Ultrafast Intersystem Crossing and Spin Dynamics of Zinc *meso*-Tetraphenylporphyrin Covalently Bound to Stable Radicals

Michael T. Colvin, Amanda L. Smeigh, Emilie M. Giacobbe, Sarah M. Mickley Conron, Annie Butler Ricks, and Michael R. Wasielewski*

Department of Chemistry and Argonne–Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois 60208-3113, United States

Supporting Information

ABSTRACT: *tert*-Butylphenylnitroxide (BPNO[•]) and α , γ -bisdiphenylene- β -phenylallyl (BDPA[•]) stable radicals are each attached to zinc *meso*-tetraphenylporphyrin (ZnTPP) at a fixed distance using one of the ZnTPP phenyl groups. BPNO[•] and BDPA[•] are oriented para (1 and 3, respectively) or meta (2 and 4, respectively) relative to the porphyrin macrocycle. Following photoexcitation of 1–4, transient optical absorption spectroscopy is used to observe excited state quenching of ^{1*}ZnTPP



by the radicals and time-resolved electron paramagnetic resonance (TREPR) spectroscopy is used to monitor the spin dynamics of the paramagnetic product states. The presence of BPNO[•] or BDPA[•] accelerates the intersystem crossing rate of ¹*ZnTPP about 10to 500-fold in 1–4 depending on the structure compared to that of ¹*ZnTPP itself. In addition, the lifetime of ³*ZnTPP in 1 is shorter than that of ³*ZnTPP itself as a result of enhanced intersystem crossing (EISC) from ³*ZnTPP to the ground state. The TREPR spectra of the three unpaired spins produced within 1 and 2 show spin-polarized excited doublet (D₁) and quartet (Q) states and subsequent formation of a spin-polarized ground state radical (D₀). All three signals are absorptive for 1 and emissive for 2. Polarization inversion of the Q state is observed on a tens of nanoseconds time scale in 2, while no polarization inversion is observed for 1. The lack of polarization inversion in 1 is attributed to the short lifetime of the doublet–quartet manifold as a result of the very large exchange interaction. The TREPR spectra of 3 and 4 show ground state radical polarization at X-band (9.5 GHz) at room temperature, but not at 85 K, and similarly no polarization is observed at W-band (94 GHz). No evidence of excited doublet or quartet states is observed, indicating that the exchange interaction is both weak and temperature dependent. These results show that although ultrafast EISC produces ^{3*}ZnTPP within 1–4, the magnitude of the exchange interactions between the three relevant spins in the resulting ^{3*}ZnTPP–BPNO[•] and ^{3*}ZnTPP–BDPA[•] systems dramatically alters their spin dynamics.

■ INTRODUCTION

Developing a fundamental understanding of spin polarization and the ability to control spin transport through organic molecules is important to the development of novel molecular materials for electronics and energy production. Photoexcitation of organic molecules can produce well-defined initial spin states,¹⁻⁶ while modern electron paramagnetic resonance (EPR) techniques provide an important means of examining these states with a view toward molecule-based spintronics.⁷⁻¹¹ The interactions of radicals with excited states have attracted attention over the past few decades. Previous studies of such systems have largely focused on (1)radical-induced excited state quenching observed optically or (2) spin polarization that results from three-spin mixing. In the past, these two topics were studied independently, with fast quenching primarily studied by fluorescence quan-tum yield and lifetime measurements,¹²⁻²⁵ and spin polarization studied by time-resolved electron paramagne-tic resonance (TREPR).^{26–39} Recently, we have studied radical-excited state interactions from the femtosecond to microsecond time scales using transient optical and TREPR

spectroscopies,^{40,41} which allows for a more complete understanding of these systems. For example, we observed ultrafast triplet state formation ($\tau = 2$ ps) in perylene-3,4:9,10-bis-(dicarboximide) (PDI) covalently attached to tert-butylphenylnitroxide radical (BPNO[•]) followed by the appearance of excited doublet and quartet states resulting from spin-spin exchange interactions within this three-spin system.⁴⁰ We also examined a similar system in which 2,2,6,6-tetramethyl-1piperidinyloxyl (TEMPO) is covalently attached to PDI.⁴¹ In this system we observed ultrafast ³*PDI formation in toluene, but electron transfer from TEMPO to PDI in tetrahydrofuran (THF). The TREPR data on TEMPO-PDI in toluene showed distinct ³*PDI and TEMPO signals as opposed to quartet and excited doublet states resulting from three exchange-coupled unpaired spins, which indicates that the exchange interactions between each of the two unpaired electrons comprising ^{3*}PDI and the single spin on TEMPO are small. In both of these

Received:	March 10, 2011
Revised:	May 27, 2011
Published:	June 01, 2011

systems ³*PDI formation results entirely from the presence of the radical and not the usual spin—orbit-induced intersystem crossing (SO-ISC) mechanism because the fluorescence quantum yield of ¹*PDI itself is nearly unity.⁴²

ZnTPP is an excellent chromophore to examine the effect of a stable free radical on excited state dynamics because it has been well characterized by transient optical experiments.⁴³ Efficient SO-ISC within ^{1*}ZnTPP yields ^{3*}ZnTPP, which has been examined in detail by TREPR spectroscopy.^{44,45} In addition, the spin dynamics of ^{3*}ZnTPP and nitroxide radicals have been studied extensively in freely diffusing mixtures,²⁸ coordinatively linked^{27,29,46–49} systems, and in one instance in a zinc porphyrin with a nitroxide covalently linked to its meso position.⁵⁰ The spin dynamics of freely diffusing ZnTPP and α , γ -bisdiphenylene- β -phenylallyl (BDPA[•]) mixtures have also been examined.⁵¹

Currently several mechanisms are used to account for spin polarization that occurs in three-spin systems: the radical—triplet pair mechanism (RTPM), ^{26–29,32,34,35,46,52–57} electron spin polarization transfer (ESPT), ^{28,29,51} and the reversed quartet mechanism (RQM). ^{37,40} The RTPM applies only to freely diffusing radical—triplet chromophore mixtures. It is a spin sorting mechanism, where the triplet and radical are mixed via the spin—spin exchange interaction (J) to produce excited doublet and quartet states as the radical and triplet diffuse together. ³⁶ Internal conversion (IC) selectively quenches the excited doublet state, with subsequent diffusion resulting in overpopulation of either the α or β state of the radical depending on the sign of J.

ESPT has usually been observed in freely diffusing systems, although diffusion is not required for this mechanism to occur. ESPT requires polarization transfer from a spin-polarized triplet state to the radical by spin exchange, resulting in quenching of the triplet state to the ground state singlet.^{28,29,58} The radical's polarization is thus independent of the sign of *J* and is determined solely by the polarization of the triplet.

