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Tuning the Triplet Excited State of Bis(dipyrrin) Zinc(II) Complexes: Symmetry Breaking Charge Transfer Architecture with Exceptionally Long Lived Triplet State for Upconversion

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Abstract: Zinc(II) bis(dipyrrin) complexes, which feature intense visible absorption and efficient symmetry breaking charge transfer (SBCT) are outstanding candidates for photovoltaics but their short lived triplet states limit applications in several areas. Herein we demonstrate that triplet excited state dynamics of bis(dipyrrin) complexes can be efficiently tuned by attaching electron donating aryl moieties at the 5,5′-position of the complexes. For the first time, a long lived triplet excited state ($\tau_T = 296\ \mu s$) along with efficient ISC ability ($\Phi_\Delta = 71\%$) was observed for zinc(II) bis(dipyrrin) complexes, formed via SBCT. The results revealed that molecular geometry and energy gap between the charge transfer (CT) state and triplet energy levels strongly control the triplet excited state properties of the complexes. An efficient triplet–triplet annihilation upconversion system was devised for the first time using a SBCT architecture as triplet photosensitizer, reaching a high upconversion quantum yield of 6.2%. Our findings provide a blueprint for the development of triplet photosensitizers based on earth abundant metal complexes with long lived triplet state for revolutionary photochemical applications.

Introduction

Triplet photosensitizers (PSs) are versatile compounds playing key roles in photocatalytic organic reactions,[1–3] photodynamic therapy,[4–6] H_2 production via photon-driven water splitting,[7–9] photovoltaics[10,11] and triplet–triplet-annihilation (TTA) assisted upconversion.[12–14] Intersystem crossing (ISC) is a crucial property of triplet PSs, whose yield can be enhanced through various strategies, including heavy atom effect (Br, I, Pt, Ru, Ir),[15–17] exciton coupling,[18] n–π*↔π–π* transition (El-Sayed rule)[19] and the use of electron spin convertor.[20] All these conventional strategies however suffer from some drawbacks, such as the high cost and toxicity of metals, long synthetic routes and shortening of triplet excited state lifetime due to the heavy atom effect.[21,22] Recently, the symmetry breaking charge transfer (SBCT) approach gained significant attention as a new strategy to develop heavy atom free triplet PSs,[23] as it facilitates charge separation with negligible energetic driving force and slow back charge recombination.[24]

SBCT plays a key role in charge separation within photosynthetic reaction centers in living systems.[25,26] This process occurs in multi-chromophoric systems formed by identical units and involves excited state charge transfer between two electronically degenerate states, producing a de-symmetrized charge transfer state.[24] SBCT can be either an intramolecular or intermolecular process and its rate varies in solvents of different polarity, being more favored in polar solvents. Molecular systems capable of SBCT have potential applications in artificial photosynthesis,[27] photonics,[28] and organic photovoltaics.[29] Indeed, it was recently found that open circuit voltage of solar cells can be significantly improved by using the SBCT approach, which increases the rate of charge transfer among the donor/acceptor layers in the device, thus improving the overall efficiency of solar cells.[29]

Zinc(II)-bis(dipyrrin) complexes are of particular interest due to their easy synthesis and intense absorption in the visible spectral region.[24,30–32] These complexes are in fact considered

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as a promising SBCT material for organic photovoltaics devices, but up to date only limited attention has been paid to study their photophysical properties. These compounds are generally weak fluorophores and recently some attempts have been made to enhance their fluorescence quantum yield.[32,33] Nevertheless, the triplet excited state properties of these complexes were rarely explored and only a few studies are available on this subject.[24,30,34] Homoleptic zinc(II) bis(dipyrrin) complexes exhibiting SBCT have been previously prepared and the occurrence of intersystem crossing (ISC) populating triplet excited states was confirmed through femtosecond transient absorption studies.[24,30] However, the reported complexes exhibited short triplet lifetime (400–800 ns) except for one homoleptic complex (zDIP1) which showed a slightly longer triplet lifetime up to 16–50 μs in solvents of different polarity. The short triplet lifetime and low triplet yield limit the applications of bis(dipyrrin) complexes, as a long triplet excited state lifetime is desired for most of the practical applications.[22,35,36]

Tuning the triplet excited state lifetime of triplet PSs is a challenging task compared to tuning the singlet excited state properties.[21] On a general basis, the mechanism of triplet population in complexes exhibiting SBCT can either be spin orbit charge transfer intersystem crossing (SOCT-ISC) or radical-pair intersystem crossing (RP-ISC).[24] A useful strategy to increase the triplet lifetime could be that of enhancing the possibility of SOCT-ISC, since simple donor/acceptor dyads following this mechanism often show long triplet lifetimes.[37] One of the probable reasons for the short triplet lifetime in the previously reported bis(dipyrrin) complexes can be envisaged in energy losses due to a radiationless deactivation channel involving intramolecular rotations and to inefficient charge recombination (CR) processes, which lead to poor triplet yield and fast triplet decay. Herein, we tried to minimize the energy losses and tune the charge transfer (CT) and triplet energy levels of bis(dipyrrin) complexes employing a structural control strategy, aimed to achieve a better matching of the CT and T_n energy which may result in high triplet yields and long lived triplet states due to efficient CR.

