Manipulating Triplet Yield Through Control Of Symmetry Breaking Charge Transfer

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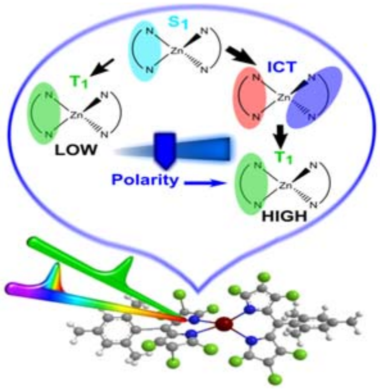
ABSTRACT

The efficiency of an organic solar cell depends on the efficacy of exciton diffusion and dissociation processes, and this can be enhanced by reducing the exciton binding energy and increasing the exciton lifetime. Zinc chlorodipyrrin (ZCl) complexes exhibit reduced exciton binding energy due to ultrafast generation of intramolecular charge transfer (ICT) states via symmetry breaking charge transfer in polar media. This paper explores the fate of the ICT states using nanosecond transient absorption. In cyclohexane, ZCl undergoes intersystem-crossing to produce triplets with ~8 ns time constant (~30% yield) and no ICT states are generated. However, in more polar solvents, triplets are generated within 1 ns via ICT state recombination with ~3 times higher yield than produced via ISC. This high triplet yield in toluene (89%) and acetonitrile (76%) via ICT state recombination is a beneficial pathway to spin-protect the excited state decay for additional charge generation from triplet excited states.

TOC GRAPHICS



KEYWORDS: Nanosecond Transient Absorption, Triplet lifetime, Charge recombination, Photophysics, Zinc chlorodipyrrin.

Organic photovoltaics (OPVs) are an attractive alternative to conventional silicon solar cells due to their many desirable properties like mechanical flexibility, inexpensive processing costs, and a broad selection of device materials.[1-4] Over last three decades, OPVs have demonstrated high potential for solar cell technology with power conversion efficiency (PCE) reaching 13%[6] from the first developed single heterojunction OPV reported in 1986 with PCE of ~1%.[7-8] Typical OPVs are comprised of an electron donor and acceptor material in separate phases, either in a bilayer structure or in a bulk-heterojunction phase.[9,10] Light is absorbed in either the donor or acceptor phase, forming a localized exciton which diffuses to the D/A interface where charge transfer and separation takes place. The localized exciton formed are typically 0.3-0.5 eV higher in energy compared to the charge transfer state; this large a driving force is typically required to achieve efficient charge transfer to form D^+/A^- by out-competing radiative and non-radiative recombination exciton losses.[11-13] Unfortunately, this 0.3-0.5 eV driving force for charge transfer reduces the available open circuit voltage (V_{OC}), which is thermodynamically limited by the energetic offset between the constituent donor HOMO and acceptor LUMO (E_{DA}).[5, 14-15]

Recent work by Bartynski *et. al.* shows that developing acceptor materials which exploit the symmetry-breaking charge transfer (SBCT) phenomena is a promising approach to move the V_{OC} closer to the thermodynamic limit.[5] SBCT is typically observed in multi-chromophoric systems, where an exciton initially formed on a single chromophore or ligand undergoes intramolecular charge transfer (ICT) to create an ICT state with broken symmetry, facilitated by the surrounding dielectric medium.[16-17] This ICT state consists of an electron and hole pair localized on two different chromophores or ligands, with very little coupling between electron and hole.[16-18] Due to their spatial displacement, symmetry-broken electron-hole pairs (ICT excitons) are expected to possess lower exciton binding energy than typical Frenkel excitons generated in organic materials.[19] Thus, charge transfer between electron donor and acceptor materials from these ICT excitons may proceed more efficiently with lower energetic requirements than that required for typical Frenkel excitons.[20-22] SBCT is an attractive strategy to achieve subsequent charge separation with negligible energetic driving force, directional specificity and a retarded back-recombination rate.[5] These advantages of the SBCT phenomena lowers recombination losses and potentially increases V_{OC}.

