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Radical Enhanced Intersystem Crossing (EISC) in New Bodipy Derivatives and Application for Efficient Triplet-Triplet Annihilation Upconversion

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Abstract: A long-lived triplet excited state of the well-known fluorophore borondipyrromethene (Bodipy) was observed for the first time via efficient radical-enhanced intersystem crossing (EISC). The triplet state has been obtained in two dyads in which Bodipy unit is linked to a nitroxide radical, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) with two different length spacers. The photophysical properties were studied with steady-state and time-resolved transient optical spectroscopies, and electron spin resonance (cw-ESR and TR-ESR). The fluorescence of Bodipy units is significantly quenched in the dyads, and the spin polarized TEMPO signal were observed with TR-ESR, generated by a Radical Triplet Pair Mechanism (RTPM). Efficient EISC ($\Phi_T = 80\%$) was observed for the dyad with shorter linker and the triplet state lifetime of Bodipy chromophore is exceptionally long (62 µs). The EISC takes 250 ps. Poor ISC was observed for the dyad with longer linker. The efficient ISC and long-lived triplet excited state in this flexible system are in stark contrast to the previously studied rigid EISC systems. EISC effect was employed for the first time to perform triplet-triplet annihilation (TTA) upconversion (quantum yield $\Phi_{UC} = 6.7\%$).

Keywords: Bodipy; Intersystem Crossing; Radical; Electron Spin Polarization; Upconversion

1. INTRODUCTION

Triplet photosensitizers are versatile compounds which have been widely used in photocatalysis,¹⁻⁶ photodynamic therapy,⁷⁻¹² photovoltaics,^{13–15} and recently in triplet-triplet-annihilation (TTA) upconversion.^{16–20} Triplet photosensitizers are expected to show strong absorption of visible light, efficient intersystem crossing (ISC) and long-lived triplet excited state, as well as feasibly derivatizable molecular structures.^{7,9} However, it is not a trivial task to tackle all these challenges. For example, it is elusive to enhance the ISC of organic compounds which are heavy atom-free (contain no transition metal atom or iodine or bromine atom, etc). It

is still a major challenge to rationally design heavy atom-free organic chromophores to show predetermined efficient ISC.^{9,21} Although some methods have been developed recently, such as using an electron spin converter or singlet fission effect,^{22–27} much room is left to explore new approaches to enhance ISC in organic chromophores.

Quenching of fluorescence by stable radicals, such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), has been known for a long time. In most of the previous studies, the quenching effect was only used for designing of fluorescent chemosensors (molecular probes) for selective detection of radicals.^{28–31} Ouenching of the singlet state by stable radical is determined by spin interactions between the photo-excited chromophores and the radicals. A series of spin states with different spin multiplicities are generated by this interaction.^{32–40} Triplet states can be formed, by enhancing the spontaneous ISC, together with radicals in non-Boltzmann distribution of population within the different spin states (this is the so-called electron spin polarization, ESP).⁴¹ ESP can be caused by a few different mechanisms, as the most frequent is the radical triplet pair mechanism (RTPM).^{32,41} The seminal paper on radical enhanced ISC (EISC) by timeresolved ESR (TR-ESR) methods is by Kawai and Obi in 1992,⁴² followed by one of us few years later.⁴³ Recently the ESP of the radical-labeled perylene,⁴⁴ phthalocyanines,^{33,34} and anthracene chromophores upon photoexcitation were studied.^{35,41} However, most studies focus on the ESP mechanisms, and the radical EISC has never been exploited to design a highly efficient triplet photosensitizers for any applications to drive a photophysical or photochemical process. On the other hand, paramagnetic compounds (mostly nitroxides) are widely used for invivo applications.⁴⁵ Thus radical EISC based triplet photosensitizers will be promising multifunctional photosensitizers. For example, the MRI-guided photodynamic therapy (PDT) based on a radical triplet photosensitizer will give an accurate delineation of the target tumor

region, and precise delivery of the treatment light by optical-fiber. As such the tumor detection, treatment and therapeutic efficiency evaluation can be accomplished with a single compound.

Radical enhanced ISC represents an interesting alternative to the conventional methods to access the triplet excited states of organic chromophores upon photoexcitation. However, there is much room remaining for the designing and application of radical EISC-based triplet photosensitizers. Concerning this aspect, herein we designed an efficient EISC-based triplet photosensitizer by linking the radical to a chromophore, boron dipyrromethene (Bodipy, Bodipy). Bodipy is of particular interest due to strong absorption of visible light, high fluorescence quantum yield (associated to an inhibited non-radiative decay of the electronic excited state) and feasibly derivatizable molecular structures.^{8,46–50} Bodipy has been used for preparation of triplet photosensitizers, ^{7,9} and the ISC of these Bodipy chromophores was achieved with various mechanisms, such as heavy atom effect, ^{10,11,21} charge recombination, ^{23,24} spin converter, ²⁴ and exciton coupling effect, ^{12,51} etc. Interestingly, production of the triplet excited state of Bodipy with radical EISC, and the ESP caused by triplet state of Bodipy, were never studied.

Moreover, application of the high-spin state of Bodipy will open a new avenue for photochemistry of Bodipy. For example, the TTA upconversion, which exploits the strong absorption of light by the photosensitizer, can reach an high upconversion quantum yield.^{16–20} Together with the flexibility in terms of excitation/emission wavelengths, the TTA upconversion has been used for luminescence bioimaging,⁵² photovoltaics,⁵³ photocatalysis⁵⁴ and optical materials.^{55–59} Among the other aspects of research on TTA upconversion, designing new triplet photosensitizers is vital for attaining highly efficient TTA upconversion. However, all the known photosensitizers for TTA upconversion are based on molecules with efficient triplet state formation, and most triplet state formation relies on heavy atom effect to enhance the ISC process. Heavy atom-free photosensitizers for TTA upconversion are rare. Previously we

developed triplet photosensitizers for TTA upconversion which are based on the use of spin converter, such as C_{60} , to enhance the ISC.^{23,24,60} Recently heavy atom-free organic triplet photosensitizers based on thermally activated delayed fluorescence (TADF) were also reported.^{61,62} Herein we prepared Bodipy-TEMPO dyads to study the EISC effect in Bodipy chromophores (Scheme 1) and we applied the new systems in TTA upconversion. A dramatic change in the photophysics of the excited states of Bodipy is induced by the flexibly linked radical unit, producing a strong visible light absorptive molecule with highly efficient ISC and a long-living

