Probing and Managing Photo-Induced Electronically Excited-State Dynamics of Molecular to Nanoscale Systems

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University

2017
ABSTRACT

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Abstract

Light-matter interactions, spectroscopically depicted by the generation and decay of materials’ photo-excited states, are the core to majority of modern optic and optoelectronic technologies that include photovoltaics (PVs), optical power limiting (OPL), bioimaging, spintronics, photodetections, etc. Achieving high performance at device levels in these applications, thus, often requires deep understanding towards excited state dynamics of the relevant materials and capabilities to manage the fate of the corresponding photo-excited species at microscopic levels. In this regard, the current study exploits spectroscopic techniques and computational analyses to probe structure-property relationships of various molecular to nanoscale conjugated materials, and then tunes their excited-state dynamical properties based on the established relationships.

The herein investigated materials include ethyne-bridged (polypyridyl)metal(II) (M)-(porphinato)metal(II) (PM) (M-(PM)n-M; M = Ru, Os; M’ = Zn, Pt, Pd) and (porphinato)metal(II) (PM)-proquinoidal spacer (Sp)-(porphinato)metal(II) (PM-Sp-PM; M = Zn, Pt, Pd) supermolecular architectures, as well as semiconducting single-walled carbon nanotubes (SWNTs) wrapped by binaphthalene-based polyanionic semconducting polymers. For majority of the work, steady-state electronic absorption, steady-state and time-resolved emission, and pump-probe transient absorption spectroscopies were employed in conjunction with time-dependent density functional
theory (TD-DFT) calculations to interrogate the nature of the photo-excited states and
the subsequent relaxation dynamics of various conjugated materials.

At a molecular level, this work shows that many unusual, but desirable
photophysical properties can be engineered through (i) coupling distinct chromophoric
oscillator photophysics via an ethyne-linkage topology; (ii) varying the nature of the
initially prepared electronically excited state wavefunctions. Along this line, two new
libraries of NIR-active supermolecular chromophores (i.e. M-(PM')ₙ-M and PM-Sp-PM)
have been established, wherein exceptional red-to-NIR spectral coverage and tunable
excited-state relaxation dynamics (i.e. S₁→S₀ radiative decay, S₁→S₀ internal conversion,
S₁→T₁ intersystem crossing, and T₁→S₀ decay rate constants) are simultaneously
attained, making M-(PM')ₙ-M and PM-Sp-PM well poised for a number of
optoelectronic applications that include OPL, triplet-triplet annihilation photon
upconversion (TTA UC), and NIR bioimaging. Moving to nanoscale systems, this work
probes the dynamics of charged excitons (i.e. trions) in electronically and
morphologically homogeneous SWNTs, which demonstrate: (i) trion quasiparticles
exclusively derive from a precursor exciton state, (ii) exciton-to-trion conversion can
approach unity under appropriate excitation and charge-doping conditions.
Importantly, because trions simultaneously carry excitation energy, charge and spin, the
findings here may guide design of new SWNT-based optoelectronic devices that include
photovoltaics, photodetectors, and spintronics.
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1. Introduction

Necessary backgrounds, the motivation as well as the organizations of this dissertation will be discussed in introduction.

1.1 Light-Matter Interactions

![NUV-NIR Spectrum Diagram]

Figure 1: Illustration of “light” wavelength range, from γ rays up to radio waves (adapted from: Turro, N. J., Ramamurthy, V. & Scaiano, J. C. Modern molecular photochemistry of organic molecules. University Science Books: Sausalito, CA, 2010)

“Light-matter interaction” occupies a vast field of natural and applied science, and is the core for a wide variety of modern technologies. The comprehensive understanding of this term started from 1900s with recognition of energy quanta (Max
Planck confidently named this as “the universal constant”, i.e. \( h = 6.55 \times 10^{-27} \text{ erg} \cdot \text{sec} \), which now is \( h = 6.6262 \times 10^{-27} \text{ erg} \cdot \text{sec} \), and reached a high peak in the 1920s with further developments of quantum physics. Light is defined as electromagnetic radiations with wave-particle dual nature, while matter is typically considered as any substance having mass and taking up space (definition of matter is somewhat more elusive and varying from one scenario to another); they are characterized by wavelength (or frequency, or energy) and length (or volume), respectively. Light and matter can both span a huge range in their corresponding dimensions. For example, as electromagnetic radiation, light ranges from \( \gamma \) rays (\( \sim 10^{-6} \mu \text{m} \)) to long radio waves (\( \sim 10^{10} \mu \text{m} \)) (Figure 1). In modern physics, the scales of matter can be down to sub-atomic level (\(< 10^{-15} \text{m} \)), and up to the observable universe (\( \sim 10^{26} \text{m} \)). Matter exists in states, and can be perturbed by light (known as the “interaction”), the consequences of which can temporally last in an enormous timescale.

Within these contexts, it is becoming obviously necessary for any researcher interested in light-matter interactions to define the scope of their work. Particularly, the investigations of this dissertation exploit light from near-ultraviolet (NUV) to near-infrared (NIR) (i.e. \( \sim 300 \sim 1400 \text{ nm} \), Figure 1)\(^6\) to interrogate matter from molecular (\( > 1 \text{ nm} \)) to nanoscale (\(< 1000 \text{ nm} \)) structures (Figure 2). The light-matter interactions of interest to this dissertation are those photo-induced transitions amongst different electronic and vibrational states that spans the sub-picosecond (sub-ps) to millisecond
(ms) time domain (Figure 3). Such a research scope within the context of light-matter interactions is characteristic of the investigations for majority of spectroscopists in chemistry and materials science.

Figure 2: Illustration of Length Scales and the Associated Objects

Figure 3: Illustration of Time Scales and the Associated Processes.
1.2 Motivation Based on a Molecular Picture

Why many scientists in chemistry and materials science are evoked by such a research scope / theme defined above? The short answer is because the fundamental understandings obtained in such a field drives the development of many modern technologies, in particular, for those relying on sourcing, detecting, and manipulating light, which are known as optoelectronics. In a practical manner, the products of these optoelectronic research have permeated every corner of our life, and provided people a more convenient and efficient living manner. For instance, with the development of light sensing technology, cameras have evolved from the early daguerreotype that capture pictures using light-sensitive silver halide coated on a copper plate to the current digital device using a small semiconductor charge-coupled devices (CCD) or complementary metal-oxide semiconductors (CMOS) as imaging sensor which enables people to simply record their daily life with a smartphone. On the other hand, the advancements of photovoltaics that absorbs solar photons, and converts them to electricity or other useful fuels could completely revolutionize the current energy architecture from the traditional fossil-fuel dominated energy sources to renewable solar energies. These and many other emerging modern optoelectronics are mostly rooted in the understandings and manipulations of materials’ responses to external optical stimulus on the time scales of sub-ps to ms, and more specifically, scientists in spectroscopic field named such responses as photo-induced transitions from one state to another.
To understand such transitions, we start with a molecular picture. Figure 4 illustrates electronic / vibrational transitions amongst various states and their associated time scales using the so-called Jablonski diagram. The lowest-energy state is labeled as $S_0$ (ground state), while the lowest-energy electronically excited state is $S_1$ state, other higher-energy excited states are written as $S_2$, $S_3$, … $S_n$. The letter “S” here indicates the singlet nature of the corresponding states, i.e. pair electrons with spin anti-parallel configuration; while on the right side of Figure 4, the letter “T” represent triplet, i.e. pair
electrons with spin parallel configuration. The closely arranged thinner lines in
proximity to each electronically excited and ground state are vibrational levels.

Molecules / materials commonly stay at ground state. However, with the
perturbation from photons of certain frequency, they can be excited to higher energy
electronic states, for example, a photo-induced $S_0 \rightarrow S_1$ transition (depicted as the blue
arrow in Figure 4). The probability of the photo-induced transitions is characterized by
“oscillator strength” ($f$), or the experimentally measured parameter, “extinction
coefficient” ($\epsilon$). Oscillator strength and extinction coefficient are related by

$$f = 4.3 \times 10^{-9} \int \epsilon \, d\nu$$  \hspace{1cm} (1.2.1)

where $\nu$ is the photon frequency. Note that, the transition from singlet to triplet state by
perturbation from linearly-polarized (laser light) or unpolarized (lamp light) light
typically has a very low probability, i.e. such a transition associates with small $f$ or $\epsilon$
values.

Following photo-excitation, the system will not stay at excited state forever, it
will relax back to the $S_0$ state through various pathways, and the such relaxation
dynamical processes are characterized by different rate constants ($k$) or their reciprocals,
the lifetimes ($\tau$). As an example shown in Figure 4, following $S_0 \rightarrow S_1$ optical transition, $S_1$
state can decay via at least three independent processes, i.e. $S_1 \rightarrow S_0$ radiative decay
(fluorescence), $S_1 \rightarrow S_0$ nonradiative decay (internal conversion), and the $S_1 \rightarrow T_1$ conversion
(called “intersystem crossing” (ISC)). These relaxation processes are in competitions and the sum of them determines the $S_i$ state lifetime, i.e.

$$\tau_{S_i} = \left(\sum k_i\right)^{-1}$$  \hspace{1cm} (1.2.2)

where $k_i$ represents different relaxation rate constant; herein, $k_i$ denotes $k_{F, S_1 \rightarrow S_0}$, $k_{IC, S_1 \rightarrow S_0}$, and $k_{ISC, S_1 \rightarrow T_1}$, respectively. In a molecular system, the excited-state decay is typically a first-order process, therefore, the decay rate of excited ($S_i$) state species can be written as

$$\frac{dn(t)}{dt} = k \cdot n(t)$$  \hspace{1cm} (1.2.3)

where $n(t)$ is the number of $S_i$ state species at time $t$, and $k = \sum k_i$; then, the integration form of (1.2.3) is

$$n(t) = n_0 e^{(kf + k_{IC} + k_{ISC})t} = n_0 e^{t/\tau_{S_i}}$$  \hspace{1cm} (1.2.4)

Where $n_0$ is the initial number of $S_i$ state species. Thus, the experimentally acquired data recording the evolution of excited state species following optical excitation can be fitted by simple exponential functions, and this is how the experimental data are translated into these relaxation rate constants.\textsuperscript{10} Again, note that, such a data fitting pattern is mainly suitable for dealing with excited state relaxation dynamics in molecular systems.

For dynamics which are not described by simple first-order processes, rate equations should be re-established according to the specific scenario.

Importantly, it is these rate constants that fundamentally determine the optoelectronic utilities of the corresponding molecules / materials. For instance, the triplet sensitizers utilized in organic light-emitting diodes should be those that display
near-unity $S_1 \rightarrow T_1$ ISC; those most efficient organic photovoltaics are composed of conjugated materials having sufficient vis-NIR absorptivity (i.e. large $f_{S_0 \rightarrow S_1}$) as well as long-lived $T_1$ state; while for bioimaging applications, the chromophores evincing large NIR fluorescence quantum yields (i.e. large $S_1 \rightarrow S_0$ radiative transition quantum yields ($\Phi_F$)) are desired. In these respects, it is particularly important to deeply understand and actively manipulate the excited state dynamics of various functional molecules / materials, and this is also the very motivation of the present dissertation.

### 1.3 Carbon Nanotube Electronic Structures

As part of the dissertation will be focused the photophysics of nanoscale semiconductors, i.e. semiconducting single-walled carbon nanotubes (SWNTs), a brief overview on SWNT electronic structures would be necessary at this stage.

Figure 5 depicts the evolution from molecular orbital picture to band structure in polyacenes. For molecules, e.g. benzene, the occupied and virtual molecular orbitals are well energetically separated. With increasing the conjugation size of the system, band gap decreases while the density of states increases. Eventually, periodic, strongly coupled molecular or atomic systems manifest a high density of delocalized orbitals which form the so-called “valence” (VB) and “conduction bands” (CB). Those bands are generally plotted against its wave vector $k$ (i.e. momentum), as shown in Figure 5B. Excitation of an electron from the VB to CB creates free carriers, i.e. the electron in CB, and the left hole in VB. For low-dimensional semiconductors, due to reduced dielectric
screening and spatial confinement, there is strong Coulomb interaction between the electron and hole, resulting in the formation of an electron-hole pair, i.e. the exciton (Figure 5C).

Figure 5: Molecular orbital picture for confined (i.e. molecular scale) systems (A), bands and molecular orbitals for extended (i.e. nanoscale) systems (B), and Excitons in extended systems (C). (adapted from reference 11)

Since the SWNT structure is equivalent to that formed by wrapping a graphene into a seamless cylinder, the graphene band structure provides a good first approximation to understand the electronic and optical properties of SWNTs. The first Brillouin zone (the primitive cell in reciprocal space) of graphene energy bands close to the Fermi level are shown in Figure 6A: there is no band gap, and the π and π* bands touch at the so-called K and K’ points. Because the available electrons just fill the π
band, the K and K' points are where the $E_F$ (the $E_F$ surface is highlighted in green in Figure 6A-C) intersects the band structure, so that undoped graphene is neither a true metal nor a true semiconductor: instead, it is a semimetal. A key effect that emerges from “rolling up graphene” to form a SWNT is the imposition of a periodic boundary condition: unlike graphene, SWNTs possess a series of allowed wave vectors in reciprocal space ($k$-space), known as quantization lines (the red lines in Figure 6B-C).\textsuperscript{12,13}

The energy band dispersion relation ($E(k)$) of a SWNT is thus a cut along the quantization lines of the graphene energy band dispersion relation, and the SWNT band gap depends on the minimum separation of the quantization lines from the K or K’ points. Therefore, there are two possible scenarios: (i) if the quantization lines run straight through the K or K’ points, the $E(k)$ dispersion close to $E_F$ is linear, giving rise to zero band gap, i.e. the band structure for metallic SWNTs (see relations in Figure 6B and D); (ii) if the quantization lines bypass the K or K’ points with a separation of $|\Delta k|$, the $E(k)$ dispersion is represented by a pair of parabolas, corresponding to a band gap $E_g$, representing the band structure for semiconducting SWNTs (see relations in Figure 6C, E).\textsuperscript{14}
Figure 6: Electronic structures of single-walled carbon nanotubes. (A) Energy bands of graphene close to the Fermi level \((E_F)\); note: the energy bands form two circular cones, connected one with the other at their extremities, which are called “Dirac cones” (as the \(E(k)\) dispersion relation near \(E_F\) of this scenario also describes massless Dirac fermions); six Dirac cones are evinced in the energy bands of graphene. (B), and (C) First Brillouin zone of graphene and the quantization lines (allowed wave vectors) in \(k\) space. (D), and (E) Schematic electronic energy dispersions close to the Dirac point and the corresponding densities of states (DOS) for metallic (D) and semiconducting (E) SWNTs.

1.4 Outline of the Dissertation

Besides Chapter 1, the Introduction, this dissertation will have three more chapters that discuss the investigations upon excited state dynamics of molecular to nanoscale systems. Below narrative will briefly describe the research scope and accomplishments in each chapter.

Chapter 2 will present a molecular roadmap to tuning ground state absorption and excited state dynamics of long-wavelength absorbers. Realizing chromophores that simultaneously possess substantial near-infrared (NIR) absorptivity and long-lived,
high-yield triplet excited states is vital for many optoelectronic applications, such as optical power limiting and triplet-triplet annihilation photon upconversion (TTA-UC). However, the energy gap law ensures such chromophores are rare, and molecular engineering of absorbers having such properties has proven challenging. In Chapter 2, we present a versatile methodology to tackle this design issue by exploiting the ethyne-bridged (polypyridyl)metal(II) \( (M; M = \text{Ru, Os})-(\text{porphinato})\text{metal(II)} \) \( (\text{PM}'; M' = \text{Zn, Pt, Pd}) \) molecular architecture \( (M-(\text{PM}')_n-M) \), wherein high-oscillator-strength NIR absorptivity up to 850 nm, near-unity intersystem crossing (ISC) quantum yields \( (\Phi_{\text{ISC}}) \), and triplet excited-state \( (T_1) \) lifetimes on the \( \mu \text{s} \) timescale are simultaneously realized. By varying the extent to which the atomic coefficients of heavy metal d-orbitals contribute to the one-electron excitation configurations describing the initially prepared singlet and triplet excited-state wavefunctions, we: (i) show that the relative magnitudes of fluorescence \( (k_F) \), \( S_1 \rightarrow S_0 \) non-radiative decay \( (k_{nr}) \), \( S_1 \rightarrow T_1 \) ISC \( (k_{\text{ISC}}) \), and \( T_1 \rightarrow S_0 \) relaxation \( (k_{T_1\rightarrow S_0}) \) rate constants can be finely tuned in \( M-(\text{PM}')_n-M \) compounds, and (ii) demonstrate designs in which the \( k_{\text{ISC}} \) magnitude dominates singlet manifold relaxation dynamics, but does not give rise to \( T_1 \rightarrow S_0 \) conversion dynamics that short-circuit a \( \mu \text{s} \) timescale triplet lifetime. Notably, the NIR spectral domain absorptivities of \( M-(\text{PM}')_n-M \) chromophores far exceed those of classic coordination complexes and organic materials possessing similarly high yields of triplet-state formation: in contrast to these benchmark materials, this work demonstrates that these \( M-(\text{PM}')_n-M \) systems realize
near unit $\Phi_{\text{isc}}$ at extraordinarily modest $S_{1}-T_{1}$ energy gaps (~0.25 eV). This study underscores the photophysical diversity of the $\text{M-}(\text{PM'})_{n}-\text{M}$ platform, and presents a new library of long-wavelength absorbers that efficiently populate long-lived $T_{1}$ states.

In Chapter 3, we will briefly discuss the utilization of the $\text{M-}(\text{PM'})_{n}-\text{M}$ supermolecular platform in NIR-to-vis triplet-triplet annihilation upconversion (TTA-UC) photochemistry, which is ultimately for solar photon frequency upconversion in photovoltaics. These $\text{M-}(\text{PM'})_{n}-\text{M}$ NIR sensitizers feature: (i) broad, high oscillator strength NIR absorptivity ($700 \text{ nm} < \lambda_{\text{max (NIR)}} < 770 \text{ nm}$; $6 \times 10^{4} \text{ M}^{-1}\text{cm}^{-1} < \text{extinction coefficient}$ ($\lambda_{\text{max (NIR)}}$) < $1.6 \times 10^{5} \text{ M}^{-1}\text{cm}^{-1}$; $820 \text{ cm}^{-1} < \text{FWHM} < 1700 \text{ cm}^{-1}$), (ii) and substantial intersystem crossing quantum yields, (iii) long, $\mu$s timescale $T_{1}$ state lifetimes, and (iv) triplet states that are energetically poised for exergonic energy transfer to the molecular annihilator (rubrene). Using low power non-coherent illumination at power densities (1 to 10 mWcm$^{-2}$) similar to that of terrestrial solar photon illumination conditions, we demonstrate that $\text{Pyr:RuPZn, Pyr:RuPZn:RuPyr}$, and $\text{Pyr:RuPZnRuPyr}$ sensitizers can be used in combination with the rubrene acceptor/annihilator to achieve TTA-UC: these studies represent the first examples whereby a low-power non-coherent NIR light source drives NIR-to-visible upconverted fluorescence centered in a spectral window within the bandgap of amorphous silicon.

Chapter 4 will describe how to actively control the excited state dynamics of low band gap, NIR absorbers via proquinoidal unit electronic structural modulations. While
the influence of proquinoidal character upon the linear absorption spectrum of low optical bandgap $\pi$-conjugated polymers and molecules is well understood, its impact upon excited-state relaxation pathways and dynamics remains obscure. In Chapter 4, we discuss the syntheses, electronic structural properties, and excited-state dynamics of a series of model highly conjugated near-infrared (NIR)-absorbing chromophores based on a (porphinato)metal(II)-proquinoidal spacer-(porphinato)metal(II) (PM-Sp-PM) structural motif. A combination of excited-state dynamical studies and time-dependent density functional theory calculations: (i) point to the cardinal role that excited-state configuration interaction (CI) plays in determining the magnitudes of $S_1 \rightarrow S_0$ radiative ($k_r$), $S_1 \rightarrow T_1$ intersystem crossing ($k_{ISC}$), and $S_1 \rightarrow S_0$ internal conversion ($k_{IC}$) rate constants in these PM-Sp-PM chromophores, and (ii) suggests that a primary determinant of CI magnitude derives from the energetic alignment of the PM and Sp fragment LUMOs ($\Delta E_L$). These insights not only enable steering of excited relaxation dynamics of high oscillator strength NIR absorbers to realize either substantial fluorescence or long-lived triplets ($\tau_{T1} > \mu s$) generated at unit quantum yield ($\Phi_{ISC} = 100\%$), but also craft those having counter-intuitive properties: for example, while (porphinato)platinum compounds are well known to generate non-emissive triplet states ($\Phi_{ISC} = 100\%$) upon optical excitation at ambient temperature, diminishing the extent of excited-state CI in these systems realizes long-wavelength absorbing heavy-metal fluorophores. This work highlights approaches to: i) modulate low-lying singlet excited-state lifetime over the
picosecond-to-nanosecond time domain, ii) achieve NIR fluorescence with quantum yields up to 25%, iii) tune the magnitude of S1→T1 ISC rate constant from $10^9$ to $10^{12}$ sec$^{-1}$ and (iv) realize T1–state lifetimes that range from ~0.1 to several µs, for these model PM-Sp-PM chromophores, and renders new insights to evolve bespoke photophysical properties for low optical bandgap π-conjugated polymers and molecules based on proquinoidal conjugation motifs.

Chapter 5 will be focused on the dynamics of charged excitons (i.e. trions) in electrostatically doped SWNTs. The trion, a three-body charge-exciton bound state, offers unique opportunities to simultaneously manipulate charge, spin and excitation in one-dimensional single-walled carbon nanotubes (SWNTs) at room temperature. Effective exploitation of trion quasiparticles requires fundamental insight into their creation and decay dynamics. Such knowledge, however, remains elusive for SWNT trion states, due to the electronic and morphological heterogeneity of commonly interrogated SWNT samples, and the fact that transient spectroscopic signals uniquely associated with the trion state have not been identified. In the word described in Chapter 5, we prepare length-sorted SWNTs and precisely control charge carrier-doping densities to determine trion dynamics using femtosecond pump-probe spectroscopy. Identification of the trion transient absorptive hallmark enables us to demonstrate that trions (i) derive from a precursor excitonic state, (ii) are produced via migration of excitons to stationary hole-polaron sites, and (iii) decay in a first-order manner.
Importantly, under appropriate conditions, exciton-to-trion conversion in SWNTs can approach 100% at ambient temperature. Our findings open up new possibilities for exploiting trions in SWNT optoelectronics, ranging from photovoltaics, photodetectors, to spintronics.
2. Molecular Roadmap to Tuning Ground State Absorption and Excited State Dynamics of Long-Wavelength Absorbers

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Michael J. Therien conceived the project, supervised the execution of all experiments, and contributed to writing the manuscript.

Yusong Bai designed, synthesized and characterized all the compounds, took the steady-state and ultrafast spectroscopic measurements, analyzed the spectroscopic data, performed the computational analyses, and contributed to writing the manuscript.

Jean-Hubert Olivier analyzed the spectroscopic data, and contributed to writing the manuscript.

Hyejin Yoo took ultrafast pump-probe measurements, analyzed spectroscopic data, and contributed to writing the manuscript.

Nicholas F. Polizzi, Jaehong Park, and Jeff Rawson analyzed the spectroscopic data, and contributed to writing the manuscript.

2.1 Introduction

Strong near-infrared (NIR) absorbing chromophores featuring long-lived triplet excited states produced at near-unit quantum yield are key to various optoelectronic applications that include long-wavelength optical power limiting (OPL),\textsuperscript{15} dye-sensitized solar cell (DSSC),\textsuperscript{16, 17} and emerging photon-upconversion (UC) technologies,\textsuperscript{18-20} such as
those based on the triplet-triplet annihilation (TTA) mechanism. However, engineering such NIR chromophores remains extremely challenging, as diminishing the optical bandgap of a given molecular absorber exponentially increases its nonradiative (S\textsubscript{1}→S\textsubscript{0}) transition rate constant congruent with the energy gap law,\textsuperscript{21} which serves to dramatically reduce the corresponding S\textsubscript{1}→T\textsubscript{1} intersystem crossing (ISC) quantum yield.\textsuperscript{6, 21-24}

Over the past several decades, long-lived triplet excited states formed at unitary conversion have been predominantly realized in (polypyridyl)metal complexes, wherein S\textsubscript{1}→T\textsubscript{1} ISC gives rise to metal-to-ligand charge transfer triplet (\textsuperscript{3}MLCT) states.\textsuperscript{25-28} However, metal complexes of this genre suffer from weak long-wavelength absorptivity relative to those evinced by many organic dyes.\textsuperscript{29-33} In this regard, porphyrin-based pigments have been widely explored for crafting NIR chromophores.\textsuperscript{34-37} While high oscillator strength (ε >10\textsuperscript{5} M\textsuperscript{-1}cm\textsuperscript{-1}), broad NIR (>700 nm) absorptivity has been achieved in selected classes of these porphyrin-based compositions,\textsuperscript{38-45} the majority of these constructs feature fast excited-state relaxation within the singlet manifolds, resulting in ISC dynamics that give rise to low triplet state yields.\textsuperscript{45-54} Within this context, engineering strong NIR-absorbing chromophores having long-lived T\textsubscript{1} excited states and fast S\textsubscript{1}→T\textsubscript{1} relaxation dynamics has remained a formidable challenge.

Here, we describe a molecular design road map to access chromophores that not only feature high oscillator strength NIR-absorptive manifolds that span the 700-900 nm
spectral domain, but also manifest near-unity population of long-lived triplet excited states following photoexcitation. This design strategy exploits the symmetric molecular architecture of highly-absorptive ethyne-bridged (polypyridyl)metal(II) \((M; M = \text{Ru, Os})\) - (porphinato)metal(II) \((PM'; M' = \text{Zn, Pt, Pd})\) compounds \((M-(PM')_n-M)\), wherein the nature of the chromophore-to-chromophore connectivity drives substantial mixing of porphyrin-based \(\pi-\pi^*\) and metal polypyridyl-based charge-resonance transitions. We analyze the influences of \(PM'\) conjugation length and the nature of the metal ion upon \(S_0\rightarrow S_1\) and \(S_0\rightarrow T_1\) energy gaps, and the \(S_1\rightarrow T_1\) ISC and \(T_1\rightarrow S_0\) relaxation rate constant magnitudes. Spectroscopic data underscore that conjugation extension along the long molecular axis achieved through \(PM'\) conjugation: i) dramatically redshifts the \(S_0\rightarrow S_1\) absorption band and enhances its NIR transition oscillator strength; ii) has a relatively modest influence on the \(S_0\rightarrow T_1\) energy gap; and iii) reduces the (terpyridyl)metal d-orbital contribution to the initially prepared \(M-(PM')_n-M\) \(S_1\) state wavefunction and hence decreases the magnitude of the ISC rate constants in the corresponding \(M-(PM')_n-M\) chromophores. These data further demonstrate that this third effect derives from the increasing contribution of porphyrin-based \(\pi-\pi^*\) character to the \(S_0\rightarrow S_1\) transition with increasing conjugation. In this regard, divalent Pt and Pd ions within the \((PM')_n\) chromophoric fragments of these \(M-(PM')_n-M\) supermolecules can be exploited as tools to tune the extent to which heavy metal d-orbitals contribute to the one-electron excitation configurations that describe the initially prepared singlet excited state. As
such, not only high oscillator strength NIR absorptivities are made possible: because the
relative magnitudes of fluorescence ($k_f$), $S_1\rightarrow S_0$ non-radiative decay ($k_{nr}$), $S_1\rightarrow T_1$ ISC ($k_{ISC}$),
and $T_1\rightarrow S_0$ relaxation ($k_{T1\rightarrow S0}$) rate constants can be finely tuned in $M-(PM')_n-M$
compounds, exceptional $T_1$-state quantum yields can be realized in these structures.
Given these enhanced photophysical properties, $M-(PM')_n-M$ chromophores stand in
sharp contrast to extensive families of conventional metal complexes, organic molecules,
and polymer materials such as (polypyridyl)metal(II) complexes, bodipy derivatives,$^{19}$
and polythiophene derivatives$^{56-58}$ that have been traditionally utilized for OPL, TTA-
UC, and DSSC applications.

2.2 Results and Discussion

2.2.1 Steady-State Electronic Absorption Spectroscopy

As shown in Figure 7, $M-(PM')_n-M$ display an unusual degree of spectral
coverage over the visible (vis) and NIR regime, tailing to 900 nm. Such high oscillator
strength vis-to-NIR absorptivities derive largely from the porphyrinic components and
the nature of chromophore-to-chromophore connectivity in these systems: the ethyne-
linkage topology aligns the chromophoric transition dipoles along the long molecular
axis (x-axis) and promotes effective mixing between the porphyrin $\pi-\pi^*$ and metal
polypyridyl-based charge-resonance transitions, resulting in redistribution of the
oscillator strength spanning vis-to-NIR spectral domain.$^{38, 39, 59-62}$ In this regard, several
characteristic electronic transitions are highlighted: (i) a broad, high-oscillator-strength
absorption manifold (ε > 100,000 M\(^{-1}\) cm\(^{-1}\)) that spans the 400-500 nm spectral window which manifests significant porphyrin-derived \(^1\pi-\pi^*\) Soret (B) band transition\(^{38, 39, 60, 62}\) (ii) the red-edge of the B-band absorption (500-550 nm) that features [Ru(tpy)_2]^{2+}-derived \(^1\text{MLCT}\) transition character\(^{60, 62}\) and (iii) the absorption band in the long-wavelength (> 600 nm) domain of the spectrum which exhibits porphyrinic \(^1\pi-\pi^*\) Q-state character (Table 1)\(^{38, 39, 60-62}\). We note that although the “B”, “Q”, and “MLCT” labels are preserved throughout this report for describing characteristic M-(PM')\(_n\)-M electronic absorption manifolds, they suggest only the dominant characters of these transitions, as the B, Q, and MLCT electronic states mix extensively in M-(PM')\(_n\)-M chromophores.
Figure 7: Electronic Absorption Spectra of M-(PZn)_n-M and the Associated Chemical Structures. Steady-state electronic absorption spectra of (a) PyrRuPZnRuPyr, (b) PyrRuPZnPzRuPyr, (c) OsPZnPzOs, (d) PyrRuPPTpRuPyr, (e) PyrRuPZnPPTpPZnRuPyr, and (f) PyrRuPZnPPTdPZnPzRuPyr. Experimental conditions: solvent = acetonitrile, ambient temperature. The R group denotes 2′6′-bis(3,3-dimethyl-1butyloxy)phenyl.

As highlighted in Figure 7, NIR spectral domain absorptive characteristics are modulated through both conjugation length and the nature of the porphyrin central metal ion. Due to a combination of symmetry breaking effects that derive from extensive x-axis conjugation and charge-transfer character stems from the ethyne linkage motif that connects the (porphinato)metal(II) and (polypyridyl)metal(II) moieties, the M-(PZn)_n-M x-polarized Q-state transition (Q_x) manifold manifests a progressive redshift
and oscillator-strength enhancement with elongation of porphyrinic conjugation,\textsuperscript{38, 39, 60, 63} highlighted in part by the \textit{Pyr}:RuPZnRuPyr\textsubscript{1} and \textit{Pyr}:RuPZn2RuPyr\textsubscript{1} spectra (Figure 7a\textendash b). Note also that the energy of Q\textsubscript{x} absorption maximum is highly sensitive to porphyrin central metal ion selection: replacing zinc(II) with palladium(II) or platinum(II) results in hypsochromic shifts due to the mixing of porphyrin π\textsuperscript{*} and metal ndπ orbitals (e.g., Figure 7b, d).\textsuperscript{64\textendash 66} In this regard, M-(PZn)\textsubscript{n}M chromophores that exploit a component (porphinato)palladium(II) moiety display a less significant hypsochromic shift of the Q\textsubscript{x} absorption maximum relative to the analogous M-(PZn)\textsubscript{n}M chromophores that leverage (porphinato)platinum(II) unit (Figure 7e-f).\textsuperscript{67}

\textbf{Table 1: Electronic Absorption Spectral Data for M-(PM')\textsubscript{n}M.}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>EAS Band Maximum / nm (ε / 10\textsuperscript{4} M\textsuperscript{-1}.cm\textsuperscript{-1})</th>
<th>FWHM\textsuperscript{b} / cm\textsuperscript{-1}</th>
<th>Oscillator Strength In NIR Regime\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B-band Region</td>
<td>1\textsuperscript{1}MLCT</td>
<td>Q-band Region</td>
</tr>
<tr>
<td>\textit{Pyr}:RuPZnRuPyr\textsubscript{1}</td>
<td>463 (1.33)</td>
<td>525 (1.06)</td>
<td>702 (1.30)</td>
</tr>
<tr>
<td>\textit{Pyr}:RuPZn2RuPyr\textsubscript{1}</td>
<td>453 (1.67), 464 (1.63) 497 (2.38)</td>
<td>522 (1.41)</td>
<td>583 (0.30) 772 (1.60)</td>
</tr>
<tr>
<td>OsPZn\textsubscript{2}Os</td>
<td>460 (1.48), 500 (2.26)</td>
<td>518 (1.22)</td>
<td>584 (0.30) 776 (1.47)</td>
</tr>
<tr>
<td>\textit{Pyr}:RuPPr\textsubscript{1}RuPyr\textsubscript{1}</td>
<td>465 (2.05)</td>
<td>515 (1.00)</td>
<td>653 (1.46)</td>
</tr>
<tr>
<td>\textit{Pyr}:RuPZnPPrPZnRuPyr\textsubscript{1}</td>
<td>477 (2.36)</td>
<td>523 (1.05)</td>
<td>582 (0.29) 746 (1.50)</td>
</tr>
<tr>
<td>\textit{Pyr}:RuPZnPdPZnRuPyr\textsubscript{1}</td>
<td>483 (2.45)</td>
<td>524 (1.19)</td>
<td>584 (0.27) 780 (1.63)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From electronic absorption spectra recorded in acetonitrile solvent. \textsuperscript{b} Taken as the spectral width of the Q-band region at half the height of the lower-energy absorption noted. \textsuperscript{c} Integrated oscillator strengths (f) were calculated based on the following expression: f = 4.3 \times 10\textsuperscript{-6} \int ε dv, where ε is the experimental extinction coefficient, and v is the energy (in wave numbers) of the absorption. Oscillator strengths were calculated over the following wavelength domains: \textit{Pyr}:RuPZnRuPyr\textsubscript{1} (700 - 800 nm); \textit{Pyr}:RuPZn2RuPyr\textsubscript{1} (700 - 900 nm); OsPZn:Os (700 - 900 nm); \textit{Pyr}:RuPPr:RuPyr\textsubscript{1} (700 - 900 nm).
Among these M-(PZn)_n-M chromophores, PyrRuPZnPdPZnRuPyr is an exceptional NIR absorber with a broad Q_x-derived manifold centered at 780 nm, having a full width at half-maximum (FWHM) of ~1700 cm^{-1}, and a substantial extinction coefficient (163,000 M^{-1} cm^{-1}). Note that, even at 850 nm, the absorptive extinction coefficients of PyrRuPZnPdPZnRuPyr still exceeds 15,000 M^{-1} cm^{-1}. These PyrRuPZnPdPZnRuPyr NIR absorptive characteristics surpass those of widely exploited long-wavelength absorbers that include conventional (polypyridyl)metal(II) derivatives, bodipy chromophores, and polythiophene-based materials.

2.2.2 Steady-State Emission Spectroscopy

The emission spectroscopy of all these M-(PM')_n-M chromophores were investigated to determine the energy levels of their respective S_1 and T_1 states (from respective S_1→S_0 fluorescence and T_1→S_0 phosphorescence data), and qualitatively map S_1→T_1 ISC efficiencies. M-(PM')_n-M emission spectra were measured at ambient temperature under both oxygenated and deoxygenated conditions (see 2.4 Materials and Methods, Figure 28-39 for details) in acetonitrile solvent. Under oxygenated conditions, O_2(1Δ) emission is observed at ~1270 nm from all the M-(PM')_n-M solution samples, suggesting the production of a low-lying \[^3[M-(PM')_n-M]^*\] state. Note, however, that the intrinsic emissive properties of these M-(PM')_n-M chromophores are relatively complex: PyrRuPZnRuPyr, OsRuPZn:Os, PyrRuPPtRuPyr, and PyrRuPZnPdPZnPdRuPyr.
manifest room-temperature phosphorescence under deoxygenated conditions, while phosphorescence for \textit{PyrRuPZnRuPyr} and \textit{PyrRuPZnPdPZnRuPyr} is only evinced under low-temperature (77K) conditions (See 2.4 Materials and Methods, Figures 38-39); moreover, fluorescence signals were observed in almost all of the M-(PM')ₙ-M compounds at ambient temperature under both deoxygenated and oxygenated conditions, except for \textit{PyrRuPPtRuPyr}, which exhibits only phosphorescence.

Table 2: Emission Energies and Quantum Yields for M-(PM')ₙ-M Chromophores.

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>Emission Energy⁺ / eV</th>
<th>Φₖ/em⁺ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₁⇒S₀</td>
<td>T₁⇒S₀</td>
</tr>
<tr>
<td>\textit{PyrRuPZnRuPyr}₁</td>
<td>1.67</td>
<td>1.25</td>
</tr>
<tr>
<td>\textit{PyrRuPZn₂RuPyr}₁</td>
<td>1.53</td>
<td>1.27</td>
</tr>
<tr>
<td>\textit{OsPZn₂Os}</td>
<td>1.52</td>
<td>1.17</td>
</tr>
<tr>
<td>\textit{PyrRuPPt₂RuPyr}₁</td>
<td>N/Aᵇ</td>
<td>1.45</td>
</tr>
<tr>
<td>\textit{PyrRuPZnPnPZnRuPyr}₁</td>
<td>1.58</td>
<td>1.24</td>
</tr>
<tr>
<td>\textit{PyrRuPZnPdPZnRuPyr}₁</td>
<td>1.53</td>
<td>1.26</td>
</tr>
</tbody>
</table>

⁺Values reported correspond to the energy of the maximal emission wavelength (λ_em(max)).ᵇ Denotes no fluorescence observed.ᶜ Emission quantum yields were determined relative to the meso-to-meso ethyne-bridged bis[(porphinato)zinc(II)] chromophore (PZn) in THF solvent (Φᵦ = 0.16).ᵈ Denotes a phosphorescence quantum yield too small to be accurately determined; only an upper limit is indicated.

Because fluorescence observed in M-(PM')ₙ-M chromophores originates from a Qₓ state-dominated relaxation to the ground state that directly competes with the S₁⇒T₁ ISC process, comparing the relative fluorescence intensities amongst these M-(PM')ₙ-M
chromophores provides a qualitative measure of their $S_1 \rightarrow T_1$ ISC efficiencies ($\Phi_{\text{ISC}}$). These data indicate $\Phi_F(\text{Pyr}_1\text{RuPPtRuPyr}) < \Phi_F(\text{Pyr}_1\text{RuPZnRuPyr}) \approx \Phi_F(\text{OsPZnOs}) \approx \Phi_F(\text{Pyr}_1\text{RuPZnPnPZnPZnPyr}) < \Phi_F(\text{Pyr}_1\text{RuPZnPdRuPyr}) < \Phi_F(\text{Pyr}_1\text{RuPZnRuPyr})$ (Figure S16). Notably, relative to $\text{Pyr}_1\text{RuPZnRuPyr}$, $\text{Pyr}_1\text{RuPZnPnPZnRuPyr}$ exhibits a $\Phi_F$ enhancement of a factor of 5 [$\Phi_F(\text{Pyr}_1\text{RuPZnRuPyr}) = 0.04 \%$, $\Phi_F(\text{Pyr}_1\text{RuPZnPnPZnRuPyr}) = 2.0 \%$, see Table 2 and Figure 37], underscoring that in $M-(\text{PM'})_n-M$ systems, long-wavelength absorptive oscillator strength enhancement based on simple conjugation expansion through additional porphyrin units [(PM')$_n$] drives diminished $\Phi_{\text{ISC}}$.