Zinc chlorodipyrrin, ZCl [bis(dodecachloro-5-mesityldipyrrinato)zinc], is a promising SBCT material for OPV devices. Devices with ZCl acceptors show significantly larger V_{OC}'s and reduced recombination losses than equivalent devices using conventional fullerene acceptors with similar LUMO energies.[5] Specifically, OPVs with tetraphenyldibenzoperyflanthrene (DBP) as a donor and ZCl as an acceptor results in a V_{OC} of 1.33 V compared to 0.88 V with analogous C_{60}-based devices. From Fourier-transform photocurrent spectroscopy and OPV electroluminescence measurements, the V_{OC} increase in DBP/ZCl analogs is attributed to the higher CT state energy (1.70 ± 0.05 eV) of ZCl than C_{60} (1.45 ± 0.05 eV) with DBP donors.[5] Comparing the V_{OC} with the CT state energy for both DBP/ZCl and DBP/C_{60} complexes reveals that there are fewer recombination losses in the DBP/ZCl complex. Additionally, it was shown that the presence of SBCT can also channel some excitation to the triplet manifold for zinc dipyrrin complexes[5,23] as well as for covalently bridged BODIPY dimers.[24-29] The triplet excitation can serve as an additional charge transfer pathway in an OPV provided the triplet energy is higher or close (within kT) to the CT state energy for donor-ZCl complex. In the case of DBP/ZCl complexes the CT state energy is ~50 meV lower than the triplet state energy of ZCl,[30] implying that any triplet excitation will still be able to undergo charge separation. This triplet excitation is beneficial for any excitation generated in the bulk ZCl (away from the D/A interface) as triplet excitons typically possess higher lifetime and thus can diffuse with greater probability to the D/A interface to charge separate. In this paper we explore the triplet yields and lifetime for ZCl in different non-polar to polar solvents. It was observed that tuning the ICT state energy in solvents with different polarity can also influence the overall triplet yield.

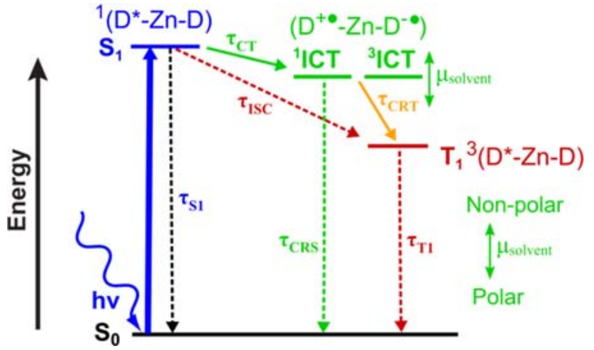


Figure 1. Simplified energy diagram showing the excited state decay pathways of ZCl in solvents of varied polarity. The energy of the ICT states is governed by solvent dipolar stabilization, $\mu_{solvent}$.

