Controlling the excited-state dynamics of low band gap, near-infrared absorbers via proquinoidal unit electronic structural modulation†

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While the influence of proquinoidal character upon the linear absorption spectrum of low optical bandgap π-conjugated polymers and molecules is well understood, its impact upon excited-state relaxation pathways and dynamics remains obscure. We report 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(i)-proquinoidal spacer-(porphinato)metal(i) (PM-Sp-PM) structural motif. A combination of excited-state dynamical studies and time-dependent density functional theory calculations: (i) points 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-state relaxation dynamics of high oscillator strength NIR absorbers to realize either substantial fluorescence or long-lived triplets (\( T_1, > \mu s \) generated at unit quantum yield (\( \Phi_{ISC} = 100\% \)), but also crafting of 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 \( S_1 \rightarrow T_1 \) ISC rate constant from \( 10^9 \) to \( 10^{12} \) s\(^{-1} \) 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.

Introduction

Low optical bandgap π-conjugated polymers and molecules have fuelled spectacular developments in optical and optoelectronic technologies.† 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 (\( E_{opt} \)) and potentiometric (\( E_{pot}^{1/2} = E_{1/2}^{1/2} \)) band gaps of the material. In contrast to the ground-state absorptive and electronic structural control enabled by proquinoidal motifs, considerable 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 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.†† Triplets–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.2 In contrast, deep tissue-penetrating in vivo imaging requires extending the absorptive and emissive wavelengths of NIR fluorophores while maintaining large \( S_1 \rightarrow S_0 \) transition dipole moments.‡§ 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 a (porphinato)metal(n)-spacer-(porphinato)metal(n) (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, Rf3P), the central metal ion is Zn(n) or Pt(n), and the proquinoidal Sp is either 4,7-diethylbenzo[1,2,5]thiadiazole (E-BTD-E) or 4,9-diethynyl-6,7-dimethyl[1,2,5]thiadiazol(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 $k_e$, $k_{ISC}$, and $k_{IC}$ 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 $k_e$, $k_{ISC}$, and $k_{IC}$ rate constants may be engineered to tightly control photophysical function of highly conjugated NIR-absorbing materials.

Results and discussion

Synthesis

Scheme 1 outlines the synthetic strategies for the PM-Sp-PM species, including ArPM-Sp-ArPM $[M = \text{Zn}(n), \text{Pt}(n); \text{Sp} = \text{E-TDQ-E}, \text{E-BTD-E}, \text{Rf}_3\text{PZnE-TDQ-ERf}_3\text{PZn}, \text{and Rf}_3\text{PZnArPPTE-TDQ-ERf}_3\text{PZnArPPt}]$. Generally, the desired PM-Sp-PM supramolecular chromophores were prepared by the metal-mediated cross-coupling of a mono meso-ethyne-functionalized (porphyrinato)metal(n) species with a dibrominated proquinoidal spacer moiety (Scheme 1). The key precursor compound $\text{Rf}_3\text{PZnArPPTE}$ was prepared via a Pd$^0$-mediated coupling reaction involving $\text{Rf}_3\text{PZnE}$ and BrArPPTEIPS, followed by deprotection of the trisopropylsilyl group. Chromophores featuring ArPM-Sp-ArPM molecular structures were isolated via column chromatography on silica using 2 : 3 CH$_2$Cl$_2$ : hexanes as the eluent, while for chromophores containing the $\text{Rf}_3\text{PZn}$ 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. Scheme 2 displays the chemical structures for previously established oligo(porphinato)metal(n) compounds that define key spectroscopic benchmarks for these newly designed PM-Sp-PM chromophores.

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, ArPZnE-TDQ-EArPZn, ArPPTE-BTD-EArPPt, and ArPPTE-TDQ-

![Scheme 1](image1.png)

Scheme 1 Synthetic routes and chemical structures for PM-Sp-PM compounds.