In order to address the above-mentioned challenges, we prepared a series of zinc(II)-bis(dipyrrin) complexes by attaching bulky aryl substituents with different electron donating strength at the 5,5′-position, and demonstrated that these complexes exhibit high triplet yield and exceptionally long lived triplet excited state. Lindsey and co-workers reported that one of the major causes of non-radiative deactivation in homoleptic bis(dipyrrin) complexes is the rotation of the phenyl group at the *meso*-position.[33] This problem is reduced in the newly synthetized complexes as the steric hindrance of the methyl groups in 5,5′-position and the use of bulky substituents restrict rotations and prevents radiationless energy losses (see Figure 1). All the newly synthetized complexes have been fully characterized and their photophysical properties have been analyzed through steady state and time resolved spectroscopic measurements. To the best of our knowledge, this is the first example of bis(dipyrrin) complexes exhibiting long lived triplet lifetimes.

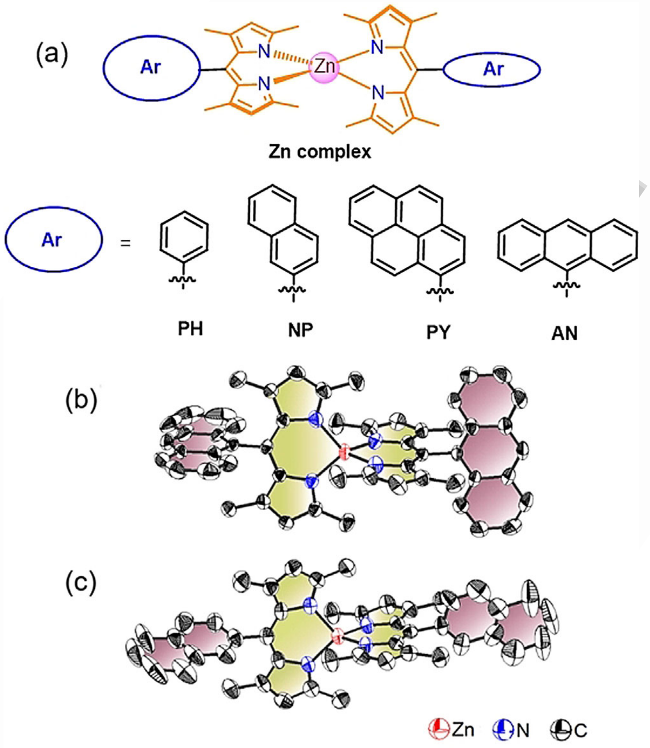


Figure 1. (a) Chemical structures of homoleptic complexes with different substituents. The complexes investigated herein are **AN-Zn**, **NP-Zn**, **PY-Zn** and **PH-Zn**. (b) ORTEP view of the single-crystal structures of **AN-Zn** and (c) **NP-Zn** (thermal ellipsoids set at 50 % probability). Hydrogen atoms and solvent molecules are omitted for clarity.

Results and Discussion

Molecular structure design and single crystal XRD analysis

Inspired by previous reports on zinc bis(dipyrrin) complexes with enhanced luminescence property,[32,33] we devised a series of the zinc bis(dipyrrin) complexes to investigate the effect of structural profile on triplet excited state dynamics and prolong the triplet lifetime of the bis(dipyrrin) complexes through structure control. Based on the previous knowledge four homoleptic zinc bis(dipyrrin) complexes were synthesized, having different bulky aryl moieties at the *meso*-position, with aim to minimize the energy losses and to achieve a better matching of CT state and triplet energy leading in turn to efficient ISC ability of the complexes through CR. The chemical structures of the complexes are shown in the Figure 1, the detailed synthetic procedure and characterization data are presented in supporting information.