In contrast to the previous two mechanisms, the RQM applies only to covalent systems. The RQM accounts for the presence of excited doublets and quartets whose polarization inverts after several hundred nanoseconds as observed in some covalently bound systems.^{37,40} The energy level diagram for the RQM is shown in Figure 1. Briefly, photoexcitation of the formally doublet ground state (D_0) produces the first excited state (D_2) , where the two electrons on the chromophore (¹*ZnTPP in our case) are still spin paired. If the exchange interactions between each of the electrons on ^{1*}ZnTPP and the unpaired electron on the radical are sufficiently large and the experiment is carried out in a static magnetic field that is much larger than the exchange interactions, excited doublet (D_1) and quartet (Q) states are formed, which are mixtures of the T_{+1} , T_0 , and T_{-1} high field eigenstates of ³*ZnTPP, and the α and β spin states of the radical. Transitions then occur from D2 to both Q and D1. The transition from D₂ to Q occurs exclusively by ISC because the overall spin multiplicity changes and the transition is formally spin forbidden. The transition from D_2 to D_1 is partially allowed since two pathways populate this state: ISC that populates ³*ZnTPP, and IC if the overall spin multiplicity between the initial and final states is unchanged. Since transitions to D_1 are more allowed, the D_1 sublevels have larger populations compared to those of Q. The zero-field-splitting interaction mixes D₁ and Q₄ causing reversible transitions, which results in the



Figure 1. Energy levels created after doublet—triplet mixing. $D_2 \rightarrow D_1$ internal conversion is more rapid (thick red arrow) than is $D_2 \rightarrow Q$ intersystem crossing (thin red arrow). The levels shown are for 3J > 0.

initial polarization. D_1 is then selectively quenched to D_0 by IC, resulting in the reversed intersystem crossing from Q to D_1 and polarization inversion. There have also been recent reports 41,59 of covalent systems that are in the weak exchange regime, where radicals and triplets are observed as opposed to doublets and quartets.

In addition to enhanced intersystem crossing (EISC) (A), electron transfer (B), energy transfer (C), and enhanced internal conversion (EIC) (D) also need to be considered as possible mechanisms that can account for radical-induced excited state quenching. We have discussed these mechanisms in detail previously.⁴⁰ Electron transfer has been observed from a radical to a triplet state in the covalently bound TEMPO–^{3*}naph-thalene-1,8:4,5-bis(dicarboximide) system⁶⁰ and in several diffusing nitroxide– C_{60} systems.^{61–63} As mentioned previously, we have recently reported conclusive evidence of electron transfer from a radical to an excited singlet state in polar media.⁴¹ EIC is rarely thought to be a dominant quenching mechanism^{16,24} and is generally perceived to be a minor contributor to the overall photophysics.^{40,41}

$${}^{1}*ZnTPP + {}^{2}R \xrightarrow{k_{EISC}} {}^{3}*ZnTPP + {}^{2}R$$
(A)

¹*ZnTPP + ²R
$$\xrightarrow{k_{\text{ET}}}$$
 ZnTPP^{•-} + R⁺ or ZnTPP^{•+} + R⁻ (B)

$${}^{1}*ZnTPP + {}^{2}R \xrightarrow{k_{EnT}} ZnTPP + {}^{2}*R$$
(C)

$${}^{1}*ZnTPP + {}^{2}R \xrightarrow{\kappa_{EIC}} ZnTPP + {}^{2}R \tag{D}$$

Förster energy transfer is generally thought to be insignificant for nitroxide radicals because their optical transitions in the visible spectrum have low oscillator strengths. Yet, exceptions have been proposed,⁶⁴ and when energyaccepting radicals are freely diffusing in solution, it is also necessary to consider the distribution of distances and the presence of multiple radicals in the proximity of one energy donor.⁶⁵ However, Förster energy transfer needs to be considered for BDPA[•] because it has an intense absorption at 485 nm and a much weaker one at 865 nm, which potentially provide the necessary spectral overlap for Förster

Scheme 1. Syntheses of $1-4^a$



^{*a*} (a) Pd(PPh₃)₄, Na₂CO₃, toluene, 95° C, 15 h, 35%; (b) TBAF, 0 °C \rightarrow room temperature, 2 h, PbO₂ 1 h, 75%; (c) Pd(PPh₃)₄, Na₂CO₃, toluene, 80 °C, 14 h, 50%; (d) TBAF, 0 °C \rightarrow room temperature, 2 h, PbO₂ 1 h, 76%; (e) Pd(dppf)₂Cl₂, KOAc, DMF, 85 °C, 4.5 h, 73%; (f) Pd₂(dba)₃, P(*o*-tolyl)₃, Ag₂O, THF, reflux, 12 h, 52%; (g) DBU, THF, benzoquinone, room temperature, 5 min, quantitative; (h) Pd(dppf)₂Cl₂, KOAc, DMF, 85 °C, 4.5 h, 73%; (i) Pd₂(dba)₃, P(*o*-tolyl)₃, Ag₂O, THF, reflux, 2 h, 42%; (j) DBU, THF, benzoquinone, room temperature, 5 min, quantitative.

transfer to occur.⁶⁶ It is also possible that through-bond Dexter energy transfer may also contribute to quenching of ¹*ZnTPP.

In this paper we present data on BPNO[•] and BDPA[•] stable radicals attached to ZnTPP at a fixed distance using one of the ZnTPP phenyl groups. BPNO[•] and BDPA[•] are oriented para (1 and 3, respectively) or meta (2 and 4, respectively) relative to the porphyrin macrocycle. The change in orientation is used to probe how the interaction between 3* ZnTPP and the radical depends on the magnitude and sign of the exchange interaction, J. Transient optical absorption experiments show that rapid EISC occurs for ^{1*}ZnTPP in 1–4 to produce ^{3*}ZnTPP, as well as significantly increasing the rate of ^{3*}ZnTPP decay back to the ground state in 1. For 1 and 2, TREPR spectroscopy reveals the presence of excited doublet and quartet states as well as a spin-polarized ground state doublet consistent with the RQM, indicating that the spin– spin exchange interaction between ^{3*}ZnTPP and BPNO[•] is large. In contrast, TREPR spectroscopy indicates that spin– spin exchange between ^{3*}ZnTPP and BDPA[•] is weaker in 3 and 4 at room temperature, and becomes negligible at cryogenic temperatures.



EXPERIMENTAL SECTION

Synthesis. The syntheses of 1-4 are summarized in Scheme 1 and described in detail in the Supporting Information.

Optical Spectroscopy. Ground state absorption measurements were made on a Shimadzu (UV-1601) spectrophotometer. The optical density of all samples was maintained between 0.1 and 0.6 at 532 nm, for both femtosecond and nanosecond transient absorption spectroscopies. Femtosecond transient absorption measurements were made using the 590 nm, 110 fs output from a optical parametric amplifier using techniques described earlier.⁶⁷ Samples were placed in a 2 mm path length glass cuvette and bubbled with nitrogen to prevent sample degradation. The samples were irradiated with 1.0 μ J/pulse focused to a 200 μ m spot. The total instrument response function (IRF) for the pump-probe experiments was 180 fs. Samples for nanosecond transient absorption spectroscopy were placed in a 10 mm path length quartz cuvette equipped with a vacuum adapter and subjected to five freeze-pump-thaw degassing cycles. The samples were excited with 6 ns, 1 mJ, 416 and 550 nm laser pulses generated using the frequency-tripled output of a Continuum 8000 Nd:YAG laser to pump a Continuum Panther OPO. The excitation pulse was focused to a 5-mm-diameter spot and matched to the diameter of the probe pulse generated using a xenon flashlamp (EG&G Electro-Optics FX-200). The signal was detected using a photomultiplier tube with high voltage applied to only 4 dynodes (Hamamatsu R928). The total instrument response time is 7 ns and is determined primarily by the laser pulse duration. Transient absorption kinetics were fit to a sum of exponentials convoluted with a Gaussian instrument function using Levenberg-Marquardt least-squares fitting.

