Quantifying Triplet State Formation in Zinc Dipyrrin Complexes

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ABSTRACT Photocatalysis is a promising method to harness solar energy and use it to form fuels and other high value chemicals, but most sensitizers used in photocatalytic reactions are complexes of rare and expensive metals such as ruthenium and iridium. Zinc dipyrromethene complexes have potential to be a more earth-abundant alternative, but their photophysical properties are largely unexplored. In this study, triplet state formation was quantified in two zinc dipyrromethene complexes, with a and without heavy atoms, by transient absorption spectroscopy. Without heavy atoms the triplet quantum yield was 16% in toluene and 27% in THF. With the addition of heavy I atoms the triplet quantum yield is increased to 62-63% and is insensitive to solvent polarity. These triplet yields meet or exceed those of successful organic photosensitizers, illustrating the potential for zinc dipyrromethene complexes as photosensitizers.

TOC GRAPHICS
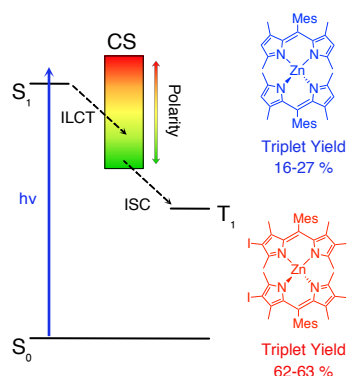
KEYWORDS Intersystem Crossing, Charge Separated State, Photosensitizer, Excited State Dynamics, Triplet Quantum Yield

Solar photocatalysis offers a mechanism to harness the sun's energy and use it to drive chemical reactions, generating fuels and other valuable products. Currently a majority of photosensitizers are based on rare second and third row transition metals such as ruthenium and iridium with comparatively few examples of earth abundant photosensitizers[1–3] It is therefore beneficial to develop novel photosensitizers incorporating more earth-abundant first row transition metals. The challenge is retaining the long excited state lifetimes and relative photostability of ruthenium and iridium complexes while using more abundant metals.

Complexes of dipyrromethene (dipyrrin) ligands have potential as sensitizers for photocatalysis. These ligands possess the intense visible absorption bands of the related porphyrins, while being more synthetically accessible. Boron dipyrromethene complexes (BODIPYs) are the most well studied class of dipyrrin complex, however their short excited state lifetimes and inefficient intersystem crossing (ISC) make bimolecular photochemical reactions with BODIPY sensitizers unlikely except in a few rare instances.[4,5] First row transition metal complexes of dipyrrin ligands are also known, but the photophysical properties of these complexes are generally unexplored.[6–10] In a few zinc dipyrrin complexes, however, formation of a long-lived triplet state has been spectroscopically observed,[11,12] meaning they have the potential to be effective photosensitizers.

Much of the previous work with zinc dipyrrin complexes has focused on enhancing their fluorescence quantum yield.[13–18] Designing an efficient photosensitizer requires the opposite approach, minimizing the energy lost through fluorescence and maximizing the yield of the long-lived, photochemically active triplet state. Zinc dipyrrin complexes offer advantages over the more widely used BODIPYs. Having two dipyrrin ligands per complex doubles the molar absorptivity. This also makes the formation of heteroleptic complexes a possibility, which will broaden the chromophore's absorption spectrum and increase the fraction of the solar spectrum absorbed.[15,19]

The presence of two dipyrrin ligands also allows for intramolecular electron transfer between the two dipyrrins to form a charge separated state (CS). This charge separated state potentially quenches the initially excited singlet state (S_1), and is theorized to facilitate ISC to the long-lived triplet state (T_1) as shown in Figure 1.[11] This same phenomenon can also be observed in orthogonal BODIPY dimers.[20]
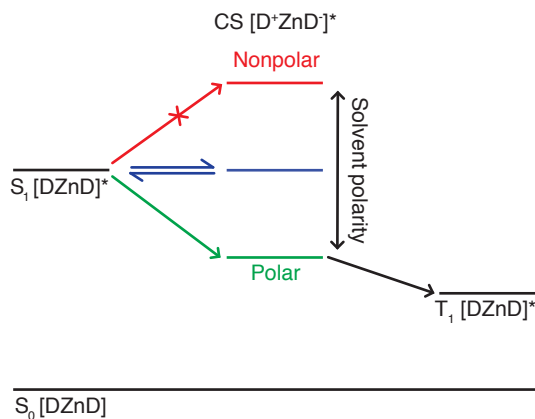
Figure 1. Qualitative Jablonski diagram for zinc dipyrrin complexes.