producing a strong visible light absorptive molecule with highly efficient ISC and a long-living excited triplet state. Linkers between the two units in the dyads with different length were used to probe the effect of the radical on the singlet excited state of Bodipy. The photophysical properties were studied with steady-state and time-resolved optical spectroscopies, continuous wave (cw) and TR-ESR spectroscopies. The fluorescence of the Bodipy unit is significantly quenched in the dyads. Exceptionally high triplet state quantum yield was observed ($\Phi_T = 80\%$), and it was found the Φ_T is highly dependent on the length of the linker between the Bodipy and the TEMPO units. The highly efficient EISC and the long triplet state lifetime ($\tau_T = 60 \ \mu$ s) are *unprecedented* in the radical-induced EISC studies, and the dyad was used as novel triplet photosensitizer for TTA upconversion.

2. Results and Discussion

2.1. Design, Synthesis and the Molecular Structure of the Compounds. Two Bodipy-TEMPO dyads were prepared (**BDP-TEMPO-1** and **BDP-TEMPO-2**, Scheme 1; **BDP** is the abbreviation of Bodipy), in which the linkers between **BDP** and TEMPO units are varied with different lengths: **BDP-TEMPO-1** is with longer linker, and **BDP-TEMPO-2** is with shorter



Scheme 1. Synthesis of the triplet photosensitizers BDP-TEMPO-1 and BDP-TEMPO-2^a

^{*a*} Key: (i) Propargyl bromide, NaH, DMF, rt, 3 h in Ar, 49 %. (ii) Et₃N, CuI, 12 h, at rt, in Ar, 65 %. (iii) Phenylacetylene, Et₃N, CuI, 12 h, at rt, in Ar, 40 %. (iv) Et₃N, CuI, 12 h, at rt, in Ar, 50 %.

linker (Scheme 1). Azide-alkyne Huisgen cycloaddition reaction was used to construct the linker.^{63,64} We expected the molecule to adopt both the extended and folded conformations, as shown from molecular dynamics (MD) simulations (it will be published elsewhere) for which we give a brief discussion.

MD studies showed that the linkers are flexible, thus these distances and the orientation of the radical with respect to the chromophore varies substantially with time. The dyads have shown to be able to display folded conformations which last for only 1 to 2 nanoseconds, then they transform rapidly to extended conformation. This is expected to play a major role on the photophysical properties of the BDP chromophore, ^{34,44,65,66} in particular in enhancing the ISC process.⁶⁵

In the extended conformations the average distance between the chromophore and the nitroxide (distance between B and O of the nitroxide group) is normally 18 and 13 Å for **BDP-TEMPO-1** and **BDP-TEMPO-2**, respectively. The first value has been confirmed by single crystal XRD studies. We failed to obtain the single crystal of **BDP-TEMPO-2** due to its poor crystability.

The single crystal of **BDP-TEMPO-1** was obtained by slow diffusion of *n*-hexane into ethanol solution of the compound. The molecular structure of **BDP-TEMPO-1** is determined (Figure 1 and Table S1). **BDP-TEMPO-1** crystallized in the triclinic crystal system in the *P*-1 space group with two molecules in the asymmetric unit.



Figure 1. The ORTEP view of the single crystal structure of **BDP-TEMPO-1** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The molecules adopt an extended conformation in the single crystal, with a distance of 18.04 Å between the spin density center (O atom of the nitroxide moiety of the TEMPO unit) and the chromophore (B atom of the Bodipy unit), and likely this is the same extended conformation found in solution by MD.

MD has also shown that the molecules can also adopt folded conformations, where the distance between the radical and the chromophore is much shorter. Folded conformations are obtained because of torsional freedom of the single bonds within the linkers. In folded conformations the distance between the two can be as short as 8 Å.

2.2. UV–vis Absorption and Fluorescence Spectra. The UV–vis absorption spectra of the dyads **BDP-TEMPO-1** and **BDP-TEMPO-2** do not show any significant difference from that of reference compounds **BDP-1** and **BDP-2** (Figure 2a). Thus we propose that electronic interaction between the Bodipy and TEMPO units at the ground state is small (it must be smaller than about 10 cm⁻¹, based on the later ESR studies). No enhanced $S_0 \rightarrow T_1$ transition was observed for the dyads, despite of the presence of the radical.⁶⁷



Figure 2. (a) UV-vis absorption spectra of BDP-TEMPO-1, BDP-1, BDP-2 and BDP TEMPO-2, $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C. (b) Fluorescence emission spectra of BDP-2, BDP-TEMPO-2 and BDP-TEMPO-2 + AIBN ($\lambda_{ex} = 508$ nm) in toluene. Optically matched solutions were used. $c = ca. 1.0 \times 10^{-5}$ M. 20 °C.

In stark contrast to the UV–vis absorption spectra, the fluorescence of the dyads are drastically different from the reference compounds **BDP-1** and **BDP-2** (Figure 2b). For example, the fluorescence intensity of **BDP-TEMPO-2** is only 25% of that of **BDP-2**, the latter is known to have a high fluorescence quantum yield and very weak ISC,^{46,48,49} i.e. the fluorescence intensity was quenched by 75% with attachment of the TEMPO unit on the Bodipy chromophore. Similar trend was observed for **BDP-1** and **BDP-TEMPO-1** (Supporting Information, Figure S16). We propose the quenching of the singlet excited state is due to EISC. This postulation was confirmed by the radical combination reaction with azobisisobutyronitrile (AIBN) under heating condition to give an ether product (Supporting Information, Scheme S1 and Figure S16 ~ Figure S19, Supporting Information). Upon this radical combination reaction and transform of the TEMPO radical into an ether structure, the fluorescence intensity was fully recovered (Figure 2b).

