** is expected to have the same orbital origins.

We next turn to the lowest-energy excited state in **1**, **2**, and **3**, which is understood to be triplet in nature due to the long observed lifetimes of 1.2 ms,^{29,43} as well as computational findings.²⁹ The long lifetime of the triplet state makes it of particular interest for bimolecular (i.e., diffusion-controlled) catalysis. Nanosecond transient absorption (NSTA) spectra collected for **1**, **2**, and **3** (Figure 3) show a broad peak at 750 nm and are indistinguishable across the series of molecules. This observation is consistent with results from previous DFT studies^{20,29} that showed a common orbital character for the lowest-lying triplet state (T_1) in each of these molecules. Each possesses a lower-lying singly occupied molecular orbital (SOMO) situated on the phenoxazine core and a higher-lying SOMO bridged across a single distal ring of the phenoxazine and an adjacent phenyl ring, which is part of one of the biphenyl substituents. The T_1 of **1**, **2**, and **3** is thus denoted as $T_{CT-Biph}$.

Despite similarities in their electronic structure, **1**, **2**, and **3** do not share comparable Φ_{ISC} values. We previously reported a wide discrepancy in Φ_{ISC} between **1** and **2** ($\Phi_{ISC,1} = 0.11$, $\Phi_{ISC,2} = 0.91$), and through time-resolved spectroscopic studies with support from electrochemistry and DFT, we attributed the high yield in the latter to its ability to access a lowest-energy singlet excited state (S_1) characterized by CT from the phenoxazine core to

the naphthyl substituent (denoted as $S_{CT-Naph}$).²⁹ Due to the structural similarity between **2** and **3**, it was our expectation at the outset that **3** would possess an electronically similar S_1 and therefore a comparable Φ_{ISC} . However, we now report $\Phi_{ISC,3} = 0.54$. This variation in Φ_{ISC} between **2** and **3** suggests that the alteration of naphthyl connectivity impacts singlet-manifold dynamics in a manner relevant to triplet formation. We thus turn to investigate the singlet dynamics of these compounds.

This exploration begins with emission measurements of **1**, **2**, and **3**. It is possible to conclude that the spectra shown in Figure 2 originate from the singlet manifold as evidenced by the relatively short lifetimes of 2.87,²⁹ 5.2,²⁹ and 4.92 ns for **1**, **2**, and **3**, respectively, measured by time-correlated singlephoton counting (TCSPC). As stated above, the emitting S_1 state of **2** has been previously assigned as $S_{CT-Naph}$. In **1**, on the other hand, the emitting state is also CT in nature, but in that case, charge moves toward a biphenyl core substituent ($S_{CT-Biph}$).²⁹ Surprisingly, the spectrum of **3** resembles that of the *N*-phenyl derivative more so than that of the *N*-1-naphthyl compound, suggesting that the emitting state of **3** has $S_{CT-Biph}$ character. However, there are two features that distinguish **3** from **1**. First, **3** possesses a slightly broader profile than **1**, and second, the quantum yield of emission (Φ_{em}) of **3** is 0.35, an intermediate value between that of **1** and **2** ($\Phi_{em,1} = 0.80$,²⁹ $\Phi_{em,2} = 0.023$ ²⁹).

To better understand the evolution of **3** following photoexcitation, we turn to femtosecond transient absorption (FSTA) spectroscopy (Figure 4). At early probe times, e.g., at 15 ps, the spectral features of **3** bear a strong resemblance to what is observed at later times for **1**. This indicates that **3** initially occupies an excited state similar to $S_{CT-Biph}$. However, over a 50 ps timescale, the molecule exhibits marked evolution resulting in the formation of a new feature centered at ~475 nm, after which no significant evolution is observed for the remainder of the experiment (~1.6 ns). Due to the similarity of this ~475 nm feature with the late-time spectrum of **2**, this excited-state absorption (ESA) is attributed to a state resembling $S_{CT-Naph}$. Importantly, in **3**, this conversion from $S_{CT-Biph}$ to $S_{CT-Naph}$ does not proceed to completion; rather, the late-time spectrum resembles a composite of those of **1** and **2** (see Figure S16 for direct comparison). In light of these observations, the late-time spectra of **3** are understood as originating from a combination of $S_{CT-Biph}$ and $S_{CT-Naph}$.

