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Wavefunction Control of Charge-Separated Excited State Lifetimes

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Supporting Information Placeholder

Abstract: Control of excited state processes is crucial to an increasing number of important device technologies that include displays, photocatalysts, solar energy conversion devices, photovoltaics, and photonics. However, the manipulation and control of electronic excited state lifetimes and properties continue to be a challenge for molecular scientists. Herein, we present the results of ground state and transient absorption spectroscopies as they relate to magnetic exchange control of excited state lifetimes. We describe a novel mechanism for controlling these excited state lifetimes, which involves varying the magnetic exchange interactions between a stable organic radical and the unpaired electrons present in the open shell configuration of a charge-separated excited state. Specifically, we show that the excited state lifetime can be controlled in a predictable manner based on an *a priori* knowledge of the pairwise magnetic exchange interactions between excited state spins. These magnetic exchange couplings affect the excited state electronic structure in a manner that introduces variable degrees of spin forbiddenness into the nonradiative decay channel between the excited state and the electronic ground state.

INTRODUCTION

Although electronic excited states have been studied by a myriad of spectroscopic techniques that have been complemented by theoretical investigations, the ability to control and manipulate excited state processes and lifetimes remains an important challenge.[1-3] Electronic relaxation between singlet and triplet excited states occurs via spin-orbit mediated intersystem crossing (ISC), and this allows access to long-lived excited states that promote photoredox reactions,[4] large spin-polarizations,[5-6] and photo-/electroluminescence.[3, 7] Recently, we developed new molecular donor-acceptor chromophores that possess a covalently-attached stable organic radical in order to generate multiple unpaired electron spins in photoexcited states.[8] These spin centers exchange couple to generate excited state spin polarizations that are a function of both the sign and magnitude of the pairwise exchange interactions and allow for ground state magnetooptical activity to arise. The same magnetic exchange interactions that determine variable excited state spin polarizations also promote magnetic exchange dependent excited state wavefunction mixing,[8] and this provides a novel way to control and manipulate excited state lifetimes via the radical-chromophore exchange interaction. Understanding these exchange interactions is important, as they figure prominently in the exciton-polaron interaction present in trion quasiparticles.[9-11] The dynamics of these trions have recently been studied in carefully charge-doped single-walled carbon nanotubes following photoexcitation and exciton formation,[12] and excited state exchange interactions are expected to affect the lifetimes of trion and higher-order multipartite quasiparticles.

While several studies have demonstrated how electron spin affects photophysical properties,[11, 13-28] the evaluation of multiple pairwise exchange interactions and their effect on photoexcited states remain relatively unexplored. Our prior work has focused on using a combination of spectroscopy and magnetometry to determine the nature of exchange-dependent wavefunction mixing between the spin doublet donor-acceptor charge transfer excited states of these radical-elaborated molecules.[8] To continue our study of magnetic exchange effects on the excited states of donor-acceptor chromophores, we desire specific chromophores that produce excited states with a high degree of biradical character.[3] An excellent chromophoric scaffold for our studies are square planar ligand-to-ligand charge transfer (LL'CT) complexes of the general formula (BPY)Pt^{II}(dichalcogenolene) (dichalcogenolene = benzene-1,2-dithiolate, catecholate, etc.; BPY = 2,2'-bipyridine), which are characterized by LL'CT transitions to excited states that are either short-lived and non-emissive ($\tau \leq 1$ ns; e.g. catecholate (CAT) complexes),[1, 29] or long-lived and emissive ($\tau \geq 10$ ns; e.g., benzene-1,2-dithiolate complexes).[1, 30-31] The short-lived, non-emissive excited states of (BPY)Pt^{II}(CAT-R) complexes (Fig. 1A,B) allow us to investigate the effects of excited state radical-chromophore exchange interactions on non-radiative excited state decay rates. Our choice of this chromophore is based not only on its short-lived, non-emissive LL'CT excited state, but also on the charge- and spin distribution of the LL'CT excited state[1, 3] (Fig. 1B) and the resemblance of the excited state SQ-NN interaction to those in our fully-characterized ground-state LZnSQ-B-NN complexes (Fig. 1C).[8, 32-38] Ground state magnetic exchange couplings between nitronylnitroxide radical (NN) and semiquinone (SQ) in LZnSQ-B-NN complexes[33-36, 38] very closely approximate the corresponding exchange couplings in the LL'CT excited states of the NN-elaborated platinum complexes since a full unit of charge is transferred in the LL'CT excited states (Fig. 1B,C).[3] Moreover, we recently demonstrated how these excited state wavefunctions can be determined from an a priori knowledge of the experimentally-determined exchange parameters.[8] In this report, we show that radical-elaborated donor-acceptor (D-A) dyads reveal a remarkable relationship between excited state lifetimes and wavefunction mixing, which derives from the pairwise excited state magnetic exchange couplings between R, D, and A spins.