Other possible mechanisms for quenching of the fluorescence of Bodipy in the radical-labeled fluorophore can be ruled out, i.e. intra- or intermolecular Förster resonance energy transfer (FRET), or Dexter energy transfer to the radical moiety, because of the small oscillator strength of the n- π * transition of the TEMPO, and the unmatched energy levels of the Bodipy with those of the radical (which is important for both the Förster and Dexter energy transfer).^{34,65} Photo-induced electron transfer (PET) can be also excluded based on both electrochemical measurements (will be published elsewhere) and TR-ESR measurements. Finally, enhanced internal conversion (EIC) is also excluded for **BDP-TEMPO-2** due to the high yield of the triplet state ($\Phi_T = 80\%$, see later section).⁴⁴ Control experiments proved that the *intermolecular* interaction of the Bodipy chromophore with TEMPO is much less efficient (the proof has been given by studying a solution contained both Bodipy and TEMPO, Figure S14, Supporting Information). These results indicate that the linker length exerts vital effect on the quenching of

the fluorescence of Bodipy chromophore, and it is most likely the spin exchange interaction between the singlet excited chromophore and the radical that quenched the fluorescence.^{32,68} This electron exchange interaction, is strongly dependent on the molecular orbital overlap,^{44,65,67} and it is reasonably favoured when the two partners are kept closer, and thus more effective in

BDP-TEMPO-2 than in **BDP-TEMPO-1**.⁶⁹

The photophysical properties were summarized in Table 1. The fluorescence lifetimes of BDP-

TEMPO-1, **BDP-1**, **BDP-TEMPO-2** and **BDP-2** were compared (Table 1). The results show that distinct double-exponential decay were observed for **BDP-TEMPO-2**, which is tentatively attributed to the change in the relative geometry between the TEMPO and the Bodipy unit, provide both large and small interactions between the two units.³³ **BDP-TEMPO-1** also show shorter fluorescence lifetime (1.4 ns) compared to **BDP-1** (3.4 ns).

	$\lambda_{\rm abs}/{\rm nm}^{a}$	\mathcal{E}^{b}	$\lambda_{\rm em}/{\rm nm}^{c}$	$\Phi_{ m F}{}^d$	$\tau_{\rm T}/\mu s^{\ e}$	$\tau_{\rm F}/{ m ns}^{f}$	$\Phi_{\Delta}{}^{g}$	$\Phi_{\mathrm{T}}{}^{h}$
BDP-1	503	8.86	515	0.90^{i}	j	3.4	j	_j
BDP-TEMPO-1	504	8.78	515	0.29	190	1.4	0.14	0.14
BDP-TEMPO-1+AIBN	504	8.81	515	0.95	j	3.8	j	_j
BDP-2	522	8.45	536	0.99	_j	5.6	j	j
BDP-TEMPO-2	523	8.33	536	0.05	62	0.2(96%)	0.56	0.80
						5.0 (4%)		
BDP-TEMPO-2+AIBN	523	8.40	536	0.98	_j	5.7	j	j

Table 1. Photophysical Parameters of the Compounds

^{*a*} Maximal UV–vis absorption wavelength in toluene $(1.0 \times 10^{-5} \text{ M})$. ^{*b*} Molar absorption coefficient at absorption maxima. $\varepsilon : 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. ^{*c*} Maximal emission wavelength in toluene $(1.0 \times 10^{-5} \text{ M})$. ^{*d*} The fluorescence quantum yields in toluene, with **BDP-1** ($\Phi_L = 0.90$, in toluene) and **IBDP** ($\Phi_L = 0.036$, in toluene) as the standard. ^{*e*} Measured by transient absorption in toluene $(1.0 \times 10^{-5} \text{ M})$. ^{*f*} The fluorescence lifetime, in toluene $(1.0 \times 10^{-5} \text{ M})$, $\lambda_{ex} = 445$ nm for **BDP-1** series, $\lambda_{ex} = 405$ nm for **BDP-2** series. ^{*g*} Singlet oxygen quantum yields in toluene, **IBDP** were

used as standard ($\Phi_{\Delta} = 0.85$ in toluene). ^{*h*} Triplet quantum yields in toluene, **Eosin Y** were used as standard ($\Phi_{T} = 0.56$ in methanol). ^{*i*} Literature values.^{70 *j*} Not applicable.

2.3. TR-ESR Measurements: EISC Process and Electron Spin Polarization (ESP). We used

TR-ESR spectroscopy to study the generation of the electron spin polarization (ESP) as a proof of the activation of the EISC channel; and the involvement of the conformational changes (folding/unfolding) both on the EISC process and on the lifetime of the triplet. ESP is produced because the interaction between TEMPO radical and the photoexcited state BDP moieties activate processes that create a non-Boltzmann population (spin polarization) of the radical electron spin sublevels that can be detected by TR-ESR: signals in enhanced Absorption (*A* polarization, lower spin level, β , is much more populated than upper spin level, α) or in *E*mission (*E* polarization, upper spin level, α , is more populated than lower spin level, β) can be observed.³³ The analysis of the polarization of the ESR spectra allowed us to obtain information on the photophysical deactivation path of the dyads.

When the chromophore is in a formal triplet state, the description of the global state of the molecule is influenced by the possible triplet - radical interaction. The Hamiltonian for the interaction is given by the exchange term as $-2J S_T \cdot S_R$, where S_T , S_R are the spin momentum of the chromophore triplet state and that of the radical respectively, and J is a measure of the separation between the doublet and the quartet states (the energy separation is 2J). As detailed in the specific section in the Supporting Information, the J values are defined as "small" or "large" when compared to the Zeeman interaction.

The electronic states that are better described in the *coupled representation*, thus with the total spin number as quantum number, when the *J*-value is larger than the Zeeman term.⁷¹ When the exchange interaction is much smaller than the Zeeman term, the *uncoupled representation* is preferred, where the two moieties are treated separately; a total spin number can be formally

provided also in this case. Because of the folding/unfolding motion, both representations have to be used to describe the molecule in the folded/extended configurations.

We will use the ${}^{2S+1}[R-T]$ notation for the strongly interacting triplet-doublet pairs, forming a doublet (D, $S_{Total} = 1/2$ and consequently 2S+1=2) or a quartet (Q, $S_{Total} = 3/2$ and consequently 2S+1=4) state, whereas the term ${}^{(2S+1)}[R,T]$ will be used to indicate weakly interacting moieties in the extended conformations. In this last case the total spin number is less essential for the description of the state.