Given the much lower Φ_{em} of $S_{CT-Naph}$ relative to $S_{CT-Biph}$, along with its red-shifted wavelength of maximum emission intensity ($\lambda_{max,em}$), the interpretation of the FSTA results is in agreement with the Φ_{em} and spectral broadening properties of **3** that were remarked on earlier. Further, the measurement of the emission kinetics of **3** via TCSPC reveals the emission decay to be monoexponential⁴⁴ (see Figure S13) with the aforementioned lifetime of 4.92 ns. This monoexponential behavior suggests that the two states are in rapid equilibrium ($S_{CT-Biph} \rightleftharpoons S_{CT-Naph}$). Temperature-dependent emission studies were employed to probe the energy splitting (G) of the two equilibrated states (see the SI for details). Interestingly, no population change was observed as the temperature was varied, indicating that $G \sim 0$. Energy-level diagrams summarizing states and photophysical dynamics for **1**, **2**, and **3** are shown in Figure 5 (top).

2.2. Modified Diphenyl System.

The excited-state equilibrium that arises in **3**, adds complexity and uncertainty in the determination of the rate constants for the depletion of a particular excited state (e.g., $S_{CT-Naph}$), particularly when measuring a rate constant (namely, that of ISC) as a function of temperature (vide infra). Therefore, a modified system is introduced, in which the energy of the singlet state nearest to that of $S_{CT-Naph}$ has been raised by reducing the extent of π -delocalization of the core substituents.²⁰ Compounds **1'**, **2'**, and **3'** (Figure 1) represent analogues of **1**, **2**, and **3**, where the biphenyl groups have been replaced with phenyl substituents.

Figure 6 presents the steady-state absorption and emission spectra of **1'**, **2'**, and **3'** in DMAc. Similar to the original dibiphenyl system, the *N*-substituent minimally perturbs the absorption spectra within the series, suggesting that each compound accesses a similar S_{FC} when excited in the near UV. As with the dibiphenyl series, emission in **1'**, **2'**, and **3'** originates from the singlet manifold, as determined by short observed lifetimes (vide infra). However, whereas **1'** exhibits high-energy, structured emission, compounds **2'** and **3'** possess highly Stokes-shifted, broad-emission profiles. This emission behavior is suggestive of CT to the naphthyl substituent in **2'** and **3'**. Notably, in contrast to the dibiphenyl series, the emission profile of the *N*-2-naphthyl analogue (**3'**) closely resembles that of its *N*-1-naphthyl analogue (**2'**) (we note that the slight shoulder **3'** displays at ~425 nm originates in early emission from a higher-lying excited state than $S_{CT-Naph}$, as indicated by TCSPC measurements (Figure S15)). Consistent with **2** and **3**, however, the emission of **3'** is higher in energy than that of **2'**, by ~70 meV, as estimated by their $\lambda_{max,em}$ values.

To understand the origin of this ~70 meV thermodynamic difference in $S_{CT-Naph}$ between **2'** and **3'**, the redox properties of each compound were measured using cyclic voltammetry in acetonitrile, a solvent with a very similar dielectric constant to DMAc (Figures S9 and S10, Table S2). However, there are insufficient differences between **2'** and **3'** in the quantity $E = E_{1/2}(PC^{*+}/PC) - E_{1/2}(PC/PC^{*-})$, where PC = photocatalyst, to account for the observed variation in emission energy ($E = 3.013$ V for **2'** and 3.038 V for **3'**; see Table S2). On the other hand, the higher CT energy in **3'** can be accounted for by considering structure differences between **2'** and **3'** and how that impacts coulombic stabilization in the CT state. Using optimized ground-state geometries,²⁰ the naphthyl-to-phenox-azine center-center distance is 4.37 Å for **2'** versus 5.33 Å for **3'**. Thus, given the larger donor-acceptor distance, **3'** experiences less coulombic stabilization in the $S_{CT-Naph}$ state. We note that in order for this ~1 Å change in distance to alter CT energies to the magnitude that is observed, the dielectric constant of the medium would need to be lower than that of DMAc ($\epsilon_{DMAc} = 38.60$ ⁴⁵). This is not wholly unexpected, as the donor-acceptor distance is on the order of the size of the solvating DMAc molecules, and a significant portion of the intervening material between the separated charges is the low-dielectric organic material of which the photocatalyst is composed, rather than the solvent.^{46–48} Thus, the use of the bulk dielectric constant in calculating coulombic stabilization may not be appropriate. In support of this, it is noted that in calculating the energy of $S_{CT-Naph}$ via the equation: $E_{CT} = E_{1/2}(PC^{*+}/PC) - E_{1/2}(PC/PC^{*-}) + E_{Coulomb}$,⁴⁹ the use of $\epsilon = 38.60$ results in a ~100 meV overestimation of the $S_{CT-Naph}$ energy, indicating that the use of a value lower than 38.60 for ϵ may be