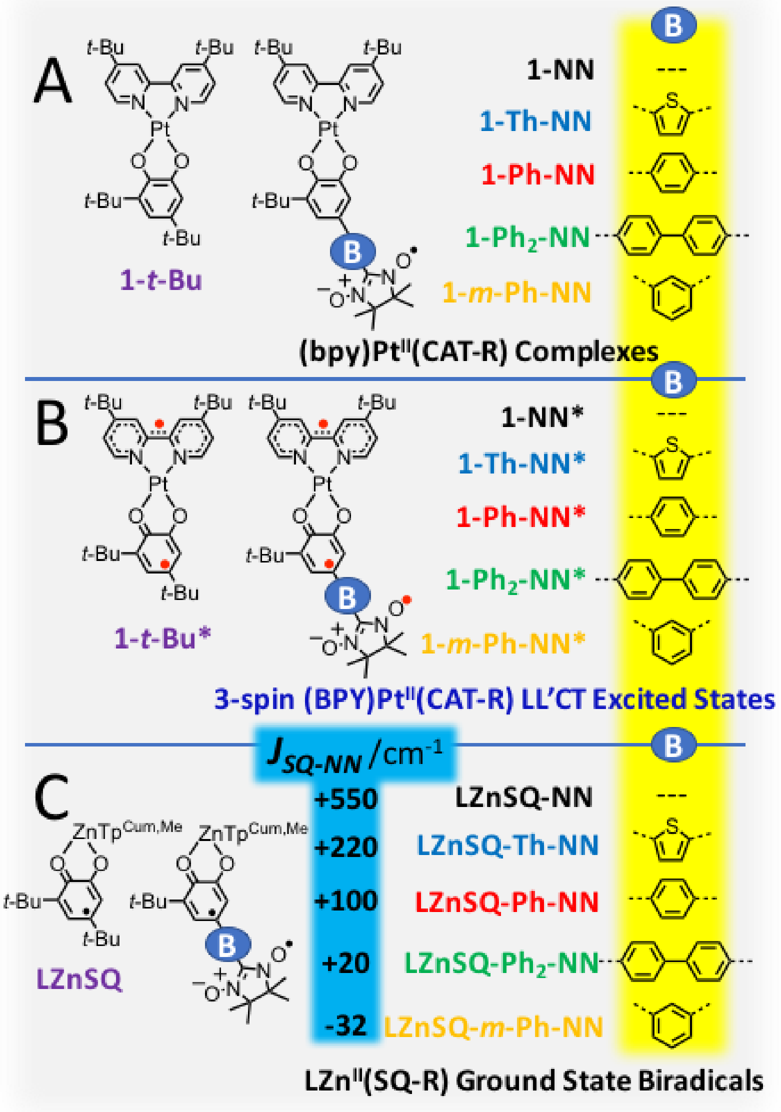

Figure 1. *A*: Platinum(II) catecholate complexes used in this study. As the *tert*-butyl groups on the bipyridine ligand have a negligible effect on both the spectroscopy and electronic structure of our complexes, they are ignored in the discussion. *B*: CAT → BPY charge-separated (LL'CT) excited states for Pt^{II} complexes in *A*. *C*: Ground state SQ-B-NN biradical complexes corresponding to the donor half of the LL'CT excited states in *B*. Values for $J_{SQ\text{-}B\text{-}NN}$ determined by magnetic susceptibility, and approximate the corresponding *J*-values in the LL'CT excited states in *B*.

RESULTS AND DISCUSSION

CAT → BPY Charge Transfer, 3-Spin LLCT Excited States, and Excited State Doublet Wavefunction Mixing. The synthesis of radical-elaborated **1-NN**, **1-Th-NN**, and **1-Ph-NN** has been reported previously,[8] and the new compounds, **1-*m*-Ph-NN** and **1-Ph₂-NN**, that have been prepared for this study and are characterized as described in the SI (Fig. 1A). The bridge fragments, B, for the (BPY)Pt^{II}(CAT-B-NN) complexes were selected because they correspond to those in our donor-acceptor biradical complexes, LZnSQ-B-NN, Fig. 1, and thus provide a range in both the magnitude and sign of $\boldsymbol{J_{SQ-NN}}$ values.[33-40] This choice results in the greatest range of wavefunction mixing allowed by this particular spin system (*vide infra*).