Unlike their BODIPY counterparts, previous studies of zinc dipyrrin complexes demonstrate that the fluorescent properties of these complexes are highly solvent dependent, with the S_1 fluorescence highly quenched in polar solvents.[11,14,21] These solvent dependent fluorescence properties are due to the presence of the CS state. In polar solvents, the CS state is stabilized, making it lower in energy than the initially excited S_1 state. In this case, intramolecular electron transfer to form the CS state becomes competitive with the radiative decay from the S_1 state. The T_1 state in these zinc complexes is non-emissive at room temperature, but phosphorescence has been observed at 77 K.[21,22] The T_1 state has also been observed in room temperature solution by transient absorption spectroscopy,[11,12] but to our knowledge the yield of triplet state formation in these complexes has not been investigated.

In this study we aim to quantify the efficiency of triplet state formation in two zinc dipyrrin complexes. Complex **1** has been previously reported[11,23] and complex **2** is a new compound, designed to probe the effect of heavy atoms on the triplet yield. In BODIPY dyes and many other fluorophores, where non-radiative decay from the S_1 state is insignificant, the ISC yield (Φ_{ISC}) can be reasonably approximated from the fluorescence quantum yield (Φ_F). In the case of zinc dipyrrin complexes, the presence of the intermediate CS state makes this approximation no longer valid. In this case the quantum yield of triplet state formation can be measured in two steps. First the molar absorptivity of the T_1 state is measured by triplet-triplet energy transfer (TTET) to a known acceptor.[24] Once the extinction coefficient is determined, the concentration and yield of the triplet state can be measured relative to a standard sample.[25]


1   2
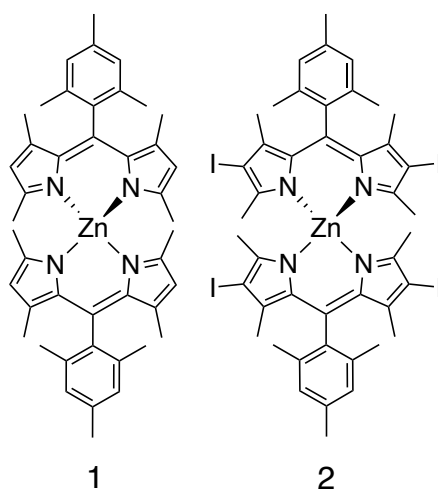
The dipyrrin ligands, 1,3,7,9-tetramethyl-5-mesityldipyrromethene[11] and 2,8-diiodo-1,3,7,9-tetramethyl-5-mesityldipyrromethene[15] were synthesized according to published procedures. The target zinc complexes, **1** and **2** were synthesized according to a modified literature procedure.[11] The dipyrrin ligand and triethylamine were dissolved in methanol, a methanol solution of zinc acetate dihydrate was added and the solution stirred at room temperature overnight. The resulting

solid was collected by vacuum filtration and purified by column chromatography and recrystallization. The complexes were characterized by ^{1}H and ^{13}C NMR, elemental analysis, and high-resolution mass spectroscopy. The characterization of **1** was consistent with previously published values.[11]

