Regulating Singlet-Triplet Energy Gaps through Substituent-Driven Modulation of the Exchange and Coulomb Interactions

Erin J. Peterson,[†] Jeff Rawson,[‡] David N. Beratan, Peng Zhang,^{*} and Michael J. Therien^{*}

Department of Chemistry, French Family Science Center, 124 Science Drive, Duke University, Durham, North Carolina, 27708-0346 USA.

ABSTRACT: Control of the singlet-triplet energy gap (ΔE_{ST}) is central to realizing productive energy conversion reactions, photochemical reaction trajectories, and emergent applications that exploit molecular spin physics. Despite this, no systematic methods have been defined to tune ΔE_{ST} in simple molecular frameworks, let alone by an approach that also holds chromophore size, and electronic structural parameters (such as the HOMO-LUMO gap) constant. Using a combination of molecular design, photophysical and potentiometric experiments, and quantum chemical analyses, we show that the degree of electron-electron repulsion in excited singlet and triplet states may be finely controlled through the substitution pattern of a simple porphyrin absorber, enabling regulation of relative electronically excited singlet and triplet state energies by the designed restriction of the electron-electron Coulomb (*J*) and exchange (*K*) interaction magnitudes. This approach modulates ΔE_{ST} magnitude by controlling the densities of state in the occupied and virtual molecular orbital manifolds, natural transition orbital polarization, and the relative contributions of one electron transitions involving select natural transition orbital pairs. This roadmap, which regulates electron density overlaps in the occupied and virtual states that define the singlet and triplet wavefunctions of these chromophores enables new approaches to preserve excitation energy despite intersystem crossing.

Controlling the energetic separation between low-lying singlet (S₁) and triplet (T₁) electronically excited states is central to the design of energy efficient light emitting diodes, many solar energy conversion schemes, and photocatalytic transformations.¹⁻⁴ The S₁-T₁ energy gap (ΔE_{ST}) in molecules is governed largely by the exchange interaction, which decays exponentially as the inter-electron distance increases. Established approaches to regulating ΔE_{ST} include: (i) designing extended molecular scaffolds that spatially separate chromophores that serve as distinct singlet and triplet excitation reservoirs, or (ii) modulating the extent of charge delocalization that characterizes molecular excited states with charge transfer character, as increased charge separation correlates with reduced exchange interaction magnitudes. While both of these tactics have impacted the development of systems that display thermally-assisted delayed fluorescence (TADF), for example, ^{1, 5-6} no systematic methods have been defined that tune ΔE_{ST} in simple chromophoric frameworks. Furthermore, it remains an open challenge to demonstrate control of S₁-T₁ state splittings via a strategy that maintains a uniform chromophore HOMO-LUMO gap.

Here we describe a strategy that minimizes the energy loss that accompanies S_1 - T_1 electronic relaxation in a molecular system where both S_1 and T_1 excitation are confined to a circular absorber. Classic circular absorbers such as (porphinato)metal chromophores possess approximate fourfold symmetry;⁷ following photon absorption, the initially prepared excited-state population randomizes between near degenerate and orthogonal Q_x and Q_y states, producing an E-symmetric excited state.⁸⁻¹⁰ As a consequence, circular absorbers feature S₁ and T₁ wavefunctions that have extraordinarily similar spatial distributions. We demonstrate that the degree of electron-electron repulsion may be finely controlled by the porphyrin macrocycle substitution pattern, enabling regulation of absolute S₁ and T₁ state energies and ΔE_{ST} through the designed restriction of the electron-electron Coulomb (*J*) and exchange (*K*) interaction magnitudes. This systematic modification of *J* and *K* is realized by controlling frontier molecular orbital (MO) density of states (DOSs) and electron density distributions in the singly occupied MOs that characterize the oneelectron transitions underpinning the S₁ and T₁ state wavefunctions.

Figure 1 highlights electronic spectra for monomeric porphyrins Rf_2PZn , Rf_2PZnE , Rf_3PZnE , and Rf_2PZnE_2 that bear combinations of perfluoroalkyl (Rf) and ethynyl (E) substituents at their respective (porphinato)zinc (PZn) meso carbon positions; fluorescence (Figure 1, red) and phosphorescence (Figure 1, blue) emission data demonstrate a marked diminution of the S_1 - T_1 energy gap as the macrocycle substitution pattern evolves in this manner. Additional photophysical data characterizing these chromophores may be found in the Supporting Information (SI).



Figure 1. Top: Molecular structures of monomeric porphyrins. Bottom: Room temperature electronic absorption spectra in THF (black). Emission spectra: room temperature fluorescence in THF (red) and 77K phosphorescence in 2-methyl-THF (blue).