Figure 3. (a) TR-ESR spectrum in frozen toluene solution of **BDP-TEMPO-2** ($c = 2 \times 10^{-4}$ M) at 80 K with excitation at 503 nm. (b) the simulation of the experimental spectrum as sum of two species: two triplet states (Tr1 and Tr2) spin coupled to the radical. The magnetic parameters of Tr1 and Tr2 were determined experimentally as reported in the Supporting information. The polarization pattern of the zero-field states were (0; 0.17; 0; 1.0; 0.67; 1.0) and (1.0; 0.0; 0.0; 0.6; 0.47; 0.33) for ⁴[R,Tr1] and ⁴[R–Tr2] respectively, while $J_{TR} = 170$ and 1.2×10^4 MHz for the two. In the simulation the D_{TR} was neglected because its value is within the linewidth value of 100 MHz.

We begin with the discussion of the results obtained at low temperature in frozen solution (at 80 K, Figure 3). The most satisfactory simulation was obtained by using two spin-polarized species, one with a strong interaction between the radical moiety, and one with a weak interaction (see J_{TR}^{Exp} values in Table 2). The simulation experimentally confirms the presence of the two possible conformations (folded and extended) for **BDP-TEMPO-2** as anticipated by MD calculations.

The simulation of this spectrum required, as parameters, the Zero-field splitting (ZFS) parameters (D, E) of the triplet state, the exchange interaction J_{TR} , the dipolar interaction D_{TR} between the triplet and the radical, and the polarization of zero-field states. Initially, the fitting was obtained by using the polarization of the zero-field states as the only free parameters. The other simulation parameters were taken either from experimental values (the g-values of the radical and of the triplet, and the zero-field splitting parameters of the triplet), or from calculation (the radical-triplet exchange interactions). The magnetic parameters of the triplet were obtained from TR-ESR measurements in a parent molecule having two iodine atoms, after reduction of the radical (the procedure and the results are reported in the Supporting Information). We noted the presence of two main conformations also in the triplet state. The exchange interaction parameter was taken from calculation for the extended conformation, and initially also for the folded conformation; we finally let also this last parameter to be varied. The best-fit value for the folded conformations was $J = 1.2 \times 10^4$ MHz (0.4 cm⁻¹. Table 2). This value is consistent with a radical-triplet distance almost 1 Å larger than the calculated one (8 Å). The dipolar interaction was neglected because within the linewidth value (100 MHz).

Table 2. Estimated distances *r* between the Bodipy moiety and the nitroxide, ZFS *D* parameter and the spin exchange interaction (*J*) for the molecules in the extended and folded conformations.

	r (Å)	$D_{TR} (\mathrm{MHz})^a$	J _{TR} ^{Calc} (MHz) ^b	$J_{\rm TR}^{\rm Exp}$ (MHz) ^c
BDP-TEMPO-1	18 ^d	8	0.03	/
	8 e	76	2×10 ⁵	/
BDP-TEMPO-2	13 ^d	23	170	170
	8 e	76	2×10 ⁵	1.2×10 ⁴

^{*a*} The calculated values for the dipolar interaction in the point dipole approximation D_{TR} (see Supporting Information for the calculation).^{72 *b*} The upper limit of the spin exchange interaction $J_{\text{TR}}^{\text{Calc}}$ according to Eq. S4 with respect to the ^{*c*} experimental value determined from simulation of the spectrum in Fig. 3b. ^{*d*} Extended conformation. ^{*e*} Folded conformation.

We pass now to present the results obtained for a diluted (10^{-4} M) fluid toluene solution at 185

K of **BDP-TEMPO-2**. Representative slices along the field taken at different delays from the laser pulse (see Figure 4a) show a time evolution of the shape of the spectrum. At early delay times, a spectrum is observed with complete *A* polarization and three broad lines centered at g = 2.0077 — relative to a nitroxide with hyperfine interaction of $a_N = 14.7 \pm 0.2$ G (dashed spectrum in Figure 4a); a structureless broad component (ca. 50 G width, see the fitting, i.e. the dotted curve, in Figure 4a) is also present. Later it evolves to another nitroxide spectrum totally with *E* polarization, a narrower linewidth and a nitrogen hyperfine interaction $a_N = 15.8 \pm 0.1$ G, and centered at g = 2.0064. At higher temperatures this is the only species observed.



Figure 4. (a) TRESR spectra of **BDP-TEMPO-2** in toluene $(1.0 \times 10^{-4} \text{ M} \text{ at } 185 \text{ K})$ upon pulsed laser excitation (532 nm, 5 ns) at the delay times of 0.3 µs (red, top) and 2 µs (black, medium) after the laser flash. The bottom spectrum in (a) is the integrated cw-ESR spectrum in the dark under the same conditions (g = 2.0063). The dashed curve is the simulation of the spectrum at 0.3 µs (g = 2.0077) as described in the text and the dotted curve a broad structureless component. (b) Time profile curve taken at 3309 G (\blacksquare in graph (a)) and the simultaneous simulation of phase II (the section of the curve representing transition from enhanced absorption to emission) and III (the section of the curve representing the relaxation of the emission) together by using

biexponential functions based on RTPM mechanism (red dashed line). Phase I represents the development of the absorption upon laser excitation. In the inset the only-absorptive signal obtained at 3304 G (* in graph (a)), relative to the formation and decay of the polarization of the species with g = 2.0077. (c) Simplified mechanism explaining the time evolution of the signals in (a) and (b, phase II and phase III); in grey the species that are observed. ^{33d} The process for formation of the *A* polarization was omitted (phase I). See text for the designation of the rate constants.

The interpretation of the evolution of the observed spectra is given by the scheme shown in Figure 4c. The upper (*intra*molecular) reaction chain accounts for the formation of signals in absorption, whereas the lower reaction accounts for the generation of signals in emission.