Previously reported femtosecond transient absorption (TA) studies reveal ultrafast formation of ICT states in ZCl from the initially excited S_1 state due to SBCT in polar media.[5] Spin conservation leads to generation of singlet ICT (^{1}ICT) state from S_1 state following SBCT with time constant τ_{CT} in polar media (Figure 1). Once generated, the ^{1}ICT ($^1[D^{+\bullet}$-Zn-$D^{-\bullet}]$) state can either undergo recombination to regenerate the ground state S_0 (via τ_{CRS}) or can undergo recombination with intersystem crossing (ISC) to relax to the triplet manifold (via τ_{CRT}). The involvement of ICT states implies a ^{1}ICT or ^{3}ICT states for the two spin alignments on the radical anion/cation pair. Typically, these two states are nearly degenerate (Figure 1) in organic semiconductors.[31-33] ^{1}ICT state can undergo two inter-system crossing (ISC) mechanisms distinct from ordinary spin-orbit induced ISC typically observed for S_1 state. One mechanism, radical pair intersystem crossing (RP-ISC) involves mixing between ^{1}ICT ($^1[D^{+\bullet}$-Zn-$D^{-\bullet}]$) and ^{3}ICT ($^3[D^{+\bullet}$-Zn-$D^{-\bullet}]$) states induced by electron-nuclear hyperfine coupling to undergo ^{1}ICT→^{3}ICT transformation followed by a rapid charge recombination to neutral lowest lying triplet state (^{3}ICT→T_1).[34-36] Alternatively, the intersystem crossing can also happen directly from ^{1}ICT→T_1 state via spin-orbit coupling provided the orbital symmetries involved are such that the spin flip is coupled with an accompanying orbital angular momentum change.[36-38] This mechanism is known as SOCT-ISC (spin-orbit, charge-transfer intersystem crossing) and this dominates when there is strong electronic coupling between the donor ($D^{+\bullet}$) and acceptor ($D^{-\bullet}$) radical pairs. Previous theoretical calculations in radical pairs illustrates that SOCT-ISC increases with orthogonality between the orbitals involved and decreases with the distance between the orbitals.[39-41] It is often difficult to distinguish between RP-ISC and SOCT-ISC mechanisms, however, the electronic coupling and thus the distance and orientation between the donor and acceptor plays an important role in determining the ISC mechanism.[42-43] In non-polar solvents, generation of the ^{1}ICT state is energetically unfavorable and thus the fate of S_1 excitation is either to decay to ground state, S_0 via τ_{S1} or to undergo conventional intersystem crossing (ISC) to T_1 via τ_{ISC}. A simplified energy diagram with all different excited states and time constants connecting them are shown in Figure 1. This work explores the long time (ns-μs) excited state dynamics of ZCl in non-polar, weakly polar, and polar solvents to quantify the entire triplet kinetic profile. These studies of ZCl in different polar media shows a dominance of triplet state photophysics with solvent polarity dependent triplet yield and generation rate.

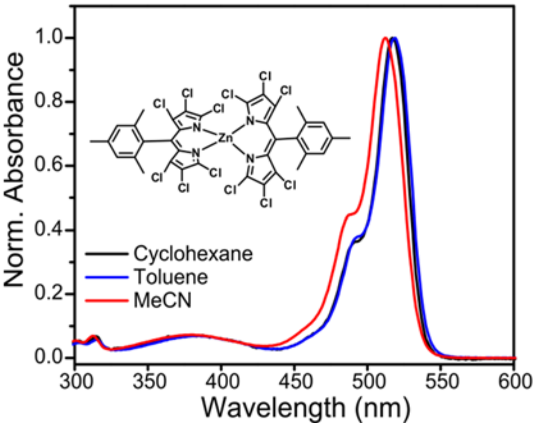


Figure 2. Normalized absorbance spectra of ZCl solution in cyclohexane, toluene and acetonitrile (MeCN). The inset shows the structure of the ZCl molecule.

The molecular structure of ZCl is shown in Figure 2 (inset). The linear absorption of ZCl in three solvents (Figure 2)—cyclohexane (non-polar with dielectric constant, ε~2), toluene (weakly polar, ε~2.4), and acetonitrile (polar, ε~38)—reveal nearly identical spectra except a 5 nm blue shift for acetonitrile, with main electronic transition at ~520 nm and a vibrational shoulder at ~490 nm. Nanosecond TA measurements were performed on these three different solutions with 532 nm excitation. Nanosecond TA spectra for ZCl in cyclohexane (Figure 3) shows an immediate depopulation of the ground state (ground state bleach between 450-540 nm) along with the formation of the excited state absorption (ESA) from S_1 at 360 nm and stimulated emission (SE) between 530-600 nm. These spectral features are consistent with previous fs TA analysis of ZCl in cyclohexane.[5] Over the first 10 ns (Figure 3a) the S_1 positive ESA and negative SE disappear with concurrent but only partial recovery (~60%) of the ground state bleach (GSB). The rate of relaxation from S_1 state to S_0 state was observed to occur with a time constant of τ_{S1}~ 3.2 ns. At longer delays a new transient absorption peak at ~450 nm is developed. This spectral feature at 450 nm is assigned to the triplet T_1 state based on previous triplet sensitization measurements of ZCl in methyl iodide (Supporting Information, S4).[5] The formation of the triplet state occurs as a result of ISC from the S_1 state. The rate constant linking S_1 to T_1 via the ISC pathway (τ_{ISC}) was determined to be ~8.3 ns. The overall relaxation time constant ($1/\tau_{S1}+ 1/\tau_{ISC}$) of S_1 state corresponds to the time-resolved photoluminescence lifetime measured for ZCl in cyclohexane (τ_{PL}: 2.5 ns, Supporting Information Figure S9).