OsPZnOs and $\text{Pyr}_1\text{RuPPtRuPyr}$, which feature conjugated frameworks essentially identical in size to that of $\text{Pyr}_1\text{RuPZnRuPyr}$, manifest enhanced $\Phi_{\text{ISC}}$ values as a result of the more substantial spin-orbit coupling induced by the respective replacement of osmium (for ruthenium) and platinum (for zinc). These data indicate that a diminished $\Phi_{\text{ISC}}$ driven by (PM')$_n$ conjugation expansion can be effectively suppressed by selective Pt or Pd metallation of porphyrin macrocycle (Figure 7A-D). For instance, compared to $\text{Pyr}_1\text{RuPZnRuPyr}$, $\text{Pyr}_1\text{RuPZnPnPZnPZnPyr}$ and $\text{Pyr}_1\text{RuPZnPdPZnPZnPyr}$ feature significantly enhanced $\Phi_{\text{ISC}}$ values, as qualitatively suggested by their relative $\Phi_F$ magnitudes. The markedly different steady-state emission spectra observed in various $M-(\text{PM'})_n-M$ supermolecular structures trace their genesis to the disparate excited-state relaxation dynamics characteristic of these chromophores (vide infra).
2.2.3 Pump-Probe Transient Absorption Spectroscopy

We discuss the common features of pump-probe transient absorption spectra recorded for M-(PM')_{n-M} chromophores following S_0→S_1 photoexcitation, and quantitatively analyze their respective excited-state dynamics relying on the time-dependent evolution of the transient absorptive signatures characteristic of their singlet and triplet excited-state manifolds. The femtosecond-to-nanosecond timescale transient spectra recorded at selected time delays for M-(PM')_{n-M} chromophores are displayed in Figures 8-10. The early time-delay (t_{delay} ~ 0.3 ps) transient spectra of these M-(PM')_{n-M} chromophores share several common features: (i) bleaching signals in the B and Q_x-band regions, (ii) weak transient absorptions between the two dominant ground-state absorption bleaching signatures, and (iii) intense NIR transient absorption manifolds that feature extraordinary spectral breadth. Moreover, these M-(PM')_{n-M} chromophores manifest qualitatively similar time-dependent transient spectral evolution in the NIR regime: the decay of the initially-prepared NIR transient absorption signal (S_1→S_n) correlates with the rise of a new lower-energy NIR transient absorption band, suggesting the evolution of a new electronically excited state. These electronically excited states persist beyond the delay limit of the femtosecond pump-probe instrument. Nanosecond-to-millisecond pump-probe transient absorption measurements determine that the lifetimes of these long-lived M-(PM')_{n-M} excited states are confined to the µs timescale under deoxygenated conditions; the lifetimes of these states are diminished to
a few hundred ns when these M-(PM')ₙ-M solutions are oxygenated (Supporting Information), indicating the triplet nature of these states. As such, the lower-energy NIR transient manifold corresponds to T₁→Tₙ transitions (as highlighted in Figures 8-10), whose rise and decay quantitatively respectively characterize the S₁→T₁ ISC dynamics and T₁ state lifetimes of these M-(PM')ₙ-M chromophores.

2.2.3.1 PyrRuPZnPyr and PyrRuPZnPyr

PyrRuPZnPyr exhibits an ultrafast ISC rate constant and near-unit ΦISC. ΦISC can be calculated via the relation ΦISC = kISC / (kISC + k₀F + k₀r), wherein kISC, k₀F, and k₀r are the respective rate constants for S₁→T₁ ISC, intrinsic S₁→S₀ fluorescence decay, and S₁→S₀ internal conversion processes. Since τS₁ = 1 / (kISC + k₀F + k₀r) and τISC = 1 / kISC, where τS₁ and τISC correspond respectively to the S₁ state lifetime and the S₁→T₁ ISC time constant, ΦISC can be expressed as ΦISC = τS₁ / τISC.⁶ As discussed above, the T₁→Tₙ transition manifold rise time quantitatively characterizes τISC, while the decay time of the S₁→Sₙ transition manifold provides a direct measure for τS₁. In this regard, a global fit of the time-dependent NIR (800-1200 nm) transient absorption dynamics for PyrRuPZnPyr enables determination of its intrinsic S₁ state lifetime and the S₁→T₁ ISC time constant: τS₁ ≈ τISC ~0.80 ps (Section 2.4, Figure 49). The evaluated magnitudes of τS₁ and τISC enable the [M-(PM')ₙ-M]⁺→[M-(PM')ₙ-M]⁺ ISC quantum yields to be determined; for PyrRuPZnPyr, note that ΦISC is ~1.
Figure 8: Transient absorption spectra determined at different time delays for (a) Pyr-RuPZnRuPyr$_1$ ($\lambda_{ex} = 680$ nm), and (b) Pyr-RuPZn:RuPyr$_1$ ($\lambda_{ex} = 800$ nm). Experimental conditions: ambient temperature, pump power = 300 $\mu$W, solvent = acetonitrile, magic angle polarization.

Compared to Pyr-RuPZnRuPyr$_1$, Pyr-RuPZn:RuPyr$_1$ displays a dramatically diminished $S_1 \rightarrow T_1$ $k_{ISC}$, and a significantly suppressed $\Phi_{ISC}$. Note that within the NIR spectral domain, Pyr-RuPZnRuPyr$_1$ manifests a $T_1 \rightarrow T_n$ transient absorption signal at the earliest time delays ($t_{delay} \sim 300$ fs), whereas electronically excited Pyr-RuPZn:RuPyr$_1$ features a NIR transient absorption dominated by a $S_1 \rightarrow S_n$ transition over $t_{delays}$ that range from 0.3-120 ps (Figure 8); these Pyr-RuPZn:RuPyr$_1$ transient spectra acquired
over these time delays resemble those evinced for the \textit{meso}-to-\textit{meso} ethyne-bridged bis[(porphinato)zinc] chromophore, PZn.\textsuperscript{48,53} Congruent with these marked differences observed in the transient spectra, \textit{Pyr}:RuPZn:RuPyr demonstrates dramatically different excited state relaxation dynamics relative to \textit{Pyr}:RuPZnRuPyr. A global fit of the time-dependent S\textsubscript{1}→S\textsubscript{n} transient absorption dynamical data evinces three time components: 970 ± 130 fs, 60 ± 7 ps, 340 ± 20 ps; these are associated respectively with acetonitrile solvent relaxation, conformational relaxation, and the intrinsic singlet lifetime of \textit{Pyr}:RuPZn:RuPyr. An analogous global fit of the T\textsubscript{1}→T\textsubscript{n} transient dynamical data provides similar characteristic time components for solvent relaxation and conformational relaxation dynamics (\(\tau_{\text{solvent}}\) ~800 fs; \(\tau_{\text{conformational}}\) ~58 ps), whereas the third time component (~610 ps) is assigned to the S\textsubscript{1}→T\textsubscript{1} ISC time constant.

\(^{1}[\textit{Pyr}:\text{RuPZn}:\text{RuPyr}]^*\rightarrow \, ^{3}[\textit{Pyr}:\text{RuPZn}:\text{RuPyr}]^*\) \(\Phi_{\text{ISC}}\) can thus be calculated as ~56%.

Considering that the fluorescence quantum yield of \textit{Pyr}:RuPZn:RuPyr has been determined to be 2%, the \(^{1}[\textit{Pyr}:\text{RuPZn}:\text{RuPyr}]^*\rightarrow \textit{Pyr}:\text{RuPZn}:\text{RuPyr}\) internal conversion (S\textsubscript{i}→S\textsubscript{0}) quantum yield (\(\Phi_{\text{IC}}\)) is ~48%, whereas that determined for \textit{Pyr}:RuPZnRuPyr is ~0%. Such marked changes in \(\Phi_{\text{IC}}\) for electronically excited \textit{Pyr}:RuPZn:RuPyr relative to \textit{Pyr}:RuPZnRuPyr correlate with not only simple energy gap law predictions,\textsuperscript{21} but also the data described above that determine significantly reduced S\textsubscript{i}→T\textsubscript{1} ISC rate constants upon conjugation extension of \textit{Pyr}:RuPZnRuPyr to \textit{Pyr}:RuPZn:RuPyr (Table 3).
Table 3: Dynamical Data and $\Phi_{\text{ISC}}$ Values for M-(PM')$_n$-M.

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>$\tau_{S1}^b$/ ps</th>
<th>$\tau_F^c$/ ps</th>
<th>$\tau_{\text{ISC}}^b$/ ps</th>
<th>$\tau_T^d$/ $\mu$s</th>
<th>$\Phi_{\text{ISC}}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyr$_1$RuPZnRuPyr$_1$</td>
<td>0.8</td>
<td>N/A</td>
<td>0.77</td>
<td>9.0</td>
<td>~1</td>
</tr>
<tr>
<td>Pyr$_1$RuPZn$_2$RuPyr$_1$</td>
<td>340</td>
<td>305</td>
<td>610</td>
<td>9.9</td>
<td>0.56</td>
</tr>
<tr>
<td>OsPZn$_2$Os</td>
<td>31</td>
<td>26</td>
<td>28</td>
<td>0.4</td>
<td>~1</td>
</tr>
<tr>
<td>Pyr$_1$RuPPt$_2$RuPyr$_1$</td>
<td>0.28</td>
<td>N/A</td>
<td>0.39</td>
<td>2.9</td>
<td>~1</td>
</tr>
<tr>
<td>Pyr$_1$RuPZnPp$_2$PnRuPyr$_1$</td>
<td>36</td>
<td>30</td>
<td>34</td>
<td>4.4</td>
<td>~1</td>
</tr>
<tr>
<td>Pyr$_1$RuPZnPp$_2$PnRuPyr$_1$</td>
<td>155</td>
<td>150</td>
<td>190</td>
<td>13.0</td>
<td>0.82</td>
</tr>
</tbody>
</table>

$^a$All data were acquired in acetonitrile solvent. $^b$ $\tau_{S1}$ and $\tau_{\text{ISC}}$ values were determined using femtosecond transient absorption spectroscopic measurements. $^c$ Fluorescence lifetimes were determined via a Hamamatsu C4780 picosecond fluorescence lifetime measurement system. $^d$ $\tau_T$ values were determined using ns-to-$\mu$s time-domain transient absorption measurements. $^e$ $\Phi_{\text{ISC}}$ values were calculated based on dynamical data acquired using femtosecond transient absorption spectroscopy.

2.2.3.2 OsPZn$_2$Os and Pyr$_1$RuPPt$_2$RuPyr$_1$

With the same conjugated framework as Pyr$_1$RuPZn$_2$RuPyr$_1$, OsPZn$_2$Os and Pyr$_1$RuPPt$_2$RuPyr$_1$ manifest substantially enhanced $S_1 \rightarrow T_1$ $k_{\text{ISC}}$ and $\Phi_{\text{ISC}}$ values due to the stronger spin-orbit coupling effect induced by osmium or platinum. A common approach to modulate ISC dynamics takes advantage of the spin-orbit coupling effect.

As the magnitude of spin-orbit coupling is roughly proportional to $Z^4$, where $Z$ represents the nuclear charge,$^6,^8$ heavier metal nuclei that bind at either of the bis(terpyridyl)metal M or (porphinato)metal M' sites of the M-(PM')$_n$-M supermolecule can be exploited as tools to tune excited state relaxation dynamics and enhance excited-state singlet-triplet wavefunction mixing. As such, OsPZn$_2$Os and Pyr$_1$RuPPt$_2$RuPyr$_1$
were synthesized to investigate the extent to which the nature of the bis(terpyridyl)metal and (porphinato)metal centers influence excited state relaxation dynamics.

**Figure 9:** Transient absorption spectra determined at different time delays for (a) OsPZnOs (λ<sub>ex</sub> = 820 nm), and (b) PyrRuPztRuPyr (λ<sub>ex</sub> = 660 nm). Experimental conditions: ambient temperature, pump power = 300 µW, solvent = acetonitrile, magic angle polarization.

Compared to PyrRuPZnRuPyr, OsPZnOs exhibits distinct excited state relaxation dynamics (Figure 9a). A global fit of the S<sub>i</sub>→S<sub>n</sub> spectral region transient dynamical data reveals two relaxation processes: 1.8 ± 0.2 ps, 31 ± 4 ps. While the fast
time constant (1.8 ps) is attributed to solvent relaxation dynamics, note that the 31 ps
time constant agrees closely with the streakscope determined fluorescence lifetime ($\tau_F$
~26 ps), and is therefore assigned as the intrinsic singlet lifetime of OsPZn:Os. Given
that the OsPZn:Os intrinsic singlet lifetime timescale resembles the PZn-to-(terpyridyl)metal torsional dynamical timescale,$^{48,69}$ OsPZn:Os conformational
dynamics may play a role in determining the S1 state lifetime. The OsPZn:Os S1 state
lifetime, an order magnitude smaller than that determined for Pyr:RuPZn:RuPyr (~340
ps), thus likely reflects faster ISC dynamics that correspondingly diminish its
fluorescence quantum yield relative to Pyr:RuPZn:RuPyr (vide supra). Two
characteristic relaxation times, 1.5 ± 0.2 ps and ~28 ± 3 ps, are obtained from global
fitting of the T1→Tn transient spectral region, which correspond respectively to the
solvent relaxation dynamics and the S1→T1 ISC time constant. The similarity between
the S1 state lifetime and $\tau_{ISC}$ in OsPZn:Os emphasizes that the S1→T1 ISC is the dominant
decay channel that depopulates the S1 state, driving a near-unit $\Phi_{ISC}$. Further transient
absorption measurements carried out in the nanosecond-to-microsecond time domain
determine an OsPZn:Os T1 state lifetime of ~0.4 µs (Table 3). Note that this T1 state
lifetime is dramatically reduced relative to that determined for Pyr:RuPZn:RuPyr (~9.9
µs), and congruent with osmium-enhanced spin-orbit coupling leading to enhanced
T1→S0 ISC dynamics.
Representative transient representative spectra acquired for \textbf{PyrRuPz:RuPyr} are shown in Figure 9b. In contrast to its analogue \textbf{PyrRuPz:RuPyr}, which exhibits strong stimulated emission and an intense \(S_1\rightarrow S_n\) NIR transient absorption that remains prominent over the 0.3-120 ps time domain, \textbf{PyrRuPz:RuPyr} transient spectra display no stimulated emission signal and a \(S_1\rightarrow S_n\) transient absorption that vanishes within 1 ps following optical excitation. Note, however, \textbf{PyrRuPz:RuPyr} displays conformational dynamics and spectral diffusion in the Q-band bleach (Figure 51) similar to that manifested in \textbf{PyrRuPz:RuPyr}. Global fitting of the \(S_1\rightarrow S_n\) spectral region transient dynamical data for \textbf{PyrRuPz:RuPyr} reveals an ultrafast decay component of 280 ± 60 fs, whereas a corresponding analysis of the \(T_1\rightarrow T_n\) transient absorption data elucidates two dynamical processes: \(\tau_1 = 390 \pm 80\) fs and \(\tau_{\text{Long}}\). The ultrafast time components evinced in the \(S_1\rightarrow S_n\) and \(T_1\rightarrow T_n\) transient absorptive spectral domains reflect the \(S_1\) state lifetime and the ISC time constant, respectively, congruent with a near-unity \(\Phi_{\text{ISC}}\). Given the timescale of the acetonitrile solvent response, it is possible that solvent dynamics may be coupled to these ultrafast excited state processes.\textsuperscript{70} The long time constant associated with the \(T_1\rightarrow T_n\) transient kinetic data corresponds to excited triplet state relaxation; a \(T_1\) lifetime of 2.91 \(\mu\)s was determined by nanosecond transient absorption measurements (Figure 44, and Table 3).

Despite the unit \(\Phi_{\text{ISC}}\) of \textbf{OsPz:Os}, the diminished \(T_1\)-state lifetime (\(\tau_T = 400\) ns), however, makes this chromophore less useful in various optoelectronic applications, e.g.
TTA-UC applications.\textsuperscript{71} In the case of \textbf{Pyr\textsubscript{1}RuP\textsubscript{2}Pt\textsubscript{2}RuPy\textsubscript{1}}, the significant hypsochromic shift of the $Q_\alpha$ transition manifold ($\Delta \nu = 2361$ cm$^{-1}$, \textit{vide supra}) of this chromophore relative to the analogous family of transitions displayed by \textbf{Pyr\textsubscript{1}RuPZ\textsubscript{n}RuPy\textsubscript{1}}, make \textbf{Pyr\textsubscript{1}RuP\textsubscript{2}Pt\textsubscript{2}RuPy\textsubscript{1}} unsuitable for NIR photon capture, despite its ultrafast and unit quantum yield conversion to a long-lived $T_1$ state. With these considerations in mind, the following section highlights the versatility of \textbf{M-(PM')}\textsubscript{n}-\textbf{M} chromophoric motif and demonstrates a molecular engineering approach that simultaneously delivers exceptional NIR absorptivity, ultrafast $S_1 \rightarrow T_1$ ISC dynamics, and long $T_1$-state lifetimes in these supermolecules.
Figure 10: Transient absorption spectra determined at different time delays for (a) Pyr$\text{RuZnPZnPZnRuPyr}$ ($\lambda_{\text{ex}} = 780 \text{ nm}$), and (b) Pyr$\text{RuZnPdPZnRuPyr}$ ($\lambda_{\text{ex}} = 800 \text{ nm}$). Experimental conditions: ambient temperature, pump power = 300 $\mu$W, solvent = acetonitrile, magic angle polarization.

2.2.3.3 Pyr$\text{RuZnPtPZnRuPyr}$ and Pyr$\text{RuZnPdPZnRuPyr}$

Representative transient absorption spectra acquired at selected time delays for Pyr$\text{RuZnPtPZnRuPyr}$ and Pyr$\text{RuZnPdPZnRuPyr}$ are shown in Figure 10; key spectral and dynamical data determined from these pump-probe transient absorption spectroscopic experiments are summarized in Table 3. As highlighted in Figure 10, Pyr$\text{RuZnPtPZnRuPyr}$ and Pyr$\text{RuZnPdPZnRuPyr}$ exhibit similar transient
absorption features over the entire vis-NIR spectral domain interrogated in these experiments. For example, at early time delays (t < 10 ps), stimulated emission contributes significantly to the S₁→Sₙ transition manifold bleaching signal centered near 800 nm. Global fitting of the NIR spectral region transient dynamical data acquired for \textit{Pyr:RuPZnPPtPZnRuPyr} and \textit{Pyr:RuPZnPdPZnRuPyr} highlight noteworthy differences in the excited state relaxation dynamics important for these supermolecules. In the S₁→Sₙ transition manifold region, \textit{Pyr:RuPZnPPtPZnRuPyr} manifests two time components: \( t₁ = 950 \pm 130 \text{ fs}, \ t₂ = 36 \pm 4 \text{ ps} \). Given the time scale of \( t₁ \), it is likely associated with solvent relaxation; the magnitude of \( t₂ \) is close to the streak-scope determined fluorescence lifetime (\( t_F = 30 \text{ ps} \)), and therefore assigned as the intrinsic S₁ state lifetime (\( t_{S₁} \)) of \textit{Pyr:RuPZnPPtPZnRuPyr}. Near-identical characteristic time constants are obtained from fitting the T₁→Tₙ transient absorption region of \textit{Pyr:RuPZnPPtPZnRuPyr}: \( t₁ = 1.2 \pm 0.2 \text{ ps}, \ t₂ = 34 \pm 2 \text{ ps} \), consistent with \( t₁ \) assignment as the solvent relaxation time, and \( t₂ \) reflecting the ISC time constant. As \( t_{S₁} \) and \( t_{ISC} \) are both \( \sim 35 \text{ ps} \), \( \Phi_{ISC}(\text{Pyr:RuPZnPPtPZnRuPyr}) \sim 1 \).

An analogous global fit of the NIR spectral region transient dynamical data acquired for \textit{Pyr:RuPZnPdPZnRuPyr} demonstrates three characteristic time components \( (t₁ = 900 \pm 60 \text{ fs}, \ t₂ = 42 \pm 5 \text{ ps}, \ t₃ = 155 \pm 9 \text{ ps}) \) in the S₁→Sₙ transition region, whereas fitting the T₁→Tₙ spectral region reveals four time constants \( (t₁ = 1.3 \pm 0.2 \text{ ps}, \ t₂ = 39 \pm 4 \text{ ps}, \ t₃ = 190 \pm 8 \text{ ps}, \ t_{long}) \). As discussed for related supermolecules detailed above,
the magnitudes of $\tau_1$ and $\tau_2$ reflect respectively solvent and conformational relaxation dynamics. The 155 ps decay time agrees well with the measured fluorescence lifetime (150 ps), and is therefore attributed to the intrinsic $S_1$ state lifetime ($\tau_{S_1}$) of $\text{Pyr:RuPZnPPdPZnRuPyr}$; consistent with the above analysis, the 190 ps time constant derived from fitting $T_1 \rightarrow T_n$ spectral region transient absorption data corresponds to the $S_1 \rightarrow T_1$ $\tau_{\text{ISC}}$; thus, $\Phi_{\text{ISC}}(\text{Pyr:RuPZnPPdPZnRuPyr})$ is calculated to be ~82%.

### 2.2.4 States Energies and Design Principles for M-(PM')$_n$-M Supermolecular Chromophores

The nonradiative transition rate constant that characterizes the intersystem crossing process between the $S_i$ and $T_1$ states in photoexcited chromophores can be expressed using a Fermi’s Golden Rule formalism, in which the rate is proportional to the square of the spin-orbit coupling ($|\langle S_1 | \hat{H}_{\text{SO}} | T_1 \rangle |^2$) between the excited singlet and triplet states.\textsuperscript{72,73} At a qualitative level, for these transition metal-containing supermolecules, it is important to note that the extent of molecular spin-orbit coupling depends on: i) the magnitude of the atomic coefficients of heavy metal d-orbitals that contribute to the one-electron excitation configurations describing the initially prepared singlet excited state wavefunction; and ii) the atomic spin-orbit coupling constants, $\xi$, of the heavy atoms in the supermolecular chromophore.\textsuperscript{68,74} Quantitative determination of the extent to which one-electron excitations that feature appreciable metal d-orbital character contribute to the configuration expansions that describe the $S_i$ and $T_1$ wavefunctions of these electronically excited supermolecular chromophores is not
computationally tractable; we describe, however, an alternative approach that qualitatively estimates the degree to which metal d orbital character contributes to the initially-prepared electronically excited singlet states in these \( M-(PM')_n-M \) chromophores.

In order to facilitate discussion of structure-property relationships important for engineering high \( \Phi_{ISC} \), long \( \tau_T \) lifetimes, and high oscillator strength NIR absorptivity, Jablonski diagrams (Figure 11) have been constructed using ground-state electronic absorption, fluorescence, and phosphorescence data acquired for these \( M-(PM')_n-M \) chromophores. Note that a Jablonski diagram for the previously established asymmetric chromophore, \textbf{PyrRuPZn}, has also been included in Figure 11 for comparative purposes.

By comparing the excited-state relaxation dynamics among \textbf{PyrRuPZn}, \textbf{PyrRuPZnRuPyr}, and \textbf{PyrRuPZn:RuPyr}, we assess the influence of the conjugated framework on \( |\langle S_i | H_{SO} | T_i \rangle|^2 \), the value of the spin–orbit coupling term upon the non-radiative \( S_i \rightarrow T_i \) transition in these \( M-(PM')_n-M \) structures. From a simple molecular-structure perspective, \textbf{PyrRuPZn:RuPyr} can be viewed as a construct built from connecting two identical \textbf{PyrRuPZn} structures via an ethyne bridge. The fact that \textbf{PyrRuPZn:RuPyr} manifests a \( k_{ISC} \) value more than three orders of magnitude smaller (Table 3) than that determined for \textbf{PyrRuPZn} underscores the disparate natures of their respective excited-state states. In contrast to \textbf{PyrRuPZn} and \textbf{PyrRuPZnRuPyr}, which
manifest broad NIR transient absorptive manifolds characteristic of extensively
delocalized T1 states having substantial MLCT character at earliest time delays, and no
evidence of stimulated emission in their respective transient absorption spectra,61,62 the
time-dependent transient spectral evolution determined for Pyr:RuPZn:RuPyr (Figure
8) resembles that characteristic of the PZn: chromophore (vide supra),48 underscoring that
the S0→S1 transition of Pyr:RuPZn:RuPyr features augmented porphyrin-based π-π*
character relative to that characterizing the S0→S1 transitions of Pyr:RuPZn and
Pyr:RuPZn:RuPyr; this insight in turn indicates a reduced contribution of [Ru(tpy)2]2+-
derived MLCT character to the initially prepared Pyr:RuPZn:RuPyr S1 state
wavefunction relative to these chromophores. Thus, the magnitude of the ruthenium d-
orbital contributions to the one-electron excitation configurations describing the
Pyr:RuPZn:RuPyr initially prepared singlet excited state is diminished relative to that
for the analogous excited state for the Pyr:RuPZn and Pyr:RuPZn:RuPyr chromophores,
congruent with the dramatically reduced kISC and ΦISC observed for Pyr:RuPZn:RuPyr.
Figure 11: M-(PM')ₙ-M Jablonski diagrams highlighting the relative energetic separations of selected electronic states and relevant excited-state relaxation processes.

The impact of the (terpyridyl)metal heavy atom spin-orbit parameter (ξₘ) on the photophysics of these supermolecules are analyzed by comparing the Jablonski diagram of OsPZn₂Os with that of PyrRuPZn₂RuPyr₁ (Figure 11). While the OsPZn₂Os and PyrRuPZn₂RuPyr₁ NIR absorbers share an identical conjugated framework, the measured $k_{ISC}$ for OsPZn₂Os ($k_{ISC} = 3.6 \times 10^{10}$ s⁻¹) is more than one order of magnitude larger than that measured for the PyrRuPZn₂RuPyr₁ supermolecule ($k_{ISC} = 1.6 \times 10^{9}$ s⁻¹). This increase of $k_{ISC}$ must trace its genesis to the higher atomic spin orbit coupling constant of osmium(II) ion (ξₘ Os = 3000 cm⁻¹) relative to ruthenium(II) ion (ξₘ Ru = 1000 cm⁻¹). These data suggest that the negative impact of conjugation expansion as chromophore structure evolves from PyrRuPZn₂RuPyr₁ to PyrRuPZn₂RuPyr₁ upon $|\langle S_1 | H_{SO} | T_1 \rangle|^2$ may be compensated by exploiting (terpyridyl)metal units having larger atomic spin-orbit coupling constants (i.e., OsPZn₂Os). While PyrRuPZn₂RuPyr₁ and OsPZn₂Os
have extraordinarily similar electronic absorption spectra (Figure 9), note that the osmium-enhanced spin-orbit coupling also drives corresponding enhanced $T_1 \rightarrow S_0$ ISC dynamics; OsPZn:Os manifests a triplet excited state lifetime ($\tau_T = 0.4 \mu s$) more than twenty times shorter than that recorded for Pyr:RuPZn:RuPyr ($\tau_T = 9.9 \mu s$). The combination of a lower-lying triplet excited state energy ($T_1 = 1.16$ eV, Figure 11) relative to Pyr:RuPZn:RuPyr ($T_1 = 1.28$ eV, Figure 11), and a diminished $T_1$ state lifetime, suggest that use of (terpyridyl)osmium centers in $M$-$\left(PM\right)_n$-$M$ supermolecules do not constitute a viable approach to develop NIR absorbers with long-lived ($\sim \mu s$) triplet excited-state lifetimes that are required by many optoelectronic applications, such as TTA UC technologies where $T_1$-state energies are a critical consideration, and $T_1$ lifetimes of at least $\mu s$ are required.\textsuperscript{18}

The Figure 11 Jablonski diagrams for Pyr:RuPZn:RuPyr, OsPZn:Os, and Pyr:RuPZn:RuPyr suggest that further engineering of NIR chromophores with long-lived ($\mu s$) $T_1$ states produced at unit quantum yield should focus on manipulation of the electronic properties of the (porphinato)metal(II) building blocks of these supermolecules. Within this context, the Zn(II) metal ions of the parent Pyr:RuPZn:RuPyr chromophore were replaced by Pt (II) metal ions. The Pyr:RuPPt:RuPyr design relies on the facts that: (i) Platinum d$\pi$ orbitals interact more strongly with the porphyrin $\pi$-electron framework relative to the analogous zinc orbitals due to its larger atomic size.\textsuperscript{75-77} As a result, the magnitude of the atomic coefficients of
metal d-orbitals in \((PM')_n\) fragment that contribute to the one-electron excitation configurations describing the initially prepared singlet excited state is increased in \(\text{Pyr:RuPPt:RuPyr}\) relative to the case in \(\text{Pyr:RuPZn:RuPyr}\). (ii) The atomic spin-orbit coupling constant of platinum \((\xi_{\text{Pt}} = 4441 \text{ cm}^{-1})\) is an order of magnitude stronger than that of zinc \((\xi_{\text{Zn}} = 390 \text{ cm}^{-1})\). Congruent with this design, population analysis of the frontier orbital (FO) electron densities shows non-modest Pt d-orbital contributions (see Materials and Methods, Section 2.4.7 for details) to orbitals important to the one-electron transitions that figure prominently in the configuration expansions that describe the low-lying excited states of the \(\text{Pyr:RuPPt:RuPyr}\) supermolecule; for example, the Pt-d orbital contributes 2.9 % of the \(\text{PPt}_2\) LUMO electron density (Table 4; Figure 12), contrasting the case for \(\text{PZn}_2\), where Zn-d orbital electron density contributes just 0.3 % to the LUMO (Figure 12). Congruent with the combination of these effects, \(k_{\text{ISC}}\) for \(\text{Pyr:RuPPt:RuPyr}\) increases by three orders of magnitude relative to that measured for \(\text{Pyr:RuPZn:RuPyr}\) (Figure 11), and \(\Phi_{\text{ISC}}\) for \(\text{Pyr:RuPPt:RuPyr}\) is driven to unity. While the large magnitude manifold hypsochromic shift of the \(\text{'Qx}-\text{derived transition manifold of PPy:RuPPt:RuPyr}\) \((\lambda_{\text{Qx}}(\text{max}) = 653 \text{ nm})\) relative to \(\text{Pyr:RuPZn:RuPyr}\) \((\lambda_{\text{Qx}}(\text{max}) = 772 \text{ nm})\) makes the \(\text{Pyr:RuPPt:RuPyr}\) supermolecule unsuitable for harvesting NIR photons (Figure 9), this composition provides important chromophore design insights: as \(\text{Pyr:RuPPt:RuPyr}\) manifests a substantial triplet excited state lifetime \((\tau_T = 2.9 \mu\text{s})\), it indicates heavy atom substitution of the \((PM')_n\) chromophoric fragment of \(\text{M-}(PM')_n-\text{M}\).
supermolecules provides a feasible path to augment $S_1$-$T_1$ ISC rate constants that will not necessarily drive $T_1\rightarrow S_0$ relaxation dynamics into the sub-$\mu$s time regime.

![Diagram of molecular orbitals](image)

**Figure 12:** Frontier molecular orbitals (0.02 isodensity surfaces) for PZn₂, PPt₂, PZnPttPZn, and PZnPdpPZn chromophores. Calculations were performed using B3LYP functional with 6-311g(d) basis set level, and minimal symmetry constraints; tight optimization criteria were applied in the geometry optimization processes.

To achieve near-unit $\Phi_{ISC}$ while maintaining high oscillator strength NIR absorbptivity within $M$-$\text{PM'}m$-$M$ supermolecules, we designed

\text{Pyr}R\text{u}ZnPM'PZnR\text{u}Pyr (M' = Pt, Pd) hybrid chromophores based on \textit{meso-to-meso} ethyne-bridged (porphinato)metal(II) trimers in which only the central porphyrin unit is complexed with Pd(II) or Pt(II) heavy metals ions. TD-DFT calculations performed on PZnPm'PZn (M = Pd, Pt) model chromophores determine that the HOMO$\rightarrow$LUMO one-electron transition figures prominently in the configuration expansions that describe the
globally delocalized $S_1$ excited states of these supermolecules (Figure 53); population analysis of the FO electron densities shows that the Pt-d orbitals contribute 1.3 % of the overall electron density of the $\text{PZnP}_{\text{Pt}}\text{PZn}$ LUMO (Table 6; Figure 12), while the analogous Pd d-orbitals account for 0.7 % (Table 7) of $\text{PZnP}_{\text{Pd}}\text{PZn}$ LUMO electron density. Due to larger magnitude of the atomic coefficients (1.3 %) of Pt-d orbitals that contribute to the FOs of $\text{PZnP}_{\text{Pt}}\text{PZn}$ relative to that (0.7 %) of the Pd-d orbitals contributing to the FOs of $\text{PZnP}_{\text{Pd}}\text{PZn}$, and the significantly larger spin-orbit coupling constant of Pt ($\xi_{\text{Pt}} = 4481 \text{ cm}^{-1}$) than that of Pd ($\xi_{\text{Pd}} = 1500 \text{ cm}^{-1}$), $\text{Pyr}_1\text{RuPZnP}_{\text{Pt}}\text{PZnRuPyr}_1$ displays larger magnitude $k_{\text{ISC}} (3.0 \times 10^{10} \text{ s}^{-1})$ and $\Phi_{\text{ISC}} (~1)$ values relative to $\text{Pyr}_1\text{RuPZnP}_{\text{Pd}}\text{PZnRuPyr}_1$ ($k_{\text{ISC}} \sim 5.3 \times 10^9 \text{ s}^{-1}$, $\Phi_{\text{ISC}} \sim 0.82$). We note that both of these supermolecular chromophores possess substantial triplet state lifetimes $[(\tau_T (\text{Pyr}_1\text{RuPZnP}_{\text{Pt}}\text{PZnRuPyr}_1) = 4.4 \mu s; \tau_T (\text{Pyr}_1\text{RuPZnP}_{\text{Pd}}\text{PZnRuPyr}_1) = 13.0 \mu s)$. These data underscore that divalent Pt and Pd ions within the $(\text{PM'})_n$ chromophoric fragment of $\text{M-}(\text{PM'})_n\text{-M}$ supermolecules can be exploited as tools to tune the magnitude of the atomic coefficients of heavy metal d-orbitals that contribute to the one-electron excitation configurations describing the initially prepared singlet excited state: introduction of a single PPt or PPd unit within the $\text{(PM')}_n$ fragment of $\text{M-}(\text{PM'})_n\text{-M}$ supermolecules makes possible both high oscillator strength NIR absorptivity and substantial ISC quantum yield, without detrimental impact upon $T_1 \rightarrow S_0$ relaxation dynamics. This ability to simultaneously fine tune the relative magnitudes of $k_{\text{nr}}$, $k_{\text{nr}}$, $k_{\text{ISC}}$,
and $k_{\text{T1-S0}}$ is currently unrivaled in other chromophoric platforms, and highlights the utility of this molecular roadmap to design NIR absorbers having highly modulated photophysical properties. **Figure 13** summarizes the overall molecular design approach to realize exceptional NIR absorbers that possess long-lived triplet excited-states produced at near-unit $\Phi_{\text{ISC}}$ through modulation of the $\text{M}-(\text{PM'})_{n}-\text{M}$ supermolecular platform.

**Figure 13**: Molecular design flow for realizing exceptional NIR absorbers that possess long-lived triplet excited-states produced at near-unit $\Phi_{\text{ISC}}$ through modulation of the $\text{M}-(\text{PM'})_{n}-\text{M}$ supermolecular platform.

With respect to **Figures 11 and 13**, it is important to consider that radiationless transition theory expresses the ISC rate constant in terms of (i) a state density factor, (ii) a matrix element describing the spin-orbit coupling between the $S_1$ and $T_1$ wave functions ($|\langle S_1|\hat{H}_{SO}|T_1\rangle|^2$), and (iii) an overlap factor that accounts for the diminution of the nonradiative rate constant magnitudes with increasing $\Delta E_{S1-T1}$.\textsuperscript{72,79} In many families of transition metal chromophores, the magnitude of $k_{\text{ISC}}$ tracks smoothly with $(\Delta E_{S1-T1})^1$. Such a dependence is clearly not manifest in the photophysics of these $\text{M}-(\text{PM'})_{n}-\text{M}$
supermolecules (Figure 11), underscoring the importance of manipulating the extent to which heavy metal d-orbitals contribute to the one-electron excitation configurations that describe the initially prepared singlet excited states of these chromophores (vide supra).

We point out that while the optical band gap can be extensively modulated within this family of M-(PM')ₙ-M supermolecules, PyrRuPZnRuPyr, PyrRuPZnPnPzRuPyr, and PyrRuPZnPdPZnRuPyr possess extraordinarily similar S₀-T₁ energy gaps (Figure 11). Such an observation is congruent with the notion that the spatial extent of the T₁-wavefunctions of M-(PM')ₙ-M supermolecules are more localized than their corresponding low-lying singlet excited states. This supposition is congruent with the previous EPR spectroscopic investigations of the electronically excited triplet states ethyne-bridged multi-porphyin compounds.⁴⁹, ⁵², ⁸⁰-⁸² Given the highly uniform S₀-T₁ energy gaps for these supermolecules, the magnitude of ΔEₛ₁₋ₐ₃ ranges from 0.42 eV (PyrRuPZnPdPZnRuPyr) to 0.27 eV (PyrRuPZnPdPZnRuPyr). In this regard, we note that the Pd-derived supermolecule, PyrRuPZnPdPZnRuPyr, manifests relative S₁-T₁ energy levels that stand in sharp contrast to those of classic porphyrinic chromophores, (polypyridyl)ruthenium(II) / osmium(II) complexes, and other π-conjugated polymers that are characterized by large Φ ISC values, as these chromophores evince ΔEₛ₁₋ₐ₃ gaps that exceed 0.4 eV.⁵⁵, ⁶⁷, ⁸³

With respect to the potential utility of these M-(PM')ₙ-M supermolecules in OPL
applications, we note that OPL schemes based on reverse saturable absorption typically requires materials having weak ground-state \((S_0 \rightarrow S_i)\) absorption, but substantial \(T_1 \rightarrow T_n\) absorptive oscillator strength in the operational wavelength regime.\(^{15, 84}\) Furthermore, the ISC time constant of such OPL materials should be shorter than the laser pulse duration.\(^{84}\) In these respects, we note that \(M-(PM')_n-M\) display weak but non-negligible absorption up to \(~1000\) nm \((\text{e.g., } \varepsilon_{\lambda} = 800\) nm \((S_0 \rightarrow S_i, \text{Pyr:RuPPt:RuPyr}) \sim 360\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\), \(\varepsilon_{\lambda} = 950\) nm \((S_0 \rightarrow S_i, \text{Pyr:RuPZnPpT:ZnRuPyr}) \sim 800\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\), \(\varepsilon_{\lambda} = 1000\) nm \((S_0 \rightarrow S_i, \text{Pyr:RuPZnPpD:ZnRuPyr}) \sim 600\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\)), but corresponding \(T_1 \rightarrow T_n\) excited-state absorption extinction coefficients that are enormous \((\varepsilon_{\lambda} = 1000\) nm \((T_1 \rightarrow T_n, \text{Pyr:RuPPt:RuPyr}) \sim 7000\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\), \(\varepsilon_{\lambda} = 1000\) nm \((T_1 \rightarrow T_n, \text{Pyr:RuPZnPpP:ZnRuPyr}) \sim 40000\) \(\text{M}^{-1}\) \(\text{cm}^{-1}\); procedures for estimating \(\varepsilon_{T_1 \rightarrow T_n}\) have been detailed elsewhere\(^{62}\) Moreov-\(\text{er, as the ISC time constants for these compounds ranges from} \sim 0.4\) to \sim 190 ps, these and related chromophores should be well poised for NIR OPL in which sub-ps to sub-ns laser pulses are exploited; the potential utility of these structures is further underscored by the paucity of high performance optical limiting materials that function near1000 nm.