Note that the potentiometrically determined HOMO-LUMO (H-L) gaps (E_p ; $E_{1/2}^{0/+} - E_{1/2}^{-/0}$) for $\mathbf{Rf_2PZn}$, $\mathbf{Rf_2PZnE}$, $\mathbf{Rf_3PZnE}$, and $\mathbf{Rf_2PZnE_2}$ (Figure 2) are all ~2.27 eV. Likewise, density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies carried out with the MN15 functional and the def2-TZVP basis set that determine the H-L gaps for these chromophores computed at the S₀, S₁, and T₁ state minima do not provide a simple rationale for the relative S₁ and T₁ state energies of these chromophores (SI, **Tables S3-4**, **S8**); these potentiometric and computational data thus suggest that other factors are at play that decrease ΔE_{ST} as the macrocycle substitution pattern evolves ($\mathbf{Rf_2PZn} \rightarrow \mathbf{Rf_3PZnE} \rightarrow \mathbf{Rf_3PZnE_} \rightarrow \mathbf{Rf_3PZnE_}$) as highlighted in the **Figure 1** data.



Figure 2. Left: ground state Rf_2PZn , Rf_2PZnE , Rf_3PZnE , and Rf_2PZnE_2 potentiometric data. Right: corresponding S₁- and T₁-state redox properties for these chromophores (see SI). Experimental conditions: 0.1 M TBAPF₆/ THF electrolyte/solvent system; ambient temperature; potential vs NHE.

 S_1 and T_1 state energies were evaluated at the S_0 , S_1 , and T_1 energy minima; these data indicate that the S_1 - T_1 electronic energy gaps computed for these chromophores are insensitive to molecular geometry, underscoring that the magnitude of ΔE_{ST} is regulated by electronic factors and not by molecular structure per se (**Table S5**). Figure 3

characterizes the nature of the T_1 states for the Rf_2PZn , Rf_2PZnE , Rf_3PZnE , and Rf_2PZnE_2 absorbers in terms of their respective dominant natural transition orbitals (NTOs) computed at the S_1 state energy minima; note that the NTOs that describe the corresponding relaxed S_1 states of these chromophores are similar (**Table S7**).

Figure 3 highlights the progressive modulation of the atom-specific electron densities reflected in the Rf₂PZn, **Rf₂PZnE**, **Rf₃PZnE**, and **Rf₂PZnE**² NTOs, and how NTO spatial electron density distributions depend on ethynyl and perfluoroalkyl substitution of the PZn ring. Figure 3 indicates that as the macrocycle substitution pattern progresses from $\mathbf{Rf}_2\mathbf{PZn} \rightarrow \mathbf{Rf}_2\mathbf{PZnE} \rightarrow \mathbf{Rf}_3\mathbf{PZnE} \rightarrow \mathbf{Rf}_2\mathbf{PZnE}_2$, the S₁ and T₁ state configurations evolve from being dominated by a single NTO to those that are better described by two NTO contributions at the S₁ state energy minimum. This effect derives from two factors: (1) macrocycle E substitution, which does not significantly alter HOMO and LUMO energies (Table S3), but amplifies DOSs in the occupied and virtual MO manifolds. Further consequences of E substitution include distortion of atomic specific NTO electron density along the molecular y axis, and alteration of the nodal pattern in the occupied NTOs of Rf₂PZnE, Rf₃PZnE, and Rf_2PZnE_2 relative to Rf_2PZn ; and (2) the σ -electron withdrawing nature of the Rf group,¹¹⁻¹⁴ which polarizes atom-specific NTO electron densities along directions defined by oppositely positioned macrocycle pyrrole units. The impact of this latter effect can be seen clearly in the nature of the increased DOS that drives an augmented contribution of the second NTO pair for Rf_3PZnE relative to Rf₂PZnE, and the nature of the electron density redistribution that accompanies this one-electron excitation (Figure 3C-D).

The data shown in Figure 3 and Table S7 depict the respective T₁ and S₁ state character for Rf₂PZn, Rf₂PZnE, **Rf₃PZnE**, and **Rf₂PZnE₂** using NTOs computed at the S₁ state energy minima. These data are striking, as they provide electronic structural insight into the exchange interaction magnitude relevant to the intersystem crossing. As the chromophore substitution pattern evolves $(Rf_2PZn \rightarrow$ $Rf_2PZnE \rightarrow Rf_3PZnE \rightarrow Rf_2PZnE_2$), the nature of electron density redistributions in the one electron transitions described by the NTO pairs [NTO₁ (H \rightarrow L); NTO₂ (H-1 \rightarrow L+1)] reduces the electron density overlap between the occupied and virtual NTOs. The fact that the NTO₂ contribution increases as electronic structural modulation progresses in this manner further reduces electron density overlap of the S_1 and T_1 wavefunctions. Because the S_1 and T_1 states of these chromophores are described by similar NTOs, Figure 3 provides insight into how substituent effects may be exploited to progressively diminish *J* and *K* magnitudes, and modulate ΔE_{ST} by design.