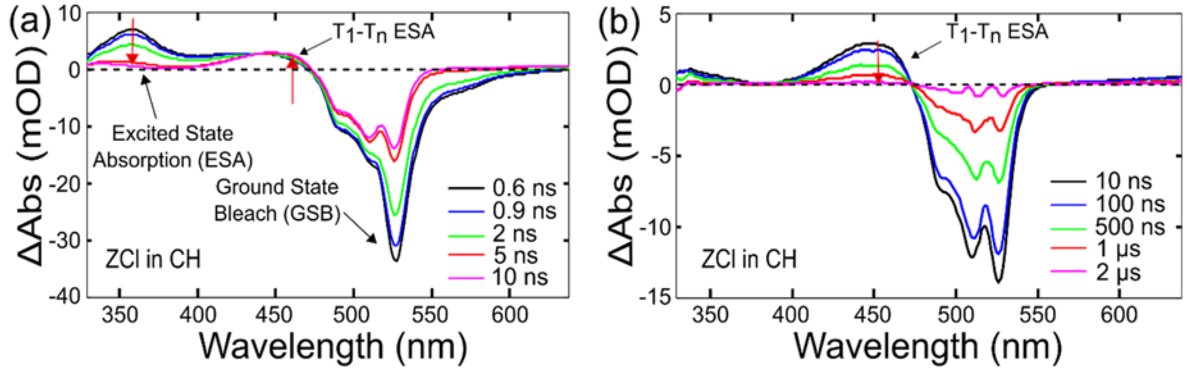


Figure 3. Nanosecond transient absorption of ZCl in cyclohexane at short time delays (a) and long time delays (b). Excitation at 532 nm was performed with a pump fluence of 106 μJ/cm^2.

As the triplet induced absorption rises, an additional structure appears to grow within the GSB region (prominently seen by a second peak at ~515 nm). Considering the growth rate for this spectral feature is the same as that of the first triplet band at 450 nm, it is likely that this spectral absorption feature is another part of the $T_1 \rightarrow T_n$ absorption spectra overlapping strongly with the GSB spectra. The nature of the $T_1 \rightarrow T_n$ absorption spectrum and its overlap with $S_0 \rightarrow S_1$ transition is discussed in Supporting information (Section S5). At longer delays (10 ns – 2 µs) (Figure 3b) the triplet excited state absorption decays with concomitant recovery of the ground state bleach with a time constant $\tau_{T_1} \sim$ 630 ns.

To understand the long time photophysics of ZCl in polar media, nanosecond TA of ZCl were performed in toluene and acetonitrile media. Nanosecond TA spectra for ZCl following excitation at 532 nm are presented in Figure 4. Unlike cyclohexane, in acetonitrile (Figure 4a) and toluene (Figure 4c) the ESA due to $S_1 \rightarrow S_n$ is not observed and instead an induced absorption band at 420 nm is observed within the instrument response (≤500 ps, Figure S1). This induced absorption band has been previously assigned to the ^{1}ICT state from femtosecond TA measurements.[5] The absence of $S_1 \rightarrow S_n$ ESA in ns TA spectra of ZCl in toluene and acetonitrile is due to ultrafast formation of the ^{1}ICT state in high polar/polarizable media.[5] This appearance of a ^{1}ICT state only in media with higher polarity/polarizability than cyclohexane indicates that dipolar stabilization is required to favor ICT state stabilization. Within 5ns, the ^{1}ICT absorption band decays with a concurrent rise of triplet absorption band at ~450 nm along with partial recovery of ground state bleach in both acetonitrile and toluene (Figure 4a & 4c). This is probably because the ^{1}ICT state can decay via two pathways to either regenerate S_0 state or to recombine to form T_1 state. The regeneration to S_0 state is more prominent in MeCN where ~50% of GSB recovery occurs within 2 ns (Figure 4a) versus 25% of GSB recovery in toluene (Figure 4c). This difference in amount of ^{1}ICT state recombination to regenerate S_0 state could arise from the difference in the ^{1}ICT state energy relative to the T_1 state for these two solutions.