Table 1: Steady state photophysical properties of **1** and **2** in aerated solutions

| Complex	Solvent	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_F (nm)	Φ_F (%)
1	Toluene	490	1.63×10^5	509	12.9
	THF	488	1.67×10^5	507	2.6
2	Toluene	516	1.72×10^5	532	2.0
	THF	513	1.70×10^5	529	0.14
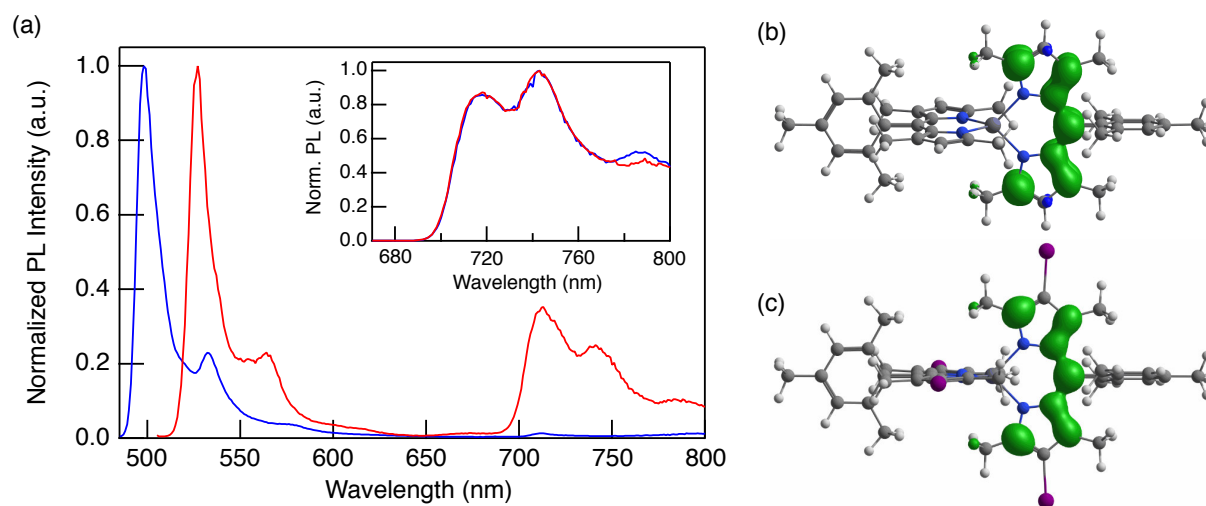
Figure 2. (a) Normalized low temperature emission spectra of **1** (blue) and **2** (red) recorded at 77 K in frozen 2-methyltetrahydrofuran solution. Inset shows normalized phosphorescence spectra collected with a 650 nm long pass filter. (b) Spin density in the lowest energy triplet state of **1** calculated in a toluene continuum. (c) Spin density in the lowest energy triplet state of **2** calculated in a toluene continuum. Computational details can be found in the supporting information.

The steady state absorption and emission spectra of **1** and **2** were measured in aerated toluene and THF solutions and the results are summarized in Table 1. At room temperature, only fluorescence is observed in the emission spectra of **1** and **2,** even in deaerated solutions. At low temperature both fluorescence and phosphorescence are visible, as seen in Figure 2. Interestingly, the addition of the electron withdrawing iodine atoms red-shifts the absorption and fluorescence energy by around 25 nm, but the phosphorescence energies of **1** and **2** are nearly identical. The calculated spin density in the lowest energy triplet states of **1** and **2** offers an explanation for this observation. In both cases, there is a node through the center of the dipyrrin ring and the substituents at the 2 and 8 positions (H or I) have very little to no unpaired spin density on them. It is therefore expected that the triplet states of these two complexes have similar energies. These calculations also support that the lowest energy triplet excited state is a ligand localized ($\pi \rightarrow \pi^*$) triplet state rather than a charge separated triplet state because all of the unpaired spin destiny is concentrated on a single dipyrrin ligand rather than being distributed between the two dipyrrin ligands.