Single crystal X-ray diffraction analysis was performed to determine the molecular geometry of homoleptic bis(dipyrrin) complexes (Figure 1). The crystallographic data are summarized in ESI and CIF files are provided for **AN-Zn** and **NP-Zn**. In both complexes, the central Zn atom adopts a distorted tetrahedral configuration, with the two dipyrrin ligands nearly perpendicular to each other. For **AN-Zn**, the Zn–N distance is in the range 1.956(7)–1.968(8) Å, consistent with the crystal structure of previously reported zinc(II) bis(dipyrrin) complexes.[30,31]

Anthracene and dipyrrin units adopt a nearly orthogonal conformation, with an average angle of 87.3°, while the angle between the mean planes of the two dipyrrin units is 89.9°—nearly orthogonal to each other. In contrast, in **NP-Zn** the dipyrrin moieties are not planar, adopting a slightly bent conformation with the two dipyrrin units slightly deviating from orthogonality (a dihedral angle of 85.09° is found between the mean planes of two dipyrrin units). The Zn–N distance is in the range 1.946(4)–1.982(5) Å. Moreover, the naphthalene moiety shows deviations from orthogonality, and a dihedral angle of 77.9° is found between the naphthalene and dipyrrin units. The different geometric features of these two complexes are in accordance with their different triplet yields.

Steady state UV/Vis absorption and fluorescence spectra

All the zinc bis(dipyrrin) complexes exhibit an intense absorption band at about 490 nm, assigned to the $^1\pi$–π^* transition of the dipyrrin core. For **AN-Zn** and **PY-Zn** an additional absorption band at about 368 nm and 340 nm is observed, which can be attributed to the $^1\pi$–π^* transition of the anthryl and pyrenyl subunits, respectively (Figure 2a). The bis(dipyrrin) complexes are weakly emissive and a broad emission profile is observed in dichloromethane (Figure 2b). As previously established, photoexcitation of these complexes induce symmetry breaking which results in charge transfer from one ligand to another, especially in polar solvents.[24,30] The emission band at about 650 nm in polar solvents can be thus assigned as a charge transfer (CT) emission, observed along with locally excited state (^{1}LE) emission band at about 515 nm. In case of **AN-Zn** and **PY-Zn** the CT emission band is more pronounced, suggesting a more efficient excited state SBCT process in these two complexes as compared to the **PH-Zn** complex. The fluorescence emission of the complexes was also studied in solvents of different polarity and fluorescence quenching was observed with increasing solvent polarity, as a further support of the occurrence of SBCT (Supporting Information, Figure S21).[30] The fluorescence decay kinetics of the bis(dipyrrin) complexes were studied in dichloromethane using the time correlated single photon counting (TCSPC) detection technique (Supporting Information, Figure S22). The emission decays follow a biexponential kinetic with an average lifetime (τ_F) 0.6–1.6 ns. In case of **AN-Zn**, the biexponential decay showed a fast component ($\tau_1 = 0.1$ ns, population ratio: 51.1%) and a slow component ($\tau_2 = 2.3$ ns, population ratio: 48.9%), with an average lifetime of 1.6 ns (Supporting Information, Figure S22a). The reference complex **PH-Zn** exhibited comparatively a shorter lifetime ($\tau_F =$ 0.6 ns). The shorter fluorescence lifetime observed for **PH-Zn** is assigned to a singlet state quenching due to an intramolecular rotation effect, which is minimized in **AN-Zn** due to steric hindrance.

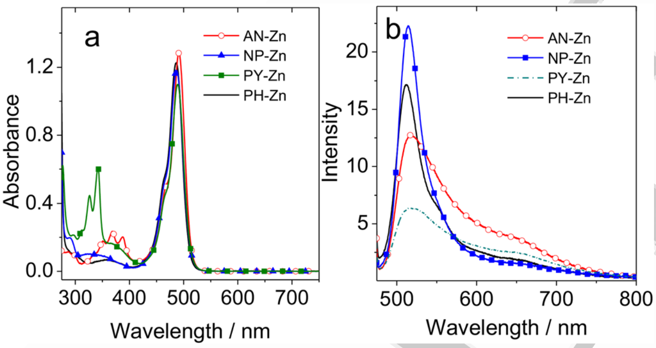


Figure 2. (a) UV/Vis absorption spectra of zinc bis(dipyrrin) complexes in dichloromethane, $c = 1.0 \times 10^{-5}$ M, 20 °C. (b) Fluorescence emission spectra of zinc bis(dipyrrin) complexes in dichloromethane, $\lambda_{ex} = 455$ nm ($A = 0.10$). Optically matched solution was used (all the solution show the same absorbance at the excitation wavelength).