![Scheme 2](image2.png)

Scheme 2 Chemical structures for previously established oligo(porphinato)metal(n) chromophores.
ArPPt) are displayed in Fig. 1. 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 (PZn$_n$ compounds), manifesting two distinct absorption manifolds that are derived from the porphyrin B- (Soret) ($S_0 \rightarrow S_1$) and Q-band ($S_0 \rightarrow S_1$) transitions. $^{6a-c,9}$ Previous investigations have demonstrated that Sp moieties modulate the respective ArPZn-Sp-ArPZn long axis-polarized Q state ($Q_2$) absorption maxima from 689 to 1006 nm, depending upon the extent of the quinoidal resonance contribution to the electronically excited singlet state. $^{24}$ 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. $^{2c}$

A comparison of the Q-band regions in the electronic absorption spectra of ArPZnE-BTD-EarPZn, ArPZnE-TDQ-EarPZn, ArPPTE-BTD-EarPPT, and ArPPE-TDQ-EarPPt reveals discrete effects correlated with the choice of spacer and (porphyrinato)metal(n) units. Compared with ArPME-BTD-EarPM, the ArPME-TDQ-EarPM analogues evince dramatically red-shifted $Q_x$-state absorption maxima and substantial oscillator strength ($f$) redistribution into the low-energy spectral domain [compound ($\lambda_{\max}(S_0 \rightarrow S_1)$, $f_{600-1000~~nm}$): ArPZnE-BTD-EarPZn (689 nm, 0.455), ArPPE-BTD-EarPPt (603 nm, 0.168), ArPZnE-TDQ-EarPZn (839 nm, 0.827), ArPPTE-TDQ-EarPPT (715 nm, 0.686); Table 1]. Furthermore, the Q-state absorption manifolds of ArPME-BTD-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 [$Q_2$(FWHM): ArPME-TDQ-EarPM ~ 2500 cm$^{-1}$; ArPME-BTD-EarPM ~ 1100 cm$^{-1}$], suggesting that the TDQ-containing chromophores give rise to $S_1$ states with greater CT character. $^{2c,10}$ Compared to ArPZn-Sp-ArPZn compounds, the ArPPt-Sp-ArPPt chromophores display blue-shifted Q-state transition manifold maxima; this phenomenon is typical of hypsochromic species and has been attributed to the enhanced mixing of metal nd and porphyrin π* orbitals. $^{6c,11}$

ArPZnE-BTD-EarPZn and ArPZnE-TDQ-EarPZn exhibit markedly different Stokes shifts and fluorescence quantum yields ($\Phi_{FL}$) (Fig. 1) in THF solvent. While ArPZnE-BTD-EarPZn displays a relatively small Stokes shift ($\Delta \nu = 1019$ cm$^{-1}$) and a large fluorescence quantum yield ($\Phi_{FL} = 0.25$) comparable to those of PZn$_n$ chromophoric benchmarks (e.g. PZn$_2$: $\Delta \nu = 711$ cm$^{-1}$, $\Phi_{FL} = 0.16$. PZn$_3$: $\Delta \nu = 806$ cm$^{-1}$, $\Phi_{FL} = 0.22$; Scheme 2),$^{10,11}$ ArPZnE-TDQ-EarPZn exhibits a significant Stokes shift of 1869 cm$^{-1}$ and negligible fluorescence ($\Phi_{FL} = 0.003$). Furthermore, the Stokes shift and fluorescence quantum yield of ArPZnE-BTD-EarPZn show modest solvent dependence [e.g., toluene.

![Figure 1](https://example.com/figure1.png)

**Figure 1**: Steady-state electronic absorption and emission spectra for: (A) ArPZnE-TDQ-EarPZn (blue colored lines, $\lambda_{\max} = 750$ nm for emission) and ArPZnE-BTD-EarPZn (red colored lines, $\lambda_{\max} = 640$ nm for emission); and (B) ArPPTE-TDQ-EarPPT (blue colored lines, $\lambda_{\max} = 650$ nm for emission) and ArPPE-BTD-EarPPt (red colored lines, $\lambda_{\max} = 540$ nm for emission). Steady-state spectra were all acquired in THF solvent at ambient condition. Ar = 2',6'-bis(3,3-dimethyl-1-butylxlo)phenyl.