EPR Spectroscopy. EPR measurements at both X-band (9.5 GHz) and W-band (94 GHz) were made using a Bruker Elexsys E680-X/W EPR spectrometer outfitted with a variable Q dielectric resonator (ER-4118X-MD5-W1) at X-band and a cylindrical resonator (EN-680-1021H) at W-band. For EPR measurements at X-band, toluene solutions of 1-4 ($\sim 10^{-4}$ M) were loaded into quartz tubes (4 mm o.d. × 2 mm i.d.), subjected to five freeze-pump-thaw degassing cycles on a vacuum line (10^{-4} mbar), and sealed using a hydrogen torch. For EPR measurements at W-band, samples of 1-4 ($\sim 10^{-4}$ M)

were loaded into quartz tubes (0.84 mm o.d. \times 0.6 mm i.d.) in a N₂-filled glovebox to a height of \sim 8 mm, and sealed with a clear ridged UV doming epoxy (Epoxies, Etc., DC-7160 UV). The EPR samples were stored in a freezer in the dark, when not being used.

Steady state CW EPR spectra were measured at X-band using 0.2-2 mW microwave power and 0.01-0.05 mT field modulation at 100 kHz. TREPR measurements were made using continuous wave (CW) microwaves with direct detection, and field swept electron spin echo (ESE) detection. A 1 kW TWT amplifier (Applied Systems Engineering 117X) was employed to generate high power microwave pulses. The resonator was fully decoupled for all pulsed experiments (Q < 200). ESE was obtained with a $\pi/2 - \tau - \pi$ pulse sequence, with a 8 ns $\pi/2$ pulse, a 16 ns π pulse, and a τ of 140 ns. After the transient species was generated by the laser pulse, the integrated echo intensity was recorded as a function of magnetic field to yield the spectrum at a given time after the laser pulse. The temperature was controlled by an Oxford Instruments CF935 continuous flow cryostat using liquid N₂. Samples 1 and 2 were photoexcited at 532 nm (0.2 mJ/pulse, 7 ns, 10 Hz) using the frequency-doubled output from a Nd:YAG laser (Quanta-Ray DCR-2), while samples of 3 and 4 were photoexcited with 6 ns, 550 nm laser pulses generated using the frequency-tripled output of a Continuum 8000 Nd:YAG laser to pump a Continuum Panther OPO, to ensure that BDPA was not photoexcited. The light from both lasers was coupled to a fiber optic sample holder (Bruker E-600-1023 L) for W-band experiments. Following photoexcitation, kinetic traces of the transient magnetization were accumulated under CW microwave irradiation (2-20 mW). The field modulation was disabled to achieve a $Q/\pi \nu \approx 30$ ns instrument response function (IRF), where Q is the quality factor of the resonator and ν is the resonant frequency, while microwave signals in emission (e) and/or enhanced absorption (a) were detected in both the real and the imaginary channels (quadrature detection). Sweeping the magnetic field gave two-dimensional spectra versus both time and magnetic field. For each kinetic trace, the signal acquired prior to the laser pulse was subtracted from the data. Kinetic traces recorded at magnetic field values offresonance were considered background signals, whose average was subtracted from all kinetic traces. The spectra were subsequently phased into a Lorentzian part and a dispersive part, and the former, also known as the imaginary magnetic susceptibility χ'' , is presented.

RESULTS

Synthesis and Steady State Characterization. The syntheses of 1–4 are described in detail in the Supporting Information. Briefly, 1 and 2 were synthesized by first making the corresponding monobrominated zinc tetraphenylporphyrin⁶⁸ and then using a Suzuki cross-coupling reaction to attach the silyl-protected BPNO[•] radical precursor,^{69,70} as shown in Scheme 1. BPNO[•] was prepared by deprotection of the silyl ether using TBAF to give the hydroxylamine, which was oxidized with PbO₂ to give BPNO[•]. The residual hydroxylamine precursor was separated from the radical by chromotography. Molecules 3 and 4 were synthesized by generating the boronic ester from brominated zinc 5-(4-bromophenyl)-10,15,20-triphenylporphyrin and performing a Suzuki cross-coupling reaction with iodo-BPDA(H)^{71,72} in THF. The BDPA radical was then prepared by treatment of the BDPA(H) porphyrin with

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and benzoquinone in THF at room temperature.

The UV-vis spectra of 1 and 2 are almost identical, with both showing the well-known Soret band of ZnTPP at 420 nm and Q-band at 550 nm (Figure 2).⁴³ There is little contribution to the UV-vis spectrum from BPNO[•], indicating that there is weak electronic coupling between radical and chromophore. The absorption spectra of 3 and 4 display an additional absorption band at 500 nm resulting from BDPA[•], as well as a broad, featureless absorption centered at approximately 330 nm, which continues to increase into the UV. The BPDA[•] extinction coefficient at 485 nm is 29 000 M⁻¹ cm⁻¹, and that of ZnTPP is 24 000 M⁻¹ cm⁻¹ at 548 nm.^{66,73}

Transient Absorption Spectroscopy. Transient absorption studies on 1-4 in toluene and THF were conducted to determine how the presence and connectivity of the radicals affects the



Figure 2. Normalized UV/vis of 1-4 in toluene.

photophysics of ZnTPP. Selective photoexcitation of ZnTPP in toluene to its lowest excited singlet state (¹*ZnTPP) at 590 nm produces a transient absorption spectrum having an absorption band at 465 nm, which then red shifts to about 480 nm with τ = 2.0 ns as ³*ZnTPP is formed (Figure S1, Supporting Information). Selective photoexcitation of the lowest energy absorption of ZnTPP in 1-4 with 590 nm, 110 fs laser pulses initially forms ¹*ZnTPP followed by ultrafast formation of ³*ZnTPP in both toluene (Figure 3) and THF (Figure S2, Supporting Information) with time constants that are all much shorter than the intrinsic SO-ISC time constant for ¹*ZnTPP (Table 1). The triplet yields were determined by comparing the absorption changes at 465 nm and 0.5 ps following the laser flash with those at 480 nm and 4.7 ns. The extinction coefficients for 1* ZnTPP and 3* ZnTPP at 465 and 480 nm are 5.6 imes 10 4 and $7.4 \times 10^4 \,\mathrm{M^{-1}\,s^{-1}}$, respectively.⁴³ The low signal-to-noise ratio from 3* ZnTPP in 3 and 4 is due to the constraint of photoexciting at 590 nm to avoid BDPA excitation. Since the extinction



compound	τ (¹ *ZnTPP \rightarrow ³ *ZnTPP) (ps)	$arphi_{ m T}$
1 (TOL)	4.0 ± 0.1	0.46 ± 0.02
1 (THF)	4.6 ± 0.3	0.49 ± 0.02
2 (TOL)	164 ± 5	0.60 ± 0.02
2 (THF)	144 ± 5	0.63 ± 0.02
3 (TOL)	19.4 ± 0.7	0.10 ± 0.02
3 (THF)	19.7 ± 0.7	0.10 ± 0.02
4 (TOL)	34 ± 1	0.20 ± 0.02
4 (THF)	39 ± 3	0.16 ± 0.02



Figure 3. Transient absorption spectra of 1-4 at times indicated in toluene and following a 110 fs, 590 nm laser pulse.