Going from the less polar toluene to the more polar THF results in very little change in either the absorption or fluorescence energies. In contrast, the fluorescence quantum yields of **1** and **2**, shown in Table 1 decrease dramatically in the more polar THF. Unlike the related BODIPY dyes, which don't have solvent dependent emission properties, interligand electron transfer between the two orthogonal dipyrrin ligands in the zinc complexes allows for the formation of a charge-separated (CS) excited state. In more polar solvents this CS state is stabilized relative to the initially excited singlet state (S_1) and quenches the S_1 fluorescence, leading to the solvent dependent

emission quantum yields that have been observed previously for **1**[11] and other zinc dipyrrin complexes.[14,26]
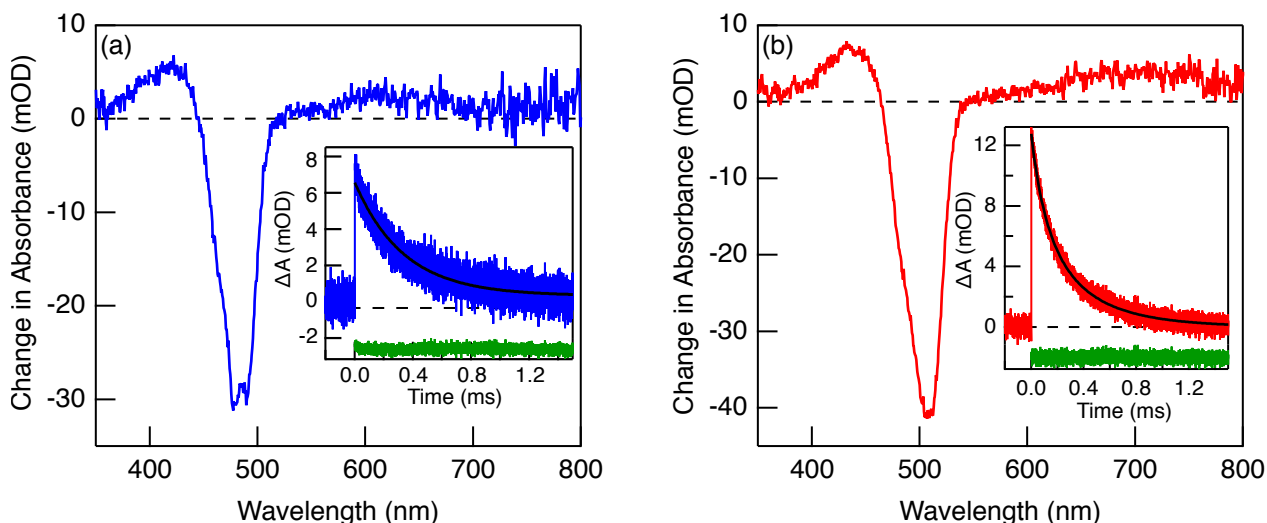
Figure 3. (a) Transient absorption spectrum of **1** in deaerated THF recorded 50 μs after 500 nm laser excitation. Inset shows the kinetic decay probed at 410 nm. The black line is a single exponential fit (τ = 340 μs) and the green line is the fit residual. (b) Transient absorption spectrum of **2** in deaerated THF recorded 50 μs after 515 nm laser excitation. Inset shows the kinetic decay probed at 440 nm. The black line is a fit to Equation 1 (k_T = 2250 s^{-1}; τ = 444 μs) and the green line is the fit residual.
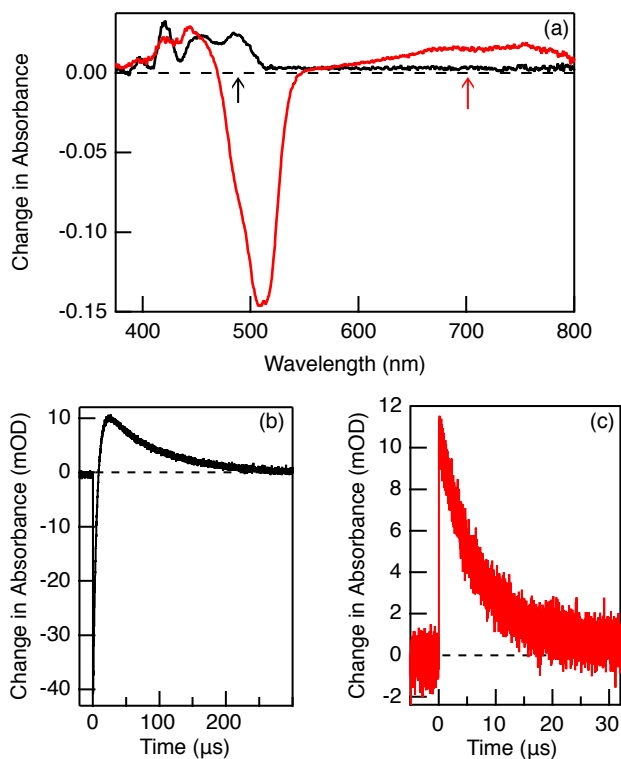
Nanosecond transient absorption spectra of **1** and **2** in deaerated toluene and THF reveals a long-lived triplet excited state as shown in Figure 3, with similar spectral features to previously reported zinc dipyrrin triplet states.[11,12] The kinetic decay of **1** can be adequately fit by a single exponential decay function but in complex **2**, triplet-triplet annihilation is a significant enough contribution to the overall triplet decay that the single wavelength decay can no longer be fit adequately with a single exponential function. As further evidence of triplet-triplet annihilation, p-type delayed fluorescence was observed in **2** with time gated emission spectroscopy (Supporting Information).