| Chromophores | $\lambda_{\max}$/nm (FWHM/cm$^{-1}$) | Stokes shift/cm$^{-1}$ | Oscillator strength in red-to-NIR$^3$ |
|--------------|------------------------------------|------------------------|--------------------------------------|
| ArPZnE-TDQ-EarPZn | 839 (2510) 995 (1778) 1869 | 0.827 | |
| ArPZnE-BTD-EarPZn | 689 (1180) 741 (1382) 1019 | 0.455 | |
| ArPPTE-TDQ-EarPPT | 715 (2415) 810 (1530) 1640 | 0.686 | |
| ArPPE-BTD-EarPPt | 603 (1061) 629 (1579) 686 | 0.168 | |
| RF$_2$PZnE-TDQ-ErP,F,PZn | 705 (1163) 750 (1370) 851 | 0.451 | |
| RF$_2$PZnArPPTE-TDQ-EarPPtRF$_2$PZn | 755 (1738) 813 (1432) 945 | 1.809 | |

$^3$ Stokes shift corresponds to the energy difference between the low-energy transition ($Q_2$) absorption and fluorescence maxima. $^4$ Integrated oscillator strengths ($f$) were calculated based on the following expression: $f = 4.3 \times 10^{-9} \int \epsilon d\nu$, where $\epsilon$ 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); ArPPE-BTD-EarPPt (600–700 nm); RF$_2$PZnE-TDQ-ErP,F,PZn (600–850 nm); RF$_2$PZnArPPTE-TDQ-EarPPtRF$_2$PZn (600–950 nm).
(Δν = 522 cm⁻¹, Φ_F = 0.27]) (Fig. S1†); in contrast, a substantial solvent-dependence of the Stokes shift and fluorescence quantum yield are evinced for ArPZnE-TDQ-EArPPZn, with less polar solvent driving smaller Stokes shifts and significantly enhanced fluorescence quantum yields [toluene (Δν_Stokes = 771 cm⁻¹, Φ_F = 0.02) vs. THF (Δν_Stokes = 1869 cm⁻¹, Φ_F = 0.003)] (Fig. S2†). These observations underscore the differing CT characters of the ArPZnE-TDQ-EArPPZn and ArPZnE-BTD-EArPPZn Q_1-states, as ArPZnE-TDQ-EArPPZn exhibits substantial CT character, the reorganization energy associated with excited-state solvent relaxation is magnified."**

Upon metal center substitution from zinc(II) to platinum(II), ArPPP-E-BTD-EArPPPt manifests weak fluorescence centered at 629 nm (Δν = 686 cm⁻¹, Φ_F = 0.001) in deoxygenated solution at ambient temperature, and phosphorescence centered at 845 nm (Δν = 4750 cm⁻¹) (Fig. S3†). Such emissive properties are similar to those observed in oligomeric (porphinato)palladium(II)/platinum(II) compounds (PM, M = Pd or Pt; Scheme 2), where phosphorescence and very weak fluorescence (77 K) are simultaneously evinced (PPd; λ_S0,max = 747 nm; λ_T1,max = 828 nm; PPT; λ_S0,max = 740 nm; λ_T1,max = 800 nm).** In contrast, ArPPP-E-TDQ-EArPPPt maintains one constant emission band centered at 810 nm, regardless of the solution oxygen content (Fig. S4†). Note that no additional emission band can be observed in deoxygenated samples of ArPPP-E-TDQ-EArPPPt even at low temperature (77 K, Fig. S5†). In light of the magnitude of the Stokes shift (Δν = 1530 cm⁻¹) and the measured lifetime of this chromophore (τ = 310 ns, Fig. S6E†), we denote the ArPPP-E-TDQ-EArPPPt 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 ArPPP-E-TDQ-EArPPPt may be best described as a “singlet-triplet”. In this regard, we emphasize that although the “fluorescence”, “phosphorescence”, “S°”, and “T°” 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 ArPPP-E-TDQ-EArPPPt (2.8%) is unusually large, considering that platinum atoms typically promote strong spin–orbit coupling, resulting in near-unit S_1 → T_1 ISC quantum yields (ΦISC values) in classic (porphinato)platinum(II) compounds.** The emissive properties observed for ArPPP-E-TDQ-EArPPPt suggest unusually low ΦISC value relative to the ArPPP-E-BTD-EArPPPt chromophore (vide infra).