Figure 4. Transient absorption spectra of 1 at the indicated times in toluene and THF following a 7 ns, 416 nm laser pulse.

coefficient of ZnTPP is small at 590 nm, we cannot increase the concentration because it diminishes probe beam transmission through the sample. The formation of ^{3*}ZnTPP within 1–4 was also observed using nanosecond transient absorption spectroscopy (Figure 4 and Figure S3 in the Supporting Information). The decay of ^{3*}ZnTPP in 1 is significantly faster than that of ^{3*}ZnTPP⁴³ itself with $\tau = 77 \pm 1$ ns in both toluene and THF, while the corresponding decay time constants of 2–4 are all >50 μ s and limited by bimolecular collisions in solution. The shorter lifetime in 1 most likely results from the quenching of ^{3*}ZnTPP by EISC back to ground state in the presence of BPNO[•].

EPR Spectroscopy. The steady state CW EPR spectra of 1 and 2 at 295 K (Figure 5a) consist of a dominant hyperfine triplet splitting due to nitrogen (I = 1) that is split further by the protons responsible for the smaller hyperfine splittings. The hyperfine coupling constants are reported in Table 2 and were obtained by simulations using WINSIM.⁷⁴ The TREPR spectrum of 1 (Figure 5b) at X-band initially consists of a broad (\sim 20 mT baseline to baseline) feature that decays with $\tau = 161 \pm 4$ ns, and three absorptively polarized signals with hyperfine splittings of 1.2 mT appearing at later times that decay with $\tau = 1206 \pm 77$ ns. No signal is observed at W-band. The TREPR spectrum of 2 at W-band (Figure 5c) shows three strongly emissive signals that appear within the instrument response time. The corresponding X-band spectrum is shown in Figure S6 in the Supporting Information. The low field signal (D_0) appears at 3362.1 mT (g = 2.0057) with a hyperfine splitting of 1.2 mT, characteristic of the nitrogen in the BPNO $^{\bullet}$. The second signal at higher field (Q) appears at 3367.0 mT (g = 2.0027), while the third signal (D₁) is at 3372.1 mT (g = 1.9998). The emissive Q, D₁, and D₀ signals appear within our resonator response time, and the Q and D_1 states evolve to absorptive polarization over time with rise times of 38 \pm 2 and 25 \pm 45 ns, respectively, followed by decay to zero with $\tau = 1036 \pm 56$ ns for Q and 934 \pm 340 ns for D₁, while the polarization of the D₀ signal does not invert and decays to zero with $\tau = 425 \pm 14$ ns. In contrast to our previously reported results, we do not observe hyperfine splitting of the quartet signal (Q). This is likely a result of uncertainty broadening due to the fast initial decay.

Figure 6a shows the steady state EPR of 3 and 4 at X-band. BDPA[•] is a carbon-centered radical with most of its spin density localized on the allyl fragment and partial delocalization into the fluorenyl rings as evidenced by the hyperfine coupling constants given in Table 2. The TREPR spectra of 3 (Figure 6b) show an absorptive signal at early times (200 ns) and an emissive signal at longer times (700 ns). However, the polarization inversion $(a \rightarrow e)$ depends on the microwave power incident on the sample, indicating that the polarization inversion is due to transient nutations.¹¹ The line width of the transient polarized signal matches that of BDPA[•] measured by CW EPR spectroscopy. The TREPR spectrum of 4 shows an emissive signal that also oscillates with the incident microwave power (Figure 6c). No transient signal is observed at W-band.

By examining the spin dynamics in frozen solution, one can determine the ISC mechanism.⁴⁵ Thus we acquired TREPR spectra of 1 and 2 at 85 K (Figure 7) to determine the influence of the radical on the ISC mechanism. The TREPR spectrum of 1 shows two overlapping features, each with absorption at low field and emission at high field. The wide feature ($7\overline{5}$ mT baseline to baseline) matches the TREPR spectrum of ³*ZnTPP, while the narrower feature (45 mT baseline to baseline) is attributed to the quartet state resulting from exchange coupling the two electrons on ³*ZnTPP with that on BPNO[•]. The absorptive feature in the center of the spectrum is assigned to the ground state radical. Similar features are observed in 2, where a narrow feature (45 mT baseline to baseline) is observed with absorption at low field and emission at high field. In contrast, the TREPR spectra of 3 and 4 at 85 K (Figure 8) show a broad feature that is absorptive at low field and emissive at high field, matching the D and E values of ³*ZnTPP.⁴⁵ No polarization is observed in the center of the spectra of 3 and $\overline{4}$ at 85 K.

DISCUSSION

Ultrafast Excited State Dynamics. We have previously discussed in detail the most common radical-induced excited state quenching mechanisms.⁴⁰ To briefly summarize, radical-induced quenching of excited states usually proceeds by one or more of the following mechanisms: electron transfer, Förster and/or Dexter energy transfer, electron-exchange-induced enhanced intersystem crossing (EISC), and enhanced internal conversion (EIC), i.e., rapid vibrational relaxation.^{12–16,18,19,21–24,60,61,75,76}

The predicted rates for Förster energy transfer were calculated using PhotochemCAD software.⁷⁷ The rate constant for Förster energy transfer is given by⁶⁵

$$k_{\rm EnT}^{\rm F}(r) = \frac{\varphi_{\rm D}\kappa^2}{\tau_{\rm D}r^6} \left(\frac{9000(\ln 10)}{128\pi^5 N\eta^4}\right) \int_0^\infty F_{\rm D}(\lambda) \,\varepsilon_{\rm A}(\lambda)\lambda^4 \,\,\mathrm{d}\lambda \quad (1)$$

where $\varphi_{\rm D}$ is the quantum yield of fluorescence of the donor, κ is a factor describing the orientation of the transition dipoles with



Figure 5. CW EPR (a) and TREPR spectra (b and c) of 1 and 2 at times indicated following a 7 ns, 532 nm laser pulse at 295 K. 1 is shown at X-band (9.5 GHz), while 2 is shown at W-band (94 GHz).

respect to each other, η is the refractive index of the solvent, $\tau_{\rm D}$ is the fluorescence lifetime of the donor, $F_{\rm D}(\lambda)$ is the normalized fluorescence intensity of the donor and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor. The calculated Förster energy transfer rates are summarized in Table 3. For 1 and 2, this mechanism is unlikely because the BPNO[•] absorbance is weak ($\varepsilon = 10.5$ M^{-1} cm⁻¹ at 476 nm), so the spectral overlap with the ¹*ZnTPP emission is poor. Moreover, the ¹*ZnTPP energy $(\sim 2.06 \text{ eV})^{78}$ is well below the lowest excited doublet state energy of ²*BPNO[•] $(\sim 2.6 \text{ eV})$,⁴⁰ making both Förster and Dexter energy transfer unlikely mechanisms for *ZnTPP quenching. In contrast, energy transfer is possible for 3 and 4 because the ¹*ZnTPP energy is 2.06 eV,⁷⁸ which is well above that of the lowest energy electronic transition of BDPA[•] at 1.4 eV (865 nm).⁶⁶ However, the calculated Förster energy transfer rates for 3 and 4 (Table 3) are about an order of magnitude slower than the experimental time constants observed for ³*ZnTPP formation, making Förster

energy transfer an unlikely quenching mechanism. Given that Dexter energy transfer is an electron exchange process, it is possible that rapid through-bond energy transfer from ¹*ZnTPP to BDPA[•] occurs in 3 and 4.