The photophysical properties of all the studied bis(dipyrrin) complexes are summarized in Table 1. Singlet oxygen quantum yield (Φ_Δ) were determined, as a preliminary evaluation of ISC ability. For **AN-Zn**, significantly high Φ_Δ of 71% in chloroform, 62% in dichloromethane and 32% in acetonitrile were observed. In case of **PY-Zn**, Φ_Δ of 35% in chloroform, 28% in dichloromethane and 14% in acetonitrile was found. The reference complex **PH-Zn** showed only $\Phi_\Delta = 10\%$ in dichloromethane and $\Phi_\Delta = 5\%$ in acetonitrile. No singlet oxygen generation was observed in nonpolar solvents in all the complexes. Solvent-dependent singlet oxygen generation ability of the complexes also supports the SOCT-ISC mechanism of triplet population.[38–40] The different ISC ability clarifies that the structural profile of bis(dipyrrin) complexes strongly controls the excited state dynamics. Notably, this is the first report of efficient singlet oxygen generation (up to 71%) of zinc(II) bis(dipyrrin) complexes. Singlet oxygen sensitizing ability of bis(dipyrrin) complexes were rarely explored, as the complexes were either with short triplet lifetime or low triplet yield. Recently Gasser et al. devised bis(dipyrrin) complexes for application in photo-

Table 1. Photophysical parameters of the compounds.[a]

	λ_{abs}[a]/nm	ε[b]	λ_{em}[a]	Φ_F[c]	τ_F[d]/ns	Φ_Δ[e]	τ_T[h]/µs	Φ_{UC}[j]
AN-Zn	491/369	1.28/0.24	518	0.007	1.6	0.62/0.71[f]/0.32[g]	295/1244[i]	6.1
PY-Zn	489/343	1.10/0.61	517	0.004	0.9	0.28/0.35[f]/0.14[g]	146/743[i]	3.3
NP-Zn	487	1.18	514	0.015	0.6	0.08/0.13[f]/0.02[g]	1.4	–[k]
PH-Zn	486	1.23	512	0.007	0.6	0.10/0.11[f]/0.05[g]	4.6/6.3[i]	–[k]

[a] In dichloromethane (1.0×10^{-5} M) and in nm. [b] Molar absorption coefficient (10^5 M^{-1} cm^{-1}). [c] Fluorescence quantum yield with Bodipy as a standard ($\Phi_F = 72\%$ in tetrahydrofuran). [d] Luminescent lifetimes, $\lambda_{ex} = 510$ nm. [e] Singlet oxygen quantum yield measured with 2,6-diiodobodipy as standard ($\Phi_\Delta = 0.87$ in DCM). [f] In chloroform. [g] In acetonitrile. [h] Triplet lifetime in dichloromethane. [i] In glycerol triacetate. [j] Upconversion quantum yield. [k] Not applicable.

Table 2. Electrochemical and optical spectral properties of the homoleptic complexes.[a]

	$E^{1/2}_{ox\,1}$ (V)	$E^{1/2}_{ox\,2}$ (V)	$E^{1/2}_{red}$ (V)	ΔE_{red}[b]	E_{00} (eV)[c]	$\Delta E_{red} - E_{00}$	ΔG_{CS} (eV)[d]
AN-Zn	+0.31	+0.48	−2.30	2.61	2.48	0.13	−0.15, −0.21[e]
PY-Zn	+0.28	+0.43	−2.30	2.58	2.48	0.10	−0.13, −0.18[e]
NP-Zn	+0.30	+0.46	−2.35	2.65	2.48	0.17	−0.11, −0.23[e]
PH-Zn	+0.27	+0.43	−2.33	2.60	2.49	0.11	−0.16, −0.23[e]

[a] Electrochemical redox values were determined by Cyclic voltammetry. Cyclic voltammetry was performed in N_2-saturated DCM containing a 0.10 M Bu_4NPF_6. Counter electrode is Pt electrode and working electrode is glassy carbon electrode, Ag/AgNO$_3$ couple is the reference electrolyte. [b] Electrochemical gap determined by energy difference between the first oxidation potential and first reduction potential. [c] The optical gap is determined by the cross point of UV/Vis absorption and fluorescence emission spectra of the compound in DCM. [d] The Gibbs free energy changes of the SBCT process in dichloromethane. [e] In acetonitrile.

dynamic therapy, but heavy atom iodine was attached at the core of the complexes to achieve efficient ISC ability and 43–57 % singlet oxygen generation was observed.[34]

To determine the thermodynamic feasibility of SBCT in solvents of different polarity, electrochemical studies were carried out (Supporting Information, Figure S23). All the complexes exhibited similar redox properties, only slight shifts (few mV) in oxidation and reduction potentials were observed. All the complexes exhibited multiple oxidation waves whereas only one reduction wave was observed in the electrical window of the solvent (CH_2Cl_2) used for electrochemical measurement.