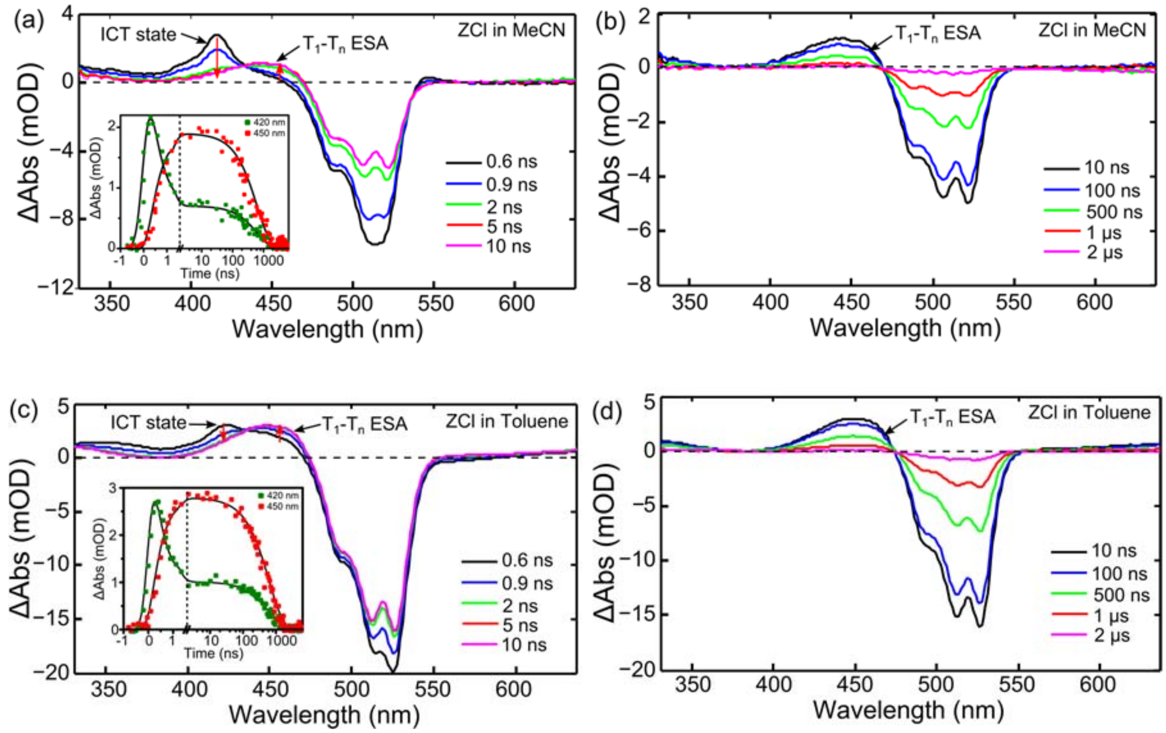


Figure 4. Nanosecond transient absorption of ZCl in (a-b) acetonitrile (MeCN) and (c-d) toluene over short time (a-c) and long time (b-d) delays. The insets in (a) and (c) show the dynamics at 420 nm and 450 nm (scaled by 2) with the fits (black line) over 6 μs. The early time dynamics upto 2 ns (broken line) shows the two state kinetics between the ICT and T_1 state. Excitation at 532 nm was performed at fluence of 106 μJ/cm^2 for ZCl in acetonitrile and 98 μJ/cm^2 for ZCl in toluene solutions.