As for the signal in absorption observed at early times, the strong spin interaction between the radical and the excited chromophore favors the formation of the triplet state of BDP unit through EISC, and consequently generates initially the doublet state ${}^{2}[R-T]$ (D). The *A* polarization of the TEMPO moiety may be formed by RTPM with doublet precursor.⁴² RTPM exploits a partial mixing between the quartet and the doublet state to transfer some population from the doublet to the triplet state (Supporting information, Figure S22). According to this mechanism, for the regular case J < 0,⁴² one of the sublevels of the doublet (D_{+1/2}) is partially depleted, whereas state Q_{-3/2} state is populated. The molecular motion brings the BDP (in triplet state) and the radical far apart rapidly, through a spin-conserved process (which preserves the total spin number). The species finally observed by TR-ESR at early times is a nitroxide with weak interaction (^(2,4)[R,T]); the distribution of population within the six sublevels of these states is the result of a population transfer from the D/Q states that have the same total M_S value; this process leads to an overall *A* polarization for the weakly coupled radical species. The magnetic parameters of the species (*g* and *a_N*) are slightly different from those of the radical in the ground state D₀ because

the interaction between the radical and the triplet is small but not negligible, and it is responsible for a quartet state contamination; the interaction, also, favors a line broadening.⁴⁴ The presence of this A polarized species at early times (Figure 4a, top), is the fingerprint of the presence of an EISC process taking place in the dyad.

At later delay times, the spectrum in Figure 4a is attributed to that of the dyad in the electronic ground state D₀ (g = 2.0063, a_N = 15.75 ± 0.05 G determined from the cw-ESR spectrum in Figure 4a; note that at room temperature the hyperfine interaction is slightly smaller $a_N = 15.45 \pm$ 0.05 G, see Supporting Information Figure S21) but spin polarized in emission. The process in the lower part of Figure 4c accounts for the formation of the ground electronic state D_0 with Epolarization; this polarization is generated by an intermolecular RTPM mechanism with quartet precursor;^{33b,65} but also the radical/quartet polarization mechanism (ROPM) is possible.^{36,40}

As regards to the time evolution of the signal of these species, the time trace recorded at 3304 G (see inset in Figure 4b) shows a quick rise (exponential growth with 0.18 µs time constant), which is time-limited by the response of the instrument (100 - 200 ns), and followed by a rather fast decay (0.4 μ s) likely due to T_l electron spin relaxation; the lifetime of the triplet is ruled out because much longer (see Table 1) and cannot contribute to the decay.

Figure 4b describes the time profiles at 3309 G, where both $^{(2,4)}[R,T]$ and polarized D₀ states are present. The rapid rise of the signal (phase I) is followed by a rapid decay to an emission (E) polarization (phase II). The E polarized band is characterized by a very slow decay (phase III of the time profile curve in Figure 4b). Overall, this time profile is in agreement with the typical RTPM mechanism, with switching from the doublet precursor to quartet precursor.⁴²

Phase I is determined by the formation/decay of the ${}^{(2,4)}[R,T]$ and its contribution is negligible for time larger than ca 1 µs. During phase II and III, a strong polarization of D₀ is generated through *inter*molecular RTPM as a consequence of an interaction between unpolarized D₀ and

the triplet moiety of $^{(2,4)}[R,T]$ molecules. The time for generation of the maximum of the *E* polarization is close to the reported intermolecular ESP generation for TEMPO (1.5 – 2 µs) through intermolecular processes.^{36,73}

We used a simple model to quantitatively fit the experimental curve (phase II and III). We assumed a pseudo-first-order reaction for ESP generation (*E* polarization) with $[D_0] \gg {}^{(2,4)}$ [R,T] (see lower reaction in Figure 4c), and included both spin relaxation T_I process for the radical and the decay of the triplet moiety to ground electronic state (τ is triplet lifetime). The details of the model are given in the Supporting Information; here we report the analytical solution for the time dependence of the *E* polarization, similar to that found for analogous systems,^{33b,33d} expressed as:

$$[D_0]_{EM} = -\frac{C}{(k_d - k_1)} \cdot \left[\exp(-k_d t) - \exp(-k_1 t)\right]$$
(1)

where $k_I = 1/T_I$, $k_d = 1/\tau$ and *C* a scaling factor.

Our fitting of phase II and III signal by using eq. 1 resulted in the determination of $\tau = 36 \pm 10 \ \mu$ s and $T_I = 0.33 \pm 0.05 \ \mu$ s. We note that lifetime of the triplet state at the same concentration at room temperature is 17 μ s (Supporting information, Figure S27), and that at lower temperature lifetime usually increases. The T_I -value can be compared with that obtained by Pulse ESR (Inversion-Recovery experiment, run on the narrower line at lower field). After inversion of the magnetization by a π -pulse, the recovery trace exhibit a biexponential behavior with $T_{Ia} = 0.2 \ \mu$ s and $T_{Ib} = 1.8 \ \mu$ s. The faster component is likely the one to be compared with the observed T_I .

As regards to **BDP-TEMPO-1**, the low triplet yield of the Bodipy moiety prevented the observation of a good-quality polarized spectrum, and only very weak emissive lines were observed (see Figure S24 and discussions in Supporting Information).

To summarize the results for **BDP-TEMPO-2**, according to MD simulation, there is a balance between folded conformation and extended conformation. The results obtained for **BDP-TEMPO-2** at 80 K (in frozen solution, Figure 3) indicated the presence of the two types of conformers (note that the equilibrium is relative to ground state). During the folding/unfolding process, for the photoexcited molecule, the interactions between the chromophore and the radical favor both the EISC and the RTPM mechanisms; the latter interaction generates ultimately ^(2,4)[R,T] spin polarized states.

Different from other systems having rigid linker between the radical and the chromophores, we attribute the high triplet quantum yield and long triplet lifetime of the dyads in this paper to the efficient EISC from $S_1 \rightarrow T_1$ but inefficient EISC of $T_1 \rightarrow S_0$ on the base of the following points: first of all the decay to the ground state is a first order perturbation and its efficiency is reciprocal to the energy gap of the states.^{34,44} As second point, we note that the folding/unfolding might disfavor EISC to the ground state by limiting the interactions between the radical and the chromophore; from our results we must conclude that there is a stiffening of the molecule in the ^(2,4)[R,T] states which prevents the folding of the dyad and therefore the EISC to the singlet (in this case S_0). It should be pointed out that the available examples of the radical enhanced ISC systems are not sufficient to draw an conclusion on the quantitative relationship between the magnitude of the exchange (*J* values) and the ISC efficiency (i.e. the triplet state quantum yield, Φ_T) because in most cases not both the *J* and the Φ_T values were reported.^{34,44,65}