necessary (see the SI for more details). Further, we note that the coulombic mechanism for the change of $S_{CT-Naph}$ energy with naphthyl connectivity can account for the previously observed energy difference in the emission spectra between *N,N*-1-naphthyl and *N,N*-2-naphthyl dihydrophenazine.²⁵ Importantly, this energy difference was observed to increase with decreasing solvent polarity, indicating that this difference in $S_{CT-Naph}$ between 1-naphthyl and 2-naphthyl analogues is due to a difference in coulombic stabilization.

Unlike **2'** and **3'**, the S_1 of **1'** is not expected to involve a CT to the *N*-substituent due to the relatively high-energy π^* of the *N*-phenyl group. What is less clear in the emission spectrum of **1'** is the extent of the involvement of the core phenyl substituents. To interrogate this, the emission spectrum of **1'** is compared to that of a related compound **1a'**, which possesses only a single core phenyl substituent but is otherwise identical to **1'** (Figure 1). The data (Figure S11) show that **1'** and **1a'** possess distinctive emission profiles: whereas **1'** exhibits features, **1a'** is broad and lacks structure. Furthermore, the measurement of emission in multiple solvents reveals that **1a'** exhibits a more significant solvatochromic shift, suggesting a larger excited-state dipole. By inference, **1'** possesses a less polar excited state, which can be explained as arising from a greater excited-state delocalization. This observation strongly suggests that the emitting state of **1'** possesses orbital character extending to both core substituents and is thus denoted as S_{deloc} . It is interesting to briefly note the significant difference in the emitting states of **1** (where arm localization occurs) versus **1'** (where delocalization occurs). This difference is attributed to the higher-lying π^* of phenyl core substituents versus biphenyl core substituents, which energetically prohibits electron localization in **1'**, with the result being a less polar excited state.

Turning to time-resolved behavior, the FSTA spectra of **1'** (Figure 7 (top)) exhibit a prominent peak at 570 nm and subtle but discernable evolution from S_{FC} . This evolution is composed of a slight blue shift and rise in ESA intensity and is consistent with cooling from the S_{FC} . The isosbestic points (e.g., at 540 nm) indicate evolution between two distinct states, which, given the subtlety of the spectral changes and the low energy of excitation (~400 nm), is interpreted as a relaxation from an excited high-frequency vibrational energy level. Data from three independent measurements are globally modeled with two exponentially decaying components ($\tau_1 = 1.9 \pm 0.4$ ps, $\tau_2 = 11 \pm 3$ ps), and afterwards, the spectra do not evolve in shape but rather uniformly decay with a time constant consistent with the singlet lifetime, as measured by TCSPC.

The FSTA of **2'** and **3'** (Figure 7 (middle and bottom)), in contrast to **1'**, exhibit marked spectral dynamics. Both compounds initially possess a strong ESA at 570 nm, but this rapidly gives way to a broad ESA, peaked at 470 nm, which remains for the duration of the experiment. The initial feature, by comparison to **1'**, can be understood as arising from a state resembling S_{deloc} . The latter feature is ascribed to the newly formed $S_{CT-Naph}$, an assignment that is strongly supported by the similarity of the 470 nm feature in **2'** and **3'** with the FSTA spectrum of **2** (Figure 4B), which is known to evolve to the $S_{CT-Naph}$ state.

The dynamics of both **2'** and **3'**, also from three independent measurements, are modeled with a minimum of three exponential components when using a global fitting procedure (see Figures S18 and S19 for DADS). The first two components ($\tau_1 < 1$ ps and $\tau_2 = 2.3 \pm 0.5$ ps