Figure 3. The dominant natural transition orbitals (NTOs) for $\mathbf{Rf_2PZn}$, $\mathbf{Rf_3PZnE}$, $\mathbf{Rf_3PZnE}$, and $\mathbf{Rf_2PZnE_2}$ that contribute to the T₁ state wave functions computed at the S₁ state equilibrium geometry at the TD-MN15/TZVP level. The NTO pairs having the two largest eigenvalues in the transition density matrix are presented. Gray and pink shading emphasizes the extent of reduced electron density overlap at selected macrocycle locations in the occupied and virtual orbitals of these NTO pairs. Eigenvalues for the NTOs that describe the H \rightarrow L (NTO₁) and H-1 \rightarrow L+1 (NTO₂) one electron transitions are highlighted in black and magenta respectively.

Figure 4 provides a quantitative picture regarding how the experimental S_1 - T_1 energy gap can be understood from the electron density differences between the one-electron NTOs that describe these states as a function of macrocycle substitution. Figure 4 highlights that the ΔE_{ST} magnitude (Figure 1) mirrors the extent of electron density overlap of the occupied and virtual components of NTO₁ (H \rightarrow L) and NTO₂ (H-1 \rightarrow L+1) as the macrocycle substitution pattern evolves (Rf₂PZn \rightarrow Rf₂PZnE \rightarrow Rf₃PZnE \rightarrow Rf₂PZnE₂).



Figure 4. The dependence of the S_1 - T_1 energy gap, ΔE_{ST} (solid line; left vertical axis) and the normalized natural transition orbital (NTO) electron density overlap (dashed and dotted lines; right vertical axis) as a function of the macrocycle substitution pattern. Progressive occupied/virtual orbital electron density overlap reduction correlates with a progressive diminution of ΔE_{ST} . The dotted line represents the electron

density overlap between NTO₁ (H→L), while the dashed line represents the electron density overlap between NTO₂ (H-1→L+1). Here, NTO electron density overlaps are normalized relative to the corresponding NTO electron density overlap for **Rf₂PZn**, and are expressed as electron density differences $\Delta \rho_1 = \rho(H) - \rho(L)$ (dotted magenta line; upper row of electron density difference maps) and $\Delta \rho_2 = \rho(H - 1) - \rho(L + 1)$ (dashed magenta line; lower row of electron density difference maps). The yellow and cyan colors in the difference maps depict the spatial distribution of the electron density differences (positive and negative). See SI for further detail.

Data displayed in **Table S9** chronicles numerically the extent to which the electron density distribution is distorted in the NTOs that characterize the T₁ state as a function of macrocycle substitution; here, reduced electron density overlap values correlate with enhanced electron density distortions,¹⁵⁻¹⁶ and track with the magnitude of the computed exchange integral (**Table S9**). Collectively, these data indicate that porphyrin macrocycle substitution patterns that manipulate ΔE_{ST} magnitude are derived from intrinsic substituent electronic properties which control the electron density distributions characteristic of the frontier orbitals.

Figure 5 highlights S_1 and T_1 state potential energy surfaces (PESs) for **Rf₂PZn**, **Rf₂PZnE**, **Rf₃PZnE**, and **Rf₂PZnE₂**, emphasizing the dependence of ΔE_{ST} and absolute relaxed S_1 and T_1 energies upon macrocycle electronic structure. The PESs are plotted showing their adiabatic energy dif-

ferences relative to the ground state. Qualitative understanding of the variations in these S₁ and T₁ state energies may be derived using a simple two-electrons in twoorbitals (HOMO and LUMO) model. In this single Slater determinant treatment, the T₁ and S₁ energies (relative to the ground state energy) are $E(T_1) = \varepsilon_L - \varepsilon_H - J_{HL}$ and $E(S_1) = \varepsilon_L - \varepsilon_H - J_{HL} + 2K_{HL} = E(T_1) + 2K_{HL}$ where ε_L and ε_H are the HOMO and LUMO energies, and J_{HL} and K_{HL} are the potential energies determined from the Coulomb and exchange integrals.