Similar to cyclohexane, the triplet growth in both solvents occurred with a concurrent rise of a peak at 510 nm, leading to a distortion of the GSB over 2 ns. This distortion of the GSB shape into a doublet structure occurs at a rate correlated to the rate of triplet formation as monitored by the 450 nm absorption band. In acetonitrile and toluene the distortion becomes evident already from 900 ps; however, the distortion in cyclohexane (τ_{ISC} = 8.3 ns) only appears after 3 ns. This indicates a faster triplet formation rate likely due to a different triplet generation mechanism in polar media via the intermediate ^{1}ICT state. At longer delays, similar to cyclohexane, the triplet feature in acetonitrile (Figure 4b) and toluene (Figure 4d) solutions completely decays (along with a concurrent recovery of the GSB signal) with a similar lifetime (within error) of ~630 ns.

Based on the nanosecond TA data reported here, no ^{1}ICT state was observed in cyclohexane and only triplet state is generated. ^{1}ICT states are observed only in toluene and acetonitrile because of the increased stabilization of the ^{1}ICT state provided by the more polar environment. In cyclohexane, the ^{1}ICT state energy is likely too high and so the S_1 state can only form triplets directly via inter-system crossing (τ_{ISC}) or alternatively relax directly to the ground state (τ_{S1}). Nanosecond TA data in toluene and acetonitrile shows a faster generation of triplets (500-700 ps) indicating that the triplets are generated via ICT recombination (τ_{CRT}) and not by ordinary ISC. In addition, a part of the population from the ICT state recombine to generate the ground state (τ_{CRS}) for both toluene and MeCN solutions. On increasing the solvent polarity from toluene to acetonitrile, triplet recombination from ICT state (τ_{CRT}) slows with an accompanied acceleration of recombination to regenerate S_0 (τ_{CRS}). However, once the triplets are generated, the triplet state decays with a lifetime (τ_{T1}) of ~630 ns in all three solvents irrespective of the solvent polarity. Based on the schematic representation of these pathways presented in Figure 1,

Table 1. Summary of ZCl electronic state lifetimes in cyclohexane, toluene, methyl iodide (MeI) and acetonitrile solvents, using the excited state kinetic scheme shown in Fig.1

Solvents (ε)	τ_{CT} (ps)*	τ_{CRT} (ps)*	τ_{CRS} (ns)	τ_{S1} (ns)	τ_{ISC} (ns)	τ_{T1} (ns)
Cyclohexane (2)	--	--	--	3.2±0.3	8.3±0.5	630±30
Toluene (2.4)	6±0.5	520±10	2.4±0.1	3.2[a]	8.3[a]	630±30
Acetonitrile (38)	1.5±0.3	720±10	2.1±0.3	3.2[a]	8.3[a]	620±30
MeI[b] (6.97)	2.8±0.3	70±2	2.4±0.3	3.2[a]	0.037±0.02	n/a

* τ_{CT} values are from previous study by Bartynski et. al.[5] and τ_{CRT} values are from previous study by Bartynski et. al. using better characterized model and more complete dataset. [a]These values were kept fixed based on the time constants extracted from ZCl in cyclohexane TA data. [b]The TA data and time constants for ZCl in MeI are shown in Supporting Information, S4 based on the triplet sensitization measurements performed in ref 5.

the fitted time constants for these pathways were estimated using a linear decomposition model (Supporting Information, S2) and are summarized in Table 1.