for $2'$ and $\tau_1 < 1$ ps and $\tau_2 = 4.6 \pm 0.7$ ps for $3'$) are associated with both the decay of the 570 nm feature and the growth of an ESA at ~ 450 nm. Therefore, both components point to dynamics associated with the formation of $S_{CT-Naph}$, although the relative amplitudes in the DADS spectra (Figures S18 and S19) suggest that the majority of this electronic transformation is accomplished by the second component (τ_2). In light of the early dynamics of $1'$, the quantity τ_1 in $2'$ and $3'$ is interpreted as $S_{CT-Naph}$ formation from the unrelaxed S_{FC} . The more dominant (and slower) τ_2 , on the other hand, is assigned as $S_{CT-Naph}$ formation from a lower-energy state analogous to the cooled S_{deloc} , which has less driving force for charge transfer and therefore is expected to exhibit slower kinetics. In discussions that follow, this kinetic component is denoted as τ_{CT} . Finally, the third component ($\tau_3 = 10 \pm 2$ ps for $2'$ and $\tau_3 = 10 \pm 3$ ps $3'$) is low in amplitude and constitutes a subtle spectral shift (see Figures S18 and S19) consistent with cooling following charge transfer.

The observation that τ_{ct} is shorter for $2'$ compared to that for $3'$ (see Table 1) can be understood because its lower $S_{CT-Naph}$ energy leads to a greater driving force for CT. Regardless, the fact that there are no competing processes of comparable speed means that $S_{CT-Naph}$ is formed in essentially quantitative yield for both compounds. In fact, even in the case of **3** discussed earlier, where τ_{ct} slows to ~ 100 ps⁵⁰ due to driving force considerations, no appreciable excited-state decay occurs on the timescale of τ_{CT} . Therefore, τ_{ct} may not prove to be a useful tunable parameter in similar naphthyl-substituted dyads.

We next move to characterize depletion pathways from $S_{CT-Naph}$. Measurement of singlet lifetimes ($\tau_{singlet}$), Φ_{em} , and Φ_{ISC} allows for the calculation of the rate coefficients for radiative decay (k_r), ISC (k_{ISC}), and nonradiative decay to the ground state (k_{nr}) (Table 1). In passing, we note that k_r for $3'$ is $\sim 25\%$ larger than that of $2'$. The higher emission energy in $3'$, the larger expected transition dipole moment resulting from the greater donor–acceptor distance, and the lower steric hindrance toward coplanarity between the naphthyl and phenoxazine moieties in $3'$ all could contribute to the larger k_r for $3'$. The quantities Φ_{ISC} and k_{ISC} , on the other hand, are of particular importance for photocatalysis applications. As can be seen in Table 1, both of the *N*-naphthyl-substituted compounds $2'$ and $3'$ possess near-unity Φ_{ISC} , indicating that k_{ISC} is the dominant singlet-decay pathway. This is in contrast to the *N*-phenyl compound $1'$, where Φ_{ISC} drops to 0.3. This overall behavior is consistent with the relationship between **2** and **1**, where the *N*-naphthyl-substituted complex has $S_{CT-Naph}$ as its S_1 , while the *N*-phenyl-substituted complex has $S_{CT-Biph}$. We note that the near-unity Φ_{ISC} observed for $2'$ and $3'$ is made possible by the very low k_r and k_{nr} values relative to k_{ISC} . Whereas the low k_r is understood as a consequence of the highly orthogonal donor–acceptor geometry,⁵¹ the suppression of k_{nr} is attributed to the high $S_{CT-Naph}$ energy, which renders $S_{CT-Naph} \rightarrow S_0$ a deeply Marcus-inverted process.⁴²

Figure 8 shows the late-time (i.e., triplet) NSTA spectra of $1'$, $2'$, and $3'$, all of which possess similar profiles. The triplet lifetimes ($\tau_{triplet}$) are also similar (Table 1). The T_1 electronic character for $3'$ has been previously explored using DFT calculations,²⁰ and its orbital character is described by a lower-lying SOMO localized on the central phenoxazine moiety and a higher-lying SOMO with electron density spread across one of the distal rings of the phenoxazine and an adjacent phenyl ring. These properties are also seen in each of the dibiphenyl analogues **1**, **2**, and **3**. The T_1 in $3'$ is therefore interpreted as a CT from the

phenoxazine to a phenyl core substituent and is thus denoted $T_{\text{CT-Phen(core)}}$. Because the T_1 of **3'** does not involve the *N*-aryl substituent and given the strong similarity of their NSTA spectra, it is expected that **1'**, **2'**, and **3'** possess similar $T_{\text{CT-Phen(core)}}$ states. See Figure 5 (bottom) for energy-level diagrams summarizing the states and photophysical dynamics of **1'**, **2'**, and **3'**.