For NIR TTA UC, a critical hurdle to real-world applications of this technology includes the lack of appropriate NIR-absorbing sensitizers that simultaneously feature: (i) broad, high oscillator strength spectral absorptivity beyond 700 nm, (ii) near-unit singlet-to-triplet intersystem crossing quantum (ISC) yields that do not occur with
significant loss of excited-state energy, (iii) \( T_1 \) states having a sufficiently long (≥ μs) lifetimes, and (iv) \( T_1 \) state energy levels that assure exergonic triplet-triplet energy transfer to the annihilator.\(^{18-20}\) In this regard, \textit{PyrRuPZnPM'PZnRuPyrr} chromophores are well suited for NIR TTA UC, as they not only meet the excited-state dynamical requirements, but also display exceptional ground-state absorptivity beyond 750 nm and \( T_1 \) state energy levels appropriate for sensitizing commonly used annihilators, (\textit{e.g.} rubrene\(^{18}\)).

\subsection*{2.3 Conclusion}

A molecular design roadmap has been described that realizes chromophores that simultaneously possess substantial near-infrared (NIR) absorptivity and long-lived, high-yield triplet excited states. These designs circumvent the critical energy-gap-law hurdle whereby diminishing absorber optical bandgap exponentially increases nonradiative \( (S_i \rightarrow S_0) \) transition rate constants and reduces \( S_i \rightarrow T_1 \) intersystem crossing (ISC) quantum yields. This chromophore design methodology exploits the ethyne-bridged (polypyridyl)metal(II) \( (M; M = \text{Ru, Os})-(\text{porphinato})\text{metal(II)} \) \( (PM'; M' = \text{Zn, Pt, Pd}) \) molecular architecture \( (M-(PM')_n-M) \), where the nature of the supermolecular conjugation drives substantial mixing of porphyrin-based \( \pi-\pi^* \) and metal polypyridyl-based charge-resonance transitions. By varying the extent to which the atomic coefficients of heavy metal d-orbitals contribute to the one-electron excitation configurations describing the initially prepared singlet and triplet excited-state
wavefunctions, the relative magnitudes of fluorescence ($k_0$), $S_1 \rightarrow S_0$ non-radiative decay ($k_{nr}$), $S_1 \rightarrow T_1$ ISC ($k_{ISC}$), and $T_1 \rightarrow S_0$ relaxation ($k_{T1,S0}$) rate constants can be finely tuned in $M$-$($PM$')_n$-$M$ compounds; such insights in turn enable molecular designs in which the $k_{ISC}$ magnitude dominates singlet manifold relaxation dynamics, but does not give rise to $T_1 \rightarrow S_0$ conversion dynamics that short-circuit a $\mu$s timescale triplet lifetime.

The $M$-$($PM$')_n$-$M$ supermolecular chromophore structure-function relationships derived from these studies are reflected, for example, in the designs of $\text{Pyr} \text{RuPZnPM'}$PZnRuPyr ($M' = \text{Pt, Pd}$) chromophores: $\text{Pyr} \text{RuPPZnPdPZnRuPyr}$ ($\varepsilon_{780}$ nm = $1.63 \times 10^5$ M$^{-1}$cm$^{-1}$, $f_{\text{NIR}} \sim 1.13$, $\Phi_{\text{ISC}} \sim 82\%$, $\tau_{T1} \sim 13.0$ $\mu$s, $\Delta E_{S1-T1} = 0.27$ eV);

$\text{Pyr} \text{RuPPZnPtPZnRuPyr}$ ($\varepsilon_{750}$ nm = $1.50 \times 10^5$ M$^{-1}$cm$^{-1}$, $f_{\text{NIR}} \sim 0.85$, $\Phi_{\text{ISC}} \sim 100\%$, $\tau_{T1} \sim 4.4$ $\mu$s, $\Delta E_{S1-T1} = 0.34$ eV). Given these enhanced NIR-absorptive and photophysical properties, $M$-$($PM$')_n$-$M$ chromophores stand in sharp contrast to extensive families of conventional metal complexes, organic molecules, and polymer materials such as (polypyridyl)metal(II) complexes,$^{55}$ bodipy derivatives,$^{19}$ and polythiophene derivatives$^{56-58}$ that have been traditionally exploited as long-wavelength absorbers that give rise to substantial electronically excited triplet state populations. Chromophores derived from $M$-$($PM$')_n$-$M$ supermolecular architectures open new opportunities to construct exceptional NIR-absorbers that not only possess long-lived triplet excited states produced at high quantum yield: as both absolute $T_1$ state energies may be controlled while ensuring modest $S_1$-$T_1$ state energy gaps, such chromophores are
uniquely poised to impact optical power limiting, dye-sensitized solar cell, and photon-upconversion applications.

2.4 Materials and Methods

2.4.1 Materials and Instrumentation

All manipulations were carried out under nitrogen or argon previously passed through an O₂ scrubbing tower (Schweitzer hall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise stated. Air sensitive solids were handled in a Braun 150-M glove box. Standard Schlenk techniques were employed to manipulate air-sensitive solutions. All solvents utilized in this work were obtained from Fisher Scientific (HPLC Grade). CH₂Cl₂ and tetrahydrofuran (THF) were distilled from CaH₂ and K/4-benzoylbiphenyl, respectively, under argon. Triethylamine (TEA) was dried over KOH pellets and distilled under vacuum. All NMR solvents were used as received. The catalysts Pd(PPh₃)₄ and tris(dibenzylideneacetone)-dipalladium(0) (Pd₂dba₃), as well as triphenylarsine (AsPh₃), were purchased from Sigma-Aldrich. Various starting materials (Scheme S1), such as ruthenium(II) (4’-bromo-2,2’;6’,2”-terpyridine)(4’-pyrrolidin-1-yl-2,2’;6’,2”-terpyridine) bis(hexafluorophosphate) (PyrRuBr)₆₂,₈₅-₉₁, osmium(II) (4’-bromo-2,2’;6’,2”-terpyridine)(2,2’;6’,2”-terpyridine) bis(hexafluorophosphate) (OsBr)₆₀,₆₂,₉₂-₉₄ [5,15-bis-ethynyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) (EPZnE)₆₀,₉₅ 1,2-bis[(10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II)]ethyne (PZn₂)₆₇,₉₅ were prepared
according to the published procedures. Flash and size exclusion column chromatography were performed on the bench top, using respectively silica gel (EM Science, 230–400 mesh) and Bio-Beads SX-1 as media.

Electronic spectra were recorded on a Varian 5000 UV/vis/NIR spectrophotometry system. NMR spectra were recorded on a 400 MHz AC-Brucker instrument. Chemical shifts for \(^1\)H NMR spectra are reported relative to residual protium in the deuterated solvents (CDCl\(_3\) = 7.26 ppm, CD\(_3\)CN = 1.93 ppm). All J values are reported in Hertz. MALDI-TOF mass spectroscopic data were obtained with a Perspective Voyager DE Instrument (Department of Chemistry, Duke University). Samples were prepared as micromolar solutions in acetone, and 2-(4’-hydroxybenzeneazo)benzoic acid (Sigma-Aldrich) was utilized as the matrix. Microwave assisted reactions were performed with Emrys Personal Chemistry System (Biotage).

### 2.4.2 Synthetic Procedures and Characterizations

\(\text{Pyr}_1\text{RuPZnRuPyr}_1\) was synthesized by cross-coupling of \(\text{Pyr}_1\text{RuBr}\) with [5,15-bis(ethynyl)-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) (Figure 14). \(\text{Pyr}_1\text{RuPZn}_2\text{RuPyr}_1\), OsPZn\(_2\)Os, \(\text{Pyr}_1\text{RuPPr}_2\text{RuPyr}_1\), \(\text{Pyr}_1\text{RuPZnPPr}_2\text{PZnRuPyr}_1\) and \(\text{Pyr}_1\text{RuPZnPdPZnPruPyr}_1\) were prepared in a similar fashion, cross-coupling bis(\textit{meso}ethynyl) ethyne-bridged oligo(porphinato)metal(II) species (EPZn\(_2\)E, EPPt\(_2\)E, EPZnPPrPZnE and EPZnPdPZnE) with either \(\text{Pyr}_1\text{RuBr}\) or OsBr (Figure 15). Overall yields (based on the
10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphyrin starting material) for the final products are outlined in Figure 27.

**Figure 14:** Syntheses and chemical structures of M-(PM’)n-M chromophores

**Figure 15:** Precursor compounds utilized for the synthesis of ethyne-bridged oligo(porphinato)metal(II)-bis(terpyridyl)metal(II) chromophores; these compounds were prepared according to previously published procedures (see Materials section above).
Figure 16: Synthesis of EPZn:E from PZn₂. (a) NBS, 0 °C, CH₂Cl₂:pyridine 20:1 mixture, 1.5 h, under argon; (b) (triisopropylsilyl)acetylene, Pd(PPh₃)₂Cl₂, CuI, THF:i-Pr₂NH 9:1 mixture, 60 °C, 16 h, under argon; (c) TBAF, THF, 0 °C, 10 min, under argon.

1,2-Bis[(5-bromo-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II)]ethyne (BrPZn₂Br). In a 500 mL round bottom flask, PZn₂ (448 mg, 0.24 mmol) was dissolved in methylene chloride (100 mL) and pyridine (10 mL). The reaction mixture was cooled to 0 °C and a solution of NBS (90 mg, 0.50 mmol) in methylene chloride (100 mL) was added via cannula. The reaction mixture was stirred at 0 °C under argon for 1.5 h and quenched by addition of H₂O (100 mL). The organic layer was separated and dried with anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography using 1:1 hexanes:methylene chloride as the eluent. Yield = 440 mg (90 %, based on 448 mg of the PZn₂ starting material). ¹HNMR (400MHz, CDCl₃ as 7.26 ppm): δ 10.33 (d, 4H, J = 4.4 Hz), 9.61 (d, 4H, J = 4.8), 9.02 (d, 4H, J = 4.4 Hz), 8.86 (d, 4H, J = 4.4 Hz), 7.74 (t, 4H, J = 8.4 Hz), 7.05 (d, 8H, J = 8.4 Hz), 3.96 (t, 16H, J = 7.4 Hz), 0.90 (t, 16H, J = 7.4 Hz), 0.36 (s, 72H). MALDI-TOF: m/z = 2033.02 (calculated for C₁₁₄H₁₃₂Br₂N₈O₈Zn₂ (M+H)+ 2031.93).

1,2-Bis[(5-triisopropylsilyl)ethynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethyne (TIPS-EPZn:E-TIPS). A 100 mL Schlenk
flask equipped with a magnetic stirbar was charged with BrP\textsubscript{Zn}Br (440 mg, 0.22 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (32 mg, 0.044 mmol) and CuI (10 mg, 0.044 mmol). A solvent mixture of THF (50 mL), diisopropylamine (5mL), and (triisopropylsilyl)acetylene (400 \(\mu\)L, 1.30 mmol) was degassed via three-pump-thaw cycles, transferred to the reaction flask and stirred at 60 °C for 16 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was poured into water, extracted with CH\textsubscript{2}Cl\textsubscript{2}, dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated. The residue was purified by column chromatography using 1:1 hexanes:methylene chloride as the eluent. Yield = 360 mg (75%, based on 220 mg of BrP\textsubscript{Zn}Br). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3} as 7.26 ppm): \(\delta\) 10.35 (d, 4H, J = 4.8 Hz), 9.73 (d, 4H, J = 4.4 Hz), 9.07 (d, 4H, J = 4.4 Hz), 8.94 (d, 4H, J = 4.4 Hz), 7.77 (t, 4H, J = 8.4 Hz), 7.08 (d, 8H, J = 8.4 Hz), 4.01 (t, 16H, J = 7.2 Hz), 1.55-1.49 (m, 42H), 0.97 (t, 16H, J = 7.4 Hz), 0.37 (s, 72H). MALDI-TOF: m/z = 2235.65 (calculated for C\textsubscript{136}H\textsubscript{174}N\textsubscript{8}O\textsubscript{8}Si\textsubscript{2}Zn\textsubscript{2} (M+H}\textsuperscript{+} 2234.87).

1,2-Bis[(5-ethynyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II)]ethyne (EPZn\textsubscript{E}). Tetrabutylammonium fluoride (1 M in THF, 220 \(\mu\)L, 0.22 mmol) was added to a solution of TIPS-EPZn\textsubscript{E}-TIPS (200 mg, 0.089 mmol) in THF (50 ml) under argon at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH\textsubscript{2}Cl\textsubscript{2}, dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated. The residue was chromatographed on silica gel using 1:1 hexanes:methylene chloride as the eluent. Yield = 166 mg (97%, based on 137 mg of TIPS-EPZn\textsubscript{E}-TIPS). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3} as 7.26 ppm): \(\delta\) 10.34 (d, 4H, J = 4.8 Hz),
9.72 (d, 4H, J = 4.4), 9.04 (d, 4H, J = 4.4 Hz), 8.92 (d, 4H, J = 4.4 Hz), 7.74 (t, 4H, J = 8.4 Hz),
7.06 (d, 8H, J = 8.4 Hz), 4.13 (s, 2H), 3.98 (t, 16H, J = 7.2 Hz), 0.93 (t, 16H, J = 7.4 Hz), 0.36
(s, 72H). MALDI-TOF: m/z = 1921.56 (calculated for C118H134N8O8Zn2 (M+H)⁺ 1923.18).

Figure 17: Synthesis of EPPt2E from TIPSEPZn2ETIPS. (a) trifluoroacetic acid, r.t., CH2Cl2, 30 min; (b) Pt(acac)2, benzonitrile, 200 °C, 4 h, microwave reaction; (c) TBAF, THF, 0 °C, 10 min, under argon.

1,2-Bis(5-triisopropylsilylethynyl)-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphyrin)ylene (TIPS-EFb2E-TIPS). In a 100 mL round bottom flask equipped with a magnetic stirring bar, TIPS-EPZn2E-TIPS (120 mg, 0.054 mmol) was dissolved by dry methylene chloride (~50 mL). Trifluoroacetic acid (1 mL) was added to the round bottom flask and the reaction was stirred at room temperature under argon for 0.5 h and then quenched by saturated NaHCO3. The organic layer was collected, washed with saturated NH4Cl, and then dried with Na2SO4. After evaporation of the solvent, the residue was purified by column chromatography using 1:1 hexanes:methylene chloride as the eluent. Yield = 112 mg (98 %, based on 120 mg of the TIPS-EPZn2E-TIPS starting material). 1H NMR (400MHz, CDCl3 as 7.26 ppm): δ 10.22 (d, 4H, J = 4.8 Hz), 9.62 (d, 4H, J = 4.4), 8.97 (d, 4H, J = 4.8 Hz), 8.85 (d, 4H, J = 4.8 Hz), 7.77
(t, 4H, J = 8.4 Hz), 7.07 (d, 8H, J = 8.4 Hz), 4.00 (t, 16H, J = 7.2 Hz), 1.55-1.49 (m, 42H), 0.99 (t, 16H, J = 7.4 Hz), 0.40 (s, 72H), -1.94 (s, 4H). MALDI-TOF: m/z = 2106.28 (calculated for \(\text{C}_{136}\text{H}_{178}\text{N}_8\text{O}_8\text{Si}_2\) (M+H)+ 2109.14).

1,2-Bis[(5-triisopropylsilylethynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)platinum(II)]ethyne (TIPS-EPPT-E-TIPS). TIPS-EFb2E-TIPS (70 mg, 0.033 mmol), platinum acetylacetonate (129 mg, 0.33 mmol) and a magnetic stirring bar were brought together into a 10 mL microwave reaction vial that was then sealed and charged with argon. These reagents were dissolved in ~6 mL of benzonitrile solvent that was previously purged with argon for 1 h. The reaction vial was stirred at 200 °C for 4 h in a microwave irradiation cavity. After the reaction, without removing the benzonitrile solvent, the reaction mixture was directly purified via silica column chromatography using 65:35 hexanes:methylene chloride eluent, and the first greenish band was collected as the desired product. Yield = 50 mg (61%, based on 70 mg of the TIPS-EFb2E-TIPS starting material). \(^1\)H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 10.08 (d, 4H, J = 5.2 Hz), 9.55 (d, 4H, J = 5.2), 8.87 (d, 4H, J = 5.2 Hz), 8.77 (d, 4H, J = 5.2 Hz), 7.71 (t, 4H, J = 8.4 Hz), 7.02 (d, 8H, J = 8.8 Hz), 3.97 (t, 16H, J = 7.2 Hz), 1.49-1.44 (m, 42H), 0.98 (t, 16H, J = 7.2 Hz), 0.31 (s, 72H). MALDI-TOF: m/z = 2491.96 (calculated for \(\text{C}_{136}\text{H}_{174}\text{N}_8\text{O}_8\text{Si}_2\text{Pt}_2\) (M+H)+ 2495.27).

1,2-Bis[(5-ethynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)platinum(II)]ethyne (EPPT-E). Tetrabutylammonium
fluoride (1 M in THF, 50 µL, 0.050 mmol) was added to a solution of TIPS-EPtE-TIPS (50 mg, 0.020 mmol) in THF (30 ml) under argon at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH₂Cl₂, dried over Na₂SO₄, and evaporated. The residue was chromatographed on silica gel using 85:15 hexanes:THF as the eluent. Yield = 41 mg (95%, based on 50 mg of TIPS-EPtE-TIPS).

¹H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 10.05 (d, 4H, J = 5.2 Hz), 9.54 (d, 4H, J = 5.2), 8.88 (d, 4H, J = 5.2 Hz), 8.76 (d, 4H, J = 5.2 Hz), 7.71 (t, 4H, J = 8.4 Hz), 7.02 (d, 8H, J = 8.8 Hz), 4.09 (s, 2H), 3.96 (t, 16H, J = 7.2 Hz), 1.49–1.45 (m, 42H), 0.96 (t, 16H, J = 7.2 Hz), 0.32 (s, 72H). MALDI-TOF: m/z = 2179.64 (calculated for C₁₁₈H₁₃₄N₈O₈Pt₂ (M+H)⁺ 2182.59).

Figure 18: Synthesis of EPZnPtZnE. (a) Pt(acac)₂, benzonitrile, 200 °C, 4 h, microwave reaction; (b) Pd(dba)₃, AsPh₃, THF/i-Pr₂NH 9:1 mixture, 50 °C, 12 h, under argon; (c) NBS, 0 °C, CH₂Cl₂:pyridine 20:1 mixture, 1.5 h, under argon; (d) (triisopropylsilyl)acetylene, Pd(PPh₃)₃Cl₂, Cul, THF/i-Pr₂NH 9:1 mixture, 60 °C, 16 h, under argon; (e) TBAF, THF, 0 °C, 10 min, under argon.

[5,15-Dibromo-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (BrPPTBr). BrFbBr (70 mg, 0.069 mmol),
platinum acetylacetonate (135 mg, 0.34 mmol) and a magnetic stirring bar were brought together into a 10 mL microwave reaction vial that was then sealed and charged with argon. These reagents were dissolved in 6 mL of benzonitrile solvent that was previously purged with argon for 1 h. The reaction vial was stirred at 200 °C for 4 h in a microwave irradiation cavity. After the reaction, without removing the benzonitrile solvent, the reaction mixture was directly purified by silica column chromatography using 65:35 hexanes:methylene chloride eluent; the first bright orange color band was collected as the desired product. This reaction was repeated three additional times in order to obtain enough material for subsequent reactions. Yield = 271 mg (products from 4 reactions in total, 81%, based on 280 mg of the BrFbBr starting material). 1H NMR (400MHz, CDCl3 as δ 7.26 ppm): δ 9.52 (dd, 4H, J = 5.2 Hz, 0.8 Hz), 8.77 (d, 4H, J = 5.2 Hz, 0.8 Hz), 7.73 (t, 2H, J = 8.4 Hz), 7.02 (d, 4H, J = 8.0 Hz), 3.95 (t, 8H, J = 7.2 Hz), 0.95 (t, 8H, J = 7.2 Hz), 0.29 (s, 36H). MALDI-TOF: m/z = 1212.84 (calculated for C56H66N4O4Br2Pt (M+H)+ 1214.06).

5,15-Bis[5’-[(10’, 20’-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)ethynyl]-[10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (PZnPtpPZn). A 100 mL Schlenk flask equipped with a magnetic stirbar was charged with PZnE (370 mg, 0.39 mmol), BrPttBr (190 mg, 0.16 mmol), Pd2(dba)3 (36 mg, 0.039 mmol) and AsPh3 (48 mg, 0.156 mmol). A solvent mixture of THF (50 mL) and diisopropylamine (5 ml) was degassed via five
freeze-pump-thaw cycles, transferred to the reaction flask, and stirred at 50 °C for 12 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was evaporated to dryness and the residue sequentially purified by silica column chromatography using 1:1 hexanes:methylene chloride as the eluent, size exclusion column chromatography using THF as the eluent, and an additional silica column chromatographic step using 1:1 hexanes:methylene chloride as the eluent. Yield = 218 mg (46%, based on 190 mg of BrPPTb).

\(^1\)H NMR (400MHz, CDCl\(_3\) as 7.26 ppm): \(\delta\) 10.38 (d, 4H, \(J = 4.4\) Hz), 10.24 (d, 4H, \(J = 5.2\) Hz), 10.11 (s, 2H), 9.29 (d, 4H, \(J = 4.4\) Hz), 9.15 (d, 4H, \(J = 4.4\) Hz), 9.00 (d, 4H, \(J = 4.4\) Hz), 8.94 (d, 4H, \(J = 5.2\) Hz), 7.76 (t, 4H, \(J = 8.4\) Hz), 7.75 (t, 2H, \(J = 8.4\) Hz), 7.08 (d, 8H, \(J = 8.4\) Hz), 7.07 (d, 4H, \(J = 8.8\) Hz), 4.04 (t, 8H, \(J = 7.2\) Hz), 3.98 (t, 16H, \(J = 7.2\) Hz), 1.06 (t, 8H, \(J = 7.2\) Hz), 0.93 (t, 16H, \(J = 7.2\) Hz), 0.35 (s, 36H), 0.31 (s, 72H). MALDI-TOF: m/z = 2957.32 (calculated for C\(_{172}\)H\(_{200}\)N\(_{12}\)O\(_{12}\)PtZn\(_2\)(M+H\(^+\)) 2953.41).

5,15-Bis[5'-[15'-bromo-10', 20'-bis(3,5-di(di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethynyl]-[10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum (II) (BrPZnPPTbZnP). In a 250 mL round bottom flask, PZnPPTbZnP (180 mg, 0.061 mmol) was dissolved in methylene chloride (50 mL) and pyridine (5 mL). The reaction mixture was cooled to 0 °C and a solution of NBS (22 mg, 0.13 mmol) in methylene chloride (50 mL) was added via cannula. The reaction mixture was stirred at 0 °C under argon for 1.5 h and quenched by addition of H\(_2\)O (100 mL). The organic layer was separated and dried with anhydrous Na\(_2\)SO\(_4\). After
evaporation of the solvent, the residue was purified by column chromatography using 6:4 hexanes:methylene chloride as the eluent. Yield = 127 mg (67 %, based on 180 mg of the \textit{PZnPptPZn} starting material). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3} as 7.26 ppm): \(\delta\) 10.27 (d, 4H, J = 4.8 Hz), 10.20 (d, 4H, J = 4.8), 9.63 (d, 4H, J = 4.8 Hz), 9.03 (d, 4H, J = 4.4 Hz), 8.92 (d, 4H, J = 5.2 Hz), 8.88 (d, 4H, J = 4.8 Hz), 7.75 (t, 6H, J = 8.4 Hz), 7.06 (d, 12H, J = 8.8 Hz), 4.03 (t, 8H, J = 7.2 Hz), 3.98 (t, 16H, J = 7.2 Hz), 1.05 (t, 8H, J = 7.2 Hz), 0.92 (t, 16H, J = 7.2 Hz), 0.38 (s, 72H), 0.34 (s, 36H). MALDI-TOF: m/z = 3114.56 (calculated for C\textsubscript{172}H\textsubscript{198}Br\textsubscript{2}N\textsubscript{2}O\textsubscript{12}PtZn\textsubscript{2} (M+H\textsuperscript{+} 3111.20).

5,15-Bis[5’-[[15’-triisopropylsilylethynyl]-10’, 20’-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethynyl]-[10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (TIPS-EPZnPPtPZnE-TIPS). A 50 mL Schlenk flask equipped with a magnetic stirbar was charged with \textit{BrPZnPptPZnBr} (80 mg, 0.026 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (9.1 mg, 0.013 mmol), and CuI (2.5 mg, 0.013 mmol). A solvent mixture of THF (25 mL), diisopropylamine (2.5 ml) and (triisopropylsilyl)acetylene (59 \textmu L, 0.26 mmol) was degassed via three-pump-thaw cycles, transferred to the reaction flask, and stirred at 60 °C for 16 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was poured into water, extracted with CH\textsubscript{2}Cl\textsubscript{2}, dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated. The residue was purified by column chromatography using 1:1 hexanes:methylene chloride as the eluent. Yield = 67 mg (78%, based on 80 mg of \textit{BrPZnPptPZnBr}). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3} as 7.26 ppm): \(\delta\) 10.28 (d,
5,15-Bis[5’-[(15’-ethynyl-10’,20’-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)ethynyl]-[10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (EPZnPnPZnE). Tetrabutylammonium fluoride (1M in THF, 37 µL, 0.037 mmol) was added to a solution of TIPS-EPZnPnPZnE-TIPS (50 mg, 0.015 mmol) in THF (20 ml) under argon at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH2Cl2, dried over Na2SO4, and evaporated. The residue was chromatographed on silica gel using 8:2 hexanes:THF as the eluent. Yield = 43 mg (97%, based on 50 mg of TIPS-EPZnPnPZnE-TIPS). 1H NMR (400MHz, CDCl3 as 7.26 ppm): δ 10.26 (d, 4H, J = 4.4 Hz), 10.17 (d, 4H, J = 4.8), 9.71 (d, 4H, J = 4.4 Hz), 9.03 (d, 4H, J = 4.4 Hz), 8.92 (t, 8H, J = 4.4 Hz), 7.75 (t, 2H, J = 8.4 Hz), 7.73 (t, 4H, J = 8.4 Hz), 7.07 (d, 4H, J = 8.8 Hz), 7.05 (d, 8H, J = 8.4 Hz), 4.07 (s, 2H), 4.00 (t, 8H, J = 7.2 Hz), 3.96 (t, 16H, J = 7.2 Hz), 1.50-1.44 (m, 42H), 1.04 (t, 8H, J = 7.2 Hz), 0.93 (t, 16H, J = 7.2 Hz), 0.32 (s, 108 H). MALDI-TOF: m/z = 3004.52 (calculated for C176H200N12O12PtZn2 (M+H)+ 3001.45).
Figure 19: Synthesis of EPZnPPdPZnE. (a) Pd$_2$(dba)$_3$, AsPh$_3$, THF/i-Pr$_2$NH 9:1 mixture, 50 °C, 12 h, under argon; (b) Pd(OAc)$_2$, benzonitrile, 200 °C, 3 h, microwave reaction; (c) NBS, 0 °C, CH$_2$Cl$_2$:pyridine 20:1 mixture, 1.5 h, under argon; (d) (triisopropylsilyl)acetylene, Pd(PPh$_3$)$_2$Cl$_2$, CuI, THF/i-Pr$_2$NH 9:1 mixture, 60 °C, 16 h, under argon; (e) TBAF, THF, 0 °C, 10 min, under argon.

5,15-Bis[5′-[10′, 20′-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl]porphinato]zinc(II)ethynyl]-10,20-bis(2′,6′-bis(3,3-dimethyl-1-butyloxy)phenyl)porphyrin (PZnFbPZn). A 100 mL Schlenk flask equipped with a magnetic stirbar was charged with PZnE (400 mg, 0.42 mmol), BrFbBr (170 mg, 0.17 mmol), Pd$_2$(dba)$_3$ (38 mg, 0.042 mmol), and AsPh$_3$ (51 mg, 0.168 mmol). A solvent mixture of THF (50 mL) and diisopropylamine (5 ml) was degassed via five freeze-pump-thaw cycles, transferred to the reaction flask and stirred at 50 °C for 12 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was evaporated to dryness and the residue was sequentially purified by silica column chromatography.
using 6:4 hexanes:methylene chloride as the eluent, size exclusion column chromatography using THF as the eluent, and another silica column chromatographic step using 1:1 hexanes:methylene chloride as the eluent. Yield = 206 mg (44%, based on 170 mg of BrFbBr).

\(^1H\) NMR (400MHz, CDCl\(_3\) as 7.26 ppm): δ 10.42 (d, 4H, J = 4.4 Hz), 10.28 (d, 4H, J = 4.8), 10.10 (s, 2H), 9.28 (d, 4H, J = 4.4 Hz), 9.15 (d, 4H, J = 4.8 Hz), 9.00 (d, 4H, J = 4.4 Hz), 8.98 (d, 4H, J = 4.8 Hz), 7.78 (t, 2H, J = 8.4 Hz), 7.77 (t, 4H, J = 8.4), 7.09 (d, 4H, J = 8.8 Hz), 7.08 (d, 8H, J = 8.4 Hz), 4.04 (t, 8H, J = 7.2 Hz), 3.99 (t, 16H, J = 7.2 Hz), 0.93 (t, 16H, J = 7.2 Hz), 0.41 (s, 36H), 0.31 (s, 72H), -1.19 (s, 2H).

MALDI-TOF: m/z = 2757.64 (calculated for C\(_{172}\)H\(_{202}\)N\(_{12}\)O\(_{12}\)Zn\(_{2}\)(M+H\(^+\)) = 2760.34).

5,15-Bis[(5'-)[10', 20'-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethynyl]-[10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]palladium(II) (PZnPPdPZn). PZnFbPZn (65 mg, 0.024 mmol), palladium acetate (32 mg, 0.144 mmol) and a magnetic stirring bar were brought together into a 10 mL microwave reaction vial that was then sealed and charged with argon. These reagents were dissolved in 6 mL of benzonitrile solvent that was previously purged with argon for 1 h. The reaction vial was stirred at 200 °C for 3 h in a microwave irradiation cavity. After the reaction without removing the benzonitrile solvent, the reaction mixture was directly purified by silica column chromatography using 65:35 hexanes:methylene chloride as the eluent; the first brownish green band was collected as the desired product. This reaction was repeated for two additional times in
order to obtain material for subsequent synthetic steps. Yield = 134 mg (products from 3 reactions, 65%, based on 195 mg of the PZnFbPZn starting material). 1H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 10.39 (d, 4H, J = 4.4 Hz), 10.29 (d, 4H, J = 4.8), 10.11 (s, 2H), 9.28 (d, 4H, J = 4.4 Hz), 9.15 (d, 4H, J = 4.4 Hz), 9.00 (d, 4H, J = 4.4 Hz), 8.97 (d, 4H, J = 4.8 Hz), 7.76 (t, 6H, J = 8.8 Hz), 7.08 (d, 8H, J = 8.4 Hz), 7.07 (d, 4H, J = 8.8 Hz), 4.03 (t, 8H, J = 7.2 Hz), 3.98 (t, 16H, J = 7.2 Hz), 1.04 (t, 8H, J = 7.2 Hz), 0.93 (t, 16H, J = 7.2 Hz), 0.30 (s, 108H). MALDI-TOF: m/z = 2860.52 (calculated for C₁₇₂H₂₉₀N₁₂O₁₂PdZn²⁺ (M+H)⁺ 2864.74).

5,15-Bis[5'-[15'-bromo-10', 20'-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethynyl]-[10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]palladium(II) (BrPZnPPdPZnBr). In a 250 mL round bottom flask, PZnPPdPZn (120 mg, 0.042 mmol) was dissolved in methylene chloride (50 mL) and pyridine (5 mL). The reaction mixture was cooled to 0 °C and a solution of NBS (15 mg, 0.088 mmol) in methylene chloride (50 mL) was added via cannula. The reaction mixture was stirred at 0 °C under argon for 1.5 h and quenched by addition of H₂O (100 mL). The organic layer was separated and dried with anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography using 6:4 hexanes:methylene chloride as the eluent. Yield = 79 mg (62 %, based on 120 mg of the PZnPPdPZn starting material). 1H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 10.29 (d, 4H, J = 4.8 Hz), 10.25 (d, 4H, J = 4.8), 9.63 (d, 4H, J = 4.8 Hz), 9.03 (d, 4H, J = 4.8 Hz), 8.96 (d, 4H, J = 4.8 Hz), 8.88 (d, 4H, J = 4.8 Hz), 7.76 (t, 2H, J = 8.4 Hz), 7.75 (t, 4H, J = 8.4 Hz),
7.07 (d, 4H, J = 8.8 Hz), 7.06 (d, 8H, J = 8.8 Hz), 4.02 (t, 8H, J = 7.2 Hz), 3.98 (t, 16H, J = 7.2 Hz), 1.03 (t, 8H, J = 7.2 Hz), 0.92 (t, 16H, J = 7.2 Hz), 0.38 (s, 72H) , 0.30 (s, 36H). MALDI-TOF: m/z = 3018.26 (calculated for C\textsubscript{172}H\textsubscript{198}Br\textsubscript{2}N\textsubscript{2}O\textsubscript{12}PdZn\textsubscript{2}(M+H)\textsuperscript{+} 3022.54).

5,15-Bis[5'-[[15'-triisopropylsilylethynyl-10', 20'-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]ethynyl]-[10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinatopalladium(II) (TIPS-EPZnPdPZnE-TIPS). A 50 mL Schlenk flask equipped with a magnetic stirbar was charged with BrPZnPdPZnBr (70 mg, 0.023 mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (8.4 mg, 0.012 mmol), and CuI (2.3 mg, 0.012 mmol). A solvent mixture of THF (20 mL), diisopropylamine (2 ml) and (triisopropylsilyl)acetylene (52 µL, 0.23 mmol) was degassed via three-pump-thaw cycles, transferred to the reaction flask and stirred at 60 °C for 16 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was poured into water, extracted with CH\textsubscript{2}Cl\textsubscript{2}, dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated. The residue was purified by column chromatography using 1:1 hexanes: methylene chloride as the eluent. Yield = 54 mg (73%, based on 70 mg of BrPZnPdPZnBr). \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3} as 7.26 ppm): \delta 10.30 (d, 4H, J = 4.4 Hz), 10.24 (d, 4H, J = 4.8), 9.70 (d, 4H, J = 4.4 Hz), 9.04 (d, 4H, J = 4.4 Hz), 8.97 (d, 4H, J = 4.8 Hz), 8.91 (d, 4H, J = 4.4 Hz), 7.75 (t, 2H, J = 8.4 Hz), 7.74 (t, 4H, J = 8.4 Hz), 7.06 (d, 4H, J = 8.4 Hz), 7.05 (d, 8H, J = 8.8 Hz), 4.02 (t, 8H, J = 7.2 Hz), 3.98 (t, 16H, J = 7.2 Hz), 1.50-1.45 (m, 42H), 1.01 (t, 8H, J = 7.2 Hz), 0.90 (t, 16H, J = 7.2 Hz), 0.33
(s, 72H), 0.29 (s, 36H). MALDI-TOF: m/z = 3221.94 (calculated for C_{194}H_{240}N_{2}O_{12}Si_{2}PdZn_{2} (M+H)^{+} 3225.48).

5,15-Bis[5’-[[15’-ethynyl-10’, 20’-bis(3,5-di(3,3-dimethyl-1-
butyloxy)phenyl]porphinato]zinc(II)]ethynyl]-[10,20-bis(2’,6’-bis(3,3-dimethyl-1-
butyloxy)phenyl]porphinato]palladium(II) (EPZnPPdPZnE). Tetrabutylammonium fluoride (1 M in THF, 43 µL, 0.043 mmol) was added to a solution of TIPS-
EPZnPPdPZnE-TIPS (54 mg, 0.017 mmol) in THF (30 ml) under argon at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, and evaporated. The residue was chromatographed on silica gel using 8:2 hexanes:THF as the eluent. Yield = 46 mg (95%, based on 54 mg of TIPS-
EPZnPPdPZnE-TIPS). $^1$H NMR (400MHz, CDCl$_3$ as 7.26 ppm): δ 10.29 (d, 4H, J = 4.4 Hz), 10.22 (d, 4H, J = 4.8), 9.69 (d, 4H, J = 4.4 Hz), 9.03 (d, 4H, J = 4.4 Hz), 8.96 (d, 4H, J = 4.8 Hz), 8.92 (d, 4H, J = 4.4 Hz), 7.76 (t, 2H, J = 8.4 Hz), 7.75 (t, 4H, J = 8.4 Hz), 7.06 (d, 4H, J = 8.4 Hz), 7.05 (d, 8H, J = 8.8 Hz), 4.08 (s, 2H), 4.01 (t, 8H, J = 7.2 Hz), 3.97 (t, 16H, J = 7.2 Hz), 1.50-1.45 (m, 42H), 1.01 (t, 8H, J = 7.2 Hz), 0.91 (t, 16H, J = 7.2 Hz), 0.34 (s, 72H), 0.30 (s, 36H). MALDI-TOF: m/z = 2908.35 (calculated for C_{194}H_{240}N_{2}O_{12}Si_{2}PdZn_{2} (M+H)$^+$ 2912.79).
General Procedure for the Preparation of PyrRuPZnRuPyr,

PyrRuPZnRuPyr, and OsPZnOs. Bis(meso-ethynyl) ethyne-bridged oligo(porphinato)zinc(II) derivatives (EPzE, EPzE) and bis(terpyridyl)metal(II) complexes (PyrRuBr, OsBr) were placed in a Schlenk flask equipped with a magnetic stir bar. Pd(dba)$_3$ (0.3 eq., based on the (porphinato)zinc synthon) and AsPh$_3$ (2 eq., based on the (porphinato)zinc synthon) were added under nitrogen atmosphere. A solvent mixture of 6:3:1 HPLC grade MeCN:THF:triethylamine was degassed by a small stream of dry argon for approximately 2 h. Enough of this solvent mixture was added to the reaction vessel via cannula to completely dissolve all reactants, and the resulting solution was heated to 60 °C for 8 h. Consumption of all the starting materials was confirmed by thin layer chromatography (90:9:1 MeCN:H$_2$O:saturated aq. KNO$_3$ as eluent). The solution was then cooled to room temperature and evaporated. The crude product was purified by column chromatography using 90:9:1 MeCN:H$_2$O:sat. aq. KNO$_3$.
as eluent for PyrRuPZnRuPyr, PyrRuPZnPPdRuPyr, PyrRuPPPtRuPyr, and OsPZnOs, whereas for PyrRuPZnPPdPZnRuPyr and PyrRuPZnPPPtPZnRuPyr, 70:20:9:1 MeCN:THF:H₂O:sat. aq. KNO₃ was employed as the eluent; the respective products eluted as the second band, following a first, small quantity of homocoupled butadiyne-bridged side-product. The product fractions was concentrated, but not to dryness. Excess ammonium hexafluorophosphate was added, followed by enough water to cause the precipitation of a dark brown-green solid, which was isolated by filtration, and washed successively with water and diethyl ether. The products were then further purified through size exclusion column chromatography (Bio-beads SX-1 medium) using 1:1 acetone:THF as the eluent, followed by a short silica gel column chromatographic step using the corresponding solvent mixture as eluent (vide supra). Additional column chromatography was performed if the level of purity was unsatisfactory as assessed by NMR spectroscopy. Counterion metathesis was then exploited again to provide the corresponding bis(hexafluorophosphate) salts as the final products.