**Femtosecond pump-probe transient absorption spectroscopy of ArPM-Sp-ArPM**

The femtosecond transient absorption spectra recorded at selected time delays for ArPM-Sp-ArPM chromophores are displayed in Fig. 2. 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 (PZn, n = 2, 3; Scheme 2). 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 → S_0 transient absorption manifolds that feature extraordinary spectral breadth.** In contrast, the ArPPP-E-TDQ-EArPPPt 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 ArPPP-E-TDQ-EArPPPt may be best described as a “singlet-triplet”. In this regard, we emphasize that although the “fluorescence”, “phosphorescence”, “S°”, and “T°” 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 ArPPP-E-TDQ-EArPPPt (2.8%) is unusually large, considering that platinum atoms typically promote strong spin–orbit coupling, resulting in near-unit S_1 → T_1 ISC quantum yields (ΦISC values) in classic (porphinato)platinum(II) compounds.** The emissive properties observed for ArPPP-E-TDQ-EArPPPt suggest unusually low ΦISC value relative to the ArPPP-E-BTD-EArPPPt chromophore (vide infra).

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![Fig. 2](Pump-probe transient absorption spectra recorded at several time delays for (A) ArPZnE-BTD-EArPPZn (λ_exc = 660 nm), (B) ArPZnE-TDQ-EArPPZn (λ_exc = 900 nm), (C) ArPPP-E-BTD-EArPPPt (λ_exc = 610 nm), and (D) ArPPP-E-TDQ-EArPPPt (λ_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.)
Femtosecond transient absorption spectroscopy of ArPZn-Sp-
ArPZn

A global fit of the NIR transient absorption dynamics observed following excitation ($\lambda_{\text{exc}} = 660$ nm), evinces three characteristic relaxation processes: 760 ± 90 fs, 24 ± 5 ps, 1.75 ± 0.1 ns (Fig. S8A†). 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-ethylene $\text{ArPZn}$-to-$\text{ArPZn}$ linkage; these dynamics have been discussed in detail for closely related structures. Over 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, Fig. S6C†). Consistent with the insensitivity of the Stokes shift and fluorescence quantum yield to solvent polarity, the $S_1$ state lifetime of ArPZnT-DQ-ArPZn manifests minimal variation with solvent dielectric constant [e.g. THF ($\tau_F = 1.67$ ns) vs. toluene ($\tau_F = 1.61$ ns, Fig. S6D†)], suggesting the electronically excited-state nature of ArPZnE-TDQ-ArPZn features negligible CT character.

The excited-state relaxation dynamics of ArPZnE-TDQ-ArPZn are also multieponential in nature. Global fitting of the NIR spectral regime transient dynamical data acquired for ArPZnE-TDQ-ArPZn evinces three relaxation processes: 950 ± 120 fs, 12 ± 2 ps, and 87 ± 6 ps (Fig. S8B†). 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 ArPZnE-TDQ-ArPZn (Fig. S6A†), 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 ArPZnE-TDQ-ArPZn, indicates substantial displacement between the ground- and singlet excited-state potential energy surfaces along the solvation coordinate. Congruent with the marked solvent-dependent ArPZnE-TDQ-ArPZn Stokes shifts observed by steady-state emission spectroscopy (vide supra). Additionally, the $S_1$ state lifetime ($\tau_{S_1} = 87$ ps) of ArPZnE-TDQ-ArPZn is much shorter than that of ArPZnE-TDQ-ArPZn, and depends strongly on solvent dielectric constant ($\epsilon_r$). For example, the $\tau_F$ determined for ArPZnE-TDQ-ArPZn measured in toluene solvent (~506 ps, Fig. S6B†) is nearly 1 order of magnitude larger than that found in THF. As such, the calculated $S_1 \rightarrow S_0$ internal conversion rate constants for ArPZnE-TDQ-ArPZn in THF and toluene differ markedly [$k_{\text{IC(THF)}} = 1.15 \times 10^{10}$ s$^{-1}$ vs. $k_{\text{IC(toluene)}} = 1.94 \times 10^{8}$ s$^{-1}$], highlighting the acceleration of the nonradiative decay process in polar solvent: since the $Q_x$-state transition features substantial CT character, solvent dipole reorientation dramatically stabilizes the polarized $S_1$ state of ArPZnE-TDQ-ArPZn, decreasing the $S_1 \rightarrow S_0$ transition oscillator strength [$\phi_F(\text{THF}) = 0.003$ vs. $\phi_F(\text{toluene}) = 0.02$].