Given the above characterization of $T_{\text{CT-Phen(core)}}$, ISC in **2'** and **3'** is understood as involving a reverse electron transfer from a molecular orbital localized to the naphthyl substituent to a molecular orbital spanning the phenoxazine core and one of its adjoining phenyl substituents. We consider it unlikely that ISC precedes the back-electron transfer (i.e., $S_{\text{CT-Naph}} \rightarrow T_{\text{CT-Naph}} \rightarrow T_{\text{CT-Phen(core)}}$) for two reasons. First, there would be minimal spin-orbit coupling for direct $S_{\text{CT-Naph}}$ to $T_{\text{CT-Naph}}$ ISC due to the similarity of the initial and final orbitals, and second, the SOMOs in $S_{\text{CT-Naph}}$ are not sufficiently spatially separated to diminish the singlet-triplet energy splitting enough to facilitate ISC via hyperfine interactions. Therefore, we assume that ISC and back-electron transfer occur in concert. As has been previously argued,^{29,30,37,38,52} this mechanism can facilitate spin-orbit coupling due to the large change of orbital angular momentum resulting from the CT between the perpendicular π -systems.

Based on the arguments above, the driving force for ISC (G_{ISC}) is estimated as the difference in energy between $S_{\text{CT-Naph}}$ and $T_{\text{CT-Phen(core)}}$, in which $E(S_{\text{CT-Naph}})$ is derived from the E_{00} of the steady-state emission (see the SI for steady-state emission analysis) and $E(T_{\text{CT-Phen(core)}}$) is approximated from the calculated T_1 energies.⁵³ Due to its lower $S_{\text{CT-Naph}}$ energy (Figure 6), **2'** possesses a lower G_{ISC} than **3'** by ~70 meV (Table 2). Despite this, its k_{ISC} is 30% larger with a value of $1.5 \times 10^8 \text{ s}^{-1}$ compared with that of $1.1 \times 10^8 \text{ s}^{-1}$ observed for **3'** (Table 1). Due to the moderate driving force (on the order of -0.5 eV; Table 2) in concert with the appreciable reorganization energy expected for this CT process in a polar medium, ISC is assumed to occur in the Marcus-normal region where driving force correlates positively with the speed of electron transfer. Therefore, the rate enhancement of **2'** compared to that of **1'** requires appropriate differences in the electronic coupling (V) and/or the reorganization energy (λ) for the two systems.

To explore this, we employ an expression from the classical Marcus theory of electron transfer (ET), where rate constants in the low coupling limit are governed by the following equation^{54,55}

$$k_{\text{ET}} = \frac{2\pi^{3/2}}{h(\lambda k_{\text{B}} T)^{1/2}} V^2 \exp\left(\frac{-(\lambda + \Delta G)^2}{4\lambda k_{\text{B}} T}\right) \quad (1)$$

In this expression, h is Planck's constant, k_{B} is Boltzmann's constant, T is the temperature, V is the diabatic coupling between reactant and product states, G is the electron-transfer reaction free energy, and λ is the reorganization energy of the reaction. This expression can be written in terms of a reaction activation energy, $G^\ddagger$, using a substitution according to eq 2, and the resulting new expression (not shown) is used to model data as described below

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G)^2}{4\lambda} \quad (2)$$

Using these equations, a temperature-dependent analysis of k_{ISC} can, in principle, yield V and λ . To approach this, it is first noted that k_{ISC} is not measured directly but rather is calculated per the equation $k_{\text{ISC}} = \Phi_{\text{ISC}} \times k_{\text{obs}}$, where $k_{\text{obs}} = 1/\tau_{\text{singlet}} = k_{\text{r}} + k_{\text{nr}} + k_{\text{ISC}}$. Thus, we sought to determine the temperature dependence of both k_{obs} and Φ_{ISC} . The first quantity was measured using temperature-dependent TCSPC, and a significant variation is observed over the range of 5–65 °C. For the second quantity, triplet amplitudes were measured using NSTA over this same temperature range. Here, no amplitude changes were resolvable, presumably because Φ_{ISC} approaches unity for both compounds at all temperatures explored. The overall set of data suggests that $k_{\text{ISC}}(T)$ can be estimated as $\Phi_{\text{ISC}}(T=20) \times k_{\text{obs}}(T)$.