Bisruthenium(II) [(5,15-bis(4'-ethynyl-(2,2';6',2''-terpyridinyl))-10,20-bis(2',6'-bis(3,3-dimethyl-1-butoxy)phenyl)porphinato)zinc(II) [4'-pyrrolidin-1-yl-2',2'';6',2'''-terpyridine] tetrakis(hexafluorophosphate) (PyrRuPZnRuPyr). Reagents: EPZnE (68 mg, 0.070 mmol), PyrRuBr (176 mg, 0.0175 mmol), Pd₂(dba)₃ (19.2 mg, 0.021 mmol), and AsPh₃ (43 mg, 0.14 mmol). Reaction solvent: 40 mL of 6:3:1 MeCN:THF:triethylamine.
Isolated yield = 160 mg of Pyr\textsubscript{1}RuPZnRuPyr (81%, based on 68 mg of EPZnE). $^3$HNMR (400MHz, CD$_3$CN as 1.93 ppm): δ 9.77 (d, 4H, J = 4.4 Hz), 9.14 (s, 4H), 8.75 (d, 4H, J = 4.4 Hz), 8.58 (d, 4H, J = 8.0 Hz), 8.30 (d, 4H, J = 8.0 Hz), 7.84 (t, 4H, J = 7.0 Hz), 7.70-7.63 (m, 10H), 7.39 (d, 4H, J = 5.0 Hz), 7.21 (d, 4H, J = 5.0 Hz), 7.12 (t, 4H, J = 6.0 Hz), 6.99 (d, 4H, J = 8.5 Hz), 6.92 (t, 4H, J = 6.0 Hz), 3.83 (t, 8H, J = 7.0 Hz), 3.63 (s, 8H), 2.07 (s, 8H), 0.66 (t, 8H, J = 7.0 Hz), 0.03 (s, 36H). MALDI-TOF: m/z = 2675.37 (calculated for C$_{128}$H$_{122}$F$_{18}$N$_{18}$O$_4$P$_3$Ru$_2$Zn (M-PF$_6$) $^+$ 2678.92).

Figure 21: $^1$H NMR spectrum of Pyr\textsubscript{1}RuPZnRuPyr in CD$_3$CN solvent, residual solvent (CH$_2$Cl$_2$, MeCN, and THF) peaks are marked with “X”.

Bisruthenium(II) [1,2-bis[(5′-ethynyl-(2,2′,6′,2′′-terpyridinyl))-10,20-bis(2′,6′-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)ethyne] [4′-pyrrolidin-1-yl-2,2′;6′,2′′-terpyridine] tetrakis(hexafluorophosphate) (Pyr\textsubscript{1}RuPZn\textsubscript{2}RuPyr\textsubscript{1}). Reagents: EPZnE (100 mg, 0.052 mmol), Pyr\textsubscript{1}RuBr (115 mg, 0.114 mmol), Pd$_2$(dba)$_3$ (14.3 mg,
0.0156 mmol), and AsPh₃ (32 mg, 0.104 mmol). Reaction solvent: 40 mL of 6:3:1 MeCN:THF:triethylamine. Isolated yield = 125 mg (63%, based on 100 mg of EPZn₂).

¹HNMR (400MHz, CD₃CN as 1.93 ppm): δ 9.97 (d, 4H, J = 4.4 Hz), 9.72 (d, 4H, J = 4.4 Hz), 9.09 (s, 4H), 8.71 (d, 4H, J = 4.8 Hz), 8.68 (d, 4H, J = 4.8 Hz), 8.49 (d, 4H, J = 8.0 Hz), 8.21 (d, 4H, J = 8.0 Hz), 7.66 (t, 4H, J = 7.6 Hz), 7.61 (t, 4H, J = 8.4 Hz), 7.57 (s, 4H), 7.49 (t, 4H, J = 7.6 Hz), 7.32 (d, 4H, J = 4.8 Hz), 7.13 (d, 4H, J = 5.6 Hz), 6.99-6.94 (m, 12H), 6.72 (t, 4H, J = 6.4 Hz), 3.81 (t, 16H, J = 7.0 Hz), 3.46 (s, 8H), ~1.90 (s, 8H) (note that this peak is not observed in the NMR spectrum below as it is completely overlapped by the residual MeCN solvent peak), 0.65 (t, 16H, J = 7.0 Hz), 0.01 (s, 72H). MALDI-TOF: m/z = 3624.87 (calculated for C₁₈₆H₁₈₆F₁₈N₂₂O₈P₃Ru₂Zn₂ (M-PF₆)⁺ 3627.49).

Figure 22: ¹H NMR spectrum of PyrRuPZnRuPyr in CD₃CN solvent, residual solvent (CH₂Cl₂, MeCN, and THF) peaks are marked with “X”.

Bisosmium(II) [1,2-bis[5-(4'-ethynyl-(2,2',6',2''-terpyridinyl))-10,20-bis(2',6'-71
bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)zinc(II)ethyne] [2,2'6',2'"-terpyridine] tetrakis(hexafluorophosphate) (OsPZnOs). Reagent: EPZnE (46 mg, 0.0238 mmol), OsBr (61.5 mg, 0.06 mmol), Pd2(dba)3 (6.6 mg, 0.0072 mmol), and AsPh3 (14.7 mg, 0.048 mmol). Reaction solvent: 25 mL of 6:3:1 MeCN:THF:triethylamine as outlined in the above procedure. Yield = 75 mg (79% yield based on 46 mg of EPZnE).

^1H NMR (400 MHz, CD3CN as 1.93 ppm): 8 10.02 (d, 4H, J = 4.4 Hz), 9.76 (d, 4H, J = 4.4 Hz), 9.18 (s, 4H), 8.76 (d, 4H, J = 7.0 Hz), 8.74 (d, 4H, J = 7.0 Hz), 8.58 (d, 4H, J = 8.4 Hz), 8.52 (d, 4H, J = 8.4 Hz), 8.27 (d, 4H, J = 8.4 Hz), 7.75 (t, 2H, J = 8.4 Hz), 7.63 (t, 4H, J = 8.8 Hz), 7.58 (t, 4H, J = 7.8 Hz), 7.52 (t, 4H, J = 7.8 Hz), 7.19 (d, 4H, J = 6.0 Hz), 7.08 (d, 4H, J = 5.6 Hz), 7.01 (d, 8H, J = 8.8 Hz), 6.87 (q, 8H, J = 6.8 Hz), 3.85 (t, 16H, J = 8.8 Hz), 0.69 (t, 16H, J = 7.0 Hz), 0.04 (s, 72H). MALDI-TOF: m/z = 3665.53 (calculated for C178H174F18N2OsP3Os2Zn2 (M-PF6)^+ 3667.49).
Figure 23: $^1$H NMR spectrum of OsPZnOs in CD$_3$CN solvent, residual solvent (CH$_2$Cl$_2$, MeCN, and THF) peaks are marked with “X”.

Bisruthenium(II) [1,2-bis[(5-(4'-ethynyl-(2,2',6',2''-terpyridinyl))-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato)platinum(II)]ethyne] [4'-pyrrolidin-1-yl-2,2';6',2''-terpyridine] tetrakis(hexafluorophosphate) (Pyr$_1$RuP$_2$RuP$_1$), Reagents: EPP$_2$E (35 mg, 0.016 mmol), Pyr$_1$RuBr (40 mg, 0.04 mmol), Pd$_2$(dba)$_3$ (8.8 mg, 0.0096 mmol), and AsPh$_3$ (15 mg, 0.048 mmol). Reaction solvent: 20 mL of 6:3:1 MeCN:THF:triethylamine. Isolated yield = 38 mg (59%, based on 35 mg of EPZnE).

$^1$HNMR (400MHz, CD$_3$CN as 1.93 ppm): δ 9.88 (d, 4H, J = 4.8 Hz), 9.68 (d, 4H, J = 5.2 Hz), 9.10 (s, 4H), 8.68 (d, 4H, J = 5.2 Hz), 8.66 (d, 4H, J = 4.8 Hz), 8.50 (d, 4H, J = 8.0 Hz), 8.24 (d, 4H, J = 8.4 Hz), 7.74 (t, 4H, J = 7.6 Hz), 7.60 (s, 4H), 7.59 (t, 4H, J = 7.6 Hz), 7.53 (t, 4H, J = 8.4 Hz), 7.33 (d, 4H, J = 5.2 Hz), 7.13 (d, 4H, J = 5.6 Hz), 7.03 (t, 4H, J = 6.4 Hz), 6.88 (d,
8H, J = 8.4 Hz), 6.81 (t, 4H, J = 6.4 Hz), 3.76 (t, 16H, J = 6.4 Hz), 3.56 (t, 8H, J = 6.4 Hz), 2.00 (t, 8H, J = 6.4 Hz), 0.67 (t, 16H, J = 6.8 Hz), -0.141 (s, 72H). MALDI-TOF: m/z = 3889.14 (calculated for C₁₈₆H₁₈₈F₁₈₂O₃₈P₃Pt₂Ru₂ (M-PF₆)⁺ 3886.90).

Figure 24: ¹H NMR spectrum of Pyr₁RuPPt₂RuPyr₁ in CD₃CN solvent, residual solvent (CH₂Cl₂, MeCN, and THF) peaks are marked with “X”.

Bisruthenium(II) [5,15-bis[5’-ethynyl-[15’-(4’-ethynyl-(2,2′;6′,2′′-terpyridinyl))-10′, 20′-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]-[10,20-bis(2′,6′-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) [4’-pyrrolidin-1-yl-2,2′;6′,2′′-terpyridine] tetrakis(hexafluorophosphate) (Pyr₁RuPZnPpZnPpRuPyr₁).

Reagents: EPZnPpZnPpE (30 mg, 0.010 mmol), Pyr₁RuBr (26 mg, 0.025 mmol), Pd₂(dbA)₃ (5.5 mg, 0.006 mmol), and AsPh₃ (9.2 mg, 0.048 mmol). Reaction solvent: 15 mL of 6:3:1 MeCN:THF:triethylamine. Isolated yield = 30 mg (63%), based on 30 mg of
\textbf{EPZnPnPZnPZnE).} $^1$HNMR (400MHz, CD$_3$CN as 1.93 ppm): $\delta$ 9.94 (d, 4H, J = 4.4 Hz), 9.91 (d, 4H, J = 4.4 Hz), 9.76 (d, 4H, J = 4.4 Hz), 9.11 (s, 4H), 8.74 (d, 4H, J = 4.4 Hz), 8.69 (d, 4H, J = 4.4 Hz), 8.62 (d, 4H, J = 4.8 Hz), 8.51 (d, 4H, J = 8.0 Hz), 8.21 (d, 4H, J = 8.0 Hz), 7.70 (t, 4H, J = 7.6 Hz), 7.58 (t, 4H, J = 8.8 Hz), 7.56 (s, 4H), 7.49 (t, 2H, J = 8.8 Hz), 7.44 (t, 4H, J = 7.6 Hz), 7.36 (d, 4H, J = 5.6 Hz), 7.12 (d, 4H, J = 5.6 Hz), 6.98 (t, 4H, J = 6.4 Hz), 6.94 (d, 8H, J = 8.8 Hz), 6.82 (d, 4H, J = 8.8 Hz), 6.67 (t, 4H, J = 6.4 Hz), 3.77 (t, 4H, J = 5.6 Hz), 3.40 (s, 8H), 1.82 (s, 8H), 0.67-0.60 (m, 24H), 0.01 (s, 72H), -0.11 (s, 36).

MALDI-TOF: m/z = 4701.82 (calculated for C$_{244}$H$_{254}$F$_{18}$N$_{26}$O$_{12}$P$_3$PtRu$_2$Zn$_2$ (M-PF$_6$)$^+$ 4705.76).

\textbf{Figure 25:} $^1$H NMR spectrum of Pyr$\text{RuPnPnPZnPZnPyr}$ in CD$_3$CN solvent, residual solvent (CH$_2$Cl$_2$, MeCN, and THF) peaks are marked with “X”.

\textbf{Bisruthenium(II)} [5,15-bis[5'-ethynyl-[15'-(4'-ethynyl-(2,2';6',2''-terpyridinyl))]-10', 20'-bis(3,5-di(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II)]-[10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]palladium(II)] [4'-pyrrolidin-1-yl-
2,2’,6’,2’’-terpyridine| tetrakis(hexafluorophosphate) (Pyr\textsubscript{1}RuPZnPPdPZnRuPyr).

Reagents: EPZnPdPZnE (32 mg, 0.011 mmol), Pyr\textsubscript{1}RuBr (28 mg, 0.027 mmol), Pd\textsubscript{3}(dba)\textsubscript{3} (6.0 mg, 0.0066 mmol), and AsPh\textsubscript{3} (10.1 mg, 0.033 mmol). Reaction solvent: 15 mL of 6:3:1 MeCN:THF:triethylamine. Isolated yield = 28 mg (54%, based on 32 mg of EPZnPdPZnE). \textsuperscript{1}HNMR (400MHz, TMS as 0 ppm): δ 10.25 (d, 4H, J = 4.4 Hz), 10.23 (d, 4H, J = 4.4 Hz), 9.36 (d, 4H, J = 4.4 Hz), 8.98-8.94 (m, 12H), 8.78 (d, 4H, J = 8.0 Hz), 8.49 (d, 4H, J = 8.4 Hz), 8.02 (t, 4H, J = 7.2 Hz), 7.87-7.77 (m, 14H), 7.60 (d, 4H, J = 4.4 Hz), 7.41 (d, 4H, J = 4.4 Hz), 7.29 (t, 4H, J = 4.8 Hz), 7.22-7.16 (m, 12H), 7.05 (t, 4H, J = 4.8 Hz), 4.05 (t, 24H, J = 6.4 Hz), 3.76 (s, 8H), ~1.90 (s, 8H) (note that this peak is not observed in the NMR spectrum below as it is completely overlapped by the residual MeCN solvent peak), 0.90 (t, 24H, J = 6.4 Hz), 0.27 (s, 72H), 0.17 (s, 36). MALDI-TOF: m/z = 4619.68 (calculated for C\textsubscript{244}H\textsubscript{254}F\textsubscript{18}N\textsubscript{26}O\textsubscript{12}P\textsubscript{3}PdRu\textsubscript{2}Zn\textsubscript{2} (M-PF\textsubscript{6})\textsuperscript{+} 4617.10).
Figure 26: $^1$H NMR spectrum of PyrRuPZnPdPZnRuPyr in CD$_3$CN solvent, residual solvent (MeCN, THF, hexanes, and TMS) peaks are marked with “X”.

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2.4.3 Steady-State Emission Spectra

Experimental conditions. The emission spectroscopy of all \( M-(PM')_n-M \) and \( (PM)_n \) supermolecular species were investigated at ambient temperature under both deoxygenated and oxygenated conditions. Deoxygenation was achieved through three freeze-pump-thaw-degas cycles; corresponding oxygenated solutions were prepared by purging with air for 30 min. Multi-wavelength excitation was performed on all these chromophores to demonstrate that no excitation wavelength dependence existed in the experiments, and the optical density under all these excitation wavelengths was \( \leq 0.1 \).
Excitation spectra confirmed the authenticity of the emission peaks. Note that the emission spectra are provided separately in two wavelength regimes: starting point (normally between 650 and 700 nm) – 1000 nm and 950 nm – 1350 nm, due to the fact that detection was provided using a combination of a vis-NIR PMT (detection range: 200-1010 nm) and a NIR-PMT (detection range: 950-1700 nm).

**Proof of Concept Study – Photophysical Properties of PZnPttPZn.** As shown in Figure 52, PZnPttPZn demonstrates a Q transition maximum absorption centered at 708 nm that is significantly red-shifted (Δλ = 72 nm) when compared to the previous established PPt benchmark. The emission and nanosecond transient absorption spectroscopic experiments chronicled in Figures 33 and 45 demonstrate that PZnPttPZn i) possesses a low-lying triplet excited state as confirmed by the emission peak centered at 1083 nm that vanishes under experimental conditions that give rise to molecular oxygen triplet sensitization and subsequent singlet oxygen radiative deactivation (λem = 1270 nm) and ii) a triplet excited state lifetime of 3.96 µs. The triplet excited state dynamics of PZnPttPZn suggest the promise of the ruthenium-derived hybrid superstructure PyrRuPZnPttPZnRuPyr, for which a near-unity ISC with µs scale triplet excited state lifetime and a strong NIR absorptivity are anticipated.
Figure 28: (A) and (B): PyrRuPZnRuPyrr emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; note that while proper long-pass filters have been applied, 2nd order transmission is observed when exciting at 452 nm (this spectroscopic feature is also manifest in some of the emission spectra that follow below). (C) Excitation scanning spectra for PyrRuPZnRuPyrr; the emission peaks centered at 745 nm, 985 nm and 1270 nm are monitored. (D) Chemical structure of PyrRuPZnRuPyrr, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.

Solvent = acetonitrile; Ambient temperature.
Figure 29: (A) and (B): PyrRuPZnRuPyr emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; the panel B inset highlights the spectral window from 1200 nm to 1340 nm (containing *O$_2$ emission peak). (C) Excitation scanning spectra for PyrRuPZnRuPyr; the emission peaks centered at 810 nm and 1270 are monitored. (D) Chemical structure of PyrRuPZnRuPyr, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.

Figure 30: O$_2$(^1Δ) emission intensity comparison between PyrRuPZnRuPyr and PyrRuPZnRuPyr. Experimental conditions: ambient temperature; solvent =
acetonitrile; \( \lambda_{\text{exc}}(\text{Pyr}_1\text{RuPZnRuPyr}_1) = \lambda_{\text{exc}}(\text{Pyr}_1\text{RuPZnRuPyr}_1) = 525 \text{ nm (O.D } \sim 0.1 \text{ at 525 nm); samples were purged under air for } \sim 30 \text{ min. Note that as the Os}^1(\Delta) \text{ emission intensity is determined not only by the } \Phi_{\text{ISC}} \text{ of the sensitizer, but also by the sensitizer-to-oxygen triplet energy transfer efficiency, this Os}^1(\Delta) \text{ emission intensity comparison only qualitatively reflects relative Pyr}_1\text{RuPZnRuPyr}_1 \text{ and Pyr}_1\text{RuPZnRuPyr}_1 \text{ ISC efficiencies.}

Figure 31: (A) and (B): OsPZn\textsubscript{2}Os emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; note that the phosphorescence signal appears on the tail of the fluorescence in (B). (C) Excitation scanning spectra for OsPZn\textsubscript{2}Os; the emission peaks centered at 815 nm, 1065 nm, and 1273 nm are monitored. (D) Chemical structure of OsPZn\textsubscript{2}Os, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.
Figure 32: (A) and (B): Pyr₁RuP₂RuPyr₁ emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; note that based on the emission quenching behavior exhibited under oxygenated conditions, all the peaks in the spectra are assigned as phosphorescence (except for the one centered at ~806 nm due to 2nd order transmission from the excitation light source, and the one centered at ~1273 nm due to O₂(1Δ) emission). (C) Excitation scanning spectra for Pyr₁RuP₂RuPyr₁; the emission peaks centered at 680 nm, 850 nm, and 1273 nm are monitored. (D) Chemical structure of Pyr₁RuP₂RuPyr₁, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.
Figure 33: (A) and (B): PZnPrtPZn emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; note that phosphorescence appears on the tail of the fluorescence in (B). (C) Excitation scanning spectra for PZnPrtPZn; the emission peaks centered at 725 nm, 1085 nm, and 1273 nm are monitored. (D) Chemical structure of PZnPrtPZn, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.

Solvent = THF; Ambient Temperature.
Figure 34: (A) and (B): Pyr\textsubscript{1}RuPZnPPI\textsubscript{1}RuPyr\textsubscript{1} emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra; note that phosphorescence appears on the tail of the fluorescence in (B). (C) Excitation scanning spectra for Pyr\textsubscript{1}RuPZnPPI\textsubscript{1}RuPyr\textsubscript{1}; the emission peaks centered at 783 nm, 985 nm, and 1273 nm are monitored. (D) Chemical structure of Pyr\textsubscript{1}RuPZnPPI\textsubscript{1}RuPyr\textsubscript{1}, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.
Figure 35: (A) and (B): PZnPPdPZn emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra. (C) Excitation scanning spectra for PZnPPdPZn; the emission peaks centered at 760 nm, and 1273 nm are monitored. (D) Chemical structure of PZnPPdPZn, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.

Solvent = THF; Ambient Temperature.
Figure 36: (A), and (B): PyrRuPZnPdPZnRuPyr\textsubscript{1} emission spectra taken under deoxygenated and oxygenated conditions, with peak assignments marked in the spectra. (C) Excitation scanning spectra for PyrRuPZnPdPZnRuPyr\textsubscript{1}; the emission peaks centered at 810 nm, and 1270 nm are monitored. (D) Chemical structure of PyrRuPZnPdPZnRuPyr\textsubscript{1}, and general experimental conditions; R group denotes 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.
Figure 37: Fluorescence intensity comparison between Pyr:RuPZn:RuPyr₁, Pyr:RuPZnRuPyr, OsPZn:Os, Pyr:RuPZnPdRuPyr₁, and Pyr:RuPZnPdPZnRuPyr₁. Spectra recorded under ambient conditions and corrected for sample concentration; all chromophores here are excited at 525 nm (MLCT band) in acetonitrile solvent.

Figure 38: NIR photoluminescence spectra of Pyr:RuPZn:RuPyr₁, measured at low temperature (77K) and room temperature (298K). Experimental conditions: $\lambda_{\text{Exc}} = 525$ nm (MLCT band), solvent = butyronitrile; prior to these measurements, the sample was subject to three freeze-pump-thaw-degas cycles.
Figure 39: NIR photoluminescence spectra of PyrPZnPdPZnPyr, measured at low temperature (77K) and room temperature (298K). Experimental conditions: $\lambda_{\text{exc}} = 525$ nm (1MLCT band), solvent = butyronitrile; prior to these measurements, the sample was subject to three freeze-pump-thaw-degas cycles.

2.4.4 Picosecond Fluorescence Lifetime Data

The fluorescence lifetimes of all chromophores were measured in acetonitrile solvent under ambient conditions (note that the extremely weak fluorescence intensity and short S1 state lifetime of PyrRuPZnRuPyr precluded a fluorescence lifetime determination by the streak camera exploited here).
Figure 40: Picosecond timescale fluorescence decays determined for: (A) Pyr\textsubscript{1}RuPZn\textsubscript{2}RuPyr\textsubscript{1}, (B) OsPZn\textsubscript{2}Os, (C) Pyr\textsubscript{1}RuPZnPdPZnRuPyr\textsubscript{1}, and (D) Pyr\textsubscript{1}RuPZnPPtPZnRuPyr\textsubscript{1}. Instrument response function and fluorescence decay are plotted in black and red solid lines, respectively. Data fitting was accomplished with Gaussian-exponential convoluted functions. Experimental conditions: $\lambda_{\text{exc}} = 405$ nm, solvent = MeCN, ambient temperature.

2.4.5 Nanosecond-to-Microsecond Transient Absorption Data

Nanosecond-to-microsecond timescale transient absorption spectra for all chromophores were recorded using an air-free spectro-cell; prior to these measurements, all samples were subject to three freeze-pump-thaw-degas cycles. When necessary, sample oxygenation was achieved by purging with air for $\sim$30 min before
measurements. Kinetic data were fitted with single-exponential decay functions to acquire the triplet excited state lifetimes.

Figure 41: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for Pyr:RuPZn:RuPyr. Experimental conditions: $\lambda_{\text{exc}} = 525$ nm, pump power = 1.2 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 700 nm for Pyr:RuPZn:RuPyr under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 525$ nm, pump power = 1.2 mJ / pulse, solvent = MeCN, ambient temperature.

Figure 42: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for Pyr:RuPZn:RuPyr. Experimental conditions: $\lambda_{\text{exc}} = 585$ nm, pump power = 0.9 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 770 nm for Pyr:RuPZn:RuPyr under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 585$ nm, pump power = 0.9 mJ / pulse, solvent = MeCN, ambient temperature.
Figure 43: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for OsPZnOs. Experimental conditions: $\lambda_{\text{exc}} = 800$ nm, pump power = 0.5 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 780 nm for OsPZnOs under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 800$ nm, pump power = 0.5 mJ / pulse, solvent = MeCN, ambient temperature.

Figure 44: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for PyrRuPPP:RuPyrr. Experimental condition: $\lambda_{\text{exc}} = 515$ nm, pump power = 1.9 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 655 nm for PyrRuPPP:RuPyrr under deoxygenated and oxygenated condition, respectively. Experimental condition: $\lambda_{\text{exc}} = 515$ nm, pump power = 1.9 mJ / pulse, solvent = MeCN, ambient temperature.
Figure 45: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for PZnPPTZn. Experimental conditions: $\lambda_{\text{exc}} = 495$ nm, pump power = 1.8 mJ / pulse, solvent = THF, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 700 nm for PZnPPTZn under deoxygenated and oxygenated conditions, respectively. Experimental condition: $\lambda_{\text{exc}} = 495$ nm, pump power = 1.8 mJ / pulse, solvent = THF, ambient temperature.

Figure 46: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for PyrRuPZnPPTZnRuPyr. Experimental conditions: $\lambda_{\text{exc}} = 500$ nm, pump power = 2.1 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 745 nm for PyrRuPZnPPTZnRuPyr under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 500$ nm, pump power = 2.1 mJ / pulse, solvent = MeCN, ambient temperature.
Figure 47: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for PZnPdPZn. Experimental conditions: $\lambda_{\text{exc}} = 498$ nm, pump power = 2.2 mJ / pulse, solvent = THF, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 725 nm for PZnPdPZn under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 498$ nm, pump power = 2.2 mJ / pulse, solvent = THF, ambient temperature.

Figure 48: (A) Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays for PyrRuPZnPdPZnRuPyr. Experimental conditions: $\lambda_{\text{exc}} = 510$ nm, pump power = 1.5 mJ / pulse, solvent = MeCN, deoxygenated, ambient temperature. (B) Nanosecond-to-microsecond transient kinetic traces recorded at 770 nm for PyrRuPZnPdPZnRuPyr under deoxygenated and oxygenated conditions, respectively. Experimental conditions: $\lambda_{\text{exc}} = 510$ nm, pump power = 1.5 mJ / pulse, solvent = MeCN, ambient temperature.
2.4.6 Other Supplementary Spectroscopic Data

Figure 49: DADS of the NIR regime, revealing near-unit ISC processes and the torsional dynamics for Pyr1RuPZnRuPyr. The negative amplitude on the red side (900–1100 nm) accounts for $S_1 \rightarrow T_1$ ISC process (~0.8 ps) and torsional dynamics (~13 ps), respectively. On the blue side (780–900 nm), the 13 ps component displays zero amplitude, whereas the 0.8 ps component is positive, representing the $S_1$ state decay process. The long-lived component accounts for the decay of the evolved excited triplet states, which persists beyond the limit of the fs pump-probe delay limit.

Figure 50: DADS of NIR regime for Pyr1RuPZn2RuPyr. Four decay components are evident in this spectral region: a long-lived component that overlaps with the $T_1 \rightarrow T_n$ transition and represents the slow decay process of the excited triplet state; an $s$-like component with a time constant of ~0.8 ps that corresponds to the solvent dynamics; another $s$-like component with a time constant of ~190 ps that represents conformational relaxation the and $S_1 \rightarrow T_1$ ISC processes; the last component of ~590 ps that overlaps with the $S_1 \rightarrow S_n$ transition accounts for non-radiative or processes that depopulate the $S_1$ state.
Figure 51: DADS of the Q-band region for PyrRuPnP2RuPyr1. Due to excitation light scattering, the signal between 655 and 671 nm was removed from the spectra. Note that a component of ~52 ps is evinced that displays positive amplitude on the blue side and negative on the red side, resulting in spectra broadening and a slight blue shift of the Q-band bleach over this time domain. This component (52 ps) is also observed in the Q-band DADS of PyrRuPZnP2RuPyr1 and originates from conformational heterogeneity and spectral diffusion following photoexcitation.

Figure 52: Electronic absorption spectra of PZnPnPPtZn (blue solid line) and PZnPnPdPZn (red solid line). These spectra were recorded under ambient conditions in THF solvent. R group represents 2’6’-bis(3,3-dimethyl-1butyloxy)phenyl.

2.4.7 TD-DFT Calculations and Population Analyses

All calculations were performed upon structures with aliphatic chains truncated to methyl groups (Figure S32, molecular structures shown at the top of the figure). For
these oligo(porphinato)metal(II) species, $C_{2v}$ conformeric minima could be formulated. Ground-state structure optimizations were performed with Density Functional Theory (DFT) using Gaussian 09, Rev C.1. The Becke three-parameter hybrid and the Lee-Yang-Parr correlation functional were employed for all calculations (B3LYP). Optimizations were performed with minimal symmetry constraints using tight optimization criteria; initial optimizations used smaller basis sets but the final optimizations and TD-DFT calculations employed the 6-311g(d) basis set as implemented in Gaussian 09. TDDFT result files were post-processed using the GaussSum package; this software partitions the wavefunction amplitudes onto molecule fragments using Mulliken population analysis.

Figure 53: Molecular structures of oligo(porphinato)metal(II) and TD-DFT determined one-electron configurations depicted as arrows with percentages representing the major excitation’s contribution to the low-lying excited-state transition (marked as “*” in the middle spectral figures) for...
oligo(porphinato)metal(II) structures. TD-DFT predicted transitions and the corresponding oscillator strength are plotted with experimentally measured ground-state absorption for comparison (middle figures).

Table 4: Mulliken Population Analysis on PPt2.

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Table 5: Mulliken Population Analysis on PZn2.

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Table 6: Mulliken Population Analysis on PZnPttPZn.

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Table 7: Mulliken Population Analysis on PZnPdPZn.

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3. Near Infrared-to-Visible Photon Upconversion Enabled by Conjugated Porphyrinic Sensitizers under Low-Power Noncoherent Illumination

This work has been published in *The Journal of Physical Chemistry A* as an article.

Michael J. Therien and Felix N. Castellano conceived the project, supervised the execution of all the experiments, and contributed to writing the manuscript.

Jearn-Huber Olivier analyzed the spectroscopic data, and contributed to writing the manuscript.

Yusong Bai designed, synthesized and characterized all the sensitizer molecules, analyzed the ultrafast pump-probe spectroscopic data, contributed to writing the manuscript.

Hyejin Yoo performed the ultrafast pump-probe spectroscopic measurements on all the sensitizer molecules, analyzed the pump-probe spectroscopic data, and contributed to writing the manuscript.

Hyounsoo Uh performed the all photon upconversion related measurements, analyzed the associated data, and contributed to writing the manuscript.

3.1 Introduction

Near infrared (NIR) photon capture and the subsequent upconversion into visible light offers one possible strategy to exceed the Shockley-Queisser limit\textsuperscript{102} and improve solar photoconversion efficiencies.\textsuperscript{103-109} Whereas well-established upconversion methods including two-photon absorption, second harmonic generation, and sequential
multiphoton absorption require high intensity coherent light sources,\textsuperscript{110-113}

photochemical upconversion (UC) based on sensitized triplet-triplet annihilation (TTA) relies on single photon absorption events, representing a more ideal approach relevant for the capture and upconversion of terrestrial solar photons.\textsuperscript{114-122} In sensitized TTA (\textbf{Figure 54}), selective excitation of the sensitizer and subsequent intersystem crossing, followed by triplet-triplet energy transfer to the acceptor/annihilator species energizes these molecules for TTA and the desired annihilation-producing fluorescence.\textsuperscript{123} Beyond the development of molecular solution-based compositions, numerous groups have expended significant effort on producing host materials/media suitable to support photochemical upconversion,\textsuperscript{115, 124-140} being cognizant of applications reaching beyond solar energy conversion.\textsuperscript{141, 142} Of particular interest to both solar energy conversion and biological imaging, only a handful of NIR-absorbing chromophores have developed for NIR-to-vis photon upconversion;\textsuperscript{143-150} real world applications, however, will require development of long-wavelength sensitizers that feature significantly enhanced energetic and photophysical characteristics.\textsuperscript{103, 107, 123}
Figure 54: Qualitative Energy Level Diagram of the Sensitized Triplet-Triplet Annihilation Process between MPZn-based NIR sensitizers and rubrene.

Figure 55: Structure of supermolecular sensitizers PyrRuPZn₂, PyrRuPZnRuPyr₁, PyrRuPZn₂RuPyr₁, OsPZn₂Os, and the rubrene acceptor/annihilator.

The development of NIR-to-Vis TTA-UC compositions relies on molecular engineering of NIR sensitizers that possess the following attributes: (i) broad NIR spectral absorptivity, (ii) large NIR absorptive extinction coefficients (e.g., $\varepsilon > 5 \times 10^4$ M$^{-1}$...
in order to be relevant for thin film devices or as a component of a thin absorptive layer interfaced to a classical semiconductor photovoltaic), (iii) singlet-triplet ISC quantum yields that approach unity, and (iv) a long-lived lowest energy triplet excited state ($\tau_{\text{triplet}} > \mu$s) energetically poised for exergonic energy transfer to the molecular annihilator. In this regard, molecular constructs composed by (porphinato)zinc(II) (PZn) and (polypyridyl)metal (M) units bridged via an ethyne connectivity (MPZn supermolecules)$^{148, 151-155}$ stand as valuable sensitizer chromophores for NIR-to-vis photon upconversion based on TTA photochemistry due to the uncommon features of their electronically excited states. In these supermolecular systems, extensive excited state interpigment electronic interaction between M and PZn subunits redistribute PZn- and (polypyridyl)metal-derived absorptive oscillator strength broadly over the UV-vis-NIR spectral domain.$^{148, 151-162}$ Furthermore, after photoexcitation, the initially prepared singlet excited states of these chromophores undergo ultrafast ISC to $T_1$ states for which $\tau_{\text{triplet}} \geq \mu$s. In this contribution, we report four supermolecular chromophores based on MPZn constructs (Figure 55: Pyr$^1$RuPZn$_2$, Pyr$^1$RuPZnRuPyr, Pyr$^1$RuPZn$^2$RuPyr, and OsPZn:Os) that fulfill critical sensitizer requirements for NIR-to-vis TTA-UC photochemistry. We show that these compositions, used in combination with low-power non-coherent NIR light activation and the high emission quantum yield rubrene acceptor/annihilator, drive NIR-to-visible upconverted fluorescence centered in a
spectral window within the bandgap of amorphous silicon\textsuperscript{106} and many other semiconducting photovoltaics and catalysts.\textsuperscript{104, 105, 109, 136}

### 3.2 Results and Discussion

As steady state phosphorescence for these chromophores is not observed at ambient temperature, nanosecond laser flash photolysis was utilized to measure the Stern-Volmer ($K_{sv}$) and bimolecular ($k_q$) quenching constants for the deactivation of these triplet sensitizers by rubrene. The magnitudes of these $K_{sv}$ and $k_q$ values provide a qualitative indication of the exoergicity of triplet energy transfer between the $^3$\textsuperscript{sensitizer}\textsuperscript{*} and rubrene. These supermolecular chromophores evince $K_{sv}$ values that range from 190 to 4600 M\textsuperscript{-1} \textbf{OsPZn:Os} ($K_{sv} = 190$ M\textsuperscript{-1}); \textbf{Pyr:RuPZn}\textsubscript{2} ($K_{sv} = 3300$ M\textsuperscript{-1}); \textbf{Pyr:RuPZn:RuPyr}\textsubscript{1} ($K_{sv} = 4400$ M\textsuperscript{-1}); \textbf{Pyr:RuPZn:RuPyr}\textsubscript{1} ($K_{sv} = 4600$ M\textsuperscript{-1}); Section 3.4] and measured $k_q$ values that span $1.9-4.2 \times 10^8$ M\textsuperscript{-1}s\textsuperscript{-1} (Figures 58–61). Note that the \textbf{Pyr:RuPZn:RuPyr}\textsubscript{1} chromophore possesses the highest $K_{sv}$ value in this series, congruent with its near-quantitative ISC quantum yield and long-lived triplet excited state ($\tau_T = 11.1$ $\mu$s); note that the $K_{sv}$ and $\tau_T$ values determined for this supermolecular chromophore exceed by $\sim$25-fold the analogous values determined for \textbf{OsPZn:Os}. Given the modest triplet lifetime of \textbf{OsPZn:Os} (400 ns), this chromophore was not further evaluated for its potential utility in NIR-to-vis TTA-UC.
Figure 56: Upconversion quantum yields measured as a function of 680 nm incident power density for A) the Pyr\textsubscript{1}RuPZn\textsubscript{2}-rubrene upconversion composition in degassed MTHF. \([\text{Pyr}_1\text{RuPZn}_2] = 2.8 \times 10^{-6} \text{ M}, [\text{rubrene}] = 3.0 \times 10^{-3} \text{ M}\) and B) the Pyr\textsubscript{1}RuPZnRuPyr\textsubscript{1}-rubrene upconversion composition in degassed 1:1 acetonitrile:toluene. \([\text{Pyr}_1\text{RuPZnRuPyr}_1] = 8.6 \times 10^{-7} \text{ M}, [\text{rubrene}] = 2.0 \times 10^{-3} \text{ M}\).