2.4. Nanosecond Transient Absorption Spectroscopy: Triplet Electronic Excited States.

In order to study the triplet excited state of both dyads upon photoexcitation, optical methods were applied, and in particular nanosecond transient absorption spectroscopy (Figure 5). With **BDP-TEMPO-1**, intense ground state bleaching (GSB) band at 500 nm was observed upon pulsed laser excitation (Figure 5a). Weak excited state absorption (ESA) bands were observed in

the regions of 410 nm – 460 nm and 550 nm – 700 nm. These are the ESA band of the T_1 state of Bodipy.^{74–76} Using triplet-triplet energy transfer (TTET) method (Eosin Y was used as reference compound, optically matched solutions were used and equal proper amount of acceptor was



Figure 5. Nanosecond time resolved transient absorption spectra of BDP-TEMPO-1 and BDP-TEMPO-2. (a) BDP-TEMPO-1 upon ns pulsed laser excitation ($\lambda_{ex} = 500$ nm) and (b) decay trace of BDP-TEMPO-1 at 510 nm. The spike is due to scattered laser. (c) BDP-TEMPO-2 upon pulsed laser excitation ($\lambda_{ex} = 516$ nm) and (d) decay trace of BDP-TEMPO-2 at 490 nm. *c* = 1.0×10^{-5} M in deaerated toluene, 20 °C.

added), according to equation S5, (Supporting Information), the triplet state quantum yield of **BDP-TEMPO-1** (Φ_T) was determined as 14% (Supporting Information, Figure S28, Table S3). This ISC efficiency is significant as compared with unsubstituted Bodipy (less than 1%). The

triplet excited state lifetime of **BDP-TEMPO-1** was determined as 190 μ s (Figure 5b). It should be pointed out that the fluorescence quenching of the Bodipy moiety in **BDP-TEMPO-1** by the TEMPO unit is much more significant (75%) than the triplet state quantum yield of **BDP-TEMPO-1** (14%), thus non-radiative decay of the S₁ state such as EIC is probable for **BDP-TEMPO-1** upon photoexcitation.⁴⁴

With **BDP-TEMPO-2**, the transient signal is more intense (Figure 5c). For example, the Δ O.D. (optical density) value at the bleaching band increased to 0.09, which is much larger than that of the **BDP-TEMPO-1** (Δ O.D. = 0.025). Δ O.D. values are proportional to the concentration of the excited molecules.^{77,78} The triplet state lifetime of **BDP-TEMPO-2** was determined as 62 μ s (Figure 5d), and the triplet state quantum yield (Φ_T) was determined as 80% (Supporting Information, Figure S29 and Table S3). By reaction with AIBN (actually 2-cyanoprop-2-yl radical) under heating conditions to produce ether, we found that no triplet state can be detected for the resulted dyads upon photoexcitation (Figure S25, Supporting Information). This evidence is a further proof that the radical moiety is vital to the formation of triplet state with the dyads. To the best of our knowledge, this is the first report of the detail study of the triplet state property of Bodipy, accessed by the radical enhanced ISC (EISC). Previously Bodipy and verdazyl radical moieties were connected by using 9,10-anthryl linker and PET effect was observed for the dyad, but the triplet state generated by photoexcitation is localized on *anthracene* moiety, *not* on Bodipy chromophore.^{36,79}

We also studied the effect of the TEMPO on production of triplet state of Bodipy chromophore by *intermolecular* interaction (studied with mixture of TEMPO and BDP, Figure S26, Supporting Information), the results show that the production of triplet state is much less efficient than the intramolecular interaction (however the triplet state lifetime is longer, which is due to the diminished self-quenching effect). These results unambiguously confirmed that the

formation of the triplet excited state with **BDP-TEMPO-1** and **BDP-TEMPO-2** is via the *intramolecular* interaction between the singlet excited state of Bodipy and the radical, and the efficiency of this radical enhanced ISC is highly dependent on the length of the linker between the Bodipy chromophore and the TEMPO unit.^{34,65,66}

The high triplet state quantum yield of our **BDP-TEMPO-2** dyad is unprecedented. In previous studies on radical labeled chromophores, normally the triplet state quantum yield for EISC is much lower,⁶⁵ or not reported. On the other hand, previously the triplet state lifetime of the chromophore obtained with EISC is much shorter than the intrinsic triplet state of the organic chromophore.^{34,44,65} For example, pervlenebisimide (PBI) chromophore was rigidly connected with TEMPO moiety with a specific distance and orientation, and radical-enhanced ISC was observed.^{34,44} However, the triplet state lifetimes are shorter than 1 μ s, although the *intrinsic* T₁ state lifetime of PBI is over 100 µs (accessed by methods other than EISC).⁶⁵ With attachment of TEMPO moiety to the phthalocyaninatosilicone, the triplet state lifetime was greatly reduced from 500 µs to ca. 15 µs.^{33b} In our case with **BDP-TEMPO-2**, the triplet state lifetime is exceptionally long (62 µs). Moreover, the triplet excited state quantum yield of BDP-TEMPO-2 is high ($\Phi_T = 80\%$). We attribute the efficient ISC and the long-lived triplet state of **BDP**-**TEMPO-2** to the weak and transient interaction between the radical moiety and the singlet excited state of Bodipy, which is sufficient for $S_1 \rightarrow T_1$ ISC, but nonsufficient for the $T_1 \rightarrow S_0$ ISC. This is reasonable since ISC is driven by first-order perturbation which is dependent on the energy gap of the states,³⁴ which leads to a relatively slow $T_1 \rightarrow S_0$ ISC. To some extent, the weak and transient interaction in our flexible system contribute to the high triplet quantum yield and long triplet lifetime, which have never been realized in rigid system. It should be pointed out that the quantitative relationship between the magnitude of the exchange (J values) and the ISC

efficiency (i.e. the triplet state quantum yield, Φ_T) is unclear because in most cases not both the *J* and the Φ_T values were reported.^{34,44,65}

Considering the wide application of Bodipy as triplet photosensitizers,²¹ we believe our results are useful for preparation of heavy atom-free organic triplet photosensitizers and for study of the fundamental photochemistry of spin-labeled chromophores. One reason for designing of heavy atom-free triplet photosensitizers is that with bulky chromophore, the ISC may become less efficient even with the heavy atom attached.⁶⁷ Heavy atom-free triplet photosensitizers, which are based on ISC via the mechanisms other than heavy atom effect, such as those with radical EISC, discussed herein, may overcome this bottleneck.