In addition to the excited state lifetime analysis, the ZCl triplet yields were calculated to compare the triplet yield via ISC versus ICT state recombination. The time dependent triplet concentrations are extracted by fitting the TA data (SI, Figure S7) with the species associated difference spectra (SADS) of the triplet state in extinction units. The SADS for triplet in extinction units is extracted from previously reported triplet sensitization TA data of ZCl in MeI (SI, section S4).[5] And the triplet yield is calculated by dividing the triplet concentration extracted with the initially excited singlet concentration. A more detailed explanation of the triplet yield calculations along with the initial excited singlet concentration is located in SI. The maximum triplet yields (Table 2) for ZCl in both toluene and acetonitrile appear to be ~2.5-3 times higher than the yield in cyclohexane. This illustrates that formation of ^{1}ICT state in polar solvents increases the overall excited state lifetime via T_1 generation and thus delays the back recombination to the ground state S_0. The higher amount of T_1 generation can potentially facilitate excitons generated in the bulk to reach D/A interface, which can undergo increased charge separation due to lowering of the ICT state energy by the polar D/A interface.

Table 2. Maximum triplet yields of ZCl in cyclohexane (measured at 15.5 ns), toluene (measured at 4.5 ns), and acetonitrile (measured at 4.5 ns).

Solvent	Maximum Triplet Yield
Cyclohexane	31 ± 5 %
Toluene	89 ± 8 %
Acetonitrile	76 ± 7 %
MeI*	97 ± 3%

*The yield reported (at 1 ns) for ZCl in methyl iodide is based on triplet sensitization measurements.

The ICT state recombination to form triplets is probably enhanced due to presence of Cl atoms at α positions in the ZCl complex. The presence of Cl atoms can facilitate spin mixing between ^{1}(ICT) and ^{3}(ICT) states to undergo $^1\text{ICT} \rightarrow {}^3\text{ICT}$ transformation and therefore can lead to faster generation of the triplet state via an RP-

ISC mechanism. Alternatively, the Cl atoms at α positions can better restrict the dihedral angle between the $D^{+\bullet}$ and $D^{-\bullet}$ units generating two orthogonally held π-orbitals; when undergoing recombination this orthogonality leads to higher spin-orbit coupling to directly generate neutral T_1 state via SOCT-ISC.[39-41] Therefore, both mechanisms are probably involved in the enhanced triplet generation of ZCl in weakly polar to polar media via the intermediate ^{1}ICT state. However, we note a ~13% lower triplet yield observed in acetonitrile compared to toluene. This lower yield along with the slower rate of triplet formation via ICT state recombination is probably due to stronger stabilization of the ICT states in acetonitrile compared to toluene,[44] bringing the ^{1}ICT and ^{3}ICT states closer or even lower than the T_1 state. This is reasonable because ZCl possesses a very small S_1-T_1 energy gap (~0.6 eV)[30], which is comparable to the stabilization energies predicted for similar SBCT compounds in polar media.[17, 45] In toluene, the stabilization energy is less and therefore the ICT states are higher relative to T_1 state and still may favor a higher recombination fraction to T_1 state. The reduction in triplet yield via enhanced stabilization of ICT states in strong polar solvents has also been observed for BODIPY dimers[29], perylenediimide dimers[46] and a variety of electron donor-acceptor systems.[47-48]

Figure 5 summarizes the solvent polarity dependent excited state dynamics of ZCl and in general can be applied to any orthogonally coupled electron donor-acceptor system. In non-polar solvents the ICT state does not get stabilized and therefore the excited state S_1 undergoes ordinary ISC (in competition with internal conversion). With increasing solvent polarity, the ICT state gets stabilized and a new pathway to generate T_1 state develops via ICT state recombination. At higher polarity, the ICT state stabilization can be such that the ICT state act as an energetic trap and thus reduces the triplet yield.