These complexes feature a broad, solvatochromic CAT → BPY LL'CT transition spanning the 450 – 800 nm region (Fig. 2). The unit charge transfer results in the LL'CT excited state of the NN radical-containing complexes possessing excited state triradical character (BPY•)Pt^{II}(SQ•-B-NN•) (B = bridge; Fig. 1B; "•" on NN and on SQ omitted hereafter for brevity). Two pairwise magnetic exchange interactions play a crucial role in defining the (BPY•)Pt^{II}(SQ-B-NN) LL'CT triradical excited state energies and photophysics: that between the BPY• and SQ radicals (J_{SQ-BPY} = 1400 cm^{-1} and constant within the series),[8] and that between the SQ and NN radicals ($J_{SQ-B-NN}$ = variable - depending on the bridge, B: -32 to +550 cm^{-1}, Fig. 1C).[32-36, 38] The J_{BPY-NN} exchange interaction is expected to be markedly smaller than the adjacent $J_{SQ-B-NN}$ and J_{SQ-BPY} couplings due to the long NN-BYP distance and poor BPY-NN orbital overlap. We therefore ignore the effects of J_{BPY-NN} in our analysis.[41-45] The J_{SQ-BPY} and $J_{SQ-B-NN}$ couplings give rise to two doublets and one quartet state in the excited state LL'CT manifold: D_{sing}, D_{trip}, and Q, respectively, Fig. 3. Importantly, D_{sing} and D_{trip} are admixed by the J_{SQ-BPY} and $J_{SQ-B-NN}$ exchange interactions,[8] and the degree of this admixture is controlled by the variable $J_{SQ-B-NN}$ exchange interaction as per Eqs. (1-3).[8] It is important to note that the $J_{SQ-B-NN}$ exchange mediated by the meta-phenylene bridge in **1-*m*-Ph-NN** is *antiferromagnetic*, and this results in the dark Q state lying energetically between the D_{sing} and the D_{trip} states. The quartet state, Q, does not mix with these doublets and is therefore unaffected by the degree of $D_{sing} – D_{trip}$ exchange mixing.[8] The cosλ and sinλ coefficients in Eqs. (1) and (2) define the degree of pure D_{sing} and D_{trip} doublet ($|S_1,1/2>$ and $|T_1,1/2>$, respectively) character that is admixed to form the magnetic exchange perturbed wavefunctions. In these equations, S_1 and T_1 represent the singlet and triplet excited states of the (BPY)Pt^{II}(CAT) core chromophore. The pairwise excited state exchange coupling constants, $J_{SQ\text{-}B\text{-}NN}$ [33, 35, 46] and $J_{SQ\text{-}BPY}$,[8] are related to this wavefunction mixing through λ as defined in Eq. (3), and the wavefunction mixing coefficients (sin λ, cos λ) are listed in Table 1. Although the Q state is included in Fig. 2, there is no evidence of intersystem crossing (ISC) to Q, and this is consistent with the lack of doublet-quartet exchange mixing and the absence of ISC to the excited ^{3}LL'CT in the parent complex, **1-*t*-Bu** (*vide supra*).[1] With respect to wavefunction control of the excited state lifetimes, our focus is solely on the excited LL'CT doublets, D_{sing} and D_{trip}, and their bridge-modulated admixture.

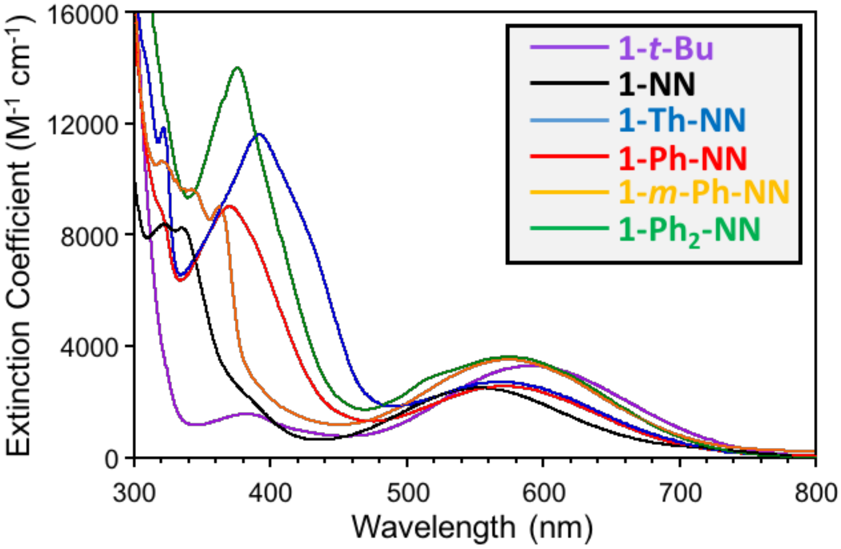

Figure 2. Electronic absorption spectra of (BPY)Pt^{II}(CAT-R) complexes recorded in CH_2Cl_2 solutions.