To examine this possibility, femtosecond transient absorption spectra of ²*BDPA[•] in toluene were obtained by direct excitation of BDPA[•]. These transient spectra display a distinct absorption band at 527 nm in addition to a ground state bleach at 485 nm (Figure S4, Supporting Information). These transient features decay completely with $\tau = 14.9 \pm 0.3$ ps. The 527 nm transient absorption has an extinction coefficient of about 10^4 M⁻¹ s⁻¹ based on the bleach of the 485 nm ground state absorption ($\varepsilon = 2.9 \times 10^4$ M⁻¹ s⁻¹). Given these extinction coefficients, it should be possible to observe ²*BDPA[•] produced by energy transfer from ¹*ZnTPP; however, the transient absorption data for 3 and 4 show no evidence of ²*BDPA[•] formation. The time constants for ¹*ZnTPP decay given in Table 1 are only slightly longer than the ²*BDPA[•] lifetime, so it is unlikely that the inability to observe the formation of ²*BDPA[•] is a consequence of inverted kinetics.

The free energies of reaction for electron transfer from ^{1*}ZnTPP to BPNO[•] ($\Delta G \simeq 0.9$ eV in toluene and $\Delta G \simeq$ 0.3 eV in THF) or from BPNO[•] to ¹*ZnTPP ($\Delta G \simeq 1.0$ eV in toluene and $\Delta G \simeq 0.4$ eV in THF) are all positive, so electron transfer is ruled out as a ¹*ZnTPP quenching mechanism for 1 and 2 (see the Supporting Information). Similarly, electron transfer from BDPA[•] to ZnTPP in both solvents is not energetically feasible ($\Delta G_{\rm CS} \simeq 1.0$ eV in toluene and $\Delta G \simeq 0.4$ eV in THF). In contrast, electron transfer from ZnTPP to BDPA[•] is energetically favorable in both 3 and 4 ($\Delta G_{CS} \simeq -0.1$ eV in toluene and $\Delta G \simeq -0.6$ eV in THF), but the absence of the strong BDPA⁻ (absorption at 600 nm $(\varepsilon = 4.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})^{80}$ in the transient absorption spectra of 3 and 4 in both toluene (Figure 3) and THF (Figure S2, Supporting Information) indicates that electron transfer is not occurring in either solvent. It is highly unlikely that the electron transfer kinetics would be inverted in both low- and high-polarity solvents. This leaves enhanced internal conversion (EIC) as the principal quenching mechanism competitive with EISC. In the case of 1 and 2, the measured triplet yields indicate that EISC and EIC each account for about half the total quenching of ¹*ZnTPP by BPNO[•], while for 3 and 4, EIC is the dominant mechanism.

The lifetime of ³*ZnTPP in 1 is shorter than that of ³*ZnTPP itself, while the lifetimes of ³*ZnTPP in 2–4 are limited by bimolecular collisions in solution, and are too long be accurately measured by our instrument (>50 μ s). The short lifetime of 1 compared to 2–4 is most likely a result of an increase in the ISC rate of ³*ZnTPP to its ground state, which is a consequence of the very large exchange interaction between ³*ZnTPP and BPNO[•] in 1, and is consistent with the TREPR data discussed in the next section. In contrast, the diffusion-limited lifetimes of ³*ZnTPP in 2–4 suggest that the radical's presence does not play a substantial role in the quenching of ³*ZnTPP.

Radical—**Triplet Spin Interactions.** The spin Hamiltonian for radical—triplet interactions is given as

$$\begin{aligned} \hat{H} &= \hat{H}_{Z} + \hat{H}_{hf} + \hat{H}_{Dip} + \hat{H}_{Ex} \\ &= g_{T}\beta_{e}B\hat{S}_{Z}^{T} + g_{R}\beta_{e}B\hat{S}_{Z}^{R} + \sum_{i}\hat{S}^{R}\cdot A\cdot I_{i} \\ &+ \hat{S}^{T}\cdot D_{T}\cdot\hat{S}^{T} + \hat{S}^{T}\cdot D_{TR}\cdot\hat{S}^{R} + J_{TR}\hat{S}^{T}\cdot\hat{S}^{R} \end{aligned}$$
(2)

where β_{e} is the Bohr magneton, g_{T} and g_{R} are the *g* values for the

Tab	le 2	2. EP	R Hyp	erfine	Coup	lings	for	1-4	(mT)
-----	------	-------	-------	--------	------	-------	-----	-----	------

	Molecule	a_N	a1	a ₂	a ₃	a4
$H_1 + H_2 + H_4 + H_4$	1	1.187	0.214	0.214	0.082	0.082
H_1 H_2 H_3 H_4 H_4	2	1.242	0.185	0.086	0.200	0.217

	Molecule	1,1',8,8'	3,3',6,6'	2,2',7,7'	4,4',5,5'	9,9'	10, 10'
$ \begin{array}{c} 10\\ 2\\ 3\\ 4\\ 5\\ 6\\ 7 \end{array} $	3	0.203	0.183	0.036	0.015	0.019	0.004
$ \begin{array}{c} 10\\ 2\\ 3\\ 4\\ 5\\ 6\\ 7 \end{array} $	4	0.207	0.174	0.031	0.026	0.009	0.004

triplet and ground state radicals, respectively, B is the magnetic field, A is the hyperfine tensor and becomes a, the isotropic hyperfine coupling constant, in fluid solution, S and I are the electron and nuclear spin operators, D is the dipolar interaction, and *J* is the exchange interaction. When the exchange interaction between the electron on the radical and the electrons on the triplet, $|J_{TR}|$, is larger than the other magnetic interactions (strong exchange regime), the exchange interaction removes the spin degeneracy resulting in the formation of excited doublet and quartet states.⁸¹ In the strong exchange regime the *g* values of the excited doublet (g_D) and quartet (g_Q) should be linear combinations of the ground state doublet (g_R) and excited triplet (g_T) , according to eqs 3 and 4,⁸¹ while the hyperfine coupling constants a_N should follow eqs 5 and 6. The zero-field-splitting parameters for a quartet state are different from those for a triplet state and obey eq 7, where $D_{\rm Q}$ is the zero field splitting of the quartet state, $D_{\rm T}$ is the zero field splitting of the triplet state, and $D_{\rm TR}$ is the dipole-dipole interaction between the electrons on the triplet and the electron on the radical. In the weak exchange limit the EPR spectrum should show separate resonances for the triplet and ground state radicals with the corresponding hyperfine splitting and g values.

$$g_{\rm D} = -\frac{1}{3}g_{\rm R} + \frac{4}{3}g_{\rm T}$$
 (3)

$$g_{\rm Q} = \frac{1}{3}g_{\rm R} + \frac{2}{3}g_{\rm T}$$
 (4)

$$a_{\rm N}^{\rm D} = -\frac{1}{3}a_{\rm N}^{\rm R} \tag{5}$$

$$a_{\rm N}^{\rm Q} = \frac{1}{3} a_{\rm N}^{\rm R} \tag{6}$$

$$D_{\rm Q} = \frac{1}{3} \left(D_{\rm T} + D_{\rm TR} \right) \tag{7}$$

TREPR Spectroscopy. We employed TREPR spectroscopy at both X- and W-bands to probe the time evolution of the spin polarization of the three-spin systems, where two electrons reside on ^{3*}ZnTPP and one electron is on BPNO[•]. The TREPR spectrum of 1 at 295 K and X-band consists of a broad absorptive feature due to the Q and D₁ signals overlapping at early times that evolves into an absorptively polarized signal having a nitrogen hyperfine splitting matching that of the ground state radical. The overlapping Q and D₁ signals are slightly broader than those observed in 2, which results from lifetime broadening. The fast decay observed by TREPR is consistent with the transient optical results. The absorptive polarization is consistent with the sign of J.⁴⁰ No signal was observed at W-band due to the short lifetime of the three-spin system in 1.