Femtosecond transient absorption spectroscopy of ArPPt-Sp-
ArPPt

A global fit of the time-dependent vis-NIR transient dynamical data acquired for ArPPtE-BTD-ArPPt following excitation at 610 nm evinces two relaxation processes: 960 ± 120 fs, 1.90 ± 0.13 ns (Fig. S8C†). Note that at an early time delay ($t_{\text{delay}} \sim 1$ ps), the initially prepared ArPPtE-BTD-ArPPt 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 (Fig. S7C and D†), suggesting that the long-lived excited state is triplet in nature. In this regard, the ultrafast component (960 fs) observed in the femtosecond transient dynamics corresponds to an ISC process, while the 1.90 ns component corresponds to the slow decay of ArPPtE-BTD-ArPPt triplet excited state. Furthermore, the decay-associated spectra (DAS, Fig. S8†) 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 $S_1 \rightarrow T_1$ conversion [i.e. $\tau_{S_1} = \tau_{\text{ISC}} \sim 960$ fs, $\Phi_{\text{ISC}} \sim 100\%$]. The ultrafast $S_1 \rightarrow T_1$ conversion and near-unit ISC quantum yield displayed by ArPPtE-BTD-ArPPt are similar to those evinced by PPTn compounds (Table 2). over the 1.90 ns component of ArPPtE-BTD-ArPPt.

In contrast to the ultrafast ISC rate constant exhibited by ArPPtE-BTD-ArPPt, the ArPPtE-TDQ-ArPPt analogue manifests dramatically different excited-state relaxation dynamics. Three time constants were obtained from fitting the ArPPtE-TDQ-ArPPt transient data acquired following Q-band excitation ($\lambda_{\text{exc}} = 750$ nm): 1.05 ± 0.15 ps, 15 ± 2 ps, 330 ± 15 ps (Fig. S8D†). 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-ArPPt ($\tau_F = 310$ ps, Fig. S6E†), and is thus assigned to the intrinsic $S_1$ state lifetime. While the ArPPtE-TDQ-ArPPt transient spectra feature complete ground state recovery within 200 ps, those of ArPPtE-TDQ-ArPPt 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 (Fig. 2D). 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
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Excited-state relaxation dynamical data, fluorescence quantum yields, and intersystem crossing quantum yields for PM-Sp-PM chromophores

| Chromophores                        | τ_S/ns | k_{\text{IC}}(S_1 \rightarrow S_0) | k_{\text{ISC}}(S_1 \rightarrow T_1) | Φ_\text{ISC}^b | Φ_\text{ISC}^c |
|-------------------------------------|--------|-----------------------------------|-----------------------------------|---------------|---------------|
| ArPZnE-TDQ-EArPZn                   | 0.087  | 1.15 x 10^{10}                    | 3.10 x 10^{7}                    | 0.003         | ~0            |
| ArPPE-TBD-EArPZn                    | 1.750  | 3.82 x 10^{8}                     | 1.43 x 10^{8}                    | 0.25          | 0.15          |
| ArPPP-TDQ-EArPPT                    | 0.310  | 1.51 x 10^{9}                     | 1.95 x 10^{9}                    | 0.028         | 0.50          |
| ArPPE-BTD-EArPPT                    | 0.001  | ≤10^{8}                           | ≤10^{2}                           | 0.001         | ~1            |
| RsPzE-TDQ-KrPzE                      | 0.785  | 9.04 x 10^{8}                     | 1.53 x 10^{8}                    | 0.12          | 0.17          |
| RsPzEAPPE-TDQ-EArPPT                    | 0.108  | 2.36 x 10^{9}                     | 1.39 x 10^{8}                    | 0.015         | 0.73          |

Note: k_{\text{IC}} denotes the S_1 \rightarrow S_0 nonradiative decay rate constant, k_{\text{ISC}} denotes the S_1 \rightarrow T_1 intersystem crossing rate constant. Excited-state relaxation rate constants were calculated based on the following equations: \( τ_S = 1/(k_{\text{IC}} + k_{\text{ISC}}) \), Φ_\text{ISC} = k_{\text{ISC}} / τ_S, and Φ_\text{ISC} can all be experimentally acquired, therefore, rate constants k_{\text{IC}}, k_{\text{ISC}}, and k_{\text{ISC}} can be calculated.

Fluorescence quantum yields were determined relative to bis[(porphinato)zinc(II)] