

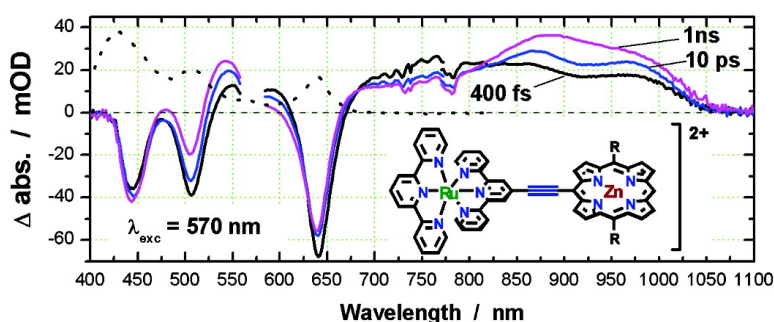
Communication

Highly Conjugated (Polypyridyl)metal–(Porphinato)zinc(II) Compounds: Long-Lived, High Oscillator Strength, Excited-State Absorbers Having Exceptional Spectral Coverage of the Near-Infrared

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Highly Conjugated (Polypyridyl)metal–(Porphinato)zinc(II) Compounds: Long-Lived, High Oscillator Strength, Excited-State Absorbers Having Exceptional Spectral Coverage of the Near-Infrared

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Examples of electronically excited chromophores that absorb strongly in the near-infrared (NIR) are limited.^{1–3} Established organic and coordination compounds that feature such NIR-absorbing excited states exploit either conjugation motifs common to conducting polymers,^{1,2a–c} linkage topologies that support intervalence charge transfer (IVCT) transitions,^{2,d,e} or lanthanide ions.³ The S_1 and T_1 states of highly π -conjugated, low band-gap materials usually express large nonradiative rate constants and correspondingly short excited-state lifetimes, while analogous electronically excited IVCT and lanthanide-ion absorbers manifest weak LaPorte-forbidden transition manifolds. We report here a class of highly conjugated supermolecular chromophores that not only feature electronically excited states that absorb over broad NIR spectral windows with considerable oscillator strength but also manifest lifetimes (1–50 μ s) that are extra-ordinarily long, relative to those of classic low band-gap organic materials.

Previous experiments establish that when (porphinato)zinc(II) (PZn) and metal(II)polypyridyl (M) units are connected via an ethyne unit that aligns the chromophoric CT transition dipoles in a head-to-tail arrangement, exceptional excited-state interpigment electronic communication within the supermolecule is enforced.⁴ Electronic absorption spectra of **RuPZn**, **OsPZn**, **RuPZnA**, **OsPZnA**, **OsPZnOs**, and **RuPZnOs** evince strong mixing of PZn-based oscillator strength with M charge-resonance bands and display a variety of low-energy electronic transitions that feature significant absorption oscillator strengths (Figure 1, Figure S1).⁴ Figure 1 displays transient absorption spectra for these species recorded over a 600–1100-nm range at a 1-ns time delay. Remarkably, all of these compounds manifest *intense* $T_1 \rightarrow T_n$ NIR transition manifolds that feature extraordinary spectral breadth and enormous absorptive extinction coefficients at $\lambda_{\max}(T_1 \rightarrow T_n)$ that span $3\text{--}10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Table 2, Supporting Information). These spectral features highlight the amenability of this structural motif for regulating excited-state absorptive cross-sections over broad NIR spectral domains [Compound ($\lambda_{\max}(T_1 \rightarrow T_n)$, fwhm): **RuPZn** (891 nm, 2800 cm^{-1}), **RuPZnA** (931 nm, 1950 cm^{-1}), **OsPZn** (960 nm, >1960 cm^{-1}), **OsPZnA** (985 nm, >2550 cm^{-1}), **RuPZnOs** (980 nm, 1700 cm^{-1}), **OsPZnOs** (~996 nm, 2220 cm^{-1}), **RuPZnOs** (~1050 nm, 2220 cm^{-1})]. Notably, the excited-state lifetimes of these chromophores are unusually long relative to those of conventional PZn and (terpyridyl)metal chromophores, ranging from 0.8 (**RuPZnOs**) to 45 μ s (**RuPZn**) (Table 2).

Photophysical properties akin to those described here lack precedent with respect to the well-established excited-state properties of monomeric porphyrin and metal polypyridyl complexes. Neither monomeric PZn^{2a} nor [bis(terpyridyl)]metal [M(tpy)₂] compounds^{2f} feature NIR transient absorption bands. The metal-to-ligand charge-transfer (MLCT) excited T_1 state lifetimes of Ru(tpy)₂²⁺ and Os(tpy)₂²⁺ are 250 ps and 269 ns, respectively,⁵ further underscoring the divergent photophysical nature of these

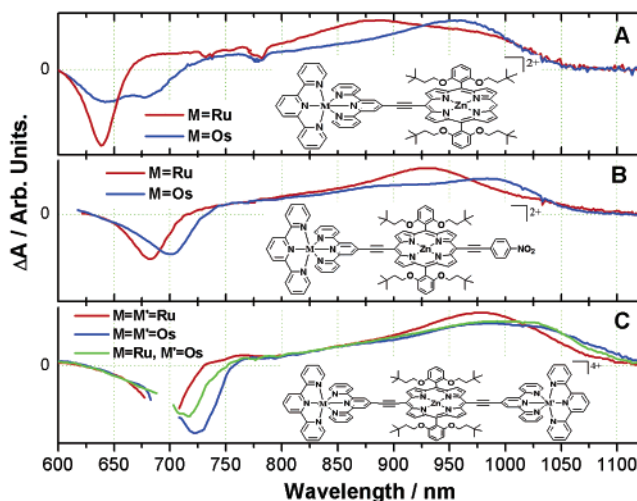


Figure 1. Magic angle transient absorption spectra recorded for: (A) **RuPZn** and **OsPZn**, (B) **RuPZnA** and **OsPZnA**, and (C) **RuPZnOs**, **RuPZnOs**, and **OsPZnOs** measured at delay times of 1 ns and normalized to the ~450 nm bleaching signature. Experimental conditions: solvent = CH₃CN, $T = 25^\circ\text{C}$, $\lambda_{\text{ex}} = 570 \text{ nm}$ (A), 605 nm (B), and 695 nm (C).

supermolecular chromophores relative to these benchmarks. Likewise, other conjugation motifs linking porphyrinoids to metal polypyridyls⁶ do not give rise to NIR absorptive excited-states of the type described here. Interestingly, a recently reported ethyne-bridged Ru(bpy)₃²⁺–Ru(tpy)₂²⁺ bis(chromophore),^{2f} featuring a 4-bipyridyl-to-4'-terpyridyl linkage topology, displays a strong NIR excited-state absorption centered at 900 nm; it is important to emphasize, however, that the Ru(tpy)₂²⁺-based **RuPZn**, **RuPZnA**, and **RuPZnOs** chromophores possess excited-state lifetimes ~2 orders of magnitude longer than that determined for Ru(bpy)₃²⁺–Ru(tpy)₂²⁺, as well as severalfold greater NIR excited-state molar absorptivity, due to the extensive contribution of porphyrin-derived oscillator strength to the $T_1 \rightarrow T_n$ manifold. The excited-state lifetimes of these Ru- and Os-based supermolecules greatly exceed those of M(tpy)₂-based chromophores that feature significant tpy ligand conjugation augmentation.¹⁰

Tables 1 and 2 emphasize the relationship between key ground- and excited-state absorptive properties of these supermolecular chromophores. Note that the magnitude of the extinction coefficients determined at $\lambda_{\max}(T_1 \rightarrow T_n)$ mirror the analogous $\lambda_{\max}(S_0 \rightarrow S_1)$ values. Evaluation of excited-state absorptive cross-section (σ_e) values and determination of the ground-state absorptive cross section (σ_g) at the $T_1 \rightarrow T_n$ absorption wavelength maximum enable computation of the three key figures of merit (σ_e , σ_e/σ_g , and $\sigma_e - \sigma_g$) for optical-limiting chromophores for sequential one-photon absorptive processes.⁷ Collectively, these σ_e , σ_e/σ_g , and $\sigma_e - \sigma_g$ values indicate that these species should be outstanding sequential one-

Table 1. Ground-State Spectral Data in Acetonitrile

	$\lambda(S_0 \rightarrow S_1)$ [nm]	$\epsilon(S_0 \rightarrow S_1)$ [M ⁻¹ cm ⁻¹]	$\epsilon_g @ (T_1 \rightarrow T_n)$ [M ⁻¹ cm ⁻¹]	$\sigma_g @ (T_1 \rightarrow T_n)$ [cm ² × 10 ⁻¹⁷]
RuPZn	638	51000	400	0.15
OsPZn	640	36000	300	0.12
RuPZnA	682	79000	355	0.13
OsPZnA	704	87000	565	0.21
RuPZnOs	710	116000	300	0.12

^a Values for ϵ_g at the $T_1 \rightarrow T_n$ λ_{\max} were determined at 3–5 mM chromophore concentrations.