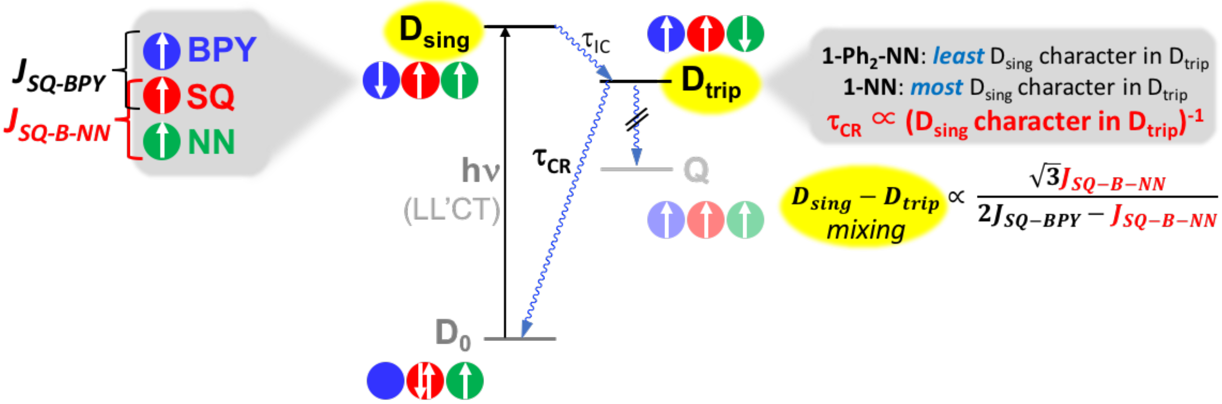

Figure 3. *Left*: Definitions of exchange parameters, *J*. *Middle*: Jablonski diagram. D_{sing} and D_{trip} are the admixed ^{2}LL'CT states for the NN-substituted complexes, τ_{CR} is the charge recombination event synonymous with LL'CT lifetime, while τ_{IC} is the internal conversion lifetime. *Right*: The two LL'CT doublets, D_{sing} and D_{trip} undergo exchange mixing which is controlled by the bridge. The greater D_{sing} character present in D_{trip} accelerates charge recombination back to D_0. Note that $J_{SQ\text{-}B\text{-}NN}$ is antiferromagnetic (negative) for **1-*m*-Ph-NN**, and this results in D_{trip} being lower in energy than Q.

Table 1. Wavefunction parameters and D_{trip} lifetimes for (BPY)Pt^{II}(CAT-B-NN) Complexes.

Complex	$J_{SQ\text{-}B\text{-}NN}$ (cm^{-1})[a]	λ[b]	%(sin λ)^2	D_{trip} Lifetime, τ_{CR} (ps)[c]
1-NN	550	11.5	3.97	250 ± 30
1-Th-NN	220	4.25	0.55	410 ± 80
1-Ph-NN	100	1.83	0.102	640 ± 30
1-*m*-Ph-NN	-32	-0.63	0.012	790 ± 20
1-Ph$_2$-NN	20	0.36	0.004	1010 ± 30

[a] Exchange coupling parameters for LZnSQ-B-NN complexes determined by variable temperature magnetic susceptibility,[33, 47-48] see text. [b] λ calculated using Eq. (3) with $2J_{SQ\text{-}BPY}$ = 2800 cm^{-1}.[8] [c] τ_{CR} lifetimes are averages of multiple experiments, see SI for details.

$$D_{trip} = cos\lambda \left|T_1, \frac{1}{2}\right\rangle + sin\lambda \left|S_1, \frac{1}{2}\right\rangle \quad (1)$$

$$D_{sing} = cos\lambda \left|S_1, \frac{1}{2}\right\rangle - sin\lambda \left|T_1, \frac{1}{2}\right\rangle \quad (2)$$

$$\lambda = \frac{1}{2} tan^{-1} \frac{\sqrt{3}J_{SQ-B-NN}}{2J_{SQ-BPY} - J_{SQ-B-NN}} \quad (3)$$

An important consequence of $D_{sing} - D_{trip}$ mixing in (BPY•)Pt^{II}(SQ-B-NN) LL'CT excited states results in a spin- and dipole-allowed $D_0 \rightarrow D_{sing}$ transition[8] that relaxes by rapid internal conversion (IC) to the D_{trip} state (Fig. 3). With respect to the (BPY)Pt^{II}(CAT) core chromophore (the "red" and "blue" spins in Fig. 3), this IC represents a localized $S_1 \rightarrow T_1$ spin conversion within the chromophore that is inaccessible to **1-*t*-Bu** and its non-radical elaborated catecholate-containing derivatives.[8] Thus, the core chromophore triplet character present in the D_{trip} excited state predicts that the non-radical $D_{trip} \rightarrow D_0$ lifetime will be dependent on the magnitude of $\sin\lambda$, and longer $D_{trip} \rightarrow D_0$ lifetimes are expected as this wavefunction mixing decreases due to the increase in chromophore spin triplet character now present in D_{trip}. Summarizing, the magnitude of the bridge-dependent $J_{SQ\text{-}B\text{-}NN}$ exchange interaction will determine the degree of D_{sing} character admixed into D_{trip}, resulting in the NN-chromophore spin exchange functioning as a molecular rheostat to modulate excited state lifetimes.