Figure 5. Schematic representation of S_1 and T_1 state potential energy surfaces for **Rf_2PZn**, **Rf_2PZnE**, **Rf_3PZnE**, and **Rf_2PZnE_2**, highlighting the dependence of absolute S_1 and T_1 energies and ΔE_{ST} upon the macrocycle substitution pattern. The relative energies of the S_1 and T_1 states are based on the computed adiabatic energy differences between the excited states and the ground state (**Tables S1**, **S6**, **S10**).

The computed values of $\varepsilon_L - \varepsilon_H$ (**Table S5**) for **Rf₂PZn**, Rf₂PZnE, Rf₃PZnE, and Rf₂PZnE₂ mirror the potentiometrically determined HOMO-LUMO gaps displayed in the Figure 2 data. The computed T₁ state PES minima in Fig**ure 5** reflect the fact that the progressive elaboration of the porphyrin macrocycle increasingly distorts the electron distribution between the occupied and virtual NTOs (Figure 4), diminishing the electron density overlap, and thereby decreasing the magnitude of the Coulomb interaction J_{HL} (**Rf₂PZn** > **Rf₂PZnE** > **Rf₃PZnE** > **Rf₂PZnE₂**; **Table** S10). This effect, combined with the exchange integral magnitude dependence of the Figure 5 S1 state PES minima, explains the unusual ΔE_{ST} dependence chronicled in the **Figure 1** spectral data. Because the exchange integral magnitude decreases progressively with macrocycle modulation (Rf₂PZn > Rf₂PZnE > Rf₃PZnE > Rf₂PZnE₂; Figure 4, Tables S9-10), Figure 5 underscores that the K_{HL} derived boost to the S1 state energy follows the opposite trend to the J_{HL} magnitude dependence of the T₁ state energy (Rf₂PZnE₂ < Rf₃PZnE < Rf₂PZnE < Rf₂PZn). The Figure 5 data thus highlight the profound divergence of relative S1 state energies from a description derived from experimentally determined E_p values (Figure 2), and that the experimental ΔE_{ST} dependences highlighted in Figure 1 derive from the opposite impact of the Coulomb and exchange interaction magnitudes on the singlet and triplet PES minima. These macrocycle-substitution dependent differences trace their genesis to the nature of and extent

to which electron density distributions are distorted in the NTOs of these chromophores (**Figures 3-4**). While electron correlation, configuration interaction, and structural contributions to the S₁ and T₁ energies are not considered in this straightforward single Slater determinant analysis (**Figure 5**), this simplified picture is consistent with TDDFT computational data described in the Supporting Information that considers all of these factors (**Tables S1-10**), and the NTO electron density overlap dependence of ΔE_{ST} described in **Figure 4**.

Electronic manipulation of chromophore HOMO and LUMO energy levels through substituent resonance and field effects¹⁷ defines the classic approach to regulate absolute S_1 and T_1 state energies, but not the S_1 - T_1 energy gap (ΔE_{ST}) . While the photophysics of rare examples of conjugated absorbers with anomalously small singlet-triplet splittings have been rationalized through analyses that illustrate atypically small HOMO-LUMO electron density overlaps,¹⁸⁻²⁰ no substituent-guided approach has been defined that enables the systematic modulation of ΔE_{ST} in any simple chromophoric platform. This work describes how the electron-electron interaction magnitude may be regulated by design in a π -conjugated chromophore. We show that the substitution pattern of two substituents ethyne and perfluoroalkyl - can be leveraged to regulate the relative S₁ and T₁ state energies at a uniform HOMO-LUMO energy gap in a simple porphyrin-based circular absorber. Combinations of these substituents provide a roadmap to amplify the densities of state in the occupied and virtual molecular orbital manifolds, modulate natural transition orbital polarization, and regulate the relative contributions of the one electron transitions involving select NTO pairs that control the electron density overlap of the occupied and virtual states describing the S_1 and T_1 wavefunctions of these chromophores. Quantum chemical analyses demonstrate that this regulation of ΔE_{ST} stems unequivocally from systematic control of the extent of exchange and Coulomb interactions. Because this approach enables control of S₁-T₁ splittings while confining S₁ and T₁ wavefunctions over uniform spatial dimensions on a single chromophoric site, it makes possible new approaches to preserve excitation energy following intersystem crossing, engineer coherence between singlet and triplet states, and promote spin polarization in electronically excited states.

ASSOCIATED CONTENT

Supporting Information. Computational data, synthetic details, compound characterization, electronic spectral, potentiometric, and excited-state dynamical data. It is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*peng.zhang@duke.edu *michael.therien@duke.edu.

Present Addresses

†Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States. ‡Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States.

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