The decay kinetics of **2** were fit with Equation 1, where β is the initial fraction of the decay occurring through triplet-triplet annihilation and k_T is the first order triplet decay rate.[27]

$$\Delta A_T = \frac{\Delta A_0\,(1-\beta)}{\exp(k_T t)-\beta} \tag{1}$$

This fitting model accounts for contribution of triplet-triplet annihilation in the excited state decay and allows the first order triplet decay rate to be extracted. For complexes **1** and **2** in both toluene and THF the observed triplet lifetimes were much longer than 100 μs, more than adequate for bimolecular sensitization applications. The observed triplet lifetimes for both complexes, however, are exceptionally sensitive to trace oxygen in the solution resulting in sample-to-sample variations in observed lifetimes.

Figure 4. Transient absorption measurements of **2** and perylene (6.0x10⁻⁵ M) in deaerated toluene. (a) Transient absorption spectra collected 100 ns (red) and 50 μs (black) after 510 nm excitation.

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Arrows indicate probe wavelengths for kinetic traces. (b) Kinetic decay trace probed at 490 nm. (c) Kinetic decay trace probed at 700 nm.

The extinction coefficient of the triplet excited states of **1** and **2** were measured by triplet-triplet energy transfer (TTET) to perylene, a triplet acceptor with a known extinction coefficient according to literature procedure.[24] This method assumes that the donor is selectively excited, all quenching of the donor excited state occurs through energy transfer rather than electron transfer, and that the triplet extinction coefficient of perylene is solvent independent. The ΔA of the initially formed donor triplet state (ΔA_D) and the acceptor triplet state (ΔA_A) were probed by transient absorption spectroscopy and the triplet extinction coefficients of **1** and **2** could be calculated using Equation 2, where the triplet extinction coefficients of perylene (14,300 M^{-1} cm^{-1} at 490 nm in benzene) was taken from the literature[28] and the efficiency of TTET (Φ_{TTET}) was estimated from the lifetime of the donor triplet state. Solutions of **1** or **2** and perylene in toluene or THF were freeze-pump-thaw degassed and excited near the maximum dipyrrin absorbance (485 nm for **1** and 510 nm for **2**). Transient absorption spectra (Figure 4a) showed the dipyrrin triplet at early times which evolved into the characteristic perylene triplet spectrum at later times. The ΔA for the dipyrrin and perylene triplets were taken from single wavelength kinetic decay traces (Figures 4b and 4c) at 490 nm (perylene) 600 nm (**1**) and 700 nm (**2**). The results are summarized in Table 2, and all values are the average of multiple independent measurements. The triplet extinction coefficient of **1** is somewhat lower than **2**, and within experimental error is independent of solvent in both complexes.