The TREPR spectrum of **2** at room temperature at both Xand W-bands differs from that of **1**. The TREPR of **2** at W-band shows an emissively polarized signal at g = 2.0057, with a 1.2 mT hyperfine splitting, which matches the *g* value and hyperfine splitting of the BPNO[•] ground state, and is thus assigned to that



Figure 6. CW EPR (a) and TREPR spectra (b and c) of 3 and 4 at 295 K, following a 6 ns, 550 nm laser pulse at times indicated.

radical. Using the *g* value of ³*ZnTPP (2.001)³⁰ and eqs 3 and 4, the predicted *g* values of the Q and D₁ states ($g_Q = 2.0026$, $g_{D_1} = 1.999$) correspond well to the measured *g* values $g_Q = 2.0027$ and $g_{D_1} = 1.998$, respectively. The hyperfine splittings for Q and D₁ predicted by eqs 5 and 6 are not observed, which likely results from lifetime broadening.

The TREPR spectra observed at X-band for 1 and 2 at 85 K look similar, and display a broad feature that matches the 3* ZnTPP spectrum, while the narrow feature at center field is assigned to the $1/2 \nleftrightarrow -1/2$ transitions of the overlapping Q and D₁ states resulting from the interaction of 3* ZnTPP with BPNO[•]. The quartet state spectrum observed in Figure 7 has been observed in other ZnTPP systems when a radical is coordinatively attached to the Zn atom.^{29,31,32} The wide feature is assigned to 3* ZnTPP, which results from a small amount of sample degradation resulting in loss of the radical due to laser damage. Similar to the transient optical and TREPR data at room temperature, the TREPR spectrum of 1 decays much faster

compared to that of 2. Since the spin polarization pattern of the quartet state in 1 and 2 is the same as that of ZnTPP, it appears that the quartet state is still formed by SO-ISC and is merely accelerated by the presence of the radical.

We consider two spin mechanisms to explain the spin polarization observed in 1 and 2: ESPT and the RQM. The RTPM is not considered as it requires diffusive motion that cannot occur in our system. The results of 2 are consistent with the RQM, as we observe excited doublet and quartet states as well as polarization inversion. ESPT is ruled out for 2 since it results in quenching of the triplet state, which is not observed optically or by TREPR spectroscopy. Assigning the spin polarization mechanism for 1 is more difficult, as the polarization inversion of the quartets and doublets observed in 2 are not observed. However, the hyperfine lines are polarized in absorption. On the basis of previous results,⁴⁰ we know that changing the position of the radical from para to meta results in a change in the sign of J and therefore we would expect to observe absorptive features in 1. The observation of a quartet at 85 K indicates that $D_1 - Q_2$ mixing is occurring. The lack of polarization inversion results from fast EIC from D_1 to D_0 , which is a result of a large exchange coupling between ³*ZnTPP and BPNO[•]. This shows that despite the observed presence of doublets and quartets at early times indicative of the RQM, fast EIC from D1 to D0 kinetically outcompetes the equilibrium between D₁ and Q that results in the usual observation of polarization inversion at later times for the RQM.

The TREPR spectra of 3 and 4 at X-band and 295 K show polarized signals matching the width and g value (2.0026) of ground state BDPA[•] and are assigned to the polarized ground state. Although polarization inversion occurs in 3, it depends on microwave power (Figure S7, Supporting Information) and is thus due to transient nutations, not polarization inversion as a result of the RQM. Transient nutations are also observed in 4 (Figure S7, Supporting Information), but they do not result in polarization inversion. No evidence of quartet and excited doublet states is observed, indicating that the RQM is not occurring in 3 and 4. It is likely that the polarization results from a weak, but nonnegligible exchange interaction between ³*ZnTPP and BDPA[•]. This is not without precedent as we have recently reported a system in which a covalently bound TEMPO radical-PDI triplet state is weakly exchange coupled.⁴¹ Whether a three-spin system is in the strong or weak exchange regime as regards TREPR observation depends on the relative contributions from the exchange and Zeeman interactions, respectively. At X-band we observe only ground state polarization, indicating that the exchange interaction is weak, while no transient signal is observed at W-band. This indicates that the exchange interaction in the three-spin system at W-band is negligible relative to the Zeeman interaction, which increases 10-fold while the exchange interaction remains unchanged. The lack of polarization observed at 85 K coupled with the presence of a triplet signal and absence of a quartet signal at 85 K indicates that the exchange interaction is also weak at low temperatures. A decrease in J as the temperature is lowered has been observed previously in radical pairs within fixed distance donor-bridge-acceptor molecules.⁸²⁻⁸⁴ The exchange interaction depends on overlap of the relevant orbitals of ZnTPP with those of BDPA[•] or BPNO[•]. The dihedral angles between the phenyl rings joining ZnTPP to BDPA[•] or BPNO[•] undergo restricted rotation in fluid solution, allowing access to conformations with greater $\pi - \pi$ orbital overlap, which increases the coupling between them, while in



Figure 7. TREPR spectra of 1 and 2 in toluene at 85 K following a 7 ns, 550 nm laser pulse at X-band at the indicated times.



Figure 8. TREPR spectra of 3 and 4 at 85 K at X-band, following a 6 ns, 550 nm laser pulse 150 ns after the laser pulse.

Table 3. Calculated Förster Energy Transfer Rates for 1-4 in Toluene

molecule	κ^2	r^{a} (Å)	$ au_{\mathrm{EnT}}\left(\mathrm{ns} ight)$		
1	0.75	10.8	82		
2	1	10.4	61		
3	0.75	13.7	6.6		
4	1	11.8	2.7		
^{<i>a</i>} D–A distances modeled using Hyperchem MM+. ⁷⁹					

frozen solution the phenyl rings are restricted to dihedral angles which diminish the coupling. Although triplet—radical systems have received significant attention, relatively few systems are weakly coupled and none have negligible interaction at any temperature. It is difficult to measure *J* with certainty in these systems; however, we can deduce upper or lower limits based on whether 1-4 are in the strong or weak exchange regime at a given applied magnetic field. Compounds 1 and 2 are in the strong exchange regime even at W-band and thus 3*J* should be larger than 3500 mT. However, **3** and **4** are in the weak exchange regime at X-band, implying that 3*J* is smaller than 350 mT at room temperature.

Finally, we address a possible reason as to why EIC is the dominant quenching mechanism in 3 and 4, whereas EISC is the dominant quenching mechanism in 1 and 2. It is possible that the smaller exchange interaction between 3* ZnTPP and BDPA[•] in 3 and 4 results in slower EISC, which allows EIC to dominate kinetically; however, both EIC and EISC may depend on *J*. In addition to the small exchange interaction in 3 and 4, we believe

that other differences between BDPA[•] and BPNO[•] may account for the difference in quenching mechanisms. IC should be related to the number of vibrations coupled to the excited state. The exchange interaction allows the electrons on ¹*ZnTPP to spend some time on the radical. The unpaired electron in BDPA[•] is delocalized into the two fluorene rings which have more bonds compared to BPNO[•] and therefore more vibrations to accelerate IC.