A careful analysis, on the basis of electrochemical gap ΔE_{redox} (energy difference between the first oxidation potential and first reduction potential) shows that only polar solvents can provide enough stabilization energy required for SBCT to take place, while the process is not thermodynamically favored in nonpolar solvents such as hexane (see Table 2 and Supporting Information).[30] The thermodynamic feasibility of SBCT was also estimated employing the Rehm–Weller analysis, which further confirmed the occurrence of SBCT in bis(dipyrrin) complexes under study (Table 2).[41,42]

Femtosecond/nanosecond transient absorption spectra: symmetry charge transfer and intersystem crossing

To understand the photophysical processes occurring upon photoexcitation and confirm the SBCT process, femtosecond transient absorption measurements were carried out. The transient absorption spectra of **AN-Zn** in dichloromethane are shown in Figure 3, while those of other complexes are reported in supporting information (Figures S24–S26).The photoexcitation at 500 nm populates the singlet excited state of the complexes, as is evident by the appearance of a ground state bleaching band (GSB) centered at about 488 nm, a stimulated emission (SE) band in the range 520–600 nm and an excited state absorption (ESA) band at 348 nm. Within a few picoseconds, the SE band mostly recovers and two new excited state absorption bands at about 385 nm and 550 nm appear, previously assigned to the formation of a charge transfer state (^{1}CT state) populated through SBCT. The observed increase in the ground state bleach during the first 10–15 ps is also taken as a further indication of SBCT.[30] At a longer timescale, charge recombination occurs, leading to population of the triplet state, as evidenced by the recovery of ^{1}CT absorption bands at 385 nm and 550 nm and the rise of a new absorption signal at about 425 nm.

To obtain the time constants of the SBCT and CR processes, global analysis of the transient absorption data was performed, retrieving the evolution associated difference spectra (EADS) and the kinetics constants describing the photodynamic of the systems. In case of **AN-Zn**, five time constants were necessary for a satisfactory fit of the data. The initial spectral component (black line in Figure 3 c) represents population of the singlet excited state. Within less than 1 picosecond (0.45 ps), SBCT occurs as evidenced by recovery of the SE band, the increase of the GSB signal and the appearance of a new ESA band at about 385 nm. Charge transfer is apparently a bi-exponential process, since a further increase of the GSB intensity and the rise of absorption at 550 nm are observed in the evolution towards the third spectral component, occurring in 1.7 ps (evolution from red to blue line in Figure 3 c). The observation of a bi-exponential kinetics of SBCT can be ascribed to the presence of slightly different conformations in solution. In the following evolution, occurring in 52 ps (evolution from the blue to the

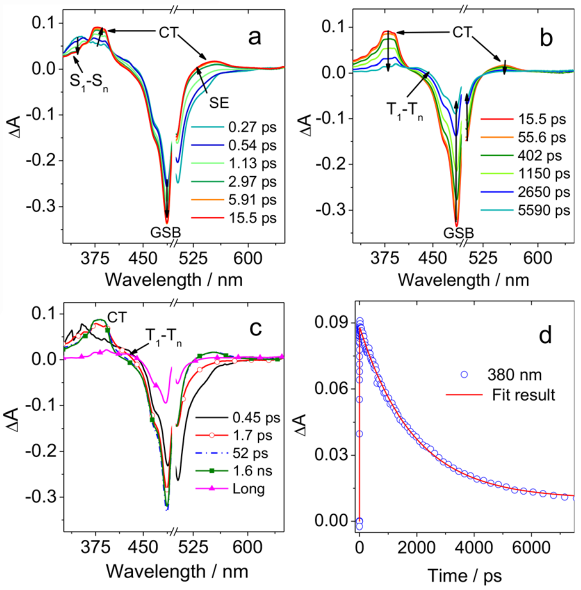


Figure 3. (a) Femtosecond transient absorption spectra of **AN-Zn** at short time delay and (b) at long time delay. (c) Evolution associated difference spectra (EADS) and (d) Decay trace at selected wavelength; $\lambda_{ex} = 500$ nm; $c = 1.0 \times 10^{-5}$ M in dichloromethane, 20 °C.

green EADS), a slight recover of the GSB signal is observed, possibly associated with a minor charge recombination process, or a slight structural relaxation of the system. The CT state principally decays in about 1.6 ns, populating the triplet state, as evidenced by the rise of absorption at about 425 nm in the last EADS. The final spectral component lives for a timescale longer than the time interval investigated with this measurement (magenta line in Figure 3c). In case of **PY-Zn**, whose spectra are reported in Supporting Information (Figure S24) SBCT occurs in 0.7/1.6 ps while CR takes place in about 1.1 ns. The reference complex **PH-Zn**, exhibits SBCT in 1.3 ps and fast CR occurs in about 770 ps, which causes inefficient triplet population, in line with the observed low triplet yield (Supporting Information, Figure S25), similarly to what observed previously for Zinc chloro-dipyrrin complexes.[24] Femtosecond transient absorption measurements of the bis(dipyrrin) complexes were also carried out in toluene (Supporting Information Figures S27–S29). All the complexes exhibited inefficient CT and triplet population in toluene. For **AN-Zn**, a small amount of CS is observed on 0.3/3.4 ps timescale and CR occurs in 252.2 ps (Supporting Information Figure S27).The results revealed that in non-polar solvents the yield of charge separation decreases and excited state lifetime is shorter than that observed in dichloromethane, decreasing the triplet yield.