A plot of $k_{\text{obs}}(T)$ is shown in Figure 9 for compounds **2'** and **3'**. With knowledge of the reaction free energy (G_{ISC} from Table 2), these data sets may be modeled using an equation that very closely resembles eq 1. Namely, k_{ET} in eq 1 is set equal to $\Phi_{\text{ISC}}(T=20) \times k_{\text{obs}}(T)$. This modified equation is then used to obtain λ and V (listed in Table 2). We note that λ and V are quite sensitive to G_{ISC} , which is partially derived from the DFT calculation of the T_1 and therefore has considerable uncertainty. However, since both **2'** and **3'** possess the same T_1 state (and therefore the same T_1 energy), and the difference in their S_1 energy is experimentally observable (vide supra), the value of G_{ISC} (defined as $G_{\text{ISC},3'} - G_{\text{ISC},2'}$) is well known. Further, the calculation of λ and V over a range of G_{ISC} values (but fixed G_{ISC}) reveals that while λ and V vary substantially with G_{ISC} , the values of λ and V for **2'** and **3'** (defined as $\lambda_{3'} - \lambda_{2'}$ and $V_{3'} - V_{2'}$, respectively) remain unchanged (see Figure S20). Therefore, while the absolute values of λ and V are uncertain, their relative values between **2'** and **3'** are known with considerably higher accuracy.

A significant, somewhat surprising, result shown in Table 2 is that the diabatic coupling for the reaction is very similar for both species. This may represent a balance between opposing impacts on coupling in **2'** versus **3'**. On the one hand, a relative lowering of electronic coupling is anticipated for **2'** versus **3'** due to steric considerations that would better enforce orthogonality between donor and acceptor π systems in **2'**. On the other hand, there are two considerations that would be expected to oppose this. First, the orbital coefficients at the point of naphthyl attachment to the N -atom are larger in **2'** than in **3'**.^{56,57} More importantly, the greater orthogonality for **2'** is expected to increase spin–orbit coupling compared to that for **3'**. While this latter factor is expected to be dominant at 90°, ^{30,31} we point out that both **2'** and **3'** explore a range of donor–acceptor dihedral angles centered at about ~90°, ³⁷ which may dampen relative impacts. In the end, the observed similarity of V between **2'** and **3'** indicates that these various influences on coupling are balancing each other out.

A second significant result from the temperature-dependent analysis is that the variation in λ is more substantial than that in V , indicating that the differences in the observed k_{ISC} are

driven by this factor. Recall that driving force considerations alone would predict the opposite trend in k_{ISC} . Due to the electronic similarity of **2'** and **3'** with respect to both donor and acceptor in the electron-transfer reaction, it is unlikely that k_{ISC} differences can be attributed to inner-sphere contributions to λ (so-called λ_i). We note that while torsional motion about the dihedral angle between the phenoxazine and naphthyl moieties should be meaningfully different between **2'** and **3'**, this motion is not expected to be a relevant nuclear reaction coordinate for ISC, since the phenoxazine–naphthyl dihedral angle is not expected to be significantly changed upon the transitioning from $S_{\text{CT-Naph}}$ to $T_{\text{CT-Phen(core)}}$. On the other hand, outer-sphere contributions due to solvent reorganization (λ_o) are expected to be impactful. As described in the Marcus two-sphere model, λ_o includes a $1/r$ dependence on the distance between the donor and acceptor (R_{DA}) in a CT complex (see the SI, Eq. S4).^{54,55,58} In **2'** and **3'**, R_{DA} can be calculated as the distance between the center of the naphthyl-anion donor and the acceptor, which, based on the DFT characterization of the T1,²⁰ is expected to be approximately centered on the C–C bond joining the phenyl core substituent to the phenoxazine moiety. The difference in geometry upon altering the naphthyl connectivity leads to **3'** having a ~ 1.1 Å larger R_{DA} than **2'**, as estimated from optimized ground-state geometries.²⁰ Calculations using the Marcus two-sphere model indicate that this difference in distance results in a ~ 132 meV difference in λ_o (λ_o) between **2'** and **3'** (see the SI for more details). While the calculation of λ_o is certainly approximate, the agreement between the calculated and experimentally determined λ_o indicates that the observed difference in λ between **2'** and **3'** is likely due to λ_o , specifically resulting from the change in donor–acceptor distance from **2'** to **3'**.

3. CONCLUSIONS

In this work, we have shown that altering the point of attachment of naphthalene N-substituents in phenoxazine photoredox catalysts has important photophysical consequences arising from both thermodynamic and kinetic factors. The overall influence on rate constant and quantum yield observables is tied to how specific attachment positions on substituents affect donor–acceptor distances. However, the way that these structural perturbations manifest depends on the state structure of the systems being compared and on the specific rate constants of interest and how they impact excited-state dynamics. It is our general conclusion that while overall structural perturbations due to inequivalent attachment positions (e.g., within naphthalene, anthracene, and pyrene) may appear subtle, the choice should be made with care in cases where intermediate CT states are mechanistically relevant.