In order to study the kinetics of the EISC in the dyads, the femtosecond transient absorption spectroscopy (fs TA) was used for characterization of the photophysical processes involved in **BDP-TEMPO-2** (the detail will be published elsewhere). The results show that the ISC of **BDP-TEMPO-2** (the detail will be published elsewhere). The results show that the ISC of **BDP-TEMPO-2** takes 250 ps. Previously a compact ring-fused perylene-nitroxide was prepared, due to the smaller distance between the radical and the perylene chromophore, a sub-ps ISC was observed.⁴⁴ In another TEMPO-labeled PBI compound with longer linker,³⁴ EISC is slower ($\tau = 45$ ps). The electron exchange interaction between the radical and the chromophore serves as the first-order perturbation that drives EISC, the magnitude of this perturbation is highly dependent on the orbital overlaps of the two moieties. Thus shorter distance between the radical and the chromophore may result in faster ISC. However, in that case the triplet state lifetime of the perylene-nitroxide dyad is only 100 ns – 500 ns,^{44,65} which is not satisfactory to be used as triplet photosensitizer for *intermolecular* electron transfer or energy transfer processes (such as photocatalysis). It should be pointed out that the photophysics of the radical-labeled organic chromophore is elusive and further investigation is needed. For example, previously pentacene

was connected with TEMPO through semi-rigid, short linker of a C=N bond, however, the ISC of the pentacene was not affected by the nitroxide radical.⁸⁰

2.5. Application of the EISC in Triplet-Triplet-Annihilation (TTA) Upconversion. To date

most of the photosensitizers for TTA upconversion are with triplet state accessed with heavy atom effect.^{16,18,19,59} Herein we demonstrated for the first time that photosensitizers with the radical group attached to visible light-harvesting chromophores, having EISC, are also efficient for TTA upconversion (**BDP-TEMPO-2**). These results are useful in terms of both fundamental photochemistry and the development of TTA upconversion.

Based on the T_1 state energy level of the Bodipy, we selected perylene as the triplet acceptor/emitter for the TTA upconversion.^{18,59,76} The overall process involves the excitation of the photosensitizer which populates the triplet excited state of the BDP unit through an EISC process. This state is responsible for photosensitization of the perylene to its triplet state, which then drives the TTA upconversion process.

First we demonstrated that excitation of **BDP-TEMPO-2** or perylene alone at 520 nm did not produce any emission in the range of 430 nm – 500 nm, where perylene is expected to give fluorescence emission (Figure 6). As second step, we determined that a solution containing the mixture of the two components (**BDP-TEMPO-2** and the perylene) produced upconverted emission in the range 430 nm – 500 nm upon excitation with 520 nm laser. The upconversion quantum yield was determined to be 6.7% (Figure 6). To the best of our knowledge, this is the first time that a photosensitizer with radical induced EISC process is exploited to produce TTA upconversion.



Figure 6. Upconversions with sensitizers **BDP-TEMPO-2** and **IBDP.** Excited with 520 nm laser (210 mW cm⁻²). Optically matched solutions were used (the solutions show the same absorbance at the excitation wavelength, A = 0.2); [perylene] = 1.1×10^{-4} M, in deaerated toluene, 20 °C.

TTA upconversion with **BDP-TEMPO-1** as the triplet photosensitizer was also studied, but much lower upconversion quantum yield ($\Phi_{UC} = 0.2 \%$) was observed. This is within expectation because the triplet state quantum yield of **BDP-TEMPO-1** ($\Phi_T = 14 \%$) is much lower than **BDP-TEMPO-2** ($\Phi_T = 80 \%$).

Scheme 2. Proposed Mechanism for the EISC promoted TTA Upconversion



We propose to use the following scheme (Scheme 2) to describe the production of the perylene triplet (³pery) and the TTA upconversion with the formation of perylene S_1 excited state (¹pery^{*}).

Based on all the above discussions, the photophysical processes of **BDP-TEMPO-1** and **BDP-TEMPO-2** upon photoexcitation can be summarized in Scheme 3. Irradiation of the two dyads at around 500 nm excite the chromophore of the dyads to an excited singlet state. The triplet state of the chromophore (state [R,T] of the molecule) is located at 1.65 eV for both molecules above the ground state. Exchange interactions between the radical and triplet moieties slightly vary the energy of the states by some GHz (expanded in the diagram) according to their total spin number (D or Q states).

Scheme 3. Jablonski Diagram Illustrating the Photophysical Processes in BDP-TEMPO-1 and BDP-TEMPO-2



The radical-chromophore pair is designated as [R,S] or [R,T] according to the spin state of the chromophore: singlet (S) or triplet (T). The superscript on left indicate the overall spin multiplicity of the pair state. For strongly interacting [R,T] pairs, exchange interaction separates doublet states (total spin S = 1/2, D in the scheme) from quartet states (S = 3/2, Q in the scheme). CTS stands for charge transfer state. The excited state of the nitroxide group is designated with red asterisks. Photoexcitation of the nitroxide moiety is obtained by irradiation at 459 nm.

Our future plan is to design radical labeled visible light-harvesting organic chromophore as novel photosensitizers, to study the photo-induced spin alignments and the high spin states, preferably to be with high yield of the long-lived quartet state, as well as the application of these molecules in optical or magnetic materials, spintronic materials, and TTA upconversion.