CONCLUSION

Transient optical spectroscopy reveals that BPNO[•] quenches ^{1*}ZnTPP competitively by EISC and EIC mechanisms, while BDPA[•] does so by a dominant EIC mechanism in covalent ZnTPP-radical systems at fixed distances. Both quenching mechanisms are essentially independent of solvent polarity. TREPR spectroscopy shows that, when J is sufficiently large, EISC results in fast quenching of ³*ZnTPP as well, and as a result, polarization inversion is not observed in the RQM. TREPR spectroscopy also shows that there is a temperature-dependent exchange interaction between ³*ZnTPP and BDPA[•] which is weak at room temperature and negligible at cryogenic temperatures because no quartet signal is observed and BDPA[•] polarization is absent. This is the first time that a negligible exchange interaction is shown at any temperature in a covalently bound radical-triplet system. This work shows that by decreasing the exchange interaction it is possible to slow down EISC to permit EIC to dominate. Moreover, it demonstrates that the magnitude of the exchange interaction is not only important in determining the rate of excited state quenching, but it can also drastically alter the excited state quenching mechanism.

ASSOCIATED CONTENT

Supporting Information. Experimental details, including synthesis, additional transient absorption, and TREPR data. This material is available free of charge via the Internet at http://pubs. acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: m-wasielewski@northwestern.edu.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant CHE-1012378. M.T.C. thanks the Link Foundation for a fellowship.

REFERENCES

- (1) Wasielewski, M. R. J. Org. Chem. 2006, 71, 5051-5066.
- (2) Verhoeven, J. W. J. Photochem. Photobiol., C 2006, 7, 40-60.
- (3) Segura, J. L.; Martin, N.; Guldi, D. M. Chem. Soc. Rev. 2005, 34, 31-47.
- (4) Holten, D.; Bocian, D. F.; Lindsey, J. S. Acc. Chem. Res. 2002, 35, 57-69.
- (5) Lukas, A. S.; Wasielewski, M. R. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001; pp 1–35.
- (6) de Silva, A. P.; Guanaratne, H. Q. N.; Gunnlaugsson, T.; Huxley,
 A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* 1997, 97, 1515–1566.
 - (7) Rajca, A. Adv. Phys. Org. Chem. 2005, 40, 153-199.

(8) Mehring, M.; Mende, J. Phys. Rev. A: At., Mol., Opt. Phys. 2006, 73, 052303/052301-052303/052312.

(9) Harneit, W. Phys. Rev. A 2002, 65, 032322.

(10) Jones, J. A. In The Physics of Quantum Information; Bouwmeester,

D., Ekert, A., Zeilinger, A., Eds.; Springer: Berlin, 2000; pp 177-189.

- (11) Schweiger, A.; Jeschke, G. Principles of Pulse Electron Paramagnetic Resonance; Oxford University Press: Oxford and New York, 2001.
- (12) Blough, N. V.; Simpson, D. J. J. Am. Chem. Soc. 1988, 110, 1915–1917.
- (13) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. J. Am. Chem. Soc. 1983, 105, 6205–6210.
- (14) Green, J. A.; Singer, L. A.; Parks, J. H. J. Chem. Phys. 1973, 58, 2690–2695.
- (15) Green, S. A.; Simpson, D. J.; Zhou, G.; Ho, P. S.; Blough, N. V. J. Am. Chem. Soc. **1990**, *112*, 7337–7346.
- (16) Herbelin, S. E.; Blough, N. V. J. Phys. Chem. B 1998, 102, 8170–8176.
- (17) Hrdlovic, P.; Chmela, S.; Sarakha, M.; Lacoste, J. J. Photochem. Photobiol, A 2001, 138, 95–109.
- (18) Karpiuk, J.; Grabowski, Z. R. Chem. Phys. Lett. 1989, 160, 451–456.
- (19) Kollar, J.; Hrdlovic, P.; Chmela, S.; Sarakha, M.; Guyot, G. J. Photochem. Photobiol., A **2005**, 170, 151–159.
- (20) Kuz'min, V. A.; Tatikolov, A. S. Chem. Phys. Lett. 1977, 51, 45–47.
- (21) Likhtenstein, G. I.; Ishii, K.; Nakatsuji, S. i. *Photochem. Photobiol.* 2007, 83, 871–881.
- (22) Medvedeva, N.; Martin, V. V.; Weis, A. L.; Likhtenshten, G. I. J. Photochem. Photobiol., A **2004**, *163*, 45–51.
- (23) Sartori, E.; Toffoletti, A.; Corvaja, C.; Moroder, L.; Formaggio, F.; Toniolo, C. *Chem. Phys. Lett.* **2004**, *385*, 362–367.
- (24) Yee, W. A.; Kuzmin, V. A.; Kliger, D. S.; Hammond, G. S.; Twarowski, A. J. J. Am. Chem. Soc. **1979**, 101, 5104–5106.

- (26) Blättler, C.; Jent, F.; Paul, H. Chem. Phys. Lett. 1990, 166, 375-380.
- (27) Fujisawa, J.; Ishii, K.; Ohba, Y.; Yamauchi, S.; Fuhs, M.; Möbius, K. J. Phys. Chem. A **1999**, 103, 213–216.
- (28) Fujisawa, J.; Ishii, K.; Ohba, Y.; Iwaizumi, M.; Yamauchi, S. J. Phys. Chem. **1995**, *99*, 17082–17084.

(29) Fujisawa, J.; Ishii, K.; Ohba, Y.; Yamauchi, S.; Fuhs, M.; Möbius, K. J. Phys. Chem. A **1997**, 101, 5869–5876.