To confirm the occurrence of ISC and triplet excited state population in the bis(dipyrrin) complexes, nanosecond–microsecond transient absorption studies were carried out (Figure 4 and Supporting Information, Figures S30–S37). All the complexes exhibited similar transient absorption features, namely a strong ground state bleaching centered at 488 nm and two excited state absorptions at 415 and 615 nm. This nanosecond transient absorption profile is characteristic for the T_1 absorption of dipyrrin derivatives (also Bodipy chromophores).[15,43] It is worth to note that here, for the first time long lived triplet excited state were observed for zinc bis(dipyrrin) complexes. For **AN-Zn**, the longer triplet lifetime of 295 μs was observed in dichloromethane (Figure 4b) and a triplet lifetime of 146 μs was recorded for **PY-Zn** (Supporting Information, Figure S30), significantly longer as compared to the reference compound **PH-Zn** (4.6 μs) and to the previously reported zinc bis(dipyrrin) complexes, all exhibiting triplet lifetimes in the range of 0.5–50 μs.[24,30] In acetonitrile, **AN-Zn** also exhibited a long lived triplet state with a lifetime of 168 μs. **PY-Zn** also showed a longer triplet lifetime of 111 μs, while a short triplet lifetime of 4.9 μs was recorded for **PH-Zn** (Supporting Information, Figures S32–S34).

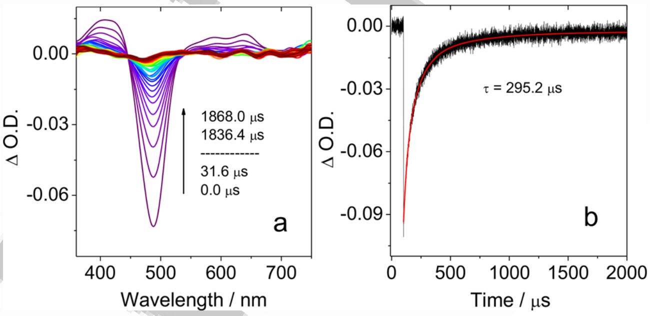


Figure 4. (a) Nanosecond transient absorption spectra of **AN-Zn** and (b) triplet state decay kinetics at 480 nm, upon ns pulsed laser excitation ($\lambda_{ex}=500$ nm); $c=5.0\times10^{-4}$ M in dichloromethane, 20 °C.

The nanosecond transient absorption measurements were also carried out in a slightly viscous solvent, glycerol triacetate, to study the effect of solvent viscosity on the triplet excited state dynamics, giving interesting results. For **PY-Zn**, the triplet excited state lifetime extended to 743 μs (Supporting Information, Figure S35), while in case of **AN-Zn** surprising results were obtained (Supporting Information, Figure S36), since the triplet state became stabilized up to the millisecond time scale ($\tau_T=1.24$ ms). In case of the reference compound **PH-Zn**, no significant stabilization of the triplet excited state in glycerol triacetate was observed as the triplet lifetime was found to be only 6.3 μs (Supporting Information, Figure S37). Our results indicate that the triplet excited state dynamics of zinc(II) bis(dipyrrin) complexes can be effectively tuned through attaching bulky aryl groups at 5,5′-position. The prolonged triplet state lifetime may be due to the inhibition of distortion at the excited state for the presence of bulky aryl groups, which is further enhanced in viscous solvents.[44,45] These results will provide a new approach to prepare SBCT based efficient triplet photosensitizers with strong absorption in the visible spectral region and long lived triplet state.

DFT computation and excited states energy diagram

In order to further elucidate the photophysical properties and get insights into the electronic structure of zinc(II) bis(dipyrrin) complexes, density functional theory (DFT) computations were performed at CAM-B3YLP/GENECP/LANL2DZ level. The ground state geometries of the complexes were optimized using the above mentioned basis set in vacuum, from which frontier molecular orbitals were obtained. As expected, the HOMO and HOMO−1 orbitals are degenerate due to the symmetrical structure of the complexes and localized over both dipyrrin ligands, while the LUMO orbital mainly spreads only on one dipyrrin ligand (Figure 5). The degeneracy or negligible energy difference (0.01 eV) between the HOMO and HOMO−1 orbitals indicates no electronic coupling between the two dipyrrin units at the ground state.[30] From the molecular orbital analysis, it is observed that the zinc atom has little or no electronic interactions with dipyrrin ligands, as no contribution was ob-