2.6. Conclusion. In summary, it is the first time that the triplet excited state of Bodipy chromophore is accessed with the radical enhanced intersystem crossing (EISC), and the electron spin polarization (ESP) along with the EISC was studied. Our strategy is to label the Bodipy chromophore with a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) via different linkers, and the EISC was studied with steady state and transient optical and ESR spectroscopies (cw ESR and TR-ESR). Significant fluorescence quenching and triplet electronic excited state production upon visible light photoexcitation was observed, with triplet state quantum yield of $\Phi_{\rm T}$ = 80%. The EISC process takes 250 ps. The triplet state of the Bodipy chromophore is exceptionally long (62 μ s). These efficient EISC and the long-lived triplet excited state are unprecedented for the radical-chromophore EISC systems. Previously the triplet state of chromophore accessed with EISC effect is short-lived (less than 1 μ s). The dyad with shorter linker between the Bodipy and the TEMPO unit shows much stronger quenching of the Bodipy fluorescence and more efficient triplet state production. The interaction of the singlet excited state of the Bodipy moiety and the TEMPO (radical moiety) was studied with TR-ESR. The analysis of the spectra confirmed the presence of EISC route to the formation of the triplet state, followed by a radical triplet pair mechanism (RTPM) leading to ESP. This heavy atom free photosensitizer with BDP triplet state accessed via EISC was used for triplet-triplet annihilation upconversion (quantum yield is 6.7%). Our future plan is to control the electron exchange interactions between the radical and the excited state of the organic chromophores and to access

high spin state of organic chromophores. These studies are useful for investigation of the interaction between triplet state of organic chromophore and radical, photo-induced electron spin polarization in organic magnetic materials and triplet-triplet-annihilation upconversion, as well as fundamental photochemistry.

3. Experimental Section

3.1. General Methods. UV–vis absorption spectra were taken on a HP8453 UV–vis spectrophotometer. Fluorescence spectra were recorded on Shimadzu RF-5301PC spectrofluorometer. Luminescence lifetimes were measured on an OB920 fluorescence/ phosphorescence lifetime instrument (Edinburgh, U.K.).

3.2. Compound BDP-TEMPO-1. Under N₂ atmosphere, compound 4 (40.9 mg, 0.1 mmol) and **2** (31.0 mg, 0.15 mmol) were dissolved in mixed solvent CHCl₃/EtOH/H₂O (12 mL, 10:0.8:0.8, v/v), then the mixture was stirred at room temperature (RT). One drop of Et₃N was added and the mixture was stirred for 5 min. Then CuI (20 mg) were added. The mixture was stirred at RT for 12 h. Then water was added and the organic layer was collected and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified using column chromatography (silica gel, DCM: MeOH = 30:1, v/v) to give a red solid. Yield: 40 mg (65%). Mp: 180.5 – 181.5 °C. The ¹H NMR spectra was recorded after treatment of the product with phenylhydrazine, to reduce the nitroxide to hydroxyl structure (no satisfactory NMR spectra can be recorded for paramagnetic compound). ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (s, 1H), 7.20 (d, 2H, *J* = 8.0 Hz), 6.99 (d, 2H, *J* = 8.0 Hz), 5.97 (s, 2H), 4.80 (t, 2H, *J* = 4.0 Hz), 1.82 (d, 2H, *J* = 8.0 Hz), 1.40–1.28 (m, 18H). ¹³C NMR (125 MHz, CDCl₃) δ = 158.75, 156.78, 145.80, 145.24, 140.96, 131.61, 128.33, 123.57, 115.36, 113.19, 85.69, 74.19, 70.61, 66.39.

61.84, 55.32, 49.65, 44.11, 31.39, 20.94, 17.24, 16.02. ESI-HRMS($C_{33}H_{42}BF_2N_6O_3 + Na^+$): calcd. m/z = 642.3277; found m/z = 642.3262.

3.3. Compound BDP-TEMPO-2. Similar procedure with compound **BDP-TEMPO-1**. Yield: 26 mg (50%). Mp: 161.5 – 162.5 °C. The ¹H NMR spectra was recorded after treatment of the product with phenylhydrazine (no satisfactory NMR spectra can be recorded for paramagnetic compound). ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (s, 1H), 6.13 (d, 2H , *J* = 8.0 Hz), 5.84 (d, 2H, *J* = 8.0 Hz), 4.60 (d, 2H, *J* = 8.0 Hz), 3.84–3.78 (m, 1H), 2.57 (s, 6H), 2.24 (d, 6H, *J* = 4.0 Hz), 2.13–2.06 (m, 2H), 1.98–1.96 (m, 2H), 1.49–1.13 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ = 157.98, 157.91, 141.52, 141.45, 132.32, 129.95, 128.48, 123.39, 123.27, 121.46, 121.38, 61.88, 45.82, 32.04, 31.71, 29.81, 22.82, 22.78, 16.23, 15.99, 15.09, 14.98, 14.29. ESI-HRMS(C₂₆H₃₆BF₂N₆O₂ + Na⁺): calcd. *m/z* = 536.2859; found *m/z* = 536.2850.

3.4. Steady State and Time-Resolved (TR) ESR Spectroscopy. Both continuous wave and TR-EPR spectra were recorded with two different generations of Bruker spectrometers, both with an extended detection bandwidth (6 MHz): a ER200D spectrometer equipped with a cylindrical cavity with optical access and cooled by a nitrogen flow for temperature control, and a ELEXSYS E580 spectrometer equipped with a dielectric cavity inside an Oxford CF900 cryostat cooled by liquid nitrogen.⁹⁴ The time resolutions for the two systems in the time-dependent experiments were different, and of the order of 150 ns for the first, and 500 ns for the second, this last having a slightly better sensitivity. Direct-detected signals (no modulation of the magnetic field was used) were recorded with LeCroy digital oscilloscopes with GHz bandwidth. Photoexcitation was obtained from Nd: YAG pulsed lasers (Quantel Brilliant, $\lambda = 532$ nm, pulse length = 5 ns; E/pulse = ca. 5 mJ) equipped with superior harmonic modules and optical parametric oscillators (OPOTECH) for tunable irradiation in the visible.

3.5. X-Ray Crystallography. X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) at 273 K using the SMART and SAINT programs. The structure was solved by direct methods (SHELXTL) and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXTL–97 program on PC. In the final stage of least–squares refinement, all non-H atoms were refined anistropically. H atoms were generated by SHELXTL–97 program. CCDC–1496015 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk. Convergence ($(\Delta/\sigma)_{max} = 0.000$, av. 0.000) for 415 variable parameters by full-matrix least-squares refinement on F^2 reached to $R_I = 0.0755$ and $wR_2 = 0.2460$ with a goodness-of-fit of 1.001, the parameters *a* and *b* for the weighting scheme were 0.1338 and 0.

S Supporting Information

Experimental procedures, nanosecond transient absorption and femtosecond transient absorption experimental details, molecular structure characterization, additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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