In the case of our initial comparison of core diphenyl photocatalysts **2** versus **3** in DMAc, exchanging the *N*-1-naphthyl substituent (**2**) with an *N*-2-naphthyl substituent (**3**) raises the $S_{\text{CT-Naph}}$ energy. Analysis of the diphenyl series reveals this increase to be ~ 70 meV and attributable to changes in donor–acceptor distance (the distance being further in **3**) and how this manifests in coulombic stabilization of the CT state. While the ~ 70 meV increase of $S_{\text{CT-Naph}}$ can be modest in terms of steady-state emission spectral shifts (see Figure 6, for example), it is photophysically impactful in **3** because of the energetically nearby $S_{\text{CT-Biph}}$ state. This leads to a significant excited-state equilibrium ($S_{\text{CT-Naph}} \rightleftharpoons S_{\text{CT-Biph}}$) that is

absent in **2**, where the driving force favoring $S_{CT-Naph}$ is more substantial. In large part because of the high radiative rate constant, k_r , for $S_{CT-Biph}$, **3** lacks the excited-state lifetime to fully engage in ISC and its quantum yield for the process caps at ~50% ($\Phi_{ISC,3} = 0.54$ in RT DMAc, while $\Phi_{ISC,2} = 0.91$). Because of the strong polarity of DMAc, it is unlikely that Φ_{ISC} for **3** can be substantially improved upon during catalysis with solvent choice, although it certainly should be possible to lower it if that is the desired effect.

Regarding performance in O-ATRP, there are important differences in the photophysical behavior of **2** and **3**. Namely, these are the much lower Φ_{ISC} in **3** and the qualitatively different character of the singlet excited state, which is also expected to participate in O-ATRP.³² A more thorough investigation of the photochemical properties of **2** and **3** will be required to understand the mechanistic underpinnings of their differing performance as O-ATRP catalysts. Such a study is currently underway in our labs.

In large part because of the $S_{CT-Naph} \rightleftharpoons S_{CT-Biph}$ equilibrium in **3**, we moved to consider a related second set of photocatalysts involving the core diphenyl-substituted **2'** and **3'**, in which core-centric singlet excited states are raised in energy, thus favoring the rapid population of $S_{CT-Naph}$ in both species. In these two photocatalysts, the impact of donor–acceptor distance is again addressed but now its role in temporally later photophysics is also explored, namely, the critical back-electron-transfer process associated with ISC ($S_{CT-Naph} \rightarrow T_{CT-Phen(core)}$). Within these dynamics, there are two competing distance-dependent effects. On one hand, the driving force for this reaction is larger in **3'** versus **2'** due to the larger donor–acceptor distance that comparatively destabilizes $S_{CT-Naph}$. Given the Marcus-normal region expectation for this reaction, such a perturbation should speed ISC in **3'** versus **2'**. However, this is not the case— k_{ISC} is 30% larger in **2'** versus **3'**—an observation that can be understood by considering the kinetic factor of solvent reorganization energy, λ_o , as uncovered by temperature-dependent measurements that implicate λ while ruling out the state coupling V . In this context, the larger donor–acceptor distance in **3'** causes a larger λ_o , which then outweighs the donor–acceptor distance benefits to driving force.

While the decrease in k_{ISC} for **3'** versus **2'** does not result in significantly smaller Φ_{ISC} for these particular systems, the effect could be of greater importance when there are competing decay pathways. In light of this consideration, it appears that given the choice, exploiting the 1-position of naphthalene N-substituents is preferable. However, there remain openings for designing excellent photocatalysts that still exploit the 2-position of naphthalene if that is desired for synthetic or unforeseen photostability reasons. For example, the photoreaction environment could be changed: it is noted that since λ is substantially larger than $-G_{ISC}$, the critical rate constant k_{ISC} is expected to increase by the use of nonpolar environments that simultaneously increase $-G_{ISC}$ by destabilizing $S_{CT-Naph}$ while decreasing λ_o through optical and static dielectric effects. Recall though, from our original comparison of **3** versus **2**, that for high triplet yields one must still ensure that $S_{CT-Naph}$ is efficiently formed after photoexcitation, and this may require imposing electronic perturbations to the naphthalene π system. Fortunately, the modularity and high degree of synthetic tunability in these types of systems, coupled with the detailed photophysical picture that is emerging, provide ample opportunities for photocatalyst design and refinement.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Photocatalysts investigated in this study.