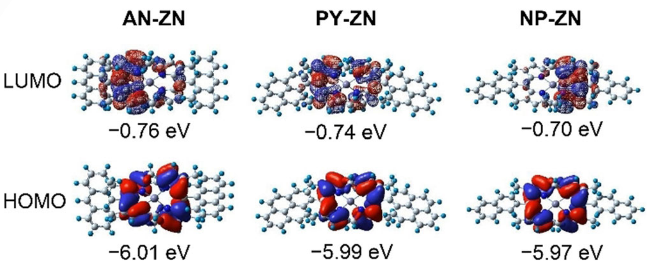
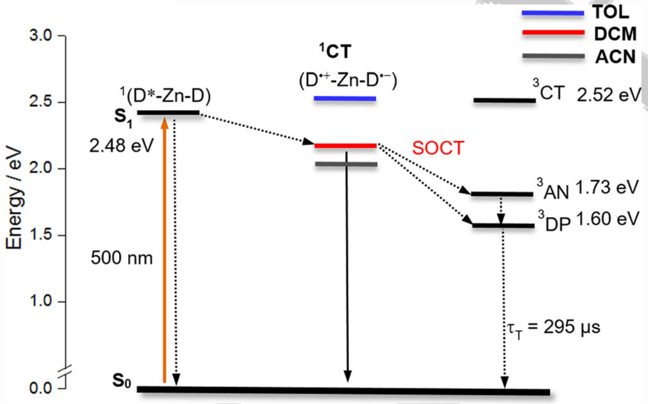


Figure 5. Frontier molecular orbitals (HOMO and LUMO) of bis(dipyrrin) complexes calculated by DFT theory at (CAM-B3YLP/GENECP/LANL2DZ) level using Gaussian 09W.

served from atomic orbital of the zinc atom in the frontier orbitals. Moreover, it was found that the attachment of organic moieties of different electronic strength has little effect on the electronic features of the complex, as the HOMO–LUMO energy gap remains nearly same in all the zinc(II) complexes.

The energy levels of the triplet state of the compounds have been estimated with DFT computations, allowing to summarize the overall photophysical processes observed in **AN-Zn** in Scheme 1. Upon photoexcitation, the singlet excited state of the dipyrrin moiety is populated, which either relaxes to the ground state or populates the CT state through SBCT. Note that SBCT occurs only in polar solvents and does not take place in non-polar solvent such as *n*-hexane. At a longer timescale the triplet excited state of the dipyrrin moiety gets populated, following the SOCT-ISC mechanism. It should be noted that the energy level matching of CT and triplet states is crucial in SOCT-ISC, which explains why **AN-Zn** exhibited efficient ISC in dichloromethane while negligible ISC was observed in toluene, due to the large energy gap between the CT state, which is destabilized in non-polar environments, and the triplet state, whose energy is mainly unaffected by solvent polarity. In the highly polar solvent acetonitrile, the ISC efficiency slightly decreased compared to dichloromethane which is probably due to low driving force for SOCT-ISC and fast CR. Similar photophysical processes were observed in case of the other zinc(II) bis(dipyrrin) complexes (Supporting Information, Schemes S1–S3). The poor ISC efficiency observed in case of the reference **PH-Zn** complex is due to the large energy gap between the CT and triplet states which is detrimental for SOCT-ISC (Supporting Information, Scheme S3), and to the increased possibility of radiationless decay, due to the less hindered structure.



Scheme 1. Simplified Jablonski diagram demonstrating the photophysical processes of **AN-ZN**. The energy levels of the excited singlet states are derived from the spectroscopic data; the energy level of charge transfer state are obtained from electrochemical data. The triplet energy levels are estimated by TD-DFT method. AN stands for Anthracene unit, D and DP stands for the dipyrrin moiety and Zn stands for the zinc metal. The number of the superscript designates the spin multiplicity.

Application for triplet–triplet annihilation upconversion

The molecules studied in this work, showing SBCT-induced ISC have strong visible light absorption and long lived triplet excited states. These properties are beneficial for intermolecular triplet–triplet energy transfer (TTET),[40] and these compounds can be useful in triplet–triplet annihilation (TTA) upconversion.

To confirm the potential application of these SBCT based bis(dipyrrin) complexes, TTA upconversion measurements were performed. Perylene was selected as triplet acceptor/emitter due to its suitable T_1 energy level (1.53 eV). Blue upconverted emission was observed upon exciting the mixture of **AN-Zn** and perylene with a 510 nm pulsed laser (Figure 6). The upconverted emission is visible to naked eye and the coordinates of CIE diagram are in agreement with photographs (Figure 6b). A high upconversion yield (Φ_{UC}) of 6.1% was observed for **AN-Zn**, **PY-Zn** exhibited 3.3% upconversion quantum yield while **PH-Zn** did not exhibit any upconversion process due to the short triplet lifetime and low ISC yield. It is worth to mention that previously Ru^{II}, Ir^{III} and Pt^{II} complexes were extensively used in TTA upconversion,[46,47] but the high cost of these metal limits their practical applications. Zinc(II) bis(dipyrrin) complexes are the cheapest and efficient SBCT materials, commonly used in photovoltaics but their short triplet lifetime has posed up to now severe limitations to their application in TTA. This is the first report of zinc(II) bis(dipyrrin) complexes showing long lived triplet states, for which practical application in TTA upconversion is demonstrated.