$$\varepsilon_D^T = \varepsilon_A^T \times \left(\frac{\Delta A_D}{\Delta A_A}\right) \times \Phi_{TTET} \tag{2}$$

Table 2. Triplet excited state properties of **1** and **2** in deaerated solutions

Complex	Solvent	ε^T (M^{-1} cm^{-1})[a]	Φ_T (%)[b]
1	Toluene	4100	16
	THF	4900	27
2	Toluene	6900	63
	THF	6800	62
[a] Error ± 20% [b] Error ± 15%			

Once the extinction coefficient of the dipyrrin triplets is known, the quantum yield of triplet state formation can be determined through relative actinometry,[25] using [Ru(bpy)$_3$]Cl$_2$ as the standard. The ΔA of the dipyrrin triplet states (ΔA^T_{unk}) and the [Ru(bpy)$_3$]$^{2+}$ triplet state (ΔA^T_{std}) were probed by transient absorption spectroscopy and the triplet quantum yield (Φ^T_{unk}) of **1** and **2** could be calculated using Equation 3, assuming a unity quantum yield for the formation of the [Ru(bpy)$_3$]$^{2+}$ triplet state (Φ^T_{std}) and a change in extinction coefficient ($\Delta\varepsilon^T_{std}$) of 2.2x10^4 M^{-1} cm^{-1} at 360 nm.[29] Solutions of **1** or **2** in toluene or THF and [Ru(bpy)$_3$]Cl$_2$ in water were optically matched, with an absorbance of 0.3 - 0.4 at 480 nm and degassed. Single wavelength kinetic decay traces were recorded at 600 nm for **1**, 700 nm for **2**, and 360 nm for [Ru(bpy)$_3$]Cl$_2$ (Supporting Information) and the maxima of these decay traces were used to calculate the triplet state yields (Φ^T_{unk}) shown in Table 2. The triplet yield of **1** nearly doubles moving from less polar toluene to THF, going from 16 to 27%, this mirrors the decreased fluorescence quantum yield. Addition of the I heavy atoms does in fact increase the triple yield to just over 60%, and this yield is insensitive to solvent polarity.

$$\Phi^T_{unk} = \Phi^T_{std} \left(\frac{\Delta A^T_{unk}}{\varepsilon^T_{unk}}\right)\left(\frac{\Delta\varepsilon^T_{std}}{\Delta A^T_{std}}\right)\left(\frac{(1-10^{Abs})_{std}}{(1-10^{Abs})_{unk}}\right) \tag{3}$$

This study has quantified the formation of long-lived triplet states in two zinc dipyrrin complexes in two different solvent environments. The presence of the I heavy atoms in **2** leads to decreased fluorescence quantum yields and increased CS state formation compared to **1**. The quantum yield of triplet state formation in **2** is also increased compared to **1**, going from 16-29% to 62-63%. While these yields don't compare to ruthenium and iridium complexes, they exceed[30] organic sensitizers like 9-cyanoanthracene[31] and eosin Y[32] that have been successfully used as photosensitizers. Interestingly, low temperature emission revealed that while the S_1 state in **2** is red-shifted relative to **1**, the T_1 states of both complexes are isoenergetic. When the solvent polarity is increased, moving from toluene to THF, **1** follows the expected trend, both the CS state formation and the triplet quantum yield increases then the solvent polarity increases, although the magnitude of the triplet quantum yield increase is less than the CS state formation, suggesting the more stabilized CS state can relax directly to the ground state more efficiently as well. In **2**, the CS state formation also increases in more polar solvent, but the triplet quantum yield is unaffected by solvent polarity. Further investigations are underway to more fully probe the effect of substituents and solvent polarity on triplet state formation in zinc dipyrrin complexes.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, NMR spectra of **2**, steady state absorption and emission, time gated emission, TA spectra and kinetic decays, optimized triplet geometries (PDF)

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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