- (30) Fujisawa, J.-i.; Ohba, Y.; Yamauchi, S. J. Am. Chem. Soc. 1997, 119, 8736–8737.
- (31) Ishii, K.; Fujisawa, J.; Ohba, Y.; Yamauchi, S. J. Am. Chem. Soc. **1996**, *118*, 13079–13080.
- (32) Ishii, K.; Fujisawa, J.-i.; Adachi, A.; Yamauchi, S.; Kobayashi, N. J. Am. Chem. Soc. **1998**, *120*, 3152–3158.
- (33) Ishii, K.; Hirose, Y.; Fujitsuka, H.; Ito, O.; Kobayashi, N. J. Am. Chem. Soc. 2001, 123, 702–708.
 - (34) Kawai, A.; Obi, K. J. Phys. Chem. 1992, 96, 52-56.
- (35) Kawai, A.; Okutsu, T.; Obi, K. J. Phys. Chem. **1991**, 95, 9130–9134.
- (36) Kawai, A.; Shibuya, K. J. Photochem. Photobiol., C 2006, 7, 89–103.
- (37) Rozenshtein, V.; Berg, A.; Stavitski, E.; Levanon, H.; Franco, L.; Corvaja, C. J. Phys. Chem. A **2005**, *109*, 11144–11154.
- (38) Teki, Y.; Kimura, M.; Narimatsu, S.; Ohara, K.; Mukai, K. Bull. Chem. Soc. Jpn. 2004, 77, 95–99.
- (39) Ohba, Y.; Nishimura, M.; Mizuochi, N.; Yamauchi, S. *Appl. Magn. Reson.* **2004**, *26*, 117–134.
- (40) Giacobbe, E. M.; Mi, Q.; Colvin, M. T.; Cohen, B.; Ramanan,
- C.; Scott, A. M.; Yeganeh, S.; Marks, T. J.; Ratner, M. A.; Wasielewski,
- M. R. J. Am. Chem. Soc. 2009, 131, 3700–3712.
- (41) Colvin, M. T.; Giacobbe, E. M.; Cohen, B.; Miura, T.; Scott, A. M.; Wasielewski, M. R. *J. Phys. Chem. A* **2010**, *114*, 1741–1748.
- (42) Giaimo, J. M.; Lockard, J. V.; Sinks, L. E.; Scott, A. M.; Wilson,
 T. M.; Wasielewski, M. R. J. Phys. Chem. A 2008, 112, 2322–2330.
- (43) Pekkarinen, L.; Linschitz, H. J. Am. Chem. Soc. 1960, 82, 2407-2411.
 - (44) Gonen, O.; Levanon, H. J. Phys. Chem. 1985, 89, 1637-1643.
 - (45) Levanon, H.; Norris, J. R. Chem. Rev. 1978, 78, 185-198.
- (46) Fujisawa, J.; Ohba, Y.; Yamauchi, S. Chem. Phys. Lett. 1998, 282, 181–186.
- (47) Fujisawa, J.; Ohba, Y.; Yamauchi, S. Chem. Phys. Lett. 1998, 294, 248–254.
- (48) Tarasov, V. F.; Saiful, I. S. M.; Iwasaki, Y.; Ohba, Y.; Savitsky, A.; Möbius, K.; Yamauchi, S. *Appl. Magn. Reson.* **2006**, *30*, 619–636.
- (49) Tarasov, V. F.; Saiful, I. S. M.; Ohba, Y.; Takahashi, K.; Yamauchi, S. Spectrochim. Acta, Part A 2008, 69, 1327–1330.

(50) Ishii, K.; Bottle, S. E.; Shimizu, S.; Smith, C. D.; Kobayashi, N. *Chem. Phys. Lett.* **2003**, 370, 94–98.

- (51) Blank, A.; Levanon, H. J. Phys. Chem. A 2001, 105, 4799-4807.
- (52) Corvaja, C.; Franco, L.; Toffoletti, A. Appl. Magn. Reson. 1994, 7, 257–269.
- (53) Goudsmit, G. H.; Paul, H.; Shushin, A. I. J. Phys. Chem. 1993, 97, 13243-13249.
- (54) Hugerat, M.; van der Est, A.; Ojadi, E.; Biczok, L.; Linschitz, H.; Levanon, H.; Stehlik, D. J. Phys. Chem. **1996**, *100*, 495–500.
- (55) Jenks, W. S.; Turro, N. J. J. Am. Chem. Soc. 1990, 112, 9009–9011.
- (56) Regev, A.; Galili, T.; Levanon, H. J. Phys. Chem. 1996, 100, 18502-18510.
- (57) Turro, N. J.; Khudyakov, I. V.; Bossmann, S. H.; Dwyer, D. W. J. Phys. Chem. **1993**, *97*, 1138–1146.
- (58) Imamura, T.; Onitsuka, O.; Obi, K. J. Phys. Chem. 1986, 90, 6741-6744.
- (59) Conti, F.; Corvaja, C.; Busolo, F.; Zordan, G.; Maggini, M.; Weber, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 495–502.
 - (60) Green, S.; Fox, M. A. J. Phys. Chem. 1995, 99, 14752-14757.

(61) Araki, Y.; Luo, H.; Islam, S. D. M.; Ito, O.; Matsushita, M. M.; Iyoda, T. J. Phys. Chem. A **2003**, 107, 2815–2820.

(62) Borisevich, Y. E.; Kuz'min, V. A.; Renge, I. V.; Darmanyan, A. P. Izv. Akad. Nauk SSSR, Ser. Khim. **1981**, 2014–2019.

(63) Samanta, A.; Kamat, P. V. *Chem. Phys. Lett.* **1992**, *199*, 635–639.
(64) Puskin, J. S.; Vistnes, A. I.; Coene, M. T. Arch. Biochem. Biophys.

1981, 206, 164–172. (65) Lakowicz, J. R. Principles of Fluorescence Spectroscopy; Kluwer:

Dordrecht, The Netherlands, 1999.

(66) Breslin, D. T.; Fox, M. A. J. Phys. Chem. 1993, 97, 13341–13347.

(67) Ahrens, M. J.; Sinks, L. E.; Rybtchinski, B.; Liu, W.; Jones, B. A.;

Giaimo, J. M.; Gusev, A. V.; Goshe, A. J.; Tiede, D. M.; Wasielewski, M. R. J. Am. Chem. Soc. 2004, 126, 8284–8294.

(68) Li, J. W.; Prentice, G. J. Electrochem. Soc. 1997, 144, 4284–4288.

(69) Baskett, M.; Lahti, P. M.; Paduan-Filho, A.; Oliveira, N. F., Jr. *Inorg. Chem.* **2005**, *44*, 6725–6735.

(70) Lahti, P. M. In *Molecular Magnetism: New Magnetic Materials;* Itoh, K., Kinoshita, M., Eds.; Kodansha and Gordon & Breach: Tokyo and Amsterdam, 2001.

(71) Plater, M. J.; Kemp, S.; Lattmann, E. J. Chem. Soc., Perkin Trans. 1 2000, 971–979.

(72) Kuhn, R.; Neugebauer, F. A. Monatsh. Chem. 1964, 95, 3-23.

(73) Barnett, G. H.; Hudson, M. F.; Smith, K. M. J. Chem. Soc., Perkin Trans. 1 1975, 1401–1403.

(74) Duling, D. R. J. Magn. Reson. B 1994, 104, 105-110.

(75) Kollar, J.; Hrdlovic, P.; Chmela, S.; Sarakha, M.; Guyot, G. J. Photochem. Photobiol, A 2005, 171, 27–38.

(76) Watkins, A. R. Chem. Phys. Lett. 1974, 29, 526-528.

(77) Du, H.; Fuh, R.-C. A.; Li, J.; Corkan, L. A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141–142.

(78) Hayes, R. T.; Walsh, C. J.; Wasielewski, M. R. J. Phys. Chem. A **2004**, 108, 2375–2381.

(79) Hypercube Inc., 1115 NW 4th St., Gainesville, FL 32601, USA, 1994.

(80) Mi, Q. Northwestern University: Evanston, IL, USA, 2009; p 325.

(81) Bencini, A.; Gatteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled Systems*; Springer-Verlag: Berlin and New York, 1990.

(82) Dance, Z. E. X.; Mi, Q.; McCamant, D. W.; Ahrens, M. J.; Ratner, M. A.; Wasielewski, M. R. J. Phys. Chem. B 2006, 110, 25163–25173.

(83) Zeidan, T. A.; Carmieli, R.; Kelley, R. F.; Wilson, T. M.; Lewis,
 F. D.; Wasielewski, M. R. J. Am. Chem. Soc. 2008, 130, 13945–13955.

(84) Carmieli, R.; Zeidan, T. A.; Kelley, R. F.; Mi, Q.; Lewis, F. D.; Wasielewski, M. R. J. Phys. Chem. A **2009**, 113, 4691–4700.