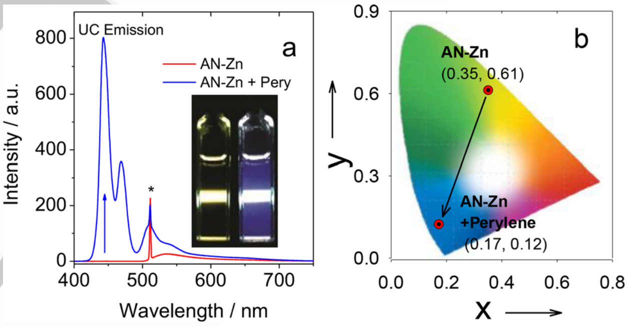


Figure 6. (a) TTA upconversion with **AN-Zn** as the photosensitizer and perylene (Pery) as the acceptor. Excited with 510 nm cw-laser (150 mW cm^{-2}); c[perylene] = 1.0×10^{-5} M, in deaerated dichloromethane, 20 °C. Inset: Photographs of **AN-Zn** alone and with added perylene (upconversion). (b) CIE diagram.

Conclusions

We prepared a series of zinc(II) bis(dipyrrin) complexes and demonstrated that their triplet excited state dynamics can be effectively tuned through structural modifications. For the first time we devised a visible light harvesting cheap SBCT architecture based on a metal organic framework, with efficient ISC capability ($\Phi_\Delta = 71\%$) and long lived triplet excited state ($\tau_T = 296$ µs). The crucial point of our strategy is tuning the energy gap between the CT and T_n states and the geometry of these bis(dipyrrin) complexes through structure alteration, which in turn controls the triplet excited state yield and lifetime. The occurrence of SBCT was confirmed through steady state and time-resolved spectroscopies, theoretical computations and electrochemical studies. Femtosecond transient absorption spectroscopy revealed a fast SBCT (0.45 ps) and slow CR (1600 ps) in **AN-Zn**, while in the reference complex **PH-Zn** comparatively faster CR (770 ps) was observed, which is in line with their different triplet yields. Notably, the zinc(II) bis(dipyrrin) complexes based on SBCT approach were employed for the first time in triplet–triplet annihilation upconversion, showing high upconversion yields of 6.1 %. These results are of particular importance in the field of photovoltaics, triplet–triplet annihilation upconversion, photodynamic therapy as well as fundamental photochemistry. It is worthy to mention here, bis(dipyrrin) complexes and Bodipy (fluorinated dipyrrin derivatives) belong to same family but due to low triplet yield and short triplet lifetime, bis(dipyrrin) complexes have been of limited interest in diverse photochemical applications such as photodynamic therapy and triplet–triplet annihilation upconversion. Our approach, leading to tuning the triplet excited state dynamics will open the doors of many applications for bis(dipyrrin) complexes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: charge transfer · intersystem crossing · photochemistry · triplet lifetime · zinc bis(dipyrrin) complexes

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FULL PAPER

Organometallic Chemistry

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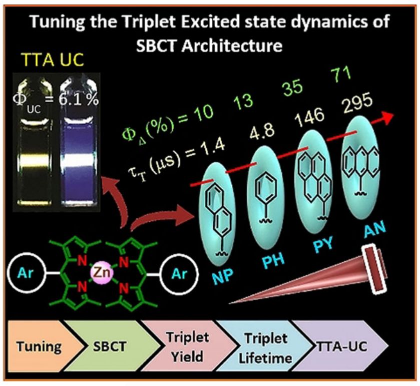
■■ – ■■

Tuning the Triplet Excited State of Bis(dipyrrin) Zinc(II) Complexes: Symmetry Breaking Charge Transfer Architecture with Exceptionally Long Lived Triplet State for Upconversion



Exploiting a structural control strategy we tuned the triplet excited state dynamics of Zinc^{II} bis(dipyrrin) complexes. Efficient intersystem crossing and long lived triplet state (296 μs) were accessed in the complexes, attaining a better matching of charge transfer and triplet energies with minimal non-radiative energy losses. This is the first attempt to utilize an earth abundant organometallic framework with efficient symmetry breaking charge transfer as a triplet photosensitizer in triplet–triplet-annihilation (TTA) upconversion.

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