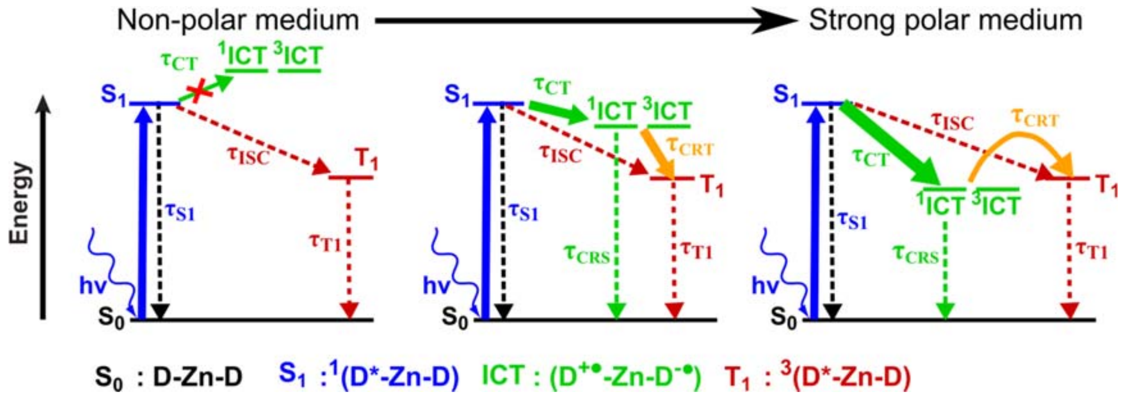


Figure 5. Summary of solvent polarity dependent excited state deactivation pathways for ZCl. The relative energy of the ICT states with respect to the T_1 state in weakly polar and strongly polar media have been deduced based on the ICT state kinetics and triplet yield observed. The ICT state energies has not been measured or calculated.

In conclusion, we extended our photophysical study of ZCl in different polar media now over sub-nanosecond to microsecond timescales. This revealed that triplets in nonpolar solvents are generated from the S_1 state via normal ISC whereas, in increasingly polar solvents, the triplet is produced more rapidly through charge recombination from the ICT states, by either RP-ISC and/or SOCT-ISC mechanisms. Additionally, triplet yield measurements reveal ~3 times as many triplets via ICT state recombination compared to conventional ISC. This observation opens up the possibility of a more controllable pathway for triplet formation via ICT state recombination rather than through conventional ISC while avoiding the use of rare elements like Pd, Pt, Ir, etc. Considering the exciton evolution in a ZCl containing device, the increased triplet yield induced by the ICT state not only increases the potential for the exciton to diffuse to the D/A interface but also allows for the unique possibility of subsequent regeneration of an ICT state when arriving at the interface, a region of increased dielectric. The manipulation of the triplet-ICT equilibrium in this manner can be used to improve overall charge separation in the device. Thus, systematic tuning of the ICT and triplet state populations within different phases of a device can be used to advantage in future OPVs.

EXPERIMENTAL METHODS

ZCl was synthesized and purified following a published procedure.[30] Nitrogen purged solutions of ZCl in cyclohexane, toluene and acetonitrile were prepared in 1 mm cuvette with absorbance of 0.18, 0.14 and 0.14, respectively at 532 nm. Nanosecond TA was performed with 532 nm pump generated from a Nd:YAG laser (Alphalas, 1kHz) externally triggered and synchronized with the femtosecond oscillator. White light continuum probe (350-650 nm) pulses are generated by pumping CaF_2 with a small portion of 800 nm ultrafast amplifier output (Coherent Legend, 1kHz). The white light generated is collimated and focused using a pair of off-axis parabolic mirrors at the sample while the 532 nm pump is focused using a 25 cm CaF_2 lens. After interacting with the sample, the white light is dispersed using a monochromator (Oriel MS127i) onto a 256-pixel Si array. The delay between pump and white light probe pulse was controlled using a Stanford Research Systems delay generator DG645. Nanosecond TA data was collected with an instrument response of ~500 ps (see SI Figure S1). The polarization of the 532 nm pump pulse was set up at a perpendicular polarization with respect to the white light polarization to reduce the pump scattering. The samples were translated perpendicular to the pump and probe path during data collection to avoid photodamage.

SUPPORTING INFORMATION

A description of the kinetic fitting model along with details of the triplet yield calculations, extinction spectra, triplet sensitization spectra, time-resolved photoluminescence and additional details for nanosecond time-resolved transient absorption are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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