Figure 2. Steady-state absorption (dashed) and emission (solid) spectra of **1**, **2**, and **3** in deaerated room-temperature (RT) DMAc.

Figure 3.
Triplet NSTA spectra of **1**, **2**, and **3** in deaerated RT DMAc. Each spectrum was taken at a delay of 40 ns.

Figure 4.

(A) FSTA spectra of **3** showing early spectral dynamics. (B) Selected FSTA spectra of **1** and **2**²⁹ (normalized) highlighting the late-time S₁ spectral features. All spectra were measured in deaerated RT DMAc using 400 nm excitation.

Figure 5.

Energy-level diagrams of the compounds studied. The arrows show the dominant decay pathways of each compound. All paths that describe at least 10% of the excited-state population decay are shown.

Figure 6. Steady-state absorption (dashed) and emission (solid) spectra of **1'**, **2'**, and **3'** in deaerated RT DMAc.

Figure 7. Selected FSTA spectra (400 nm excitation) of **1'** (top), **2'** (middle), and **3'** (bottom) in deaerated RT DMAc.

Figure 8.

Triplet NSTA spectra of **1'**, **2'**, and **3'** in deaerated RT DMAc. Each spectrum was taken at a delay of 40 ns.

Figure 9. Temperature-dependent k_{obs} of $2'$ and $3'$, measured by TCSPC in deaerated DMAc, and the corresponding fits.

Table 1.

Photophysical Parameters of the Diphenyl-Substituted Series

	τ_{CT} (ps)	τ_{singlet} (ns)	τ_{triplet} (ms)	Φ_{em}^b	Φ_{ISC}	k_r^{ab} (s ⁻¹)	k_{ISC}^a (s ⁻¹)	k_{nr}^{ab} (s ⁻¹)
1'		3.24 ± 0.04	1.5 ± 0.2	0.68 ± 0.09	0.30 ± 0.08	2.1 × 10 ⁸ ± 0.3 × 10 ⁸	9.3 × 10 ⁷ ± 0.2 × 10 ⁷	6 × 10 ⁶ ± 4 × 10 ⁷
2'	2.3 ± 0.5	6.32 ± 0.02	1.5 ± 0.2	0.019 ± 0.005	0.95 ± 0.09	3.0 × 10 ⁶ ± 0.8 × 10 ⁶	1.5 × 10 ⁸ ± 0.1 × 10 ⁸	5 × 10 ⁶ ± 1 × 10 ⁷
3'	4.6 ± 0.7	8.03 ± 0.06	1.4 ± 0.3	0.030 ± 0.007	0.92 ± 0.14	3.7 × 10 ⁶ ± 0.9 × 10 ⁶	1.1 × 10 ⁸ ± 0.2 × 10 ⁸	6 × 10 ⁶ ± 2 × 10 ⁷

^aRate constants calculated using the following equations: $k_T = \Phi_{\text{em}}/\tau_{\text{singlet}}$, $k_{\text{ISC}} = \Phi_{\text{ISC}}/\tau_{\text{singlet}}$, and $k_{\text{nr}} = \tau_{\text{singlet}}^{-1} - k_T - k_{\text{ISC}}$.

^bThese values refer exclusively to S1 → ground-state decay pathways.

Table 2.Key Kinetic Parameters for $T_{CT-Phen(Core)}$ Formation in Diphenyl Series

	$G_{ISC} (eV)^a$	$G^\ddagger (eV)$	$\lambda (eV)^a$	$V (eV)^a$
2'	-0.500	0.050 ± 0.007	(0.93)	(2.5×10^{-4})
3'	-0.567	0.057 ± 0.002	(1.06)	(2.6×10^{-4})
3' - 2'	-0.067	0.007 ± 0.007	0.13 ± 0.04	$0.1 \times 10^{-4} \pm 0.4 \times 10^{-4}$

^aNo attempt is made to propagate error associated with how computational (DFT) uncertainty impacts the reported G_{ISC} numbers in this table. While specific λ and V values that are determined are sensitive to the input G_{ISC} , the differences in λ and V between **2'** and **3'** are much less so. See Figure S20 for the dependence of λ and V on G_{ISC} .