Table 2. Excited-State Spectral Data in Acetonitrile

	τ_1^c [μ s]	$\lambda_{e,\max}$ [nm]	$\epsilon_e^{a,b}$ [M ⁻¹ cm ⁻¹]	σ_e^a [cm ² × 10 ⁻¹⁷]	$\sigma_e - \sigma_g$ [cm ² × 10 ⁻¹⁷]	σ_d/σ_g
RuPZn	44	884	29900	11.4	11.3	75
OsPZn	0.86	964	48900	18.7	18.5	163
RuPZnA	24	931	77100	29.5	27.4	227
OsPZnA	1.08	985	74200	28.4	28.2	135
RuPZnOs	0.79	1000	97400	37.3	37.2	324

^a Excited-state values ϵ_e and σ_e were determined from transient absorption spectra recorded at a 1-ns time delay; reported values were determined at the $T_1 \rightarrow T_n$ λ_{\max} . ^b ϵ_e were calculated using standard methods (see Supporting Information). ^c Triplet lifetimes reported were measured under anaerobic conditions.

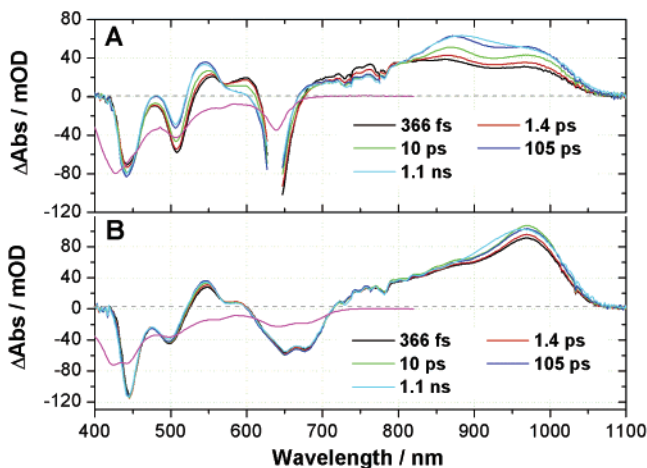


Figure 2. Representative transient absorption dynamics at several time delays for: (A) RuPZn and (B) OsPZn. Experimental conditions: solvent = acetonitrile, $T = 25$ °C, $\lambda_{\text{ex}} = 633$ nm. Scaled steady-state absorption, inverted, is displayed for comparison.

photon absorbers;⁸ based on these parameters, these chromophores are without rival in the NIR spectral regime.

While detailed excited-state dynamical studies will be reported elsewhere,⁹ representative time-resolved transient absorption spectral data for RuPZn and OsPZn (Figure 2) provide insight into the general photophysical properties of this collection of chromophores. Note that at time delays that range from 250 fs to several ns, there is no evidence for stimulated emission from RuPZn and OsPZn excited-states; furthermore, these complexes do not manifest steady-state spontaneous emission in the NIR. These photophysics contrast the established excited-state dynamical behavior of: (i) ethyne-bridged multiporphyrin compounds, which manifest stimulated emission,^{2a} and (ii) metal polypyridyl complexes that feature μ s MLCT lifetimes, which exhibit typically substantial radiative rate constants. Note also that the low-energy absorption manifolds of these RuPZn and OsPZn transient spectra bear no resemblance to ligand-localized $T_1 \rightarrow T_n$ transitions; further, the fact that no stimulated emission is observed regardless of pump-wavelength (data not shown)⁹ confirms that electronic relaxation is fast for these species. While RuPZn and OsPZn excited states display multi-

exponential relaxation dynamics,⁹ the fact that the NIR absorptive manifolds of both these species exhibit time-dependent increases in amplitude with identical 16-ps time constants suggests that the magnitude of the $T_1 \rightarrow T_n$ oscillator strength is coupled to PZn-to-(terpyridyl)metal torsional dynamics.^{2a} In sum, these spectral and dynamical features are consistent with an extensively delocalized T_1 -state wave function for these complexes characterized by substantial charge-separated (CS) character. Such highly polarized RuPZn and OsPZn CS excited states would exhibit dramatically attenuated $T_1 \rightarrow S_0$ Franck–Condon overlap relative to that manifested for emissive metal polypyridyls, and excited-state lifetimes determined by charge recombination dynamics.

In conclusion, we show that coupled oscillator photophysics can be exploited to design and fabricate supermolecular chromophores that possess high oscillator strength excited-state absorptions over broad spectral windows of the NIR. The excited-state absorptive domains of these strongly coupled multipigment ensembles can be extensively modulated. For sequential one-photon absorptive processes, these materials evince large σ_e , σ_e/σ_g , and $\sigma_e - \sigma_g$ values, and excited-state lifetimes ranging from 1 to 50 μ s. As the combination of all these properties within a single chromophoric entity have heretofore lacked precedent within the NIR, these and closely related structures may find particular utility in long-wavelength optical-limiting applications.¹¹

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Supporting Information Available: Electronic absorption spectra, details regarding data acquisition and analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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