LL'CT Excited State Transient Absorption Spectroscopy. Transient absorption spectra ($\Delta OD > 0$ for transient absorption and $\Delta OD < 0$ for bleaching of ground state absorption bands; OD = optical density), recorded following photoexcitation into the low-energy envelope of the LL'CT bands for **1-NN**, **1-Th-NN**, **1-Ph-NN**, **1-*m*-Ph-NN** and **1-Ph$_2$-NN** display transient features between 415-550 nm and 650-800 nm (e.g., Fig. 4A; see SI) that are characteristic of LL'CT excited states having a (BPY•)Pt^{II}(SQ-B-NN) charge and spin distribution.[1, 8, 38] As an example, the transient absorption spectra for **1-Ph$_2$-NN** are shown in Fig. 4A, and these data are characteristic of the spectra for the other radical-elaborated complexes (see SI). As seen in Fig. 4A, these spectra exhibit bleaching of both the ground state UV band ~380 nm and the LL'CT band ~575 nm, as well as transient absorptions in the visible region of the spectrum (~550 and 750 nm). Transient absorption spectral features are in good agreement with the optical transitions observed in the ground state absorption spectra of the LZnSQ-B-NN complexes.[33-36, 38, 40] The transient absorption spectra at early delay times (~ 1-5 ps) in Fig. 4A display spectral features that span the same wavelengths as those at longer delay times (44~650 ps), but they possess distinctly different spectral band shapes. This observation suggests that more than two electronic states contribute to the transient absorption spectral envelope, and we assign these states to D_0, D_{sing}, and D_{trip} (Fig. 3). The D_{sing} and D_{trip} LL'CT excited states possess the same electronic configuration[8] and are therefore expected to exhibit nearly identical excited state distortions relative to the electronic ground state. This results in highly nested D_{sing} and D_{trip} excited state potential energy surfaces and very similar transient absorption features.

The kinetic traces of the spectral transients for each radical-substituted complex are shown in Figs. 4B-F. These data may be fit with as many as four kinetic decay components on the order of hundreds of femtoseconds (τ_{SR}; solvent reorganization), ~1 ps (τ_{VR}; vibrational relaxation), tens of ps (τ_{IC}; internal conversion), and hundreds of ps (τ_{CR}; charge recombination), (Fig. 5; Global analysis kinetic fits give charge recombination lifetimes that agree with those from single-wavelength kinetics, see SI for a complete fit analysis of the kinetic data). The short-lived components τ_{SR} and τ_{VR} can be assigned to solvent reorganization, and vibrational relaxation and redistribution, as has been reported previously for **1-*t*-Bu**.[29] The τ_{IC} is tentatively assigned to $D_{sing} \rightarrow D_{trip}$ internal conversion. Finally, the longest lifetime component is easily assignable as the $D_{trip} \rightarrow D_0$ charge recombination step (τ_{CR}). Since the measured charge recombination time constant, τ_{CR}, is markedly longer than any of the other time constants, it is not convoluted with the short-lived components included in our analysis of the kinetic data. A Jablonski diagram that shows only doublet states and summarizes the photophysical events with their characteristic time constants is shown in Fig. 5. Importantly, the magnitude of τ_{CR} is a function of the excited state exchange-mediated D_{sing}

– D_{trip} mixing and therefore the ensuing discussion will focus on this important exchange-dependent relaxation process.