Examination of the upconversion sensitization properties of the Pyr\textsubscript{1}RuPZn\textsubscript{2}, Pyr\textsubscript{1}RuPZnRuPyr\textsubscript{1}, and Pyr\textsubscript{1}RuPZnRuPyr\textsubscript{1} chromophores used in conjunction with the rubrene acceptor/annihilator under NIR laser excitation conditions yielded fluorescence and dynamical data in the visible consistent with sensitized triplet-triplet annihilation, exhibiting characteristic weak and strong annihilation kinetic limits, Figures 62-63.\textsuperscript{123,137} Unfortunately, solubility limitations of these sensitizers in non-polar solvents along with that of rubrene in polar solvents required the use of a mixed solvent system for all UC experiments. Therefore, ideal concentrations of both sensitizer and annihilator could not be achieved in these compositions and the maximal observed UC quantum yields in the strong annihilation regime merely represent lower limits, with Pyr\textsubscript{1}RuPZn\textsubscript{2}/rubrene being the largest at 6.6\% (Figures 56 and 64). In order to evaluate the compatibility of these RuPZn-based supermolecular upconversion compositions for terrestrial solar
photon capture, non-coherent excitation was utilized; the corresponding double logarithmic plots of the upconversion emission signals in the yellow measured as a function of the incident power density from a Xe lamp/monochromator light source are presented in Figure 57. Note that in these studies, the excitation wavelength corresponded to the respective sensitizer NIR absorption maximum. It is critical to emphasize that while accessing the optically saturated linear regime is important from a mechanistic determination standpoint, it is not a prerequisite for formulating UC compositions intended for real-world applications. For example, sub-bandgap sensitization of WO₃ photoanodes in a prototypical water splitting photoelectrochemical cell was shown to function effectively under low non-coherent light flux.¹⁰⁹

While the TTA-UC compositions highlighted in Figure 57 are stationed in the weak annihilation limit as manifested by the quadric dependence of upconversion emission intensity upon power density (slope = 2.0), note that low power non-coherent illumination (> 1 mW cm⁻²) readily gives rise to fluorescence upconversion at power densities well below that of terrestrial solar photon illumination conditions. These \textit{PyrRuPZn₂, PyrRuPZnRuPyr,} and \textit{PyrRuPZnRuPyr;} sensitizers used in combination with rubrene acceptors/annihilators represent the first examples whereby low-power non-coherent NIR light stimulation achieves NIR-to-visible upconversion centered in a spectral window within the bandgap of amorphous silicon as well as many other semiconductor photovoltaics.
Figure 57: Double logarithmic plots of the upconverted emission generated from selective excitation of supermolecular NIR Sensitizers PyrRuPZn₂, PyrRuPZnPyr, and PyrRuPZnPyr₁ in presence of rubrene annihilator/acceptor rubrene in vacuum degassed solvents at RT measured as a function of excitation power density. Experimental conditions: λ<sub>ex</sub> = 740 ± 10 nm for PyrRuPZn₂ (black); 710 ± 10 nm for PyrRuPZnPyr (red); 760 ± 10 nm for PyrRuPZnPyr₁ (green). [PyrRuPZn] = 40 µM; [PyrRuPZnPyr] = 14 µM; [PyrRuPZnPyr₁] = 10 µM; [rubrene] = 2.0-3.0 mM. Upconverted emission at 590 ± 15 nm was recorded for 60 seconds and averaged. Inset shows the upconverted emission spectrum of rubrene.

3.3 Conclusion

Summarizing, we report four supermolecular chromophores based on (porphinato)zinc(II) (PZn) and (polypyridyl)metal (M) units bridged via ethyne connectivity (Chart 1: PyrRuPZn₂, PyrRuPZnPyr, PyrRuPZnPyr₁, and OsPZn₂Os) that fulfill critical sensitizer requirements for NIR-to-vis TTA-UC photochemistry. These NIR sensitizers feature: (i) broad, high oscillator strength NIR absorptivity (700 nm < λ<sub>max</sub> (NIR) < 770 nm; 6 × 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup> < extinction coefficient (λ<sub>max</sub> (NIR))
<1.6 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}; 820 \text{ cm}^{-1} < \text{FWHM} < 1700 \text{ cm}^{-1}), (ii) and substantial intersystem
crossing quantum yields, (iii) long, $\mu$s timescale $T_1$ state lifetimes, and (iv) triplet states
that are energetically poised for exergonic energy transfer to the molecular annihilator
(rubrene). Using a coherent light source and NIR excitation, these chromophores enable
the strong annihilation regime to be readily accessed where the photochemical
upconversion process is kinetically limited by the $^3\text{annihilator^*}$ decay rate, and
demonstrate the ability to achieve substantial anti-Stokes energy gain (0.5 eV) via TTA-UC. Using low power non-coherent illumination at power densities (1 to 10 mWcm$^{-2}$)
similar to that of terrestrial solar photon illumination conditions, we demonstrate that
Py$_r$RuPZ$_n$, Py$_r$RuPZ$_n$:Ru$_p$Y$_r$, and Py$_r$RuPZ$_n$Ru$_p$Y$_r$ sensitizers can be used in
combination with the rubrene acceptor/annihilator to achieve TTA-UC: these studies
represent the first examples whereby a low-power non-coherent NIR light source drives
NIR-to-visible upconverted fluorescence centered in a spectral window within the
bandgap of amorphous silicon. We posit that this class of supermolecular chromophores
offers exceptional promise to further enhance the harvesting of sub-bandgap NIR
photons that are not captured by conventional solid-state semiconductor materials, and
facilitate their subsequent upconversion to light of wavelengths suitable for capture by
commercial photovoltaic devices.
3.4 Methods and Supplementary Figures

Spectroscopic Measurements on Upconversion Samples. All luminescence samples were prepared in a specially designed 1 cm$^2$ quartz optical cell with a side arm round-bottomed flask and degassed with a minimum of three freeze-pump-thaw cycles. Static absorption spectra were measured with an 8453 diode array spectrophotometer (Agilent). Steady-state photoluminescence spectra were recorded using either a FLS-920 or FLS-980 fluorescence spectrophotometer (Edinburgh Instruments). A Ti:Sapphire oscillator, Chameleon Ultra II (Coherent) was utilized as the excitation light source which provided tunable photons (690-800 nm) at a repetition rate of 80 MHz (nJ pulse energies), considered here as a continuous wave photon source. Incident laser power was varied using a series of neutral density filters. The incident laser power was measured using either a Power Max 5200 power meter (Molelectron) or a Nova II/PD300-UV power meter (Ophir).

Upconversion Quantum Yield Measurements. The sensitized upconverted fluorescence quantum yield measurements of rubrene in 1:1 acetonitrile:toluene were measured relative to [Os(phen)$_3$](PF$_6$)$_2$ in acetonitrile using 690 nm excitation, measured under identical conditions utilizing Eq. 1,

$$\Phi_{UC} = 2\Phi_{std} \left( \frac{A_{std}}{A_{UC}} \right) \left( \frac{I_{UC}}{I_{std}} \right) \left( \frac{\eta_{UC}}{\eta_{std}} \right)^2$$

(3.4.1)

where $\Phi_{uc}$, $A_{uc}$, $I_{uc}$ and $\eta_{uc}$ represents the quantum yield, absorbance, integrated photoluminescence intensity, and refractive index of the upconversion sample at the
excitation wavelength. No corrections were made for the small differences in refractive index between the sample and standard. The corresponding terms for the subscript “std” is for the reference quantum counter at the corresponding excitation wavelength. The quantum yield standard was [Os(phen)$_3$(PF$_6$)$_2$ in acetonitrile, whose $\Phi_{std} = 0.03 \pm 0.002$, determined using an absolute photoluminescence quantum yield system (Hamamatsu, C11347). The integrated intensity of the upconverted fluorescence was analyzed over the 500-680 nm spectral regime while that of [Os(phen)$_3$(PF$_6$)$_2$ was analyzed over 600-850 nm. Quantum yield values reported herein represent an average of at least two independent measurements. Even though the emission profile of the standard sample does not overlap the upconverted photoluminescence evident at shorter wavelengths, note that the experimentally determined quantum yields were reproducible using this relative actinometric method.

**Stern-Volmer Quenching.** Transient absorption decays were collected with an LP 920 laser flash photolysis system from Edinburgh Instruments. The pump excitation source was a Vibrant LD 355 II Nd:YAG/OPO nanosecond laser system from OPOTEK. Absorption transients of the NIR supermolecular sensitizers in the presence and absence of rubrene were collected with both PMT and InGaAs detectors and fit with single exponential functions using either IGOR Pro 6 or Origin Pro 9.0. The Stern-Volmer ($K_{SV}$) and the bimolecular quenching constants ($k_a$) for rubrene triplet sensitization were obtained according to the dynamic Stern-Volmer relation, $\tau_0/\tau = 1 + K_{SV}[Q]$, where $\tau_0$ and
τ are lifetimes of sensitizers in the absence or presence of the quencher, respectively. $K_{SV}$ is the Stern-Volmer constant, $K_{SV} = k_q \tau_0$, and [Q] is the molar concentration of the rubrene quencher present in the solution.

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q]$$

$$K_{SV} = k_q \tau_0$$

Figure 58: Dynamic Stern-Volmer plot of Pyr1RuPZn2 triplet excited state quenching by rubrene in MTHF. Changes in the Pyr1RuPZn2 lifetime were ascertained by first-order analysis of the transient absorption kinetics, $\lambda_{ex} = 700$ nm.
Figure 59: Dynamic Stern-Volmer analysis of Pyr:RuPZnRuPyr triplet excited state quenching by rubrene in deaerated 1:1 acetonitrile:toluene. Changes in the Pyr:RuPZnRuPyr lifetime were ascertained by first-order analysis of the transient absorption kinetics monitored at 1010 nm, $\lambda_{ex} = 530$ nm. The inset presents the kinetic transients used in the Stern-Volmer analysis.

Figure 60: Stern-Volmer plot of Pyr:RuPZn:RuPyr triplet excited state quenching by rubrene in deaerated 1:1 acetonitrile:toluene. Changes in the Pyr:RuPZn:RuPyr lifetime were ascertained by first-order analysis of the transient absorption kinetics, $\lambda_{ex} = 700$ nm.
Figure 61: Stern-Volmer plot of OsPZn2Os triplet excited state quenching by rubrene in deaerated 1:1 acetonitrile:toluene. Changes in the OsPZn2Os lifetime were ascertained by first-order analysis of the transient absorption kinetics, $\lambda_{\text{ex}} = 710$ nm.

Figure 62: Double logarithmic plot of the upconverted emission generated from selective excitation of the PyrRuPZn2 supermolecular sensitizer in the presence of the rubrene annihilator/acceptor in vacuum degassed MTHF at RT measured as a function of incident laser fluence, $\lambda_{\text{ex}} = 770$ nm. $[\text{PyrRuPZn}_2] = 17 \, \mu\text{M}$, $[\text{rubrene}] = 3.0 \times 10^{-10}$ M.
mM. Inset: upconversion emission profile of rubrene displayed as a function of excitation power density.

Figure 63: Double logarithmic plots of the upconverted emission generated from selective excitation of the Pyr\textsubscript{1}RuPZnRuPyr\textsubscript{1} (A) and Pyr\textsubscript{1}RuPZnRuPyr\textsubscript{1} supermolecular sensitizers (B) in the presence of the rubrene annihilator/acceptor in vacuum degassed MTHF at RT measured as a function of incident laser fluence.
Figure 64: Upconversion quantum yields measured as a function of 680 nm incident power density for the Pyr$_1$RuPZnRuPyr$_1$-rubrene upconversion composition in degassed 1:1 acetonitrile:toluene. [Pyr$_1$RuPZnRuPyr$_1$] = 8.6 \times 10^{-7} \text{ M}, [\text{rubrene}] = 2.0 \times 10^{-3} \text{ M}.
4. Controlling the Excited-State Dynamics of Low Band Gap, Near-Infrared Absorbers via Proquinoidal Unit Electronic Structural Modulation

This work has been published in Chemical Science as an article.

Michael J. Therien conceived the project, supervised the execution of all experiments, and contributed to writing the manuscript.

Yusong Bai designed, synthesized and characterized all the supermolecular structures, took the steady-state and ultrafast spectroscopic measurements, analyzed the spectroscopic data, performed the computational analyses, and contributed to writing the manuscript.

Jeff Rawson contributed to the molecular design and synthesis, performed part of the computational analyses, contributed to writing the manuscript.

Sean A. Roget measured the fluorescence quantum yields from most of the supermolecular structures.

Jean-Hubert Olivier contributed to writing the manuscript.

Jiaxing Lin, Peng Zhang, and David N. Beratan contributed to performing the computational analyses and writing the manuscript.

4.1 Introduction

Low optical bandgap π-conjugated polymers and molecules have fueled spectacular developments in optical and optoelectronic technologies.\(^{15, 164-167}\) A common strategy to realize polymer bandgap reduction relies on augmenting the π-backbone
quinoidal character. Introduction of so-called proquinoidal units into the conjugation main chain drives well understood perturbations to the ground-state electronic absorption spectrum, where augmented proquinoidal character diminishes both the optical (E_{op}; E_{1/2}^{0/0} – E_{1/2}^{-0/0}) band gaps of the material.\textsuperscript{168-177} In contrast to the ground-state absorptive and electronic structural control enabled by proquinoidal motifs,\textsuperscript{170, 171, 174-178} considerably less insight exists concerning the impact of proquinoidal character on excited-state relaxation pathways and dynamics of extensively π-conjugated molecules and materials.

Control over the excited-state relaxation dynamics of highly conjugated NIR-absorbing materials would broadly boost their broad utility for optical and optoelectronic applications. For instance, long-wavelength optical power limiting (OPL) relies upon reverse-saturable absorption, demanding materials whose photoexcitation is followed by rapid intersystem crossing (ISC) with near-unit quantum yield to a long-lived triplet excited state.\textsuperscript{15, 84, 179} Triplet-triplet annihilation photon-upconversion (TTA-UC), which has applications that include solar energy harvesting, places a premium on enhancing near-infrared (NIR) absorptive oscillator strength and engineering ultrafast ISC.\textsuperscript{18-20} In contrast, deep tissue-penetrating \textit{in vivo} imaging requires extending the absorptive and emissive wavelengths of NIR fluorophores while maintaining large $S_1 \rightarrow S_0$ transition dipole moments.\textsuperscript{167, 180-182} Advancing these applications motivates the
development of design approaches to regulate the natures of initially prepared photo-
excited states and the subsequent relaxation dynamics of long-wavelength absorbers.

Here, we combine molecular design and synthesis, time-resolved spectroscopic
methods, and quantum chemical analyses to delineate the excited-state properties of a
series of model highly conjugated NIR-absorbing chromophores based on
(porphinato)metal(II)-spacer-(porphinato)metal(II) (PM-Sp-PM) structural motif170 in
which: the porphyrin ligand is either electron rich (10,20-diarylporphyrin, ArP) or
electron deficient (10,15,20-tris(perfluoroalkyl)porphyrin, Rf3P), the central metal ion is
Zn(II) or Pt(II), and the proquinoidal Sp is either 4,7-diethynylbenzo[c][1,2,5]thiadiazole
(E-BTD-E) or 4,9-diethynyl-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (E-TDQ-E).
Steady-state absorption, emission, and pump-probe transient absorption spectroscopic
experiments, and time-dependent density functional theory (TD-DFT) computational
studies, unambiguously correlate the extent of configuration interaction (CI) and charge
transfer (CT) character of the initially prepared excited state with the relative
magnitudes of \( S_1 \rightarrow S_0 \) radiative \( (k_r) \), \( S_1 \rightarrow T_1 \) intersystem crossing \( (k_{ISC}) \), and \( S_1 \rightarrow S_0 \) internal
conversion \( (k_{IC}) \) rate constants. Collectively, these studies demonstrate how electronic
modulation of proquinoidal conjugation motifs, conventionally utilized to regulate the
ground-state absorptivity of low optical bandgap \( \pi \)-conjugated polymers and molecules,
can also be exploited to steer their excited state relaxation pathways. This work: (i)
underscores how modulation of the extent of excited-state CI for conjugation motifs that
rely on proquinoidal units can produce either exceptional NIR fluorophores or chromophores that generate long-lived electronically excited state triplets at high quantum yield, and (ii) describes a roadmap via which the relative magnitudes of $k_r$, $k_{ISC}$, and $k_{IC}$ rate constants may engineered to tightly control photophysical function of highly conjugated NIR-absorbing materials.

4.2 Results and Discussion

4.2.1 Synthesis

Figure 64 outlines the synthetic strategies for the PM-Sp-PM species, including ArPM-Sp-ArPM [M = Zn(II), Pt(II); Sp = E-TDQ-E, E-BTD-E], Rf3PZnE-TDQ-ERf3PZn, and Rf3PZnArPPtE-TDQ-ERf3PZnArPPt. Generally, the desired PM-Sp-PM supermolecular chromophores were prepared by the metal-mediated cross-coupling\(^{59,63,183,184}\) of a mono meso-ethyne-functionalized (porphinato)metal(II) species with a dibrominated proquinoidal spacer moiety (Figure 65). The key precursor compound Rf3PZnArPPtE was prepared via Pd\(^{0}\)-mediated coupling reaction involving Rf3PZnE and BrArPPtETIPS, followed by deprotection of the triisopropylsilyl group.

Chromophores featuring ArPM-Sp-ArPM molecular structures were isolated via column chromatography on silica using 2:3 CHCl\(_3\):hexanes as the eluent, while for chromophores containing the Rf3PZn fragment, 3:7 THF:hexanes was employed due to their solubility in this mobile phase. Size exclusion column chromatography with THF eluent was employed for purification of each chromophore after silica column
chromatography. Figure 66 displays the chemical structures for previously established oligo(porphinato)metal(II) compounds\textsuperscript{38, 39, 53, 67, 95} that define key spectroscopic benchmarks for these newly designed PM-Sp-PM chromophores.

Figure 65: Synthetic routes and chemical structures for PM-Sp-PM compounds.

Figure 66: Chemical structures for previously established oligo(Porphinato)metal(II) chromophores.

4.2.2 Steady-State Absorption and Emission Spectroscopy of ArPM-Sp-ArPM Chromophores

Steady-state electronic absorption and fluorescence spectra recorded for ArPM-Sp-ArPM species (ArPZnE-BTD-EArPZn,\textsuperscript{170} ArPZnE-TDQ-EArPZn,\textsuperscript{170} ArPpE-BTD-EArPp, and ArPpE-TDQ-EArPp) are displayed in Figure 67. The gross features of the electronic absorption spectra for these complexes resemble those of dimeric and multimeric porphyrin compounds that feature a meso-to-meso ethyne-linkage topology
(PZnₙ compounds), manifesting two distinct absorption manifolds that are derived from the porphyrin B- (Soret) (S₀→S₂) and Q-band (S₀→S₁) transitions. Previous investigations have demonstrated that Sp moieties modulate the respective ArPZn-Sp-ArPZn long axis-polarized Q state (Qₓ) absorption maxima from 689 to 1006 nm, depending upon the extent of the quinoidal resonance contribution to the electronically excited singlet state. Further, semi-empirical electronic structure calculations and electrochemical data underscored the cardinal role that ArPZn and Sp fragment orbital energy differences played in fixing the radical cation and anion state energy levels in these ArPZn-Sp-ArPZn structures.

A comparison of the Q-band regions in the electronic absorption spectra of ArPZnE-BTD-EArPZn, ArPZnE-TDQ-EArPZn, ArPPtE-BTD-EArPPt, and ArPPtE-TDQ-EArPPt reveals discrete effects correlated with the choice of spacer and (porphinato)metal(II) units. Compared with ArPME-BTD-EArPM, the ArPME-TDQ-EArPM analogues evince dramatically red-shifted Qₓ-state absorption maxima and substantial oscillator strength (f) redistribution into the low-energy spectral domain [Compound (λₘₐₓ(S₀→S₁), f₆₀₀-₁₀₀₀ nm): ArPZnE-BTD-EArPZn (689 nm, 0.455), ArPPtE-BTD-EArPPt (603 nm, 0.168), ArPZnE-TDQ-EArPZn (839 nm, 0.827), ArPPtE-TDQ-EArPPt (715 nm, 0.686); Table 8]. Furthermore, the Qₓ-state absorption manifolds of ArPME-TDQ-EArPM species manifest much broader full width at half maxima (FWHM) and less discernable vibrational structures relative to those evinced by ArPME-
BTD-EArPM chromophores \[Q_x (\text{FWHM})\]: ArPME-TDQ-EArPM \(\sim 2500 \text{ cm}^{-1}\); ArPME-BTD-EArPM \(\sim 1100 \text{ cm}^{-1}\), suggesting that the TDQ-containing chromophores give rise to \(S_1\) states with greater CT character.\(^{170,6,185,186}\) Compared to ArPZn-Sp-ArPZn compounds, the ArPPt-Sp-ArPPt chromophores display blue-shifted \(Q_x\)-state transition manifold maxima; this phenomenon is typical of hypso porphyrin species and has been attributed to the efficient mixing of metal nd- and porphyrin \(\pi^*\) orbitals.\(^{65-67,187}\)

**Figure 67:** Steady-state electronic absorption and emission spectra for: (A) ArPZnE-TDQ-EArPZn (blue colored lines, \(\lambda_{\text{exc}} = 750 \text{ nm for emission}\)) and ArPZnE-BTD-EArPZn (red colored lines, \(\lambda_{\text{exc}} = 640 \text{ nm for emission}\)); and (B) ArPPtE-TDQ-EArPPt (blue colored lines, \(\lambda_{\text{exc}} = 650 \text{ nm for emission}\)) and ArPPtE-BTD-EArPPt (red colored lines, \(\lambda_{\text{exc}} = 540 \text{ nm for emission}\)). Steady-state spectra were all acquired in THF solvent at ambient condition. Ar = 2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl.
Table 8: Steady-State Absorption and Emission Data for PM-Sp-PM.

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>$\lambda_{\text{max}}$ / nm (FWHM / cm$^{-1}$)</th>
<th>Stokes Shift / cm$^{-1}$</th>
<th>Oscillator Strength in Red-to-NIR $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArPZnE-TDQ-EArPZn</td>
<td>$S_0 \rightarrow S_1$ 839 (2510) $S_1 \rightarrow S_0$ 995 (1778)</td>
<td>1869</td>
<td>0.827</td>
</tr>
<tr>
<td>ArPZnE-BTD-EArPZn</td>
<td>689 (1180) 741 (1382)</td>
<td>1019</td>
<td>0.455</td>
</tr>
<tr>
<td>ArPPtE-TDQ-EArPPt</td>
<td>715 (2415) 810 (1530)</td>
<td>1640</td>
<td>0.686</td>
</tr>
<tr>
<td>ArPPtE-BTD-EArPPt</td>
<td>603 (1061) 629 (1579)</td>
<td>686</td>
<td>0.168</td>
</tr>
<tr>
<td>Rf$_3$PZnE-TDQ-ERf$_3$PZn</td>
<td>705 (1163) 750 (1370)</td>
<td>851</td>
<td>0.451</td>
</tr>
<tr>
<td>Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn</td>
<td>755 (1738) 813 (1432)</td>
<td>945</td>
<td>1.809</td>
</tr>
</tbody>
</table>

$^a$ Stokes shift corresponds to the energy difference between the low-energy transition ($Q_x$) absorption and fluorescence maxima. $^b$ Integrated oscillator strengths ($f$) were calculated based on the following expression: $f = 4.3 \times 10^9 \int \varepsilon \, dv$, where $\varepsilon$ is the experimental extinction coefficient, and $\nu$ is the energy (in wave numbers) of the absorption. Oscillator strengths were calculated over the following spectral domains: ArPZnE-TDQ-EArPZn (600 – 1000 nm); ArPZnE-BTD-EArPZn (600 – 800 nm); ArPPtE-TDQ-EArPPt (600 – 850 nm); ArPPtE-BTD-EArPPt (600 – 700 nm); Rf$_3$PZnE-TDQ-ERf$_3$PZn (600 – 850 nm); Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn (600 – 950 nm).

ArPZnE-BTD-EArPZn and ArPZnE-TDQ-EArPZn exhibit markedly different Stokes shifts and fluorescence quantum yields ($\Phi_F$) (Figure 67) in THF solvent. While ArPZnE-BTD-EArPZn displays a relatively small Stokes shift ($\Delta \nu = 1019$ cm$^{-1}$) and a large fluorescence quantum yield ($\Phi_F = 0.25$) comparable to those of PZn$_n$ chromophoric benchmarks (e.g. PZn: $\Delta \nu = 711$ cm$^{-1}$, $\Phi_F = 0.16$, PZn$_2$: $\Delta \nu = 806$ cm$^{-1}$, $\Phi_F = 0.22$; Figure 66),$^{48,53}$ ArPZnE-TDQ-EArPZn exhibits a significant Stokes shift of 1869 cm$^{-1}$ and negligible
fluorescence ($\Phi_F = 0.003$). Furthermore, the Stokes shift and fluorescence quantum yield of ArPZnE-BTD-EArPZn show modest solvent dependence [e.g., toluene ($\Delta \nu = 522$ cm$^{-1}$, $\Phi_F = 0.27$)] (Figure 77); in contrast, a substantial solvent-dependence of the Stokes shift and fluorescence quantum yield are evinced for ArPZnE-TDQ-EArPZn, with less polar solvent driving smaller Stokes shifts and significantly enhanced fluorescence quantum yields [toluene ($\Delta \nu_{\text{Stokes}} = 771$ cm$^{-1}$, $\Phi_F = 0.02$) vs. THF ($\Delta \nu_{\text{Stokes}} = 1869$ cm$^{-1}$, $\Phi_F = 0.003$)] (Figure 78). These observations underscore the differing CT characters of the ArPZnE-TDQ-EArPZn and ArPZnE-BTD-EArPZn $Q_z$-states; as ArPZnE-TDQ-EArPZn exhibits substantial CT character, the reorganization energy associated with excited-state solvent relaxation is magnified.$^{48,62}$

Upon metal center substitution from zinc(II) to platinum(II), ArPPtE-BTD-EArPPt manifests weak fluorescence centered at 629 nm ($\Delta \nu = 686$ cm$^{-1}$, $\Phi_F = 0.001$) in deoxygenated solution at ambient temperature, and phosphorescence centered at 845 nm ($\Delta \nu = 4750$ cm$^{-1}$) (Figure 79). Such emissive properties are similar to those observed in oligomeric (porphinato)palladium(II)/platinum(II) compounds ($\text{PM}_3$, $M = \text{Pd}$ or $\text{Pt}$; Figure 66), where phosphorescence and very weak fluorescence (77K) are simultaneously evinced ($\text{PPd}_3$: $\lambda_{S1\rightarrow S0}(\text{max}) = 747$ nm; $\lambda_{T1\rightarrow S0}(\text{max}) = 828$ nm; $\text{PPt}_3$: $\lambda_{S1\rightarrow S0}(\text{max}) = 740$ nm; $\lambda_{T1\rightarrow S0}(\text{max}) = 800$ nm).$^{67}$ In contrast, ArPPtE-TDQ-EArPPt maintains one constant emission band centered at 810 nm, regardless of the solution oxygen content (Figure 80). Note that no additional emission band can be observed in
deoxygenated samples of ArPPtE-TDQ-EArPPt even at low temperature (77K, Figure 81). In light of the magnitude of the Stokes shift (Δν = 1530 cm⁻¹) and the measured lifetime of this chromophore (τ = 310 ps, Figure 82E), we denote the ArPPtE-TDQ-EArPPt emission band centered at 810 nm as fluorescence. Given the (porphinato)platinum(II) components of this chromophore, it is recognized that the low-lying emissive state of ArPPtE-TDQ-EArPPt may be best described as a “singletriplet”. In this regard, we emphasize that although the “fluorescence”, “phosphorescence”, “S₁”, and “T₁” labels are preserved throughout this report for describing the respective higher and lower energy emissive states of the platinum-containing PM-Sp-PM compounds, they suggest only the dominant characters of these excited states. Note that the fluorescence quantum yield determined for ArPPtE-TDQ-EArPPt (2.8%) is unusually large, considering that platinum atoms typically promote strong spin-orbit coupling, resulting in near-unit S₁→T₁ ISC quantum yields (ΦISC values) in classic (porphinato)platinum(II) compounds.⁶⁷, ¹⁸⁸, ¹⁸⁹ The emissive properties observed for ArPPtE-TDQ-EArPPt suggest an unusually low ΦISC value relative to the ArPPtE-BTD-EArPPt chromophore (vide infra).
4.2.3 Pump-Probe Transient Absorption Spectroscopy of ArPM-Sp-ArPM

Figure 68: Pump-probe transient absorption spectra recorded at several time delays for (A) ArPZnE-BTD-EArPZn ($\lambda_{\text{exc}} = 660$ nm), (B) ArPZnE-TDQ-E ArPZn ($\lambda_{\text{exc}} = 900$ nm), (C) ArPPtE-BTD-EArPPt ($\lambda_{\text{exc}} = 610$ nm), and (D) ArPPtE-TDQ-EArPPt ($\lambda_{\text{exc}} = 750$ nm). Experimental conditions: solvent = THF; ambient temperature; magic angle polarization. Steady-state absorption (orange solid line) and fluorescence (magenta dash line) are provided as inverted spectra. Ar = 2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl.

The femtosecond transient absorption spectra recorded at selected time delays for ArPM-Sp-ArPM chromophores are displayed in Figure 68. The early time-delay (< 1 ps) transient spectra of these ArPM-Sp-ArPM chromophores share several common features that resemble the transient spectral signatures of ethyne-bridged multimeric (porphinato)zinc(II) structures ($\text{PZn}_n$, $n = 2, 3$; Figure 66).\textsuperscript{48, 69} These include: (i) bleaching signals in the Soret and $Q_x$ band regions, (ii) weak transient absorptions between the two dominant ground-state absorption bleaching signatures, and (iii) intense NIR $S_1 \rightarrow S_n$ transient absorption manifolds that feature extraordinary spectral breadth.\textsuperscript{48, 53, 67}
Conventional $PZ_n$ excited-state dynamics include fast $S_2 \rightarrow S_1$ internal conversion ($< 1$ ps),\textsuperscript{69} nanosecond timescale $S_1$ state lifetimes,$^ {48, 67}$ and small Stokes shifts in virtually all solvents;\textsuperscript{48, 53} this latter point suggests minimal degrees of solvent repolarization and inner-sphere chromophore nuclear reorganization are associated with excited-state relaxation of these species. Furthermore, upon metal center substitution with palladium(II) or platinum(II), the corresponding $PPd_n$ or $PPt_n$ chromophores (Figure 66) manifest ultrafast intersystem crossing on sub-picosecond to picosecond timescales.\textsuperscript{67}

For corresponding $ArP-M-Sp-ArP$ species, however, it is clear that the proquinoidal spacer units regulate electronically excited-state electron density spatial distributions (Figure 67).

**Femtosecond Transient Absorption Spectroscopy of ArPZn-Sp-ArPZn.** A global fit of the NIR transient absorption dynamics observed following excitation ($\lambda_{exc} = 660$ nm), evinces three characteristic relaxation processes: $760 \pm 90$ fs, $24 \pm 5$ ps, $1.75 \pm 0.1$ ns (Figure 84A). The $760$ fs and $24$ ps components are assigned to respective solvent relaxation, and structural relaxation processes associated with torsional dynamic about the ethyne-Sp-ethyne $ArPZn$-to-$ArPZn$ linkage; these dynamics have been discussed in detail for closely related structures.\textsuperscript{48, 69} The $1.75$ ns component corresponds with ground-state recovery and is assigned to the intrinsic $S_1$ state lifetime, in close agreement with the fluorescence lifetime determined by streak-scope ($\tau_f = 1.67$ ns, Figure 82C). Consistent with the insensitivity of the Stokes shift and fluorescence quantum yield to
solvent polarity, the S\textsubscript{1} state lifetime of \textit{ArPZnE-BTD-EArPZn} manifests minimal
variation with solvent dielectric constant [e.g. THF (\(\tau_F = 1.67\) ns) vs toluene (\(\tau_F = 1.61\) ns, Figure 82D)], suggesting the electronically excited-state nature of \textit{ArPZnE-BTD-EArPZn}
features negligible CT character.

The excited-state relaxation dynamics of \textit{ArPZnE-TDQ-EArPZn} are also
multiexponential in nature. Global fitting of the NIR spectral regime transient dynamical
data acquired for \textit{ArPZnE-TDQ-EArPZn} evinces three relaxation processes: 950 ± 120 fs,
12 ± 2 ps, and 87 ± 6 ps (Figure 84B). While the 950 fs and 12 ps components correspond,
respectively, to the solvent relaxation and structural relaxation dynamics, the 87 ps
component is very close to the streak-scope determined fluorescence lifetime (\(\tau_F = 76\) ps)
of \textit{ArPZnE-TDQ-EArPZn} (Figure 82A), and is thus assigned to the intrinsic singlet
excited-state lifetime. Notably, the THF solvent relaxation component mirrors the
timescale for the time-dependent red shift of the stimulated emission from 910 to 1020
nm (\(\Delta\nu = 1185\) cm\(^{-1}\)). This dynamic Stokes shift, absent for \textit{ArPZnE-BTD-EArPZn},
indicates substantial displacement between the ground- and singlet excited-state
potential energy surfaces along the solvation coordinate\textsuperscript{,185,190,191} congruent with the
marked solvent-dependent \textit{ArPZnE-TDQ-EArPZn} Stokes shifts observed by steady-
state emission spectroscopy (\textit{vide supra}). Additionally, the S\textsubscript{1} state lifetime (\(\tau_{S1} = 87\) ps) of
\textit{ArPZnE-TDQ-EArPZn} is much shorter than that of \textit{ArPZnE-BTD-EArPZn}, and
depends strongly on solvent dielectric constant (\(\varepsilon_s\)). For example, the \(\tau_F\) determined for
ArPZnE-TDQ-EArPZn measured in toluene solvent (~ 506 ps, Figure 82B) is nearly 1 order of magnitude larger than that found in THF. As such, the calculated S₁→S₀ internal conversion rate constants for ArPZnE-TDQ-EArPZn in THF and toluene differ markedly [k_{IC} (THF) = 1.15 × 10^{10} \text{ sec}^{-1} vs. k_{IC} (toluene) = 1.94 × 10^{9} \text{ sec}^{-1}], highlighting the acceleration of the nonradiative decay process in polar solvent: since the Q₂-state transition features substantial CT character, solvent dipole reorientation dramatically stabilizes the polarized S₁ state of ArPZnE-TDQ-EArPZn, decreasing the S₁→S₀ transition oscillator strength [Φ_{F} (THF) = 0.003 vs. Φ_{F} (toluene) = 0.02].

**Femtosecond Transient Absorption Spectroscopy of ArPPt-Sp-ArPPt.** A global fit of the time-dependent vis-NIR transient dynamical data acquired for ArPPtE-BTD-EArPPt following excitation at 610 nm evinces two relaxation processes: 960 ± 120 fs, 1.90 ± 0.13 ns (Figure 84C). Note that at an early time delay (t_{delay} ~ 1ps), the initially prepared ArPPtE-BTD-EArPPt electronically excited state has already evolved to a long-lived excited state that persists beyond the delay limit of the femtosecond pump-probe instrument. Nanosecond pump-probe transient absorption measurements determine that the lifetime of this long-lived excited state is 2.5 µs, which is reduced to 0.24 µs under oxygenated conditions (Figure 83C-D), suggesting that the long-lived excited state is triplet in nature. In this regard, the ultrafast component (960 fs) observed in femtosecond transient dynamics corresponds to ISC process, while the 1.90 ns component corresponds to the slow decay of ArPPtE-BTD-EArPPt triplet excited state.
Furthermore, the decay-associated spectra (DAS, Figure 84) connected with the ultrafast component manifests an S-like shape in the 900-1200 nm domain, displaying a decay on the blue side and rise on the red side of the transient, suggesting unit quantum yield S1→T1 conversion (i.e. τS1 = τISC ~ 960 fs, ΦISC ~ 100%). The ultrafast S1→T1 conversion and near-unit ISC quantum yield displayed by ArPPtE-BTD-EArPPt are similar to those evinced by PPTb compounds (Table 9).

Table 9: Dynamical data for PM-Sp-PM chromophores

<table>
<thead>
<tr>
<th>Chromophores</th>
<th>τS1 / ns</th>
<th>Relaxation Rate from S1 / sec⁻¹</th>
<th>ΦF</th>
<th>ΦISC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kIC (S1→S0)</td>
<td>kF (S1→S0)</td>
<td>kISC (S1→T1)</td>
</tr>
<tr>
<td>ArPZnE-TDQ-EArPZn</td>
<td>0.087</td>
<td>1.15×10¹⁰</td>
<td>3.10×10⁷</td>
<td>≤ 10⁷</td>
</tr>
<tr>
<td>ArPZnE-BTD-EArPZn</td>
<td>1.750</td>
<td>3.82×10⁸</td>
<td>1.43×10⁸</td>
<td>8.57×10⁷</td>
</tr>
<tr>
<td>ArPPtE-TDQ-EArPPt</td>
<td>0.310</td>
<td>1.51×10⁹</td>
<td>9.15×10⁷</td>
<td>1.67×10⁹</td>
</tr>
<tr>
<td>ArPPtE-BTD-EArPPt</td>
<td>0.001</td>
<td>≤ 10⁸</td>
<td>- 10⁸</td>
<td>1.04×10¹²</td>
</tr>
<tr>
<td>Rf₂PZnE-TDQ-ERP₂PZn</td>
<td>0.785</td>
<td>9.04×10⁸</td>
<td>1.53×10⁸</td>
<td>2.17×10⁸</td>
</tr>
<tr>
<td>Rf₂PZnArPPtE-TDQ-EArPPtRf₂PZn</td>
<td>0.108</td>
<td>2.36×10⁹</td>
<td>1.39×10⁸</td>
<td>6.76×10⁹</td>
</tr>
</tbody>
</table>

* kIC denotes the S1→S0 nonradiative decay rate constant, kF denotes the intrinsic fluorescence rate constant, kISC denotes the S1→T1 intersystem crossing rate constant. Excited-state relaxation rate constants were calculated based on the following equations: τS1 = 1 / (kIC + kF + kISC), ΦF = kF / τS1, ΦISC = kISC / τS1, since τS1, ΦF, and ΦISC can all be experimentally acquired, therefore, rate constants kIC, kF, and kISC can be calculated. b Fluorescence quantum yields were determined relative to bis[(porphinato)zinc(II)] (PZn) in THF (0.16). c ΦISC were determined based on femtosecond transient absorption spectra, for details see Supporting Information.

In contrast to the ultrafast ISC rate constant exhibited by ArPPtE-BTD-EArPPt, the ArPPtE-TDQ-EArPPt analogue manifests dramatically different excited-state relaxation dynamics. Three time constants were obtained from fitting the ArPPtE-TDQ-
 transient data acquired following Q-band excitation ($\lambda_{\text{exc}} = 750$ nm): $1.05 \pm 0.15$ ps, $15 \pm 2$ ps, $330 \pm 15$ ps (Figure 84D). Analogous to the characteristic relaxation times evinced for ArPZn-Sp-ArPZn chromophores, the two fast time constants (1.05 ps and 15 ps) correspond respectively to established THF solvational and structural relaxation dynamics. The 330 ps component is comparable to the streak-scope determined fluorescence lifetime of ArPPtE-TDQ-EArPPt ($\tau_F = 310$ ps, Figure 82E), and is thus assigned to the intrinsic $S_1$ state lifetime. While the ArPZnE-TDQ-EArPZn transient spectra feature complete ground state recovery within 200 ps, those of ArPPtE-TDQ-EArPPt evolve at long-time delays to give rise to a new transient absorption band that spans the 800-1050 nm spectral domain. This transient absorption manifold persists beyond the delay limit of the femtosecond instrument (Figure 68D). Nanosecond transient absorption spectroscopy determines the lifetime of this long-lived excited state to be 250 ns in deoxygenated solutions, while in ambient atmosphere saturated solutions it is reduced to 140 ns (Figure 83A-B), suggesting that the corresponding excited state is dominated by triplet character. Femtosecond timescale transient absorption spectral data allow direct evaluation of the $S_1 \rightarrow T_1$ ISC quantum yield and rate constant ($\Phi_{\text{ISC}} \sim 51\%$; $k_{\text{ISC}} \sim 1.67 \times 10^9 \text{ s}^{-1}$) for ArPPtE-TDQ-EArPPt (Supporting Information; Table 9). The excited-state relaxation dynamics of ArPPtE-TDQ-EArPPt thus contrast those evinced in classic oligomeric highly conjugated (porphinato)platinum(II) species where near-unit ISC quantum yields and sub-picosecond ISC time constants are manifested.\textsuperscript{67} Also note
that the $S_1$ state lifetime of ArPPtE-TDQ-EArPPt is about four times longer than that of its ArPZnE-TDQ-EArPZn analogue, whereas PPTe evince significantly diminished $S_1$ state lifetimes relative to the corresponding PZnE chromophores due to ultrafast $S_1 \rightarrow T_1$ ISC dynamics (Figure 66).\textsuperscript{53, 67} In this regard, the longer $S_1$ state lifetime (Table 9) of ArPPtE-TDQ-EArPPt relative to ArPZnE-TDQ-EArPZn originates from two factors: (i) diminution of the nonradiative decay rate constant as the optical bandgap is widened when platinum(II) replaces zinc(II) in this chromophoric motif, and (ii) an unconventionally slow ISC rate constant. The origin of this slow ISC will be discussed in the context of TD-DFT calculations (vide infra).

These data (Figures 67-68; Tables 8-9) demonstrate that varying the nature of the intervening proquinoidal spacer units drives substantially different absorptive and excited-state dynamical properties in ArPM-Sp-ArPM chromophores: (i) ArPZn-Sp-ArPZn chromophores, such as ArPZnE-TDQ-EArPZn, having significant excited-state proquinoidal character, exhibit broad long-wavelength absorptive manifolds and substantial NIR oscillator strength, negligible ($\Phi_F < 0.01$) fluorescence, and short-lived (~tens of ps) singlet excited state lifetimes. (ii) ArPZn-Sp-ArPZn chromophores, such as ArPZnE-BTD-EArPZn, that feature less electronically excited-state proquinoidal character, exhibit narrower long-wavelength absorptive manifolds and less substantial NIR oscillator strength, long-lived (ns) $S_1$ states and large ($\Phi_F \sim 0.25$) fluorescence quantum yields. (iii) ArPPt-Sp-ArPPt chromophores, characterized by ArPPtE-TDQ-
EArPPt and ArPPtE-BTD-EArPPt, evince similar dependences of absorptive oscillator strength distribution upon the nature of the proquinoidal spacer, but show an unusual dependence of the degree of electronically excited-state proquinoidal character upon the magnitude of \( k_{ISC} \): ArPPtE-BTD-EArPPt, which features a modest extent of excited-state proquinoidal character, features a \( S_1 \rightarrow T_1 \) ISC rate constant \( (k_{ISC} = 1.04 \times 10^{12} \text{s}^{-1}) \) three orders of magnitude greater than that for ArPPtE-TDQ-EArPPt. The origins of these disparate photophysical properties modulated by these Sp units are explored below using TD-DFT calculations.

**4.2.4 Computed Electronic Structures of ArPM-Sp-ArPM Chromophores**

The differing \( S_1 \) state CT characters of these ArPM-Sp-ArPM chromophores are underscored by population analyses of their frontier orbitals (FOs) and the transition matrix eigenvectors computed by TD-DFT methods (Figure 69). The \( S_1 \) state of ArPZnE-TDQ-EArPZn is dominated (~ 80%) by the HOMO→LUMO configuration, where ~ 30% of the HOMO wavefunction amplitude and > 70% of the LUMO amplitude is assigned to atoms in the TDQ spacer (see Section 4.4.7 for molecular orbital population analyses). Photo-excitation of the ArPZnE-TDQ-EArPZn \( Q_x \)-band region, thus, redistributes electron density from the ArPZn to the TDQ unit, resulting in a delocalized \( S_1 \) state with substantial CT character. In contrast, ArPZnE-BTD-EArPZn manifests an \( S_1 \) state composed of multiple single-excitation configurations that involve FOs from HOMO-3 to LUMO+3, where the shares of HOMO and LUMO wavefunction amplitudes that can
be assigned to ArPZn and TDQ subunits are comparable. These data indicate that the S1 state for ArPZnE-BTD-EArPZn exhibits negligible CT character and substantial CI, more akin to classic porphyrin π→π* transitions and those characteristic of PZn supermolecular chromophores.38, 39, 48, 95 These computational figures buttress the finding that the ArPZnE-TDQ-EArPZn Qx transition has greater quinoidal character than that of ArPZnE-BTD-EArPZn,170 as demonstrated by analyses of the Qx manifold FWHM and vibronic structures, fluorescence quantum yields, and the dynamic and solvent dependent Stokes shifts exhibited by these chromophores.

Figure 69: TD-DFT determined energy level diagrams and frontier molecular orbitals for ArPM-Sp-ArPM [M=Zn(II) or Pt(II), Sp = E-TDQ-E, or E-BTD-E], with arrows depicting the one-electron configurations that contribute most significantly to the low-energy (Qx) transitions. Calculations were performed at the M11 / 6-311g(d) theory level.

The contrasts outlined above regarding the S1 state CT characters of the (porphinato)zinc(II) compounds are sustained in their (porphinato)platinum(II) counterparts. A further distinction that may be drawn for these latter ArPPtE-TDQ-
EA_

EArPPt and ArPPtE-BTD-EArPPt chromophores is that a lesser share of the S₁ state wavefunction amplitude lies proximal to the platinum atom for the TDQ-based compound than for the BTD-based analogue. Note that the ArPPtE-TDQ-EArPPt S₀→S₁ transition is mainly described by the HOMO→LUMO configuration, and population analysis demonstrates that the (porphinato)platinum(II)-derived electron density contributes ~ 23% to the ArPPtE-TDQ-EArPPt LUMO amplitude. In contrast, the ArPPtE-BTD-EArPPt S₀→S₁ transition features the interaction of several configurations involving FOs beyond the HOMO and LUMO, and all of the virtual FOs evince dominant (> 50%) wavefunction amplitude assigned to the (porphinato)platinum(II) fragment. These population analyses rationalize the correlation of large k isc for the ArPPtE-BTD-EArPPt S₁ state with its strong CI character, and smaller k isc for the ArPPtE-TDQ-EArPPt S₂ states with its strong CT character: as ISC can be induced by spin-orbit coupling (a local effect induced by wavefunction density proximal to a heavy atom),⁶,⁶⁸ it is clear that the wavefunction spatial distribution of the initially prepared singlet excited state of ArPPtE-BTD-EArPPt is responsible for its considerably greater S₁-T₁ mixing relative to that manifested for ArPPtE-TDQ-EArPPt.

4.2.5 Schematic Potential Energy Surfaces Summarizing the Electronic and Dynamical Properties of ArPM-Sp-ArPM

The spectroscopic, dynamical, and computational results for these ArPME-Sp-EArPM structures can be schematically illustrated using a series of qualitative potential energy surfaces as displayed in Figure 70. In these schematic illustrations, the free
energies of \textit{ArPM-Sp-ArPM} chromophores in their ground states and low-lying singlet excited states are given as functions of a solvation coordinate, as spectroscopic and dynamical investigations indicate solvation dynamics plays a prominent role in determining the excited-state relaxation pathways. TD-DFT calculations show that the \textit{ArPME-TDQ-EArPM} \(S_1\) states feature stronger proquinoid contributions and greater CT character than those of \textit{ArPME-BTD-EArPM} analogues (Figure 69). The CT character of the \textit{ArPME-TDQ-EArPM} Franck-Condon state initiates solvent dipolar reorientation, which in turn augments excited-state electronic polarization. The evolving solvent reorganization creates a ladder of stabilized states with progressively enhanced CT character relative to the initially prepared \(S_1\) state, funneling excited-state energy through \(S_1 \rightarrow S_0\) nonradiative conversion that competes with \(S_1 \rightarrow T_1\) ISC (Figure 70A). In this regard, note that the 1 ps characteristic solvent relaxation timescale (marked on potential energy surfaces for \textit{ArPME-TDQ-EArPM}, Figure 70A,C) corresponds to the timescale of the potential energy curve displacement (\(\Delta q\)) dynamics between \(S_0\) and \(S_1\) states that are driven along the solvent coordinate. The \(S_0 \rightarrow S_1\) vertical transition of \textit{ArPPtE-TDQ-EArPPt} manifests a lower degree of CI relative to that for \textit{ArPPtE-BTD-EArPPt} (vide supra), and the major single-excitation configuration involves virtual FOs featuring spacer-dominant (~77\%) electron density, resulting in diminished \(S_1\)-\(T_1\) mixing (Figure 70C), and hence the experimentally observed slow ISC rate constant \((1.67 \times 10^9\) sec\(^{-1}\)). In contrast, the low-energy transition for \textit{ArPPtE-BTD-EArPPt} exhibits a higher
degree of CI, and (porphinato)platinum(II)-derived electron density makes prominent (>50%) contributions to the amplitudes of all the ArPPE-BTD-EArPPt virtual orbitals involved in the corresponding transition, relative to that in the ArPPE-BTD-EArPPt chromophore, thus giving rise to stronger S₁-T₁ mixing and the ultrafast ISC rate constant $(1.04 \times 10^{12} \text{ sec}^{-1})$ (Figure 70D). Moreover, as the nature of the initially prepared S₁ state of ArPPE-BTD-EArPPt is barely perturbed by solvent dynamics, S₁→T₁ ISC dominates excited-state relaxation processes, giving rise to the near-unity ΦISC in ArPPE-BTD-EArPPt.

Figure 70: Schematic potential energy surfaces summarizing the spectroscopic and dynamical features, and computed electronic structures, for ArPME-Sp-EArPM chromophores [M=Zn(II) or Pt(II), Sp = thiadiazoloquinoxaline (TDQ), or benzothiadiazole (BTD)].

4.2.6 Relative Frontier Orbital Energies of ArPM and Spacers, and Implications for New Chromophore Designs

The disparate CT characters of the ArPME-TDQ-EArPM and ArPME-BTD-EArPM S₁ states trace their origins to relative (porphinato)metal and spacer fragment FO
energies; DFT calculations thus suggest rules for the rational engineering of excited state dynamics in these supermolecular chromophores (Figure 71). Here, a critical distinction is the energetic alignment of the ArPM and Sp fragment LUMOs (ΔE_L). For ArPME-BTD-EArPM compounds, which feature multiconfigurational S1 states of modest CT character, ΔE_L between ArPME and E-BTD-E is smaller than 0.3 eV. For ArPME-TDQ-EArPM chromophores, which feature HOMO→LUMO-dominated S1 states of substantial CT character, ΔE_L is larger than 1 eV. If the extent of CT character and degree of CI that describe the S1 states of ArPME-Sp-EArPM chromophores define the dominant factors that determine their ISC rate constants and fluorescence quantum yields, then minimizing ΔE_L for ArPZnE-Sp-EArPZn chromophores will be the key to designing new long wavelength fluorophores, while minimizing ΔE_L for ArPPtE-Sp-EArPPt chromophores will enable elucidation of NIR absorbers that manifest substantial ISC quantum yields.
Figure 71: TD-DFT determined frontier molecular orbitals of the precursor fragments (ArPZnE, ArPPtE, Rf₃PZnE, Rf₃PZnArPPtE, E-TDQ-E, and E-BTD-E) plotted as 0.02 isodensity surfaces along with the corresponding calculated energy level bars. Calculations were performed at the M11 / 6-311g(d) theory level.

Supermolecules built from the TDQ spacer and porphyrin fragments endowed with LUMO energies that are substantially more stable than those of the meso-aryl derivatives mentioned so far permit the validation of this hypothesis. An established approach that uniformly stabilizes porphyrin macrocycle FOs by an inductive σ-electron withdrawing effect exploits meso-perfluoroalkyl substitution. The recently described electron-deficient meso-tris(perfluoroalkyl)porphyrin Rf₃PZnE is an ideal building for this purpose, as its HOMO and LUMO are both substantially stabilized relative to those of the [(5,10,20-diphenylporphinato)zinc(II)]ethynyl (ArPZnE) unit (Figure 71). Furthermore, as the computed Rf₃PZnArPPtE LUMO is energetically close...
to that of $\text{Rf}_3\text{PZnE}$ (Figure 71), the $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtERf}_3\text{PZn}$ compound was designed with the expectation that it would display attenuated electronically excited-state proquinoidal character compared to $\text{ArPPtE-TDQ-EArPPt}$, and thus an ISC rate constant substantially larger than that of the parent chromophore $\text{ArPPtE-TDQ-EArPPt}$. Likewise, $\text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}$ was designed with the expectation that this electronic structural engineering would provide a NIR fluorophore, and contrast those photophysics delineated above for $\text{ArPZnE-TDQ-EArPZn}$.

Figure 72: Steady-state and pump-probe transient absorption spectra recorded for $\text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}$ and $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtERf}_3\text{PZn}$: steady-state electronic absorption and emission spectra for (A) $\text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}$ ($\lambda_{\text{exc}} = 650$ nm for emission) and (B) $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtERf}_3\text{PZn}$ ($\lambda_{\text{exc}} = 700$ nm for emission), solvent = THF, ambient condition. Pump-probe transient absorption spectra recorded at representative time delays for (C) $\text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}$ ($\lambda_{\text{exc}} = 680$ nm) and (D) $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtERf}_3\text{PZn}$ ($\lambda_{\text{exc}} = 800$ nm), solvent = THF, ambient temperature, magic angle polarization, steady-state absorption (orange solid line) and fluorescence (magenta dash line) are displayed as inverted spectra. Ar = 2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl; Rf = heptafluoropropyl.

To that end, $\text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}$ and $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtERf}_3\text{PZn}$ were synthesized by methods closely analogous to those that provided the
chromophores discussed above. The steady-state electronic absorption and emission spectra for Rf₃PZnE-TDQ-ERf₃PZn reveal features that significantly differ from those of ArPZnE-TDQ-EArPZn, while resembling those of ArPZnE-BTD-EArPZn (Figure 72A, Table 8); Rf₃PZnE-TDQ-ERf₃PZn spectroscopic highlights include a narrow lowest-energy absorption manifold (Qₓ(FWHM) = 1163 cm⁻¹), a modest Stokes shift (Δν = 851 cm⁻¹), and a substantial fluorescence quantum yield (Φₓ = 0.12) in THF solvent. Likewise, Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn manifests spectral signatures that reflect attenuated S₁ state CT character relative to the parent chromophore ArPPtE-TDQ-EArPPt, and features a low-energy transition having a reduced Qₓ(FWHM) (1738 cm⁻¹) and a smaller Stokes shift (Δν = 945 cm⁻¹) relative to that evinced by ArPPtE-TDQ-EArPPt. These steady-state spectroscopic signatures evinced by the meso-perfluoroalkyl(porphinato)metal(II) supermolecules vindicate the prediction based on TD-DFT calculations: due to the minimization of ∆Eₓ, Rf₃PZnE-TDQ-ERf₃PZn and Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn possess globally delocalized S₁ states having reduced CT character relative to those of ArPME-TDQ-EArPM.

Representative transient absorption spectra recorded at selected time delays for Rf₃PZnE-TDQ-ERf₃PZn and Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn are displayed in Figure 72C-D; key spectral data are highlighted in Table 9. Rf₃PZnE-TDQ-ERf₃PZn evinces no dynamic Stokes shift in the femtosecond transient absorption spectra, indicating modest CT character of the Franck-Condon state congruent with the minimal
ΔE_L calculated for this chromophore. As a result, S₁→S₀ internal conversion along the solvation coordinate is greatly diminished, and the S₁ state lifetime of Rf₃PZnE-TDQ-ERf₃PZn reaches ~0.8 ns, comparable to that of ArPZnE-BTD-EArPZn. For Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn, because of the low ΔE_L between the Rf₃PZnArPPtE wings and the central TDQ unit, the S₀→S₁ vertical transition involves less electron density redistribution than that of ArPPtE-TDQ-EArPPt. As a result, Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn manifests an ISC rate constant about four times as large as that of the parent chromophore ArPPtE-TDQ-EArPPt (6.76 × 10^{12} sec⁻¹ vs. 1.67 × 10^{12} sec⁻¹), and now manifests photophysics that approach those of ArPPtE-BTD-EArPPt. Note that these changes of ISC rate constant reflected in the evolution of supermolecular structure from ArPPtE-TDQ-EArPPt to Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn strikingly contrast the corresponding photophysics evinced in classic PZnₙ (Figure 66) multimeric species, where ISC rate constants decrease dramatically with increasing PZnₙ conjugation length. The spectroscopic features displayed by ArPPtE-TDQ-EArPPt and Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn highlight the cardinal role of S₁ state proquinoidal character in tuning the ground-state absorption in NIR, fluorescence quantum yield, and ISC rate constant for long-wavelength absorbing (porphinato)metal(II) species.

4.3 Conclusion

While the influence of proquinoidal character upon the linear absorption spectrum of low optical bandgap π-conjugated polymers and molecules is well
understood, less insight exists concerning its impact upon excited-state relaxation pathways and dynamics. Exploiting a series of model highly conjugated NIR-absorbing chromophores based on a (porphinato)metal(II)-spacer-(porphinato)metal(II) (PM-Sp-PM) structural motif in which the porphyril ligand is either electron rich (10,20-diarylporphyrin, ArP) or electron deficient (10,15,20-tris(perfluoroalkyl)porphyrin, RfsP), the central metal ion is Zn(II) or Pt(II), and the proquinoidal Sp is either 4,7-diethynylbenzo[c][1,2,5]thiadiazole (E-BTD-E) or 4,9-diethynyl-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (E-TDQ-E), we elucidate design principles important for controlling the excited-state dynamics of highly conjugated NIR-absorbing materials that feature conjugation motifs that rely on proquinoidal units, and define strategies through which $S_1 \rightarrow S_0$ radiative ($k_r$), $S_1 \rightarrow T_1$ intersystem crossing ($k_{ISC}$), and $S_1 \rightarrow S_0$ internal conversion ($k_{IC}$) rate constants may be manipulated over many orders of magnitude.

A combination of excited-state dynamical studies and TD-DFT calculations: (i) point to the cardinal role that excited-state configuration interaction (CI) plays in determining the magnitudes of $k_r$ ($S_1 \rightarrow S_0$), $k_{ISC}$ ($S_1 \rightarrow T_1$), and $k_{IC}$ ($S_1 \rightarrow S_0$) in these PM-Sp-PM chromophores, and (ii) suggests that a primary determinant of CI magnitude derives from the energetic alignment of the PM and Sp fragment LUMOs. The chromophore ArPZnE-BTD-EArPZn, whose low-lying excited state is characterized by a substantial degree of CI, defines a NIR emitter having a substantial fluorescence.
quantum yield ($\lambda_{em}(S_1 \rightarrow S_0) = 740$ nm; $\Phi_F = 0.25$); in contrast, ArPZnE-TDQ-EArPZn, whose low-lying excited state is described by a modest degree of CI and substantial charge transfer (CT) character, features an internal conversion rate constant, $k_{IC}$, more than two orders of magnitude larger than its BTD analogue. Optical excitation of ArPPtE-BTD-EArPPt likewise generates a low-lying excited state having a substantial extent of CI, and gives rise to unit quantum yield formation of its electronically excited triplet state. In contrast, excitation of ArPPtE-TDQ-EArPPt demonstrates an unusually fluorescent Pt(II) complex, with an $k_{ISC}$ three orders of magnitude smaller than its BTD analogue; the low CI/high CT character of the excited state provides a path to short-circuit the large magnitude spin-orbit coupling associated with heavy metal chromophores by minimizing $S_i$-state wavefunction density proximal to the heavy Pt nuclei, thus realizing a rare if not unique example of a fluorescent (porphinato)platinum(II) chromophore at ambient temperature having ISC dynamics on the ns timescale.\textsuperscript{67, 189, 195-197}

As TD-DFT computations and excited-state dynamical studies correlate high CI with modest energy gaps ($\Delta E_l$) between PM and Sp fragment LUMOs in PM-Sp-PM chromophores, RfsPZnE-TDQ-ERfsPZn and RfsPZnArPPtE-TDQ-EArPPtRfsPZn were synthesized: the $\sigma$-electron withdrawing effect of RfsPZnE meso-perfluoroalkyl moieties serves to align the Sp and PM LUMOs of these chromophores, defining NIR absorbers having low-lying excited states characterized by extensive CI. RfsPZnE-TDQ-ERfsPZn
thus contrasts ArPZnE-TDQ-EArPZn in that NIR fluorescence dominates its photophysics. Likewise, Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn, because of the low $\Delta E_i$ between the Rf$_3$PZnArPPtE wings and the central TDQ unit, features expansive excited-state CI and a large $k_{isc}$, displaying photophysics congruent with large magnitude spin-orbit coupling.

For non-heavy-metal containing low optical bandgap $\pi$-conjugated structures that produce long-lived triplet states at high quantum yield, this work shows that these photophysics trace their genesis to modest degree of CI that describes the low-lying excited states of these systems; however, if electronic structural modifications are introduced that give rise to high CI excited states, exceptional fluorophores may be produced. For heavy metal-containing low optical bandgap $\pi$-conjugated motifs, this work enables proquinoidal NIR chromophores having counter-intuitive properties to be evolved: for example, while (porphinato)platinum compounds are well known to generate non-emissive triplet states at unit quantum yield upon optical excitation at ambient temperature, diminishing the extent of excited-state CI in these systems realizes long-wavelength absorbing heavy-metal fluorophores. In sum, this work highlights approaches to: i) modulate low-lying singlet excited-state lifetime over the picosecond-to-nanosecond time domain, ii) achieve NIR fluorescence with quantum yields up to 25%, iii) tune the magnitude of $S_1$-$T_1$ ISC rate constant from $10^9$ to $10^{12}$ sec$^{-1}$ and (iv) realize $T_1$–state lifetimes that range from $\sim 0.1$ to several $\mu$s, for these model PM-Sp-PM
chromophores, and renders new insights to evolve bespoke photophysical properties for low optical bandgap π-conjugated polymers and molecules based on proquinoidal conjugation motifs.

Given the disparate photophysical requirements for NIR absorbers for applications ranging from optical power limiting to triplet-triplet annihilation photochemistry to in vivo bioimaging, this work underscores the photophysical diversity that may be engineered in supermolecular chromophores, and demonstrates how electronic modulation of proquinoidal conjugation motifs, conventionally utilized to regulate the ground-state absorptivity of low optical bandgap π-conjugated polymers and molecules, can also be exploited as powerful means to modulate their excited-state relaxation pathways.

4.4 Materials and Methods

4.4.1 Materials and Instrumentation

**Materials.** All manipulations were carried out under nitrogen or argon previously passed through an O₂ scrubbing tower (Schweitzerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise stated. Air sensitive solids were handled in a Braun 150-M glove box. Standard Schlenk techniques were employed to manipulate air-sensitive solutions. All solvents utilized in this work were obtained from Fisher Scientific (HPLC Grade). CH₂Cl₂ and tetrahydrofuran (THF) were distilled from CaH₂ and K/4-benzoylbiphenyl, respectively, under argon. Triethyleamine (TEA)
was dried over KOH pellets and distilled under vacuum. All NMR solvents were used as received. The catalysts Pd(PPh$_3$)$_4$ and tris(dibenzylideneacetone)-dipalladium(0) (Pd$_2$dba$_3$), as well as triphenylarsine (AsPh$_3$), were purchased from Sigma-Aldrich.

Various starting materials (Figure 73), such as 4,9-bromo-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (Br-TDQ-Br)$_{170}$, 4,7-diethynylbenzo[c][1,2,5]thiadiazole (Br-BTD-Br)$_{170}$, [5-triisopropylsilylthiophenyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyl)phenyl)porphinato]zinc(II) (ArPZnETIPS)$_9$, [5-ethynyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyl)phenyl)porphinato]zinc(II) (ArPZnE)$_{38,39,62,67,95}$, [5-triisopropylsilylthiophenyl-10,15,20-tri(heptafluoropropyl)porphinato]zinc(II) (Rf$_3$PZnETIPS)$_{202}$, and [5-ethynyl-10,15,20-tri(heptafluoropropyl)porphinato]zinc(II) (Rf$_3$PZnE)$_{202}$ were prepared according to the published procedures (Figure 73). The synthesis of and NMR characterization of 4,9-bis[(10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyl)phenyl)porphinato]zinc(II)-5-yethynyl]-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (ArPZnE-TDQ-EArPZn) and 4,7-bis[(10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyl)phenyl)porphinato]zinc(II)-5-yethynyl]benzo[c][1,2,5]thiadiazole (ArPZnE-BTD-EArPZn) have been reported previously (Figure 73)$_{170}$ Flash and size exclusion column chromatography were performed on the bench top, using respectively silica gel (EM Science, 230–400 mesh) and Bio-Beads SX-1 as media.
Instrumentation. Electronic spectra were recorded on a Varian 5000 UV/vis/NIR spectrophotometry system. NMR spectra were recorded on a 400 MHz AC-Brucker instrument. Chemical shifts for \(^1\)H NMR spectra are reported relative to residual protium in the deuterated solvents (CDCl\(_3\) = 7.26 ppm, THF-\(d_8\) = 1.72, 3.58 ppm). All J values are reported in Hertz. MALDI-TOF mass spectroscopic data were obtained with a Perspective Voyager DE Instrument (Department of Chemistry, Duke University). Samples were prepared as micromolar solutions in acetone, and 2-(4'-hydroxybenzeneazo)benzoic acid (Sigma-Aldrich) was utilized as the matrix. Microwave assisted reactions were performed with Emrys Personal Chemistry System (Biotage).
4.4.2 Synthetic Procedures and Characterizations

Figure 74: Synthesis of ArPPtE from ArPZnETIPS. (a) trifluoroacetic acid, r.t., CH2Cl2, 30 min; (b) Pt(acac)2, benzonitrile, 200 °C, 2h, microwave reaction; (c) TBAF, THF, 0 °C, 10 min, under argon.

5-Triisopropylsilylethynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyl)oxy)phenyl)porphyrin (ArFbETIPS). In a 100 mL round bottom flask equipped with a magnetic stirring bar, ArPZnETIPS (300 mg, 0.270 mmol) was dissolved by dry methylene chloride (~50 mL). Trifluoroacetic acid (5 mL) was added to the round bottom flask and the react was stirred at room temperature under argon for 0.5 h and then quenched by saturated NaHCO3. The organic layer was collected, washed with saturated NH4Cl, and then dried with Na2SO4. After evaporation of the solvent, the residue was purified by a short column chromatography using 1:1 hexanes: methylene chloride as the eluent. Yield = 275 mg (98 %, based on 300 mg of the ArPZnETIPS starting material). 1H NMR (400MHz, CDCl3 as 7.26 ppm): δ 10.02 (s, 1H), 9.67 (d, 2H, J = 4.8), 9.16 (d, 2H, J = 4.4 Hz), 8.87 (d, 2H, J = 4.8 Hz), 8.85 (d, 2H, J = 4.4 Hz), 7.71 (t, 2H, J = 8.4 Hz), 7.01 (d, 4H, J = 8.4 Hz), 3.91 (t, 8H, J = 7.2 Hz), 1.49-1.43 (m, 21H), 0.85 (t, 8H, J = 7.2 Hz), 0.32 (s, 36H), -2.56 (s, 2H). MALDI-TOF: m/z = 1045.65 (calculated for C67H91N4O4Si (M+H)+ 1045.57).
[5-Triisopropylsilylethynyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (ArPPtETIPS). ArFbETIPS (70 mg, 0.067 mmol), platinum acetylacetonate (132 mg, 0.335 mmol) and a magnetic stirring bar were brought together into a 10 mL microwave reaction vial that was then sealed and charged with argon. These reagents were dissolved in ~6 mL of benzonitrile solvent that was previously purged with argon for 1 h. The reaction vial was stirred at 200°C for 2 h in a microwave irradiation cavity. After the reaction without removing the benzonitrile solvent, the reaction mixture was directly purified through a silica column chromatography using 65:35 hexanes: methylene chloride eluent, and the first greenish band was collected as the desired product. Yield = 174 mg (70%, products from 3 reactions in total, based on 210 mg of the ArFbETIPS starting material). 1H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 9.92 (s, 1H), 9.58 (d, 2H, J = 4.8), 9.03 (d, 2H, J = 4.8 Hz), 8.80 (d, 2H, J = 4.8 Hz), 8.78 (d, 2H, J = 4.8 Hz), 7.69 (t, 2H, J = 8.4 Hz), 6.98 (d, 4H, J = 8.4 Hz), 3.90 (t, 8H, J = 7.2 Hz), 1.47-1.41 (m, 21H), 0.88 (t, 8H, J = 7.6 Hz), 0.24 (s, 36H).

MALDI-TOF: m/z = 1235.36 (calculated for C₆₇H₉₁N₄O₄PtSi (M+H)+ 1237.63).

[5-Ethylnyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II) (ArPPtE). Tetrabutylammonium fluoride (1M in THF, 126 µL, 0.126 mmol) was added to a solution of ArPPtETIPS (120 mg, 0.097 mmol) in THF (50 ml) under argon at 0°C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH₂Cl₂, dried over Na₂SO₄, and evaporated.
The residue was chromatographed on silica gel using 85:15 hexanes:THF as the eluent. Yield = 100 mg (95%, based on 120 mg of ArPPtETIPS). \(^1\)H NMR (400MHz, CDCl\(_3\) as solvent): \(\delta\) 9.93 (s, 1H), 9.59 (d, 2H, \(J = 4.8\)), 9.01 (d, 2H, \(J = 4.8\) Hz), 8.82 (d, 2H, \(J = 4.8\) Hz), 8.80 (d, 2H, \(J = 4.8\) Hz), 7.66 (t, 2H, \(J = 8.4\) Hz), 6.96 (d, 4H, \(J = 8.4\) Hz), 4.13 (s, 1H), 3.90 (t, 8H, \(J = 7.2\) Hz), 0.88 (t, 8H, \(J = 7.6\) Hz), 0.24 (s, 36H). MALDI-TOF: m/z = 1082.12 (calculated for C\(_{58}\)H\(_{70}\)N\(_4\)O\(_4\)Pt (M+H)+ 1081.29).

Figure 75: Synthesis of Rf\(_3\)PZnArPPtE from ArPZnETIPS and Rf\(_3\)PZnE. (a) NBS, 0 °C, CH\(_2\)Cl\(_2\):pyridine 20:1 mixture, 1 h, under argon; (b) trifluoroacetic acid, r.t., CH\(_2\)Cl\(_2\), 30 min; (c) Pt(acac)\(_2\), benzonitrile, 200 °C, 2h, microwave reaction; (d) Pd\(_2\)(dba)\(_3\), AsPh\(_3\), THF/i-Pr\(_2\)NH 10:1 mixture, 60 °C, 16 h, under argon; (e) TBAF, THF, 0 °C, 10 min, under argon.

[5-Bromo-15-triisopropylsilylthynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) (BrArPZnETIPS). In a 250 mL round bottom flask, ArPZnETIPS (180 mg, 0.163mmol) was dissolved in methylene chloride (50 mL) and pyridine (5 mL). The reaction mixture was cooled to 0 °C and a solution of NBS (32
mg, 0.179 mmol) in methylene chloride (50 mL) was added via cannula. The reaction mixture was stirred at 0 °C under argon for 1 h and quenched by addition of H₂O (100 mL). The organic layer was separated and dried with anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography using 6:4 hexanes: methylene chloride as the eluent. Yield = 155 mg (80 %, based on 180 mg of the ArPZnETIPS starting material). ¹H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 9.72 (d, 2H, J = 4.4), 9.66 (d, 2H, J = 4.4), 8.93 (d, 2H, J = 4.4 Hz), 8.90 (d, 2H, J = 4.8 Hz), 7.74 (t, 2H, J = 8.4 Hz), 6.98 (d, 4H, J = 8.4 Hz), 3.96 (t, 8H, J = 7.2 Hz), 1.53-1.47 (m, 21H), 0.91 (t, 8H, J = 7.2 Hz), 0.32 (s, 36H). MALDI-TOF: m/z = 1184.57 (calculated for C₆₇H₈₈BrN₄O₄SiZn (M+H)+ 1186.83).

5-Bromo-15-triisopropylsilylethynyl-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphyrin (BrArFbETIPS). In a 100 mL round bottom flask equipped with a magnetic stirring bar, BrArPZnETIPS (120 mg, 0.101 mmol) was dissolved by dry methylene chloride (~50 mL). Trifluoroacetic acid (2 mL) was added to the round bottom flask and the react was stirred at room temperature under argon for 0.5 h and then quenched by saturated NaHCO₃. The organic layer was collected, washed with saturated NH₄Cl, and then dried with Na₂SO₄. After evaporation of the solvent, the residue was purified by a short column chromatography using 1:1 hexanes: methylene chloride as the eluent. Yield = 111 mg (98 %, based on 120 mg of the BrArPZnETIPS starting material). ¹H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 9.61 (d, 2H, J = 4.4), 9.54 (d,
2H, J = 4.4), 8.82 (d, 2H, J = 4.4 Hz), 8.78 (d, 2H, J = 4.8 Hz), 7.68 (t, 2H, J = 8.4 Hz), 6.91 (d, 4H, J = 8.4 Hz), 3.92 (t, 8H, J = 7.2 Hz), 1.53-1.47 (m, 21H), 0.89 (t, 8H, J = 7.2 Hz), 0.31 (s, 36H), -2.48 (s, 2H). MALDI-TOF: m/z = 1123.92 (calculated for C_{67}H_{90}BrN_{4}O_{4}Si (M+H)^{+} 1123.46).

[5-Bromo-15-triisopropylsilylethynyl-10,20-bis(2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinate]platinum(II) (BrArPpETIPS). BrArFbETIPS (70 mg, 0.062 mmol), platinum acetylacetonate (123 mg, 0.312 mmol) and a magnetic stirring bar were brought together into a 10 mL microwave reaction vial that was then sealed and charged with argon. These reagents were dissolved in ~6 mL of benzonitrile solvent that was previously purged with argon for 1 h. The reaction vial was stirred at 200^\circ C for 2 h in a microwave irradiation cavity. After the reaction without removing the benzonitrile solvent, the reaction mixture was directly purified through a silica column chromatography using 65:35 hexanes: methylene chloride eluent, and the first greenish band was collected as the desired product. Yield = 55 mg (68%, products from 3 reactions in total, based on 70 mg of the BrArFbETIPS starting material). ^1H NMR (400MHz, CDCl₃ as 7.26 ppm): δ 9.56 (d, 2H, J = 4.8), 9.51 (d, 2H, J = 4.8), 8.77 (d, 2H, J = 4.8 Hz), 8.75 (d, 2H, J = 4.8 Hz), 7.72 (t, 2H, J = 8.4 Hz), 7.01 (d, 4H, J = 8.4 Hz), 3.95 (t, 8H, J = 7.2 Hz), 1.51-1.44 (m, 21H), 0.95 (t, 8H, J = 7.2 Hz), 0.31 (s, 36H). MALDI-TOF: m/z = 1316.71 (calculated for C_{67}H_{88}BrN_{4}O_{4}PtSi (M+H)^{+} 1316.53).
1-[(5-,10,15,20-Tri(heptafluoropropyl)porphinato)zinc(II)]-2-[(5’,15’-(triisopropylsilyl)ethynyl)-10’,20’-bis(2,6-bis(3,3-dimethyl-1-butyloxy)-phenyl)porphinato)platinum(II)]-ethyne (Rf3PZnArPPtETIPS). A 100 mL Schlenk flask equipped with a magnetic stirbar was charged with Rf3PZnE (60 mg, 0.067 mmol), BrArPPtETIPS (55 mg, 0.042 mmol), Pd2(dba)3 (23 mg, 0.025 mmol) and AsPh3 (38 mg, 0.126 mmol). A solvent mixture of THF (50 mL) and diisopropylamine (5 ml) was degassed via five freeze-pump-thaw cycles, transferred to the reaction flask and stirred at 60 °C for 16 h. After the reaction endpoint was confirmed by TLC, the reaction mixture was evaporated to dry and the residue was sequentially purified by silica column chromatography using 1:1 hexanes: methylene chloride as the eluent, size exclusion column chromatography using THF as the eluent, and another silica column chromatography using 1:1 hexanes: methylene chloride as the eluent. Yield = 43 mg (48%, based on 55 mg of BrArPPtETIPS). 1H NMR (400 MHz, CDCl3 as 7.26 ppm): δ 10.49 (d, 2H, J = 4.8), 10.12 (d, 2H, J = 4.8), 9.75 (s, 2H), 9.69 (s, 2H), 9.63 (s, 2H), 9.56 (d, 2H, J = 4.8), 8.99 (d, 2H, J = 4.8), 8.80 (d, 2H, J = 4.8), 7.73 (t, 2H, J = 8.4), 7.03 (d, 4H, J = 8.4), 3.99 (t, 8H, J = 7.2), 1.52-1.43 (m, 21H), 1.00 (t, 8H, J = 7.2), 0.33 (s, 36H). MALDI-TOF: m/z = 2138.19 (calculated for C98H96F21N8O8PtSiZn (M+H)+ 2137.41).

1-[(5-,10,15,20-Tri(heptafluoropropyl)porphinato)zinc(II)]-2-[(5’,15’-(ethynyl)-10’,20’-bis(2,6-bis(3,3-dimethyl-1-butyloxy)-phenyl)porphinato)platinum(II)]-ethyne (Rf3PZnArPPtE). Tetrabutylammonium fluoride (1M in THF, 26 μL, 0.026 mmol) was
added to a solution of \textbf{Rf$_3$PZnArPPtETIPS} (43 mg, 0.020 mmol) in THF (20 ml) under argon at 0°C. The reaction mixture was stirred for 10 min at 0 °C, quenched with water, extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, and evaporated. The residue was chromatographed on silica gel using 85:15 hexanes:THF as the eluent. Yield = 38 mg (95%, based on 43 mg of \textbf{Rf$_3$PZnArPPtETIPS}). $^1$H NMR (400MHz, CDCl$_3$ as 7.26 ppm): δ 10.47 (d, 2H, J = 4.8), 10.11 (d, 2H, J = 4.8), 9.73 (s, 2H), 9.67 (s, 2H), 9.61 (s, 2H), 9.55 (d, 2H, J = 4.8), 8.97 (d, 2H, J = 4.8), 8.78 (d, 2H, J = 4.8), 7.72 (t, 2H, J = 8.4), 7.03 (d, 4H, J = 8.4), 4.12 (s, 1H), 3.99 (t, 8H, J = 7.2), 0.98 (t, 8H, J = 7.2), 0.32 (s, 36H). MALDI-TOF: m/z = 1979.36 (calculated for C$_{89}$H$_{76}$F$_{21}$N$_8$O$_8$PtZn (M+H)$^+$ 1981.06).

**General Procedure for the Preparation of ArPPtE-TDQ-EArPPt, ArPPtE-BTD-EArPPt, Rf$_3$PZnE-TDQ-ERf$_3$PZn, and Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn.** *meso-*ethynyl functionalized (porphinato)metal(II) derivatives (ArPPtE, Rf$_3$PZnE, and Rf$_3$PZnArPPtE) and proquinoidal spacer moieties (Br-TDQ-Br, and Br-BTD-Br) were placed in a Schlenk flask equipped with a magnetic stir bar. Pd$_2$(dba)$_3$ (0.3 eq., based on the (porphinato)zinc synthon) and AsPh$_3$ (2 eq., based on the (porphinato)zinc synthon) were added under nitrogen atmosphere. A solvent mixture of 10:1 HPLC grade THF:triethylamine was degassed by a small stream of dry argon for approximately 2 h. Enough of this solvent mixture was added to the reaction vessel via cannula to completely dissolve all reactants, and the resulting solution was heated to 50-60 °C for 16 h. Consumption of all the starting materials was confirmed by thin layer
chromatography (6:4 hexanes:CH$_2$Cl$_2$ as eluent for ArPPtE-TDQ-EArPPt and ArPPtE-BTD-EArPPt, 65:35 hexanes:THF as eluent for Rf$_3$PZnE-TDQ-ERf$_3$PZn and Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn). The solution was then cooled to room temperature and evaporated. The crude product was purified by column chromatography using 6:4 hexanes:CH$_2$Cl$_2$ as eluent for ArPPtE-TDQ-EArPPt and ArPPtE-BTD-EArPPt, 65:35 hexanes:THF as eluent (due to solubility reason) for Rf$_3$PZnE-TDQ-ERf$_3$PZn and Rf$_3$PZnArPPtE-TDQ-EArPPtRf$_3$PZn. The product fractions was concentrated to dryness, then further purified through size exclusion column chromatography (Bio-beads SX-1 medium) using THF as the eluent, followed by a short silica gel column chromatography using the corresponding solvent mixture as eluent (vide supra). Additional column chromatography was performed if the level of purity was unsatisfactory as assessed by NMR spectroscopy.
Figure 76: Schematic summary for the synthesis of ArPME-TDQ-EArPM, ArPME-BTD-EArPM (M = Zn$^{II}$, or Pt$^{II}$), Rf$^3$PZnE-TDQ-ERf$^3$PZn, and Rf$^3$PZnArPPtE-TDQ-EArPPtRf$^3$PZn.

4,9-Bis[(10,20-bis[2',6'-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)platinum(II)-5-ylethynyl]-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (ArPPtE-TDQ-EArPPt). Reagents: ArPPtE (50 mg, 0.046 mmol), Br-TDQ-Br (9 mg, 0.023 mmol), Pd$_2$(dba)$_3$ (13 mg, 0.014 mmol), and AsPh$_3$ (28 mg, 0.092 mmol). Reaction solvent: 22 mL of 10:1 THF:triethylamine. Isolated yield = 30 mg of ArPPtE-TDQ-EArPPt (56%, based on 9 mg of Br-TDQ-Br). $^1$H NMR (400MHz, CDCl$_3$ as 7.26 ppm): δ 10.39 (d, 4H, J = 4.8), 9.94 (s, 2H), 9.05 (d, 4H, J = 4.8), 8.98 (d, 4H, J = 4.8), 8.80 (d, 4H, J = 4.4), 7.76 (d, 4H, J = 8.4), 7.05 (d, 8H, J = 8.8), 3.97 (t, 16H, J = 7.2), 3.14 (s, 6H), 0.95 (t, 16H, J = 7.2), 0.25 (s, 72H). MALDI-TOF: m/z = 2371.35 (calculated for C$_{126}$H$_{141}$N$_{12}$O$_{8}$Pt$_2$S (M+H)$^+$ 2373.81).
4,7-Bis[(10,20-bis[2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl]porphinato)platinum(II)-5-ylethynyl]benzo[12,5]thiadiazole 
(ArPPtE-BTD-EArPPt). Reagents: ArPPtE (50 mg, 0.046 mmol), Br-BTD-Br (7 mg, 0.023 mmol), Pd2(dba)3 (13 mg, 0.014 mmol), and AsPh3 (28 mg, 0.092 mmol). Reaction solvent: 22 mL of 10:1 THF:triethylamine. Isolated yield = 28 mg of ArPPtE-BTD-EArPPt (53%, based on 7 mg of Br-BTD-Br). 1H NMR (400MHz, CDCl3 as 7.26 ppm): δ 9.92 (d, 4H, J = 4.8), 9.80 (s, 2H), 8.94 (s, 4H), 8.92 (d, 4H, J = 4.8), 8.79 (d, 4H, J = 4.8), 7.98 (s, 2H), 7.75 (t, 4H, J = 8.4), 7.04 (d, 8H, J = 8.4), 3.97 (t, 16H, J = 7.2), 0.97 (t, 16H, J = 7.2), 0.26 (s, 72H). MALDI-TOF: m/z = 2294.81 (calculated for C122H137N10O8Pt2S (M+H)+ 2293.72).

4,9-Bis[(10,15,20-Tri(heptafluoropropyl)porphinato)zinc(II)-5-ylethynyl]-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (Rf3PZnE-TDQ-ERf3PZn). Reagents: Rf3PZnE (42 mg, 0.046 mmol), Br-TDQ-Br (9 mg, 0.023 mmol), Pd2(dba)3 (13 mg, 0.014 mmol), and AsPh3 (28 mg, 0.092 mmol). Reaction solvent: 22 mL of 10:1 THF:triethylamine. Isolated yield = 23 mg of Rf3PZnE-TDQ-ERf3PZn (50%, based on 9 mg of Br-TDQ-Br). 1H NMR (400MHz, THF-d8 as 1.72, 3.58 ppm): δ 10.35 (s, 4H), 9.68 (s, 4H), 9.60 (s, 4H), 9.32 (s, 4H), 3.28 (s, 6H). MALDI-TOF: m/z = 2014.76 (calculated for C72H23F42N12O8Pt2S (M+H)+ 2016.80).

4,9-Bis[(15’-(10’,15’,20’-tri(heptafluoropropyl)porphinato)zinc(II)-5’-ylethynyl]-10,20-bis(2’,6’-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]platinum(II)-5-ylethynyl]-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (Rf3PZnArPPtE-TDQ-
EArPPtRfsPZn). Reagents: RfsPZnE (42 mg, 0.046 mmol), Br-TDQ-Br (9 mg, 0.023 mmol), Pd(db)3 (13 mg, 0.014 mmol), and AsPh3 (28 mg, 0.092 mmol). Reaction solvent: 22 mL of 10:1 THF:triethylamine. Isolated yield = 23 mg of RfsPZnArPPtE-TDQ-EArPPtRfsPZn (50%, based on 9 mg of Br-TDQ-Br). 

$^1$H NMR (400MHz, THF-$d_8$ as 1.72, 3.58 ppm): δ 11.02 (d, 4H, J = 4.8), 10.66 (d, 4H, J = 4.8), 10.29 (s, 4H), 10.23 (s, 4H), 10.17 (s, 4H), 10.10 (d, 4H, J = 4.8), 9.53 (d, 4H, J = 4.8), 9.34 (d, 4H, J = 4.8), 8.27 (t, 4H, J = 8.4), 7.57 (d, 8H, J = 8.4), 4.53 (t, 16H, J = 7.2), 3.25 (s, 6H), 1.54 (t, 16H, J = 7.2), 0.89 (s, 72H).

MALDI-TOF: m/z = 4174.16 (calculated for C$_{188}$H$_{155}$F$_{42}$N$_{20}$O$_8$Pt$_2$S$_2$Zn$_2$ (M+H)$^+$ 4173.35).

### 4.4.3 Steady-State Emission Spectra

The emission spectroscopy for all the PM-sp-PM supermolecular species were investigated at ambient temperature under both deoxygenated and oxygenated condition. Deoxygenation was achieved through three cycles of freeze-pump-thaw, oxygenation was done by purging with air for 30 min. The optical density at all the different excitation wavelengths is ≤ 0.1. For low-temperature experiments, prior to freezing the sample by liquid nitrogen, three cycles of freeze-pump-thaw was applied for deoxygenation.
Figure 77: Comparative steady-state electronic absorption (solid lines) and emission spectra (dash lines) of ArPZnE-BTD-EArPZn in THF (blue lines) and toluene (orange lines). Stokes shift is computed based on the difference of the lowest-energy absorption and emission maxima.

Figure 78: Comparative steady-state electronic absorption (solid lines) and emission spectra (dash lines) of ArPZnE-TDQ-EArPZn in THF (black lines) and toluene (red lines). Stokes shift is computed based on the difference of the lowest-energy absorption and emission maxima.
Figure 79: Steady-state emission spectra of ArPPtE-BTD-EArPPt measured under deoxygenated (black line) and oxygenated (red line) condition. Experimental conditions: $\lambda_{\text{exc}} = 480$ nm, ambient temperature, solvent = THF.

Figure 80: Steady-state emission spectra of ArPPtE-TDQ-EArPPt measured at deoxygenated (black line) and oxygenated (red line) condition. Experimental conditions: $\lambda_{\text{exc}} = 649$ nm, ambient temperature, solvent = THF.
Figure 81: Steady-state emission spectra of ArPPtE-TDQ-EArPPt measured at low temperature (77K, green line) and room temperature (298K, red line). Experimental conditions: $\lambda_{\text{exc}} = 649$ nm, solvent = Methyl-THF.

4.4.4 Picosecond Fluorescence Lifetime

Time-resolved emission spectra were recorded using a Hamamatsu C4780 picosecond fluorescence lifetime measurement system. This system employs a Hamamatsu Streakscope C4334 as its photon-counting detector; a Hamamatsu C4792-01 synchronous delay generator electronically generated all time delays. The excitation light source chosen was a Hamamatsu 405 nm diode laser. All fluorescence data were acquired in single-photon-counting mode using Hamamatsu HPD-TA software. The data were analyzed using the Hamamatsu fitting module; both non-deconvoluted and deconvoluted data analyses were performed to ascertain whether or not any emissive processes were excitation pulse-limited.
Figure 82: Picosecond fluorescence decay of ArPZnE-TDQ-EArPZn in THF (A) and toluene (B), ArPZnE-BTD-EArPZn in THF (C) and toluene (D), ArPPtE-TDQ-EArPPt in THF (E), Rf₃PZnE-TDQ-ERf₃PZn in THF (F), and Rf₃PZnArPPtE-TDQ-
EA/EPPf/PZn in THF (G). Experimental conditions: $\lambda_{\text{exc}} = 405$ nm, instrument response function (IRF) $\sim 150-160$ ps, ambient temperature, magic angle polarization.

### 4.4.5 Nanosecond-to-Microsecond Transient Absorption

Nanosecond-to-microsecond transient absorption for all chromophores were measured with air-free spectro-cell, three cycles of freeze-pump-thaw was applied for deoxygenation prior to measurement. Oxygen quenching experiments were performed by purging the sample with air for $\sim 30$ min before measurement. Kinetic traces were fitted with single-exponential decay model to acquire the excited triplet state lifetime.

**Figure 83:** Nanosecond-to-microsecond transient absorption spectra recorded at selected time delays (under deoxygenated condition) and transient kinetic traces.
(under deoxygenated and oxygenated condition, respectively) for ArPPtE-TDQ-EArPPt (A) and (B), ArPPtE-BTD-EArPPt (C) and (D), and Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn (E) and (F). Experimental condition: λₑₓᶜₑ = 480 nm (ArPPtE-TDQ-EArPPt, ArPPtE-BTD-EArPPt), 500 nm (Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn), pump power = 1.5 mJ / pulse (ArPPtE-TDQ-EArPPt, ArPPtE-BTD-EArPPt), 1.3 mJ / pulse (Rf₃PZnArPPtE-TDQ-EArPPtRf₃PZn), solvent = THF, ambient temperature.

4.4.6 Other Supplementary Spectra

**Global Fitting and Decay Associated Difference Spectra**

![Figure 84: DADS of the NIR regime for ArPZnE-BTD-EArPZn (A), ArPZnE-TDQ-EArPZn (B), ArPPtE-BTD-EArPPt (C), and ArPPtE-TDQ-EArPPt (D), revealing solvent relaxation dynamic (~ 1 ps), structural (torsional) relaxation dynamics (~ 10-30 ps), and the intrinsic S₁ state decay. Offsets account for the transient absorption signal of the evolved excited triplet states, which persists beyond the delay limit of the transient optical system. Steady-state absorption and emission are plotted as the inverted dash lines.](image)

*Estimation of ISC Quantum Yields for ArPPtE-TDQ-EArPPt.* The ISC quantum yield for ArPPtE-TDQ-EArPPt was determined from fs transient absorption spectral
data via comparison of spectra acquired at $t = 30$ ps, which probes the excited singlet population without influence from solvent and structural relaxation dynamics (these processes are in the time domain of $\sim 1$ ps and 10-30 ps), and at a delay time (e.g., $t = 1.32$ ns) at which only ground and excited triplet state populations of $\text{ArPPtE-TDQ-EArPPt}$ exist. The ISC quantum yield can be estimated using equation (1).

$$\Phi_{\text{ISC}} = \frac{\Delta A (715 \text{ nm}, t = 1.32 \text{ ns})}{\Delta A (715 \text{ nm}, t = 30 \text{ ps})}$$ (4.4.6.1)

To ensure the accuracy of the calculated $\Phi_{\text{ISC}}$, the $\Delta A$ utilized in equation (1) has to be a pure signal from ground state bleach (GSB). In this regard, note that the Q-band region (600-800 nm) GSB at $t = 30$ ps overlaps well with the ground-state absorption (Figure S9A), and due to the large Stokes shift, stimulated emission signal is greatly separated from the GSB signal, suggesting $\Delta A (715 \text{ nm}, t = 30 \text{ ps})$ can be attributed only to the depletion of ground state populations (due to excited singlet populations). However, the Q-band region GSB at $t = 1.32$ ns does not overlap with the ground-state absorption (Figure S9A), particular in the spectral domain of 700-800 nm that is due to the triplet excited state absorption. To eliminate the influence from the triplet excited state absorption on the Q-band region GSB at $t = 1.32$ ns, spectra deconvolution is required. The Q-band ground-state electronic absorption can be deconvoluted using three Gaussian peaks (Figure S9B), therefore, a similar deconvolution pattern was utilized for Q-band region GSB at $t = 1.32$ ns (Figure S9C, Fit Peak 3-5). Another two Gaussian peaks that account for the triplet excited state absorption were required to fit transient absorption spectra ($t = 1.32$ ns) in the 575-1075 nm spectral domain (Figure S9C, Fit Peak 1-2). Thus, the pure signal from Q-band region GSB at $t = 1.32$ ns can be acquired by addition of the three negative Gaussian peaks in Figure S9C (Fit Peak 3-5), and $\Delta A (715 \text{ nm}, t = 1.32 \text{ ns})$ obtained based on such deconvoluted spectra can be attributed only to the depletion of ground state populations (due excited triplet populations) (Figure S9D). Then, $\Phi_{\text{ISC}} (\text{ArPPtE-TDQ-EArPPt}) = \Delta A (715 \text{ nm}, t = 1.32 \text{ ns}) / \Delta A (715 \text{ nm}, t = 30 \text{ ps}) = (\ldots$
28.66 mOD) / (-14.37 mOD) = 0.5. In the similar manner, the $\Phi_{ISC}$ for RfsPZnArPPtE-TDQ-EArPPtRfsPZn can also be calculated, resulting in $\Phi_{ISC} (RfsPZnArPPtE-TDQ-EArPPtRfsPZn) = 0.73$.

Figure 85: Spectral deconvolution for transient absorption at t = 1.32 ns. Comparative spectra among ground-state electronic absorption (red dotted lines, rescaled), transient absorption at t = 30 ps (black solid line), and transient absorption at t = 1.32 ns (green solid line) (A). Spectral deconvolution of Q-band ground-state electronic absorption (B). Spectra deconvolution of transient absorption at t = 1.32 ns in the spectral domain of 575-1075 nm. Q-band region ground state bleach recovery calculations (D).
Figure 86: (A) Femtosecond transient absorption spectra of Q-band bleach and stimulated emission region in the time domain of solvation dynamics, experimental condition: $\lambda_{\text{exc}} = 900$ nm, power = 260 nJ / pulse, solvent = THF, ambient temperature, magic angle polarization. (B) Schematic illustration of dynamics Stokes shift of ArPZnE-TDQ-EArPZn in THF, where potential energy curve displacement ($\Delta q$) between $S_0$ and $S_1$ states along the solvation coordinate plays a key role.

4.4.7 TD-DFT Calculations and Population Analysis

All calculations were performed upon structures with aliphatic chains truncated to methyl groups (Figure S59, molecular structures on top). For these oligo(porphinato)metal(II) species, $C_{2v}$ conformeric minima could be formulated. Ground-state structure optimizations were performed with Density Functional Theory (DFT) using Gaussian 09, Rev C.1. The M110 functional was employed for all calculations. Optimizations were performed with minimal symmetry constraints using tight optimization criteria; initial optimizations used smaller basis sets but the final optimizations and TD-DFT calculations employed the 6-311g(d) basis set as implemented in Gaussian 09. TDDFT result files were post-processed using the GaussSum package; this software partitions the wavefunction amplitudes onto molecule fragments...
using Mulliken population analysis.\textsuperscript{101}

Figure 87: Comparison of TD-DFT predicted transitions and experimentally determined ground-state absorption spectra for ArPZnE-TDQ-EArPZn (A), ArPZnE-BTD-EArPZn (B), ArPPtE-TDQ-EArPPt (C), and ArPPtE-BTD-EArPPt (D).
Figure 88: Frontier orbitals plotted as 0.02 isodensity surfaces for (left) ArPZnE-TDQ-EArPZn and (right) ArPZnE-BTD-EArPZn, along with a diagram comparing their calculated energies. Arrows depict the major one-electron configurations with percentages representing each excitation’s contribution to the lowest-energy transition. The coefficients of each molecular orbital contributed by porphyrin, spacers (ETDQE and EBTDE), and zinc atoms are listed, determined by population analysis.
Figure 89: Frontier orbitals plotted as 0.02 isodensity surfaces for (left) ArPPtETDQ-EOarPPt and (right) ArPPtEBTD-EOarPPt, along with a diagram comparing their calculated energies. Arrows depict the major one-electron configurations with percentages representing each excitation’s contribution to the lowest-energy transition. The coefficients of each molecular orbital contributed by porphyrin, spacers (ETDQE and EBTDE), and zinc atoms are listed, determined by population analysis.
5. Dynamics of Charged Excitons in Electronically and Morphologically Homogeneous Single-Walled Carbon Nanotubes

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**Michael J. Therien** conceived the project, supervised the execution of all experiments, and contributed to writing the manuscript.

**Yusong Bai** designed the experiments, performed the steady-state and ultrafast spectroscopic measurements, analyzed the ultrafast spectroscopic data, and contributed to writing the manuscript.

**Jean-Hubert Olivier** prepared the single-walled carbon nanotube samples, performed steady-state spectroscopic measurements, and contributed to analyzing the spectroscopic data and writing the manuscript.

**George Bullard** acquired high-resolution Transmission electron microscopy and atomic force microscopy images for the single-walled carbon nanotubes samples.

**Chaoren Liu** contributed to analyzing the spectroscopic data and writing the manuscript.

5.1 Introduction

The trion, comprised of an exciton and a charge \(^{212}\), defines a unique quasiparticle species by its hybrid nature: it simultaneously carries excitation energy, net charge and unpaired spin. Exploitation of trions in optoelectronics have been impeded by their small...
binding energies ($\Delta E_{Tr}$) in conventional three-dimensional (3D, $\Delta E_{Tr} \sim 0.01$-0.3 meV) and 2D ($\Delta E_{Tr} \sim 1$-5 meV) semiconductors, wherein trion observation is made possible under cryo-conditions. In sharp contrast, optical excitation of the semiconducting single-walled carbon nanotube (SWNT) charged ground state ($E^{\text{g0}}$) gives rise to trions even at room temperature, due to the drastically increased $\Delta E_{Tr}$ ($\sim 100$ meV) in 1D SWNTs that arises from reduced dielectric screening. Owing to the substantial $\Delta E_{Tr}$, the tightly-bound trion quasiparticles in SWNTs offer new opportunities to manipulate charge, spin, and excitonic energy at room-temperature. To fully understand and exploit the exceptional potential of SWNT trion species, it is vitally important to attain fundamental insights into the dynamics and mechanisms that characterize their creation and decay.

Various transient optical methods have been used to indirectly assess trion dynamics in SWNTs; such studies report trion formation and decay time constants that vary by many orders of magnitude. Furthermore, corresponding mechanistic descriptions of trion generation and decay are ambiguous, due to the heterogeneity of the nanotube samples studied and the lack of a clear trion spectral fingerprint. Indeed, recent experimental and theoretical evidence for the suppression of exciton-free carrier scattering in SWNTs challenged the exciton-free hole scattering mechanism for ultra-fast (~50 fs) trion formation. Additionally, linear optical studies for charge-doped SWNTs demonstrate a new lower-energy absorption, which has been attributed to a direct
ground-to-trion optical transition \((E_{00} \rightarrow \text{Tr}^{*11}, \text{where Tr}^{*11} \text{denotes a low-lying electronically-excited trion state})^{216,219}\); no experimental evidence, however, has confirmed the nature of the state produced by SWNT \(E_{00}\) photon absorption.

Here, we describe the transient absorptive and dynamical properties of hole trions in length-sorted semiconducting \((6,5)\) SWNTs, wherein hole polaron densities are rigorously controlled. Owing to the electronic and morphological homogeneity of these SWNT samples, we clearly identify a trion transient absorptive hallmark, which in turn enables us to correlate dynamical processes characteristic of bright excitons, hole polarons, and trions, and thus unambiguously unveil trion formation and decay dynamics. By comparing trion dynamics acquired from pumping in resonance with the \(E_{00} \rightarrow E_{11}\) exciton transition, with those obtained from excitation of the previously assigned “trion transition”, we ascertain, for the first time, charge-doped 1D SWNTs do not possess a direct \(E_{00} \rightarrow \text{Tr}^{*11}\) optical transition. Moreover, these dynamical studies demonstrate, that under appropriate carrier-doping conditions, optical stimuli can result in near-unit conversion of excitons to trions, opening up new possibilities for SWNT-based optoelectronic devices that rely upon manipulating spin, energy and charge.

5.2 Results and Discussion

5.2.1 Acquiring Homogeneously-Engineered SWNTs

As a primary task for identifying trion dynamics, we acquired SWNTs having high uniformity of electronic structure (chirality) and length. Dispersion of these SWNTs
in the condensed phase by exploiting a binaphthalene-based polyanionic semiconducting polymer (S-PBN(b)-Ph5) that exfoliates, individualizes, and disperses SWNTs via a single-chain helically chiral wrapping mechanism, assures morphological homogeneity of these samples (Figure 90a)\(^{229}\). These semiconducting polymer-SWNT superstructures maintain a fixed polymer helical pitch length on the SWNT surface (Figure 90 b). The robustness of the polymer-SWNT superstructures in various aqueous and organic solvents enable multiple rigorous separation procedures that permit isolation of highly-enriched \(^{230}\) (purity > 90%), length-sorted\(^{231}\) (700 ± 50 nm) (6,5) SWNTs: these S-PBN(b)-Ph5-[(6,5) SWNTs] thus define uniquely engineered, consistent nanoscale carbon nanotube superstructures (Figure 90b, and Section 5.4.1 Figure 94) with which to probe transient absorptive signatures and dynamics of trions. Figure 90c provides benchmark transient absorption spectra for neutral S-PBN(b)-Ph5-[(6,5) SWNTs] in D\(_2\)O solvent, following E\(_{10}\)→E\(_{11}\) (1000 nm) optical excitation. Owing to the high homogeneity of these (6,5) SWNT superstructures, transient absorptive hallmarks for a broad range of quasiparticles are clearly visualized: these include a dominant E\(_{10}\)→E\(_{11}\) bleach centered at ~1000 nm \(^{232}\) and three positive transient absorption bands observed to the red of this bleach, at ~1100 nm (E\(_{11}\)→E\(_{11,\text{BX}}\)),\(^{231}\) ~1150 nm (\(^{3}\)E\(_{11}\)→\(^{3}\)E\(_{nm}\)) \(^{233}\), and ~1200-1300 nm (fast-decay signal, \(\tau\) ~0.7 ps) \(^{234}\).
Unambiguous analysis of trion dynamics also requires SWNTs with rigorously controlled carrier-doping densities. For this reason, we prepared hole-doped SWNTs through established methods that exploit K$_2$IrCl$_6$ as an oxidant capable of stoichiometrically transferring holes to S-PBN(b)-Ph$_5$-[(6,5) SWNT] superstructures in D$_2$O solvent$^{235}$. We emphasize that spectroscopic data demonstrate that the S-PBN(b)-Ph$_5$ polymer remains unoxidized by this procedure, as the semiconducting polymer valence band energy is stabilized by over 400 meV relative to that of the (6,5) SWNT$^{235}$. With length-sorted SWNTs in hand, and known nanotube concentrations in solution, the stoichiometric oxidant enables precise control over hole density ($[h^+]$) in S-PBN(b)-Ph$_5$-[(6,5) SWNTs] (see Section 5.4.2 for details).
Figure 91a electronic absorption data that chronicle the oxidative titration of the S-PBN(b)-Ph5-[(6,5) SWNT] superstructure highlight the progressive diminution of $E_{00} \rightarrow E_{11}$ transition oscillator strength and the correlated rise of a new lower-energy transition at $\sim1150$ nm, with increasing $[h^{+}]$ from 0 to 14.3 (100 nm)$^{-1}$. The new transition centered at 1150 nm has usually been ascribed to trion optical transition ($E_{00}^{+} \rightarrow Tr_{11}^{+}$)\textsuperscript{216, 219}; consistent with data described below, we denote this 1150 nm transition as $E_{00}^{+} \rightarrow E_{11}^{+}$, an exciton transition dressed by the interactions with hole polarons.

5.2.2 Identification of SWNT Trion Transient Absorptive Signature

To identify the trion transient absorptive signature, we acquired broadband pump-probe transient data on hole-doped on SWNTs in which $[h^{+}]$ was fixed and known; these studies unveiled a suspicious transient absorption band centered at 1190 nm. Representative transient absorption spectra of a heavily hole-doped S-PBN(b)-Ph5-[(6,5) SWNT] superstructure ($[h^{+}] \sim14.3$ (100 nm)$^{-1}$) manifest $E_{00} \rightarrow E_{11}$ ($\sim1000$ nm) and $E_{00}^{+} \rightarrow E_{11}^{+}$ ($\sim1150$ nm) bleaches, as well as a signal having an absorption maximum near 1190 nm (Figure 91b), the nature of which has not been previously determined. Importantly, this transient absorption manifold centered at 1190 nm is absent in undoped, neutral S-PBN(b)-Ph5-[(6,5) SWNTs], suggesting its correlation with nanotube hole polarons.
Figure 91: Ground-state absorption and pump-probe transient absorptive dynamical data for hole-doped SWNTs. (a) NIR ground-state absorption spectra that chronicle the extent of hole injection into S-PBN(b)-Ph5-(6,5) SWNTs. Experimental conditions: [(6,5) SWNTs] ~72.3 nM; SWNT length = 700 ± 50 nm; argon atmosphere; solvent = D2O; T = 293 K; optical path length = 2 mm; hole source (oxidant) = K2IrCl6. (b) Representative 2-D transient absorption spectral plot for a heavily hole-doped ([h+]~14.3 (100 nm)-1) S-PBN(b)-Ph5-(6,5) SWNT sample at the time delays noted; dotted lines highlight the major transition manifolds. Experimental conditions: λexc = 1000 nm; solvent = D2O; T = 293 K; magic angle polarization; excitation pump power = 140 µJ/cm². (c) Single wavelength, ps-time domain kinetic traces that chronicle the dynamics for E11 excitons (λprobe = 1000 nm): black – neutral SWNTs, red – hole-doped SWNTs; corresponding kinetic trace (green) highlighting the dynamics for hole trions (λprobe = 1190 nm). Kinetic traces plotted with absolute ΔAbsorption normalized.

The 1190 nm transient absorption signal is ascribed to a trion transient absorptive hallmark (Tr11→Tr,mnm, where Tr,mnm denotes a higher-lying hole-trion electronically excited state) based on dynamics analysis. Kinetic traces (λprobe = 1000 nm) representing E11 exciton dynamics in neutral and hole-doped S-PBN(b)-Ph5-[6,5] SWNTs, and the 1190 nm kinetic trace evinced in hole-doped S-PBN(b)-Ph5-[6,5] SWNTs, are plotted in Figure 91c for comparison (absolute ΔAbsorption normalized). E11 exciton dynamics in
neutral S-PBN(b)-PhS$_2$[(6,5) SWNTs] are governed by a 1D diffusion-controlled exciton-exciton annihilation (EEA) process ($2E_{11} \rightarrow E_{11,2} + E_{00} \rightarrow E_{11} + E_{00}$, where $E_{11,2}$ represents an $E_{11}$ exciton within the second manifold)\textsuperscript{232,236}, giving rise to a signal reduction of ~50\% within 2 ps (Figure 91c). On the other hand, $E_{11}$ exciton dynamics evinced in hole-doped SWNTs manifest faster decay relative to that determined in their neutral analogues (Figure 91c). Given the excess of hole polarons relative to excitons in SWNTs for this pump-probe experiment ([E$_{11}$]~0.6 (100 nm)$^{-1}$; [h$^+$]~14.3 (100 nm)$^{-1}$), we hypothesize that prior to EEA events, optically generated $E_{11}$ excitons diffuse to nearby hole-polaron sites and are trapped, forming hole trions. Furthermore, $E_{11}$ exciton decay in hole-doped SWNTs clearly correlates with the rise of the nascent transient absorption signal at 1190 nm within ~0.5 ps. As such, the correspondingly evolved transient absorption manifold centered at 1190 nm is attributed to a trion transient absorptive hallmark ($Tr_{+11} \rightarrow Tr_{+nm}$).

5.2.3 Unveiling Trion Dynamics by 1D Diffusion Kinetic Model

Kinetic modeling of these exciton and trion signals reveals that trions form via the diffusion of excitons to hole polaron sites; once formed, these quasiparticles decay in a first-order manner (schematically illustrated in Figure 92a). We evaluated trion formation and decay dynamics using a 1D diffusion kinetic model depicted in Figure 92b, that also takes into account 1D diffusion-controlled EEA processes explicitly described by Lüer\textsuperscript{232}. In this model, we assume that hole polarons in 1D SWNTs in D$_2$O are stationary sites on the timescale of these experiments (akin to 1D Wigner crystal)\textsuperscript{237},
contrasting the mobile nature of excitons. This assumption is justified by considering the long-range Coulomb repulsion amongst positively charged quasi-particles, and the fact that migration of such species is accompanied with significant outer-sphere reorganization energy in the condensed phase. We fit the E11 exciton and hole trion kinetic data with numerical solutions of the coupled differential equations that describe the kinetic model in Figure 92b (see Section 5.4.3 for details). As shown in Figure 92c, the agreement between our kinetic model and the experimental data provide compelling proof of a diffusion-controlled trion formation mechanism, and determine directly SWNT hole trion formation and decay constants ($k_{Tr} \sim 5.4 \times 10^{11}$ s$^{-1}$, and $k_{E-Tr} \sim 4.5 \times 10^6$ nm s$^{-1/2}$).

Figure 92: 1D diffusion kinetic model describing hole trion formation. (a) Schematic description of hole trion formation in hole-doped, optically-excited semiconducting SWNTs. (b) Diagrammatic representation of the four-state model used to fit the $E_{00} \rightarrow E_{11}$ and $Tr^{+}_{11} \rightarrow Tr^{+}_{nm}$ kinetic traces, where the $N_X(t)$ ($X = E_{11}, E_{11,2},$
\( \text{Tr}^*_{11}, \text{or } h^* \) corresponds to the densities \([(100 \text{ nm})^{-1}] \) of these quasi-particles at a certain time \( t \), \( k_{k0} \) is the intrinsic first-order decay rate constant for bright singlet excitons in (6,5) SWNTs, \( k_{k1} \) is the rate constant for the first-order decay from the second to the first exciton sub-band, \( k_{kT} \) is the first-order decay rate constant of trions, \( k_{\text{EEA}} t^{-1/2}N_{E11} \) is the EEA rate constant, and \( k_{\text{EEA}} t^{-1/2}N_{h^+} \) is the trion formation rate. Note, all rate constants are in units of \( \text{ps}^{-1} \).

(c) Kinetic traces for \( E_{00} \rightarrow E_{11} \) bleaching oscillator strength (red, scatter square) and \( \text{Tr}^*_{11} \rightarrow \text{Tr}^*_{nm} \) transient absorption oscillator strength (green, scatter circle), and corresponding numerical fits (solid curves) obtained using the kinetic model depicted in b. Note that data represented in c do not correspond to single-wavelength kinetics, as they are acquired from integrated Gaussian functions fitted to the corresponding spectral signals (Section 5.4.3).

We further studied the dependences of trion formation and decay dynamics upon hole polaron densities, and examined how \([h^+]\) impacts the diffusive behavior of excitons. As can be seen in Figure 93, a striking feature – manifest clearly in these dynamical data – is that the trion formation rate constant, \( k_{E-\text{Tr}}^* = k_{E-\text{Tr}} t^{-1/2}N_{h^+} \), depends on initial \([h^+]\), with \( k_{E-\text{Tr}}^* \) increasing monotonically from \( 3 \times 10^{11} \) to \( 1 \times 10^{12} \text{ s}^{-1} \) as \([h^+]\) increases from 0.3 to 14.3 \((100 \text{ nm})^{-1}\), while \( k_{\text{Tr}} \) does not \((\overline{k_{\text{Tr}}} = 3.9 \times 10^{11} \text{ s}^{-1}, \sigma_{SD} \sim 1.3 \times 10^{11} \text{ s}^{-1}\), where \( \overline{k_{\text{Tr}}} \) is the average value for \( k_{\text{Tr}} \), and \( \sigma_{SD} \) is the standard deviation) (Section 5.4.3). These observations are congruent with the 1D diffusion-controlled trion formation/decay picture highlighted in Figure 92a. Additionally, as \( k_{\text{EEA}} \sim \sqrt{32D_{E11}/\pi} \), where \( D_{E11} \) represents the exciton diffusion constant, we obtained a \( D_{E11} \) value of \( \sim 0.9 \text{ cm}^2\text{s}^{-1} \) for S-PBN(b)-Phi-[(6,5) SWNTs] dispersed in D$_2$O; note that this value is the same order of magnitude compared to exciton diffusion constants derived from pump-probe measurements of xerogel-dispersed SWNTs \footnote{232} and fluorescence quenching studies of SWNTs suspended in agarose gels \footnote{239}. Furthermore, an exciton diffusion length may be...
determined from the relation $L_{E11} = \sqrt{D_{E11} \tau_{E11}}$ (where $\tau_{E11}$ is the exciton decay time constant). For $[h^+] \sim 14.3 \text{ (100 nm)}^{-1}$ SWNTs, $\tau_{E11}$ is $\sim 0.5 \text{ ps}$, indicating that $L_{E11}$ is $\sim 6 \text{ nm}$, which matches closely the half spatial separation between hole polarons ($d_{h^+}/2 \sim 3.5 \text{ nm}$). This correlation between $L_{E11}$ and $d_{h^+}/2$ is consistent with the notion that trion formation in optically excited hole-doped SWNTs derives from an exciton diffusion process that occurs on a timescale over which hole polarons are effectively stationary.

![Figure 93: Hole trion formation and decay rate constants as a function of $[h^+]$. Summary plot of hole trion formation and decay rate constants as a function of $[h^+]$. Note that the hole trion formation rate constant is determined from the expression $k_{E-\text{Tr} \cdot t^{-1/2}N_{h^+}}$ (as both exciton and hole polaron concentrations vary as a function of time); here $t$ is selected at $0.5 \text{ ps}$; as $[h^+]$ is a function of time, this value is acquired from numerical simulation based on rate equations derived from the kinetic model in Figure 92b; hole trion decay rate constants are directly represented by $k_{\text{Tr} \cdot t}$, as trion decay is a first-order process. Error bars represent the uncertainty from fitting the exciton and trion kinetic traces.

Importantly, these experimental and the corresponding numerical simulation of these results (Section 5.4.4) indicate that exciton-to-trion conversion can approach unity under hole-doping levels that range from 6.1-14.3 (100 nm)$^{-1}$ (Figure 106). Based on the kinetic model in Figure 92b, the exciton decay rate in hole-doped SWNTs is determined
by \( \frac{d N_{E_{11}}}{dt} \) = \(-k_1 N_{E_{11}}\) + \((-k_{EEA} t^{-1/2} N_{E_{11}}^2)\) + \((-k_{E-Tr} t^{-1/2} N_{h} N_{E_{11}})\), wherein \((-k_1 N_{E_{11}})\), \((-k_{EEA} t^{-1/2} N_{E_{11}}^2)\), and \((-k_{E-Tr} t^{-1/2} N_{h} N_{E_{11}})\) represent the three exciton decay channels (intrinsic first-order decay, EEA, and trion formation, respectively). Using the \(k_{EEA}\) and \(k_{E-Tr}\) values obtained in these studies, our numerical simulations demonstrate that trion formation defines the dominant exciton decay channel for hole-doped SWNTs in which \([h^+]\) ranges from 6.1-14.3 (100 nm).¹

5.2.4 The Nature of Previously-Assigned Trion Optical Transition

The nascent 1150 nm band in Figure 91a, previously ascribed to trion optical transition (\(E_{00}^* \rightarrow Tr_{11}^*\))²¹₆,²¹₉, is purely excitonic (\(E_{00}^* \rightarrow E_{11}^*\)) in nature. If the 1150 nm absorption in Figure 91a originates from a direct \(E_{00}^* \rightarrow Tr_{11}^*\) optical transition, optically pumping this band should result in instantaneous formation of hole trions in hole-doped SWNTs, and hence an immediate observation of the trion transient absorption signal, \(Tr_{11}^* \rightarrow Tr_{nm}^*\). However, pump-probe transient optical measurements of hole-doped SWNTs (\([h^+] \approx 14.3\) (100 nm)) in which excitation is centered in this absorption manifold, demonstrate a gradual rise \(Tr_{11}^* \rightarrow Tr_{nm}^*\) signal (Section 5.5.5). These data indicate that a \(E_{00}^* \rightarrow Tr_{11}^*\) transition possesses little or no oscillator strength at 1150 nm. Moreover, following excitation at ~1130 nm, the resultant transient kinetic traces representative of \(E_{11}\) exciton and hole trion dynamics mirror those obtained for excitation at 1000 nm (Figure 108). Such dynamical similarities further demonstrate the 1150 nm absorption characteristic of hole-doped SWNTs is not an \(E_{00}^* \rightarrow Tr_{11}^*\) transition,
but a signature of an exciton absorption that is dressed by a Fermi sea of excess carriers, congruent with the $E^{*0} \rightarrow E^{*11}$ assignment in Figure 91a.

5.3 Conclusion

In summary, we have shown that trion quasi-particles form from exciton migration to stationary hole polaron sites in an optically excited, charged semiconducting SWNTs, while trion decay is a first-order process. These data demonstrate that under the experimental conditions here, trions are not produced by direct optical excitation of any ground-state absorption associated with hole-doped SWNTs, contrasting sharply the photophysics of carrier-doped conventional semiconductors, wherein trions may be produced via an optical transition from the ground state. This work further establishes a SWNT hole trion transient absorptive signature ($\text{Tr}^{*11} \rightarrow \text{Tr}^{*nm}$): as trion formation requires the co-existence of an exciton and a charge carrier, we emphasize that $\text{Tr}^{*11} \rightarrow \text{Tr}^{*nm}$ transition defines an unequivocal spectroscopic fingerprint for any study that aims to investigate optically-driven free-carrier generation in SWNTs. Importantly, under appropriate charge-doping conditions ($[h^{+}] \approx 6.1-14.3$ (100 nm)$^{-1}$), exciton-to-trion conversion can approach 100% following optical stimuli. Because these tightly-bound trions undergo drift in electric field $^{241}$, which results in simultaneous transportation of energy, charges and spin, these trion formation and decay dynamical data may guide design of new SWNT-based optoelectronic devices that include photovoltaics, photodetectors, and spintronics.
5.4 Materials and Methods

5.4.1 Preparation of Polymer-Wrapped (6,5) SWNTs and Morphological Characterization

Preparation of polymer-wrapped (6,5) SWNTs. Approximately 10 mg of nanotubes (Sigma Aldrich 704148-1G Lot# MKBJ6336V) were added to a vial containing 20 ml of aqueous 1.04% (w/v) sodium deoxycholate. The vial was bath sonicated for 15 min and then tip sonicated for 2 h (MISONIX, Ultrasonic Liquid Processors, S-4000) at a power level of 12W. The mixture was centrifuged (Optima TLX Ultracentrifuge) at 90,000 g for 1 h and the top 80% of the supernatant was collected. (6,5) SWNT purification was performed using an aqueous two phase extraction (ATPE)\textsuperscript{230}. Briefly, after addition of SWNTs to the “ATPE system”, (6,5) SWNTs were isolated in a given phase by varying sodium dodecyl sulfate concentration of the system. Once isolated, the layer containing the desired SWNTs was collected and an equal volume of aqueous 2% (w/v) sodium cholate was added. To prepare polymer-wrapped SWNTs, the previous solution was added to an aqueous mixture of the desired polymer dispersant. Surfactant and unbound polymer were removed by exchanging the solution into a buffer solution and subjecting to gel permeation chromatography (this step yielded length-sorted polymer-wrapped (6,5) SWNTs). The resulting sample was desalted via centrifugal filtration. The sample was washed with and then taken up in the desired solvent mixture \textsuperscript{229}. This solution was used with no further modifications.
**Morphological characterization.** The as-prepared polymer-SWNTs were characterized by atomic force microscopy (AFM), and the corresponding topographic intermittent contact AFM image associated with height profiles are provided in Figure 94. AFM images of S-PBN(b)-Phs-[(6,5) SWNT] dispersed in aqueous solvent corroborate the well-defined periodicities with constant pitch length of ~10 nm (Figure 94b). Also, the polymer-wrapped SWNTs are well individualized, as highlighted in Figure S1c.

![AFM characterization of S-PBN(b)-Phs-[(6,5) SWNT] samples. a, Topographic intermittent contact AFM image of S-PBN(b)-Phs-[(6,5) SWNT] from an aqueous suspension on a Si surface. b, The height profile along the blue arrow in the panel a; distances between two dash lines highlight the pitch length (~10 nm) of polymer-SWNT. c, The height profile along the red arrow in the panel a; the well separated peaks with height of ~1 nm highlight such polymer-wrapped SWNTs are individualized.](image)

**5.4.2 Determination of Hole Polaron and Exciton Densities in SWNT**

* Determination of hole polaron densities. The protocol for rigorously controlling hole polaron densities in SWNT has been explicitly described in a previous investigation (1). In brief, (i) SWNTs having uniform length \(l = 700 \pm 50\) nm distribution are obtained by gel permission chromatography (GPC) separation; (ii) the mass concentration \(\rho\) of SWNTs can be determined using the value from Zheng et al., which correlated OD =1 in
1 cm beam path length at $E_{00} \rightarrow E_{11}$ transition to 6.5 $\mu$g mL$^{-1}$ of (6,5) tubes (2); (iii) the molar concentration of the oxidant is experimentally determined. As the SWNT length is known, the “molecular weight” of these SWNTs, $M$ (g mol$^{-1}$) can be estimated. Then the molar concentration of SWNTs is calculated by $[\text{SWNTs}] = \rho \times 10^{-3} / M$ (for oxidative titration experiments, $[\text{SWNTs}] \sim 72$ nM). With known molar centration of the oxidant $[\text{K}_2\text{IrCl}_6]$ and $[\text{SWNTs}]$, and the SWNT length, the hole polaron densities can be calculated by $[h^+] = ([\text{K}_2\text{IrCl}_6] \times V_1) / ([\text{SWNTs}] \times V_2) / l$, where $V_1$ and $V_2$ are the volume of the titrant and SWNTs solution sample, respectively.

**Determination of exciton densities.** The protocol for rigorously controlling exciton densities in SWNTs has been described previously (3). Generally, from the measurement of excitation power, the number of incident photons ($P_I$) was calculated. 2) From the measurement of the transmitted excitation power of the SWNT solution and a blank solvent, the numbers of photons absorbed by the SWNTs ($P_A$) and solvent ($P_{Sol}$), as well as the number of photons scattered by the cuvette ($P_{Sc}$), were obtained using $P_A = P_I - P_{Sc} - P_{Sol} - P_T$, where $P_{Sc}$: the number of scattered photons, $P_{Sol}$: the number of photons absorbed by solvent, $P_T$: the number of transmitted photons, $P_A$: the number of absorbed photons. 3) From the linear absorbance of the SWNT solution, the SWNT concentration was determined. 4) From the beam diameter measurement, the illuminated volume ($V$) was obtained. 5) From the SWNT concentration and $V$, the number of SWNTs in the given $V$ was obtained. 6) From the computed number of absorbed photons and the
number of SWNTs in V, the number of excitons generated per 100 nm of SWNT unit length was calculated. We note that, for SWNTs samples having different $[h^+]$, the exciton densities are varying as a function of $[h^+]$, even though identical excitation conditions are applied throughout the measurements for all the hole-doped SWNTs samples; this phenomenon is due to phase space filling (4).

5.4.3 Model Description and Data Fitting

*Further description of the kinetic model and rate equations.* The kinetic model is derived based on 1D diffusion mechanism, where exciton-exciton and exciton-hole interactions are both considered. We adapted the simplified exciton-exciton annihilation (EEA) model described by Lüer and co-workers (5) that is derived based on pure one-dimensional diffusion and by assuming immediate annihilation upon contact. In addition to the assumptions that have been justified in the main text for this adapted model, we have two additional notes here: (i) in the differential equations describing the decay rate of excitonic species, dissociation of a trion into one $E_{11}$ exciton and one $h^+$ was initially considered by involving a term of $k_{T-E}N_{T_{11}^*}$, where $k_{T-E}$ represents the first-order trion dissociation rate constant (See below equation (5.4.3.1)-(5.4.3.4) for the corresponding changes); however, fitting kinetic data ($E_{11}$ exciton decay traces and hole trion evolution and decay traces acquired with differing $[h^+]$ but identical excitation conditions) using such a model consistently gives rise to $k_{T-E}$ ranging from $10$ to $10^3$ s$^{-1}$, that is negligible relative to other dynamical processes. In this regard, such a term
(k_{Tr-E}N_{Tr_{11}}^{+}) can be removed from the rate equations. (ii) In our rate equations, we express the intrinsic decay of singlet exciton as a term of \(-k_{10}N_{E_{11}}\) (\(k_{10} \sim 0.048 \text{ ps}^{-1}\)), contrasting to some previously used treatment, where singlet exciton decay was expressed as dispersive first-order decay (5, 6). Pump fluence-dependent measurements have been carried out here (\(\lambda_{\text{Pump}} = 1000 \text{ nm}\), and the kinetic traces (\(\lambda_{\text{Probe}} = 1010 \text{ nm}\)) are compared in Figure 95a, Figure 95b displays the corresponding kinetic data normalized at \(t_{\text{delay}} = 3\) ps. As can be seen in Figure 95b, variation of the pump fluence from 6.4 \(\mu\text{J cm}^{-2}\) to 228 \(\mu\text{J cm}^{-2}\) induces no observable changes to the kinetics in the longer delay range (\(t_{\text{delay}} > 3\) ps), and these kinetic traces beyond \(t_{\text{delay}} = 3\) ps can be fitted consistently using exponential functions, resulting in an averaged lifetime of \(\sim 20.7\) ps, congruent with data obtained from photoluminescence measurements (7-9). As such, in the present kinetic model, we describe the intrinsic decay of singlet excitons as a first-order process with a rate constant of \(k_{10} \sim 0.048 \text{ ps}^{-1}\), based on the data from pump-probe measurements with the S-PBN(b)-Ph-[(6,5) SWNT] samples. In summary, rate equations describing dynamics of E_{11} excitons, trions, and hole polarons can be derived as following:

\[
\frac{dN_{E_{11}}}{dt} = -k_{10}N_{E_{11}} + k_{EAA}(t-t_0)N_{E_{11}}^2 + k_{21}N_{E_{11},2} - k_{E-Tr_1}(t-t_0)N_{h^+}N_{E_{11}} + k_{Tr-E}N_{Tr_{11}}^+ \quad (5.4.3.1)
\]

\[
\frac{dN_{E_{11},2}}{dt} = \frac{1}{2}k_{EAA}(t-t_0)N_{E_{11}}^2 - k_{21}N_{E_{11},2} \quad (5.4.3.2)
\]

\[
\frac{dN_{Tr_{11}}^+}{dt} = k_{E-Tr}(t-t_0)N_{h^+}N_{E_{11}} - k_{Tr}N_{Tr_{11}}^+ \quad (5.4.3.3)
\]

\[
\frac{dN_{h^+}}{dt} = k_{E-Tr}(t-t_0)N_{h^+}N_{E_{11}} + k_{Tr}N_{Tr_{11}}^+ \quad (5.4.3.4)
\]
where, the $N_X$ ($X = E_{11}, E_{11}, 2, Tr_{11}$, or $h^*$) values correspond to the densities (/ 100 nm) of these quasi-particles, $k_{10} = 0.022 \text{ ps}^{-1}$ is the intrinsic first-order decay rate constant for bright singlet excitons in (6,5) SWNTs(7), $k_{21} = 23 \text{ ps}^{-1}$ is the rate constant for the first-order decay from the second to the first exciton sub-band(10), $k_{Tr}$ is the first-order decay rate constant of trions, $k_{EEA}$ is the EEA rate constant, and $k_{E-Tr}$ is the trion formation rate constant. Note that: (i) the $t^{-1/2}$ dependence of EEA and hole trion formation processes originate from 1D diffusion(11); (ii) $k_{E-Tr} = k_{EEA} / 2\sqrt{2}(5)$; and (iii) $t_0$ is fitting parameter for time zero.

**Figure 95:** $E_{11}$ exciton dynamics in neutral S-PBN(b)-Ph$_5$-[6,5) SWNT]. a, Excitation fluence-dependence of $E_{00} \rightarrow E_{11}$ bleaching signal intensity at 1010 nm. b, $E_{00} \rightarrow E_{11}$ bleach kinetics (same data as that displayed in a) normalized at $t_{\text{delay}} = 3 \text{ ps}$, and the exponential function fitting of the kinetic traces (fitting range: 3-2500 ps). Experimental conditions: solvent = D$_2$O, $T = 293 \text{ K}$, magic angle polarization, $\lambda_{\text{pump}} = 1000 \text{ nm}$, pump fluence = 6.4 $\mu$J cm$^{-2}$ (black), 24.0 $\mu$J cm$^{-2}$ (red), 80.0 $\mu$J cm$^{-2}$ (green), 288.0 $\mu$J cm$^{-2}$ (orange).

**Extraction of trion transient signal and fitting description.** As shown in Figure 96, overlap of transient signals is observed in the spectral domain of 1100 - 1350 nm, these include the $E_{00} \rightarrow E_{11}$ bleach (highlighted as “2”), $Tr_{11} \rightarrow Tr_{nm}$ transient absorption (highlighted as “3”), and a fast-decay near-infrared transient signal (highlighted as “1”).
An accurate fitting of trion kinetics requires signal separation among “1”, “2”, and “3”. We exploit Gaussian peak analyses to accomplish such signal separations. Gaussian peak deconvolution analyses involving multiple peaks without boundary conditions can lead to arbitrary fitting results that do not reflect real peak information. To avoid such possible fitting “errors”, we acquire the general peak information (including photon energy at peak maximum \( h\nu_{\text{Max}} \), and peak full-width at half maximum [FWHM]) for (i) signal “1”, and “2”, while keeping the peak information of signal “3” as a free parameter in the fitting. Note that, (i) \( h\nu_{\text{Max}} \) and FWHM for signal “1”, the fast-decay broad NIR transient absorption signal of hole-doped SWNTs, can be obtained from the transient spectral data of neutral SWNTs (identical excitation conditions as that for hole-doped SWNTs samples), as that highlighted by “1” in Figure 97; (ii) \( h\nu_{\text{Max}} \) and FWHM for signal “2”, the \( E^0_{\text{00}} \rightarrow E_{11}^+ \) bleach signal of hole-doped SWNTs, can be obtained from the linear absorption spectrum of the corresponding sample, as shown in Figure 98.

Figure 96: Two-dimensional pump-probe spectral data for hole-doped S-PBN(b)-Ph5-[6,5] SWNT. Two-dimensional pump-probe spectral data acquired in the NIR spectral domain (900-1350 nm). The signal intensity Δabsorption is given by the
The \( \text{E}^*_{\infty} \rightarrow \text{E}^*_{11} \) bleach, \( \text{Tr}^*_{11} \rightarrow \text{Tr}_{nm} \) transient absorption, and fast-decay NIR transient signal are highlighted as “2”, “3”, and “1”, respectively. Experimental conditions: solvent = D\(_2\)O, \( T = 293 \) K, magic angle polarization, \( [h^\ddagger] \sim 14 \) (100 nm)\(^3\), \( \lambda_{\text{Pump}} = 1000 \) nm, pump fluence = 140.0 µJ cm\(^{-2}\).

**Figure 97:** Two-dimensional pump-probe spectral data for neutral S-PBN(b)-Ph\(_5\)-[(6,5) SWNTs]. Two-dimensional pump-probe spectral data acquired in the NIR spectral domain (900-1350 nm). The signal intensity \( \Delta \text{absorption} \) is given by the color scale on the right. The fast-decay NIR transient signal is highlighted as “1”. Experimental conditions: solvent = D\(_2\)O, \( T = 293 \) K, magic angle polarization, \( \lambda_{\text{Pump}} = 1000 \) nm, pump fluence = 140.0 µJ cm\(^{-2}\).

**Figure 98:** Linear absorption spectrum for hole-doped S-PBN(b)-Ph\(_5\)-[(6,5) SWNTs]. Linear absorption spectrum of hole-doped SWNTs acquired over the 850-1300 nm spectral domain. Gaussian peak analysis was exploited to acquire the peak information for \( \text{E}^*_{\infty} \rightarrow \text{E}^*_{11} \) transition. Experimental conditions: solvent = D\(_2\)O, \( T = 293 \) K.
We utilized the following Gaussian distribution function to accomplish the spectral fitting for selective time delays:

\[
f(x, \mu_i, \sigma_i, A_i) = \sum_{i=1}^{3} A_i \frac{1}{\sigma_i \sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{x - \mu_i}{\sigma_i} \right)^2} + y_0
\]  

(5.4.3.5)

where \( x \) is the photon energy (unit in eV) as variable, \( \mu_i \) is the expected value (\( \hbar \nu_{\text{Max}} \)) of the \( i \)th signal, \( \sigma_i \) is related to FWHM of the \( i \)th signal by FWHM = \( 2\sqrt{2\ln2} \sigma \), \( A_i \) is the peak area of the \( i \)th signal, and \( y_0 \) is an offset (viewed as baseline). Utilizing such a Gaussian function while applying boundary conditions for signal “1” and “2” (acquired as noted above) allows successful signal extraction for trion transient absorption at selected time delays. Figure 99 displays the separated signal for “1”, “2”, and “3” at selected time delays. We note that the E_{00} \rightarrow E_{11} bleaching signal was not involved in this signal processing, as it is intrinsically well separated from “1”, “2”, and “3” (i.e. signals in the energy domain of 0.918 – 1.148 eV were treated with Gaussian peak analyses). Likewise, dynamical analyses for SWNT samples with varying hole-doping levels can all be accomplished in the similar manner as described above. The transient absorption spectra for SWNTs samples with [\( h \tau \)] = 0.3, 0.7, 3.5, and 6.1 (100 nm)\(^{-1}\) are also provided in Figure 100.
Figure 99: Two-dimensional mapping of separated transient signals in the NIR domain. 

a, Extracted transient signals for $E^\ast_{10} \rightarrow E^\ast_{11}$ bleach.  
b, Extracted transient signals for $Tr^\ast_{11} \rightarrow Tr^\ast_{nm}$ absorption.  
c, Extracted transient signals for the fast-decay NIR absorption as highlighted in Figure 98.  

Note: (i) data processing range spans the time domain of 0.07 – 5.48 ps, and the spectral domain of 1080 – 1350 nm; (ii) data processing was accomplished based with equation (5) using Python for coding; (iii) certain extremely noisy data points were removed from this analysis.
Figure 10: Two-dimensional pump-probe spectra for S-PBN(b)-Ph-[(6,5) SWNT] having varying \([h^+]\). a, Two-dimensional pump-probe spectra of hole-doped SWNTs with \([h^+] = 0.3 (100 \text{ nm})^{-1}\). b, Two-dimensional pump-probe spectra of hole-doped SWNTs with \([h^+] = 0.7 (100 \text{ nm})^{-1}\). c, Two-dimensional pump-probe spectra of hole-doped SWNTs with \([h^+] = 3.5 (100 \text{ nm})^{-1}\). d, Two-dimensional pump-probe spectra of hole-doped SWNTs with \([h^+] = 6.1 (100 \text{ nm})^{-1}\). Experimental conditions: solvent = D_2O, \(T = 293 \text{ K}\), magic angle polarization, \(\lambda_{\text{Pump}} = 1000 \text{ nm}\), pump fluence = 140.0 \(\mu\text{J cm}^{-2}\).

Data fitting for each kinetic trace starts from \(t_{\text{delay}} = 130 \text{ fs}\). Initial values for the densities of \(E_{11}\) excitons ([\(E_{11}\)]), \(E_{11}\) excitons in the second manifold ([\(E_{11, 2}\)]), trions ([\(\text{Tr}^{+11}\)]) and hole polarons ([\(h^+\)]) are required in order to numerically solve these ordinary differential equations (ODEs). The initial values for \([E_{11, 2}]\) and \([\text{Tr}^{+11}]\) are set as zero, while the initial values for \([E_{11}]\) and \([h^+]\) can be experimentally determined (details see Section 5.4.2). The fitting is accomplished by using the nonlinear curve-fitting function (‘lsqcurvefit’) coupled with ‘ODE45’ function in MATLAB. Curve-fitting ranges from 195.
$t_{\text{delay}} = 100 \text{ fs to } t_{\text{delay}} = 20 \text{ ps}$. Numerical solutions of these ODEs are plotted as decay curves for $E_{11}$ excitons, $E_{11}$ excitons in the second manifold, trions and hole polarons, as shown in Figure 101a ($[E_{11}] \sim 0.7 \text{ (100 nm)}^{-1}$, $[h^+] \sim 14 \text{ (100 nm)}^{-1}$). Figure 101b displays the same results, but with densities of the corresponding species being normalized. In this regard, we note that although there is no direct spectroscopic signature for monitoring the population densities for $E_{11}$ excitons in the second manifold and hole polarons, these numerical solutions provide a track for the historical changes of $[E_{11}, 2]$ and $[h^+]$ that are not spectroscopically measurable.

**Figure 101**: Numerical solutions for $[E_{11}]$, $[E_{11,2}]$, $[\text{Tr}^+_{11}]$, and $[h^+]$. a, Numerical solutions for $[E_{11}]$, $[E_{11,2}]$, $[\text{Tr}^+_{11}]$, and $[h^+]$ obtained by fitting hole-doped S-PBN(b)-Ph5-[(6,5) SWNT] ($[h^+] \sim 14.0 \text{ (100 nm)}^{-1}$) using equations (1)-(4). Initial values are provided as following: $[E_{11}] = 0.7 \text{ (100 nm)}^{-1}$, $[E_{11,2}] = 0.0 \text{ (100 nm)}^{-1}$, $[\text{Tr}^+_{11}] = 0.0 \text{ (100 nm)}^{-1}$, $[h^+] = 14.0 \text{ (100 nm)}^{-1}$. b, Same data plot as that in a, but with population densities of the corresponding species being normalized.

**Trion formation and decay rate constants**. In Figure 93, trion formation and decay dynamics are presented by 2-D plot at a selected time point ($t_{\text{delay}} = 0.5 \text{ ps}$) for a parallel comparison between trion formation rate constant $(k_{E-\text{Tr}}t^{-1/2}N_{h^+})$ and trion decay rate constant $(k_{\text{Tr}})$. In fact, as $k_{E-\text{Tr}}t^{-1/2}N_{h^+}$ varies as a function of both $[h^+]$ and $t$, a 3-D plot conveys a more comprehensive picture of these trion dynamics (Figure 102). As trion
decay is a first order process, the corresponding rate constant is not varying as a function of time and \([h^+]\). In contrast, trion formation rate constant \((k_{E\rightarrow Tr} - \frac{1}{2}N_{h^+})\) not only varies as a function of time, but also, at each selected time point, changes its value based on the \([h^+]\) characteristic of that time. These **Figure 102** data are clearly congruent with the conclusion that trions are formed via migration of excitons to stationary hole polaron sites, while these states decay in a first-order manner.

**Figure 102**: Hole trion formation and decay rate constants as a function of both \([h^+]\) and \(t\). Trion formation \((k_{E\rightarrow Tr} - \frac{1}{2}N_{h^+})\) and decay \((k_{Tr})\) rate constants (in ps\(^{-1}\) unit) obtained from fitting values for \(k_{E\rightarrow Tr}\) and \(k_{Tr}\), and the numerical solutions for \([h^+]\) (see **Figure S8**).

**Figure 103**: Standard deviations of diffusion-controlled vs non-diffusive models as a function of hole polaron density. **a**, Standard deviations of exciton dynamical data fitting based on a diffusion-controlled trion formation model (black)
and a non-diffusive trion formation model (red). b, Standard deviations from trion dynamical data fitting based on a diffusion-controlled trion formation model (black) and a non-diffusive trion formation model (red).

A non-diffusive trion formation model has also been examined here. The corresponding ODEs can be derived as below:

\[
\frac{dN_{E_{11}}}{dt} = -k_{10}N_{E_{11}} - k_{E_{11}}(t-t_0)^{\frac{1}{2}}N_{E_{11}}^2 + k_{E_{11}}N_{E_{11}}N_{H_{11}}N_{E_{11}} + k_{E_{11}}N_{E_{11}}N_{Tr_{11}} \tag{5.4.3.6}
\]

\[
\frac{dN_{E_{11}}}{dt} = \frac{1}{2}k_{E_{11}}(t-t_0)^{\frac{1}{2}}N_{E_{11}}^2 - k_{E_{11}}N_{E_{11}} \tag{5.4.3.7}
\]

\[
\frac{dN_{Tr_{11}}}{dt} = k_{E_{11}}N_{H_{11}}N_{E_{11}} - k_{E_{11}}N_{Tr_{11}} \tag{5.4.3.8}
\]

\[
\frac{dN_{Tr_{11}}}{dt} = k_{E_{11}}N_{H_{11}}N_{E_{11}} + k_{E_{11}}N_{Tr_{11}} \tag{5.4.3.9}
\]

Compared to the diffusion-controlled model (equation (5.4.3.1) – (5.4.3.4)), this non-diffusive model lacks a time-dependent term \((t-t_0)^{\frac{1}{2}}\) in the trion formation rate constant. The suitability of these two models can be evaluated based on their standard deviations \((\sigma)\). As can be seen in Figure 103, these two models display quite similar \(\sigma\) values for fitting the exciton and trion dynamics in the low hole density regime (i.e. \([h] \sim 0.3 – 0.7\) (100 nm)\(^{-1}\)); however, fitting of the dynamical data in the medium-to-high hole density regime (i.e. \([h] \sim 3.5 – 14.3\) (100 nm)\(^{-1}\)) clearly shows that the diffusion-controlled trion formation model manifests significantly smaller \(\sigma\) values relative to the non-diffusive model (see Figure 104-105 for raw data and fitting curves). In this regard, the diffusion controlled model mathematically displays global suitability for reproducing the experimentally determined exciton and trion dynamics, while the non-diffusive
model is only capable of reproducing the dynamics when trion formation makes a minor
collection to the overall exciton decay dynamics (i.e. in low hole doping regime).

![Numerical fitting of the diffusion-controlled vs non-diffusive models in the low hole density regime. a and b, diffusion-controlled vs non-diffusive model fitting of exciton and trion dynamical data at \([h'] \sim 0.3 \text{ (100 nm)}^{-1}\). c and d, diffusion-controlled vs non-diffusive model fitting of exciton and trion dynamical data at \([h'] \sim 0.7 \text{ (100 nm)}^{-1}\). Furthermore, the non-diffusive model generates unrealistic fitting parameters.

For example, for \([h'] \sim 14.3 \text{ (100 nm)}^{-1}\) dynamical data, the non-diffusive model results in
\(k_{\text{EEA}} \sim 1.66 \times 10^4 \text{ nm s}^{0.5}\), corresponding to \(D_{\text{E11}} \sim 2.7 \times 10^7 \text{ cm}^2 \text{ s}^{-1}\), a value many orders of magnitude removed from the independently established exciton diffusion constants in
SWNTs. Also, for the first-order trion decay process, the diffusion-controlled model gives rise to an average (from all $[h^+]$) trion decay rate constant of $\sim0.42$ ps$^{-1}$, a value close to the result ($\sim0.36$ ps$^{-1}$, averaged from all $[h^+]$) from simple single exponential fitting of the trion decay dynamics, thus mathematically making sense (as a simple single exponential model corresponds to a first-order process described in the diffusion-controlled model). In the non-diffusive model, although trion decay maintains the same form as that in the diffusion-controlled model, i.e. $k_{\text{Tr-E}}N_{\text{Tr}_i}$, the lack of the $(t-t_0)^{1/2}$ term in the description of trion formation mathematically forces a fit for the average $k_{\text{Tr-E}}$ of $\sim0.9$ ps$^{-1}$, which is incongruent with simple inspection of the data. These fitting results point to the fact that compared to the non-diffusive trion formation model, a diffusion-controlled trion formation model is more appropriately describes the exciton and trion dynamical data acquired for hole-doped SWNTs.
Figure 105: Numerical fitting of diffusion-controlled vs non-diffusive models in the medium-to-high hole density regime. a and b, diffusion-controlled vs non-diffusive model fitting of exciton and trion dynamical data at \([h^+] = 3.5 \text{ (100 nm)}^{-1}\). c and d, diffusion-controlled model vs non-diffusive model fitting of exciton and trion dynamical data at \([h^+] = 6.1 \text{ (100 nm)}^{-1}\). e and f, diffusion-controlled model vs non-diffusive model fitting of exciton and trion dynamical data at \([h^+] = 14.3 \text{ (100 nm)}^{-1}\).
5.4.4 Evaluation of Exciton-to-Trion Conversion

*Simple qualitative estimation of the exciton-to-trion conversion yield.* We note that the exciton-to-trion formation quantum yield ($\Phi_{E\rightarrow Tr}$) may be directly estimated from the relation $\Phi_{E\rightarrow Tr} \sim k_{E\rightarrow Tr} / (k_{E\rightarrow Tr} + k_{EEA} + k_{10})$, where $k_{E\rightarrow Tr}$ is trion formation rate constant, $k_{EEA}$ is EEA rate constant, and $k_{10}$ is the intrinsic first-order decay rate constant for singlet exciton. Here, a simple bi-exponential function may be used to fit the trion transient absorption signal for obtaining a phenomenological $k_{E\rightarrow Tr}$ in the dimension of ps$^{-1}$ (this value is $\sim 2.38$ ps$^{-1}$). The phenomenological $k_{EEA}$ and $k_{10}$ are readily acquired from bi-exponentially fitting the neutral SWNTs E$11$ kinetic trace, which are $\sim 0.67$ ps$^{-1}$ and 0.048 ps$^{-1}$, respectively. Therefore, $\Phi_{E\rightarrow Tr} \sim 2.38$ ps$^{-1} / (2.38$ ps$^{-1} + 0.67$ ps$^{-1} + 0.048$ ps$^{-1}) = 0.77$.

Additionally, if the E$11$ exciton bleaching signature dynamics of heavily hole-doped (e.g. [$hr$] $\sim 6.1 - 14.3$ (100 nm)$^{-1}$) SWNTs samples were fitted bi-exponentially, a fast decay time constant, whose value is close to the bi-exponentially-fitted trion formation time constant of the same sample, can always been obtained; this fast decay components depletes at least 70% of E$11$ exciton population. Based on this simple dynamical correlation and the above estimated $\Phi_{E\rightarrow Tr}$ (without applying any complex models), we estimate that the lower limit for exciton-to-trion conversion in (6,5) SWNTs with [$hr$] $\sim 6.1-14.3$ (100 nm)$^{-1}$ should be $\sim 70\%$. Additionally, in the absence of any mathematical model, the dynamical correlation between the decay of E$11$ excitons and rise of trions may be directly visualized by looking at the raw kinetic data in Figure 92c, particularly
for the initial ~1 ps.

Note that this qualitative analysis is congruent with the notion that trion formation serves as the dominant decay channel that depletes excitons in SWNTs where $[h^+]$ ranges from 6.1-14.3 (100 nm)$^{-1}$.

**Quantitative estimation on exciton-to-trion conversion yield based on numerical simulation.** Based on equations (5.4.3.1)-(5.4.3.4), the exciton decay rate in hole-doped SWNTs is determined by

$$\left(\frac{dN_{E11}}{dt}\right)_{\text{decay}} = (-k_{10}N_{E11}) + (-k_{\text{EEA}}t^{-1/2}N_{E11}^2) + (-k_{\text{E-Tr}}t^{-1/2}N_{h^+}N_{E11}),$$

wherein $(-k_{10}N_{E11})$, $(-k_{\text{EEA}}t^{-1/2}N_{E11}^2)$, and $(-k_{\text{E-Tr}}t^{-1/2}N_{h^+}N_{E11})$ represent the excitons decay channels through excitons intrinsic first-order decay, EEA, and trion formation, respectively (note, $t = t-t_0$). Among there parameters, $k_{10}$ is a constant acquired from experiment, $k_{\text{EEA}}$ and $k_{\text{E-Tr}}$ are acquired from fitting the exciton and trion dynamics, $N_X (X = h^+, \text{or} E_{11})$ are the numerical solutions of equations (5.4.3.1)-(5.4.3.4) following fitting the excitons and trions dynamics. As such, the exciton decay rates through different decay channels can be plotted as Figure 106. As can be seen in Figure 106, for $[h^+] \sim 6.1-14.3$ (100 nm)$^{-1}$, trions formation predominates in excitons decay channels, while for $[h^+] \leq 3.5$ (100 nm)$^{-1}$, EEA process starts to compete with the trion formation process in exciton decay channels. The $\Phi_{\text{E-Tr}}$ (exciton-to-trion conversion yield) can further be quantified by comparing the integration area of the different decay channels shown in Figure 106. Particularly, for $[h^+] \sim 14.3$ (100 nm)$^{-1}$, $\Phi_{\text{E-Tr}} = 0.91$; for $[h^+] \sim 6.1$ (100 nm)$^{-1}$, $\Phi_{\text{E-Tr}} = 0.80$; while for $[h^+] \sim 3.5$ (100 nm)$^{-1}$, $\Phi_{\text{E-Tr}} = 0.48$. Such $\Phi_{\text{E-Tr}}$ determinations are highly
consistent with the above qualitative estimations, and they point to the conclusion that under appropriate hole-doping densities (i.e. \([h^+] \sim 6.1-14.3\) (100 nm)\(^{-1}\)), exciton-to-trion conversion yield can approach unity.

**Figure 106:** Exciton decay rate evaluated as a function of exciton intrinsic decay, EEA, and trion formation decay channels. 

- a. Excitons intrinsic decay rate, EEA rate, and trions formation rate as a function of time, initial \([h^+] = 14.3\) (100 nm)\(^{-1}\). 
- b. Same as a, except initial \([h^+] = 6.1\) (100 nm)\(^{-1}\). 
- c. Same as a, except initial \([h^+] = 3.5\) (100 nm)\(^{-1}\).

### 5.4.5 Examination of Excitation Wavelength Dependence

To examine the nature of the 1150 nm-centered absorption band, we optically excited hole-doped ([\(h^+] \sim 14\) (100 nm)\(^{-1}\)) S-PBN(b)-Ph\(_5\)·[(6,5) SWNT] sample with a pump wavelength of 1130 nm, and pump photon flux of \(1.1 \times 10^{12}\) pulse\(^{-1}\). The corresponding transient spectra and selected single-wavelength kinetic traces are presented in comparison with that obtained from optical excitation at 1000 nm (photon flux: \(9.1 \times 10^{11}\) pulse\(^{-1}\)) (Figure 107, and Figure 108, respectively). As can been in these spectra and kinetic traces, no evident differences can be observed. Again, we denote the ~1190 nm absorption band observed in hole-doped SWNTs as an \(E^{*00} \rightarrow E^{*11}\) transition. Optical pumping at this band should generate lower-energy (relative to the energy of \(E^{*11}\) exciton) excitons that are diffusive in nature. Such excitons can interact with hole
polarons and form trions. Congruent with this interpretation, we observe the fact that optically pumping at 1190 nm with a photon flux close to that of pumping at 1000 nm gives rise to similar trion transient signal intensity relative to that obtained under 1000 nm optical pump, even though the oscillator strength of \( \text{E}_0^0 \rightarrow \text{E}_{11}^+ \) transition is about twice as that of the \( \text{E}_0^0 \rightarrow \text{E}_{11}^+ \) transition at 1130 nm (Figure 98).

Figure 107: Representative transient absorption spectra obtained for heavily hole-doped S-PBN(b)-Ph-(6,5) SWNTs. a, Transient absorption spectra at selected time delays for hole hole-doped S-PBN(b)-Ph-(6,5) SWNTs following excitation at 1000 nm (excitation photon flux: \( 9.1 \times 10^{11} \) pulse\(^{-1} \)). b, Transient absorption spectra at selected time delays for hole hole-doped S-PBN(b)-Ph-(6,5) SWNTs following excitation at 1130 nm (excitation photon flux: \( 1.1 \times 10^{12} \) pulse\(^{-1} \)). Experimental conditions: \( [r^+] = 14.0 \) (100 nm)\(^2\), solvent = D\(_2\)O, \( T = 293 \) K, magic angle polarization.
Figure 108: Kinetic traces representative of dynamics for $E_{11}$ excitons and hole trions in heavily hole-doped S-PBN(b)-Ph$_5$-[(6,5) SWNTs]. Representative kinetic traces selected at $\lambda_{\text{Probe}} = 1000$ nm (representative of $E_{00} \to E_{11}$ transition; $\lambda_{\text{Pump}} = 1000$ nm: black, $\lambda_{\text{Pump}} = 1130$ nm: green) and $\lambda_{\text{Probe}} = 1190$ nm (representative of $Tr^{+11} \to Tr^{+nm}$ transition; $\lambda_{\text{Pump}} = 1000$ nm: red, $\lambda_{\text{Pump}} = 1130$ nm: orange) in ps time-domain for hole-doped S-PBN(b)-Ph$_5$-[(6,5) SWNT] ($[hr] = 14.0$ (100 nm)$^{-1}$). Kinetic curves are plotted with absolute $\Delta$Absorption being normalized.

5.4.6 Laser Pulse Characterization and Nature of the $E_{00} \to E_{11}$ Pumping

The deconvoluted steady-state absorption spectra shown in Figure S5 point to the fact that SWNTs with chiralities other than (6,5) are present and contribute to the electronic absorption spectrum of the ground-state sample in the spectral domain of 900-1300 nm. To address the potential issue that transient optical signals following (6,5) SWNTs $E_{00} \to E_{11}$ optical pumping could be contaminated by the transient absorptive contributions of other SWNT species other than (6,5) SWNTs, we characterized our laser pulse with the TOPAS output being set to 1.24 eV, and the corresponding laser pulse shape is shown in Figure 109. As can be seen in Figure 109, the 1.24 eV laser pulse display maximum overlap with (6,5) SWNT $E_{00} \to E_{11}$ transition, and is energetically...
separated from the corresponding $E_{00} \rightarrow E_{11}$ transitions of SWNTs of other chiralities (the combined concentration of which are one order of magnitude smaller than the (6,5) SWNT population); thus, these other SWNT populations will in no way impact the transient signal analysis of (6,5) SWNT excitonic dynamics.

Figure 109: Characterization of excitation laser pulse. a, 1.24 eV energy laser pulse characterized using a fiber optic path cable (Ocean Optics); data were collected using Ocean Optics SpectraSuite software; the FWHM (0.012 eV) and center energy ($X_c \sim 1.24$ eV) of the laser pulse in fitted (red curve of the inset) by Gaussian function. b, An overlap of the 1.24 eV laser pulse with the deconvoluted steady-state absorption spectra (Figure 98) of hole-doped SWNTs.
6. Conclusions

At a molecular level, this work shows that many unusual, but desirable photophysical properties can be engineered through (i) coupling distinct chromophoric oscillator photophysics via an ethyne-linkage topology; (ii) varying the nature of the initially prepared electronically excited state wavefunctions. Along this line, two new libraries of NIR-active supermolecular chromophores (i.e. M-(PM')ₙ-M and PM-Sp-PM) have been established, wherein exceptional red-to-NIR spectral coverage and tunable excited-state relaxation dynamics (i.e. S₁→S₀ radiative decay, S₁→S₀ internal conversion, S₁→T₁ intersystem crossing, and T₁→S₀ decay rate constants) are simultaneously attained, making M-(PM')ₙ-M and PM-Sp-PM well poised for a number of optoelectronic applications that include OPL, triplet-triplet annihilation photon upconversion (TTA UC), and NIR bioimaging. Moving to nanoscale systems, this work probes the dynamics of charged excitons (i.e. trions) in electronically and morphologically homogeneous SWNTs, which demonstrate: (i) trion quasiparticles exclusively derive from a precursor exciton state, (ii) exciton-to-trion conversion can approach unity under appropriate excitation and charge-doping conditions. This work further establishes a SWNT hole trion transient absorptive signature (Tr₊₁→Tr₊₀): as trion formation requires the co-existence of an exciton and a charge carrier, we emphasize that Tr₊₁→Tr₊₀ transition defines an unequivocal spectroscopic fingerprint for any study that aims to investigate optically-driven free-carrier generation in SWNTs. Importantly, because trions simultaneously carry excitation energy, charge and spin, the findings here
may guide design of new SWNT-based optoelectronic devices that include photovoltaics, photodetectors, and spintronics.
References


Biography

Yusong Bai was born in Zhuozhou, Hebei Province, P. R. China, in July 1988. He received his B.S. degree in School of Chemistry and Environment in Beijing University of Aeronautics and Astronautics in June 2011.

In August 2011, Yusong became a graduate student in the Department of Chemistry, Duke University, wherein he works in the Therien Group. In Duke, Yusong’s research interest lies in probing and controlling light-matter interactions in condensed phase, with particular emphasis on interrogating and managing photo-induced electronically excited-state dynamics of various supermolecular to nanoscale structures that include ethyne-bridged highly-conjugated (porphinato)metal(II) architectures, semiconducting single-walled carbon nanotubes, etc. His work in Ph.D. has given rise to two first-author published manuscripts (one more first-author manuscript has been submitted, three others first-author work are to be submitted), and four co-author published manuscripts. Yusong has previously been awarded Undergraduate Distinction Award (Duke), GPNANO Fellowship, Paul M. Gross Fellowship, Burroughs Wellcome Fellowship, and the John T. Chambers Scholar from The Fitzpatrick Institute of Photonics.