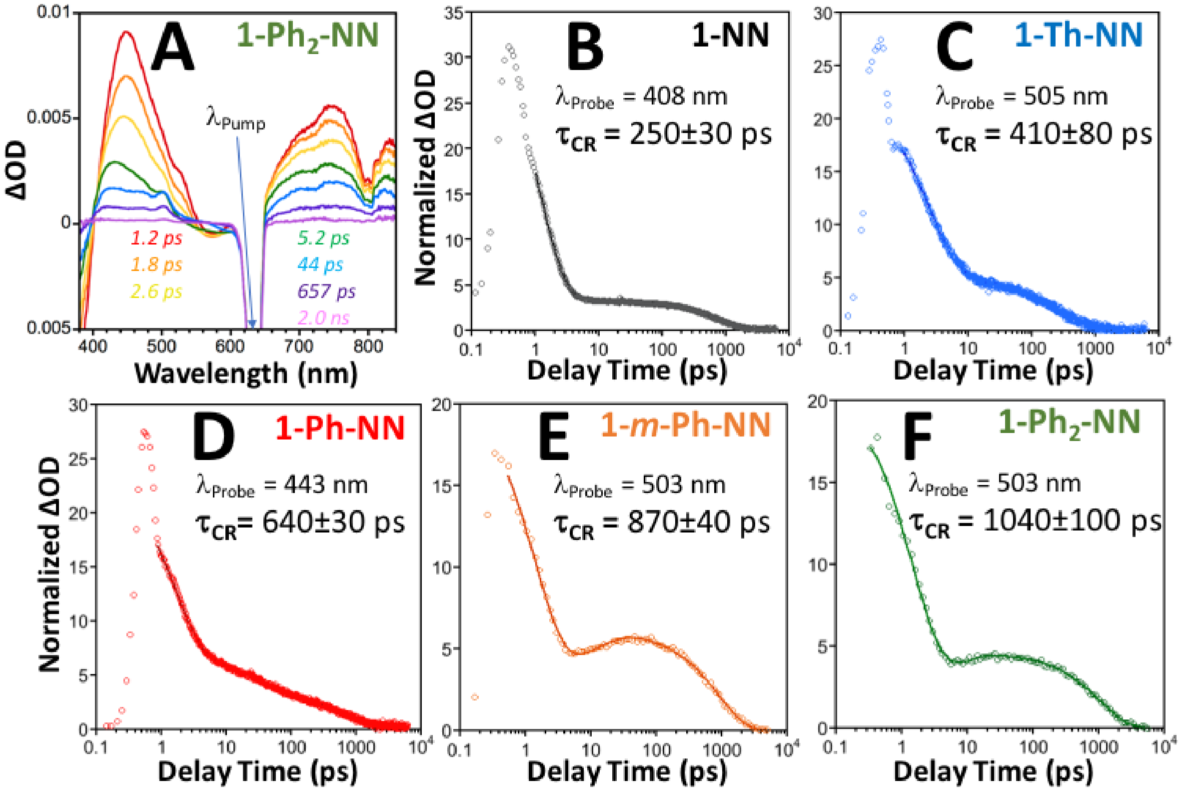

Figure 4. *A*: Transient absorption spectra of **1-Ph$_2$-NN** recorded at various delay times following a 100 fs, 630 nm excitation pulse (λ_{Pump}, 0.55 μJ/pulse). Spectra for other complexes display similar features (see SI). *B-F*: Representative normalized ΔOD traces obtained for wavelengths in the 400-550 nm probe region. Wavelengths for kinetic fits correspond to either absorption of the ground state LL'CT (~575 nm), or strong excited state absorptions (~450 nm or >650 nm). The latter wavelength is characteristic of the semiquinone chromophore which is present in the LL'CT excited state. Averaged charge recombination lifetimes (τ_{CR}) are shown as insets. For details see SI.

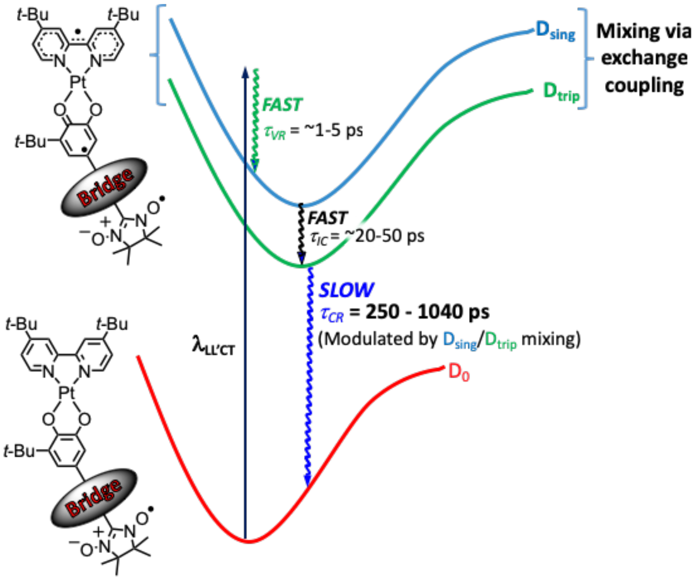

Figure 5. Representations of doublet potential energy surfaces for (BPY)Pt^{II}(CAT-Bridge-NN) complexes. The fastest process is vibrational relaxation (τ_{VR}) followed by internal conversion (τ_{IC}), with the slowest process being charge recombination (τ_{CR}) back to the ground doublet state, D_0. The vertical doublet is D_{sing} since it, like the ground state, possesses singlet (BPY)Pt^{II}(CAT) chromophoric character. Excited doublets, D_{sing} and D_{trip} are expected to be highly nested since they have the same orbital parentage and differ only in their spin wavefunctions.

Exchange-Modulated LL'CT Lifetimes. As predicted from our understanding of the excited state D_{sing} – D_{trip} interdoublet mixing in (BPY•)Pt^{II}(SQ-B-NN),[8] the charge recombination lifetimes (τ_{CR}) vary as a function of the $J_{SQ\text{-}B\text{-}NN}$ exchange interaction. Plotting τ_{CR} as a function of the D_{sing} – D_{trip} interdoublet mixing $(\sin\lambda)^2$ for radical elaborated **1-NN** (250 ± 30 ps), **1-Th-NN** (410 ± 80 ps), **1-Ph-NN** (640 ± 30 ps), **1-*m*-Ph-NN** (790 ± 30 ps), and **1-Ph$_2$-NN** (1010 ± 100 ps) clearly shows that there is a marked increase in lifetime as the excited state exchange coupling between the SQ and NN radical centers decreases ($J_{SQ\text{-}B\text{-}NN}$, Table 1 and Fig. 6). The observed increase in the $D_{trip} \rightarrow D_0$ charge recombination lifetime is counter to what is predicted by the energy gap law,[49] using LL'CT energies observed in the electronic absorption spectra and the results of our electrochemical studies (see SI). Additionally, the observed lifetime increase is also inconsistent with a vibrational "loose bolt" effect [49] whereby **1-Th-NN**,

1-Ph-NN, **1-*m*-Ph-NN**, and **1-Ph₂-NN** would be expected to undergo more rapid relaxation to D_0 resulting from the increase in the vibrational density of states relative to **1-NN**. Finally, the observed lifetimes are inconsistent with a decay process that occurs via an NN-localized excited state, since the observed lifetime for the lowest energy **Ar-NN** (Ar = 3,4-dimethoxy-5-*tert*-butyl-phenyl) excited state is 70 ± 5 ps and there are marked differences between the **Ar-NN** and (BPY)Pt^{II}(CAT-B-NN) transient absorption spectra (see SI).

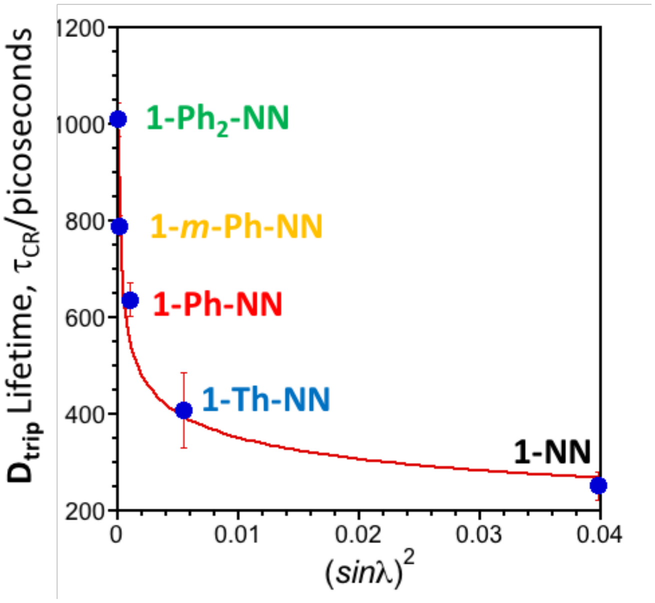

Figure 6. Plot of D_{trip} lifetimes vs. the square of the mixing coefficients, $(\sin\lambda)^2$. The solid line is a power law function fit to the data that serves as a phenomenological guide to the eye.

The analysis presented above points to exchange-mediated $D_{trip}\rightarrow D_0$ relaxation as the dominant mechanism that accounts for the observed differences in ground state recovery rates between **1-Ph₂-NN**, **1-*m*-Ph-NN**, **1-Ph-NN**, **1-Th-NN**, and **1-NN** (Fig. 6). This excited state exchange mechanism reveals itself in the form of a dramatic power-law dependence of the charge recombination lifetimes, τ_{CR}, as a function of $(\sin\lambda)^2$, the latter of which is the amount of D_{sing} character admixed into the D_{trip} wavefunction by the $J_{SQ-B-NN}$ exchange interaction (Eq. 1, Fig. 3 and Table 1). We observe that τ_{CR} asymptotically approaches large values as the D_{trip}

wavefunction tends toward the “pure” D_{trip} = |T_1,½> that has zero D_{sing} character. Thus, as $(\sin\lambda)^2 \rightarrow 0$, the $D_{trip} \rightarrow D_0$ charge recombination event takes on a larger degree of spin forbiddeness due to the increased chromophore triplet character (e.g., **1-Ph$_2$-NN**). This leads to dramatic exchange-modulated increases in the charge recombination lifetime. Conversely, an increase in D_{sing} character admixed into the D_{trip} function (e.g., **1-NN**), reduces the spin forbiddeness and the D_{trip} lifetime is observed to decrease. Importantly, the covalently attached NN radical provides a mechanism for these complexes to attain lifetimes characteristic of the chromophoric triplet state, *but without spin-orbit mediated ISC*. The new excited state exchange interactions that result from covalent attachment of a radical spin to a chromophore have previously been shown to be important in changing excited state spin dynamics,[16, 21-22, 50-52] and it was suggested[8] that this could be used as a strategy to exert wave function control over excited state lifetimes, including the charge recombination process observed here. In our prior work, we used MCD spectroscopy and magnetic susceptibility measurements to determine excited state magnetic exchange couplings that between the electron spins in the excited states of these molecules, and that there was no direct spin-orbit coupling matrix element that connects the D_{sing} and D_{trip} functions. Mixing between D_{sing} and D_{trip} was shown to occur via the exchange interaction. Our results therefore provide a unique example of creating entangled triad of electron spins with concomitant spin polarization using visible light. These results are of interest to efforts in molecule-based quantum information science since this excited state spin polarization may be transmitted to the recovered ground state. $D_{trip} \rightarrow D_0$ charge recombination is supported by the functional form of the D_{trip} lifetime vs. $(\sin\lambda)^2$ plot and the fact that that D_{trip} lies *below* the Q state in **1-*m*-Ph-NN**. Thus, the effect of excited state exchange on lifetime can be described as a non-radiative decay counterpart to the exchange mechanism that activates spin forbidden electronic transitions, originally proposed by Tanabe,[53] indicating that spin-orbit coupling using heavy metals is not required to access the core chromophore triplet state when multiple exchange interactions are operative.

CONCLUSIONS

We have presented a time-resolved kinetic and spectroscopic study of NN radical-substituted (BPY)Pt^{II}(CAT-B-NN) complexes with charge recombination lifetimes that are inversely proportional to the magnitude of the excited state D_{sing} – D_{trip} mixing. This wavefunction mixing and lifetime modulation is a direct consequence of the radical-chromophore magnetic exchange coupling. We show that τ_{CR} represents an exchange-mediated $T_1 \rightarrow S_0$ ISC process that is not present in the (BPY)Pt^{II}(CAT) core chromophore. Our study provides an important mechanism for precise control of charge-separated excited state lifetimes, including IC ground state recovery rates without the stringent requirement of spin-orbit coupling. Exchange-mediated wavefunction mixing[8] and its effects on excited state lifetimes may play an important role in charge-doped materials including conjugated organic polymers and carbon nanotubes. More specifically, the implications for further manipulation of these exchange coupled excited states is tremendous, and the concepts detailed here will translate to furthering our understanding of spin-coupled trion states, such as those found in hole-doped carbon nanotubes.[12] This is impactful, for it suggests that exchange coupling of a singlet exciton with a hole polaron could result in the formation of a triplet exciton without the need for SOC. We note that the $\boldsymbol{J_{SQ-NN}}$ values ($|\boldsymbol{J_{SQ-NN}}|$ ~30-550 cm^{-1}) are small compared to most excited state singlet triplet gaps (>1000 cm^{-1} depending on the chromophore), and small compared to heavy transition metal spin orbit coupling constants (~1000 cm^{-1}). Remarkably, the magnitude of the excited state exchange interaction will not have to be large to affect the D_{sing} - D_{trip} spin interconversion and have a dramatic and predictable effect on lifetimes. We have shown that $J_{SQ\text{-}B\text{-}NN}$ exchange interactions as small as 20 cm^{-1} in **1-Ph$_2$-NN** can dramatically affect charge recombination lifetimes relative to **1-NN.** The data presented in Fig. 6 clearly show that even smaller **1-B-NN** exchange interactions will lead to markedly longer charge recombination lifetimes. Importantly, the $J_{SQ\text{-}B\text{-}NN}$ exchange interaction must be large enough to enable conversion from D_{trip} to D_{sing}, but small enough to maximize the chromophore triplet character in D_{trip}.

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Supporting Information.

Synthesis and characterization of **1-*m*-Ph-NN** and **1-Ph$_2$-NN** and transient absorption decay kinetic analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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COMPETING INTERESTS

The authors declare no competing interests.

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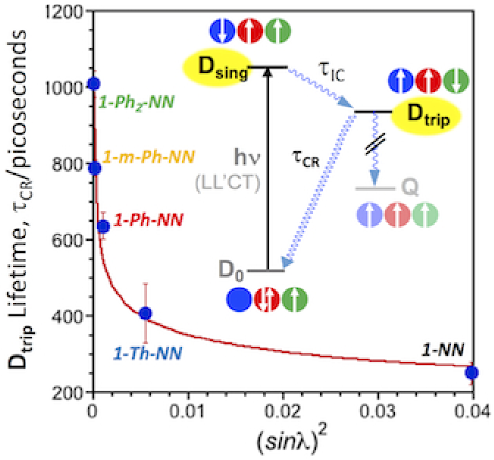

TOC Graphic

57x44mm (300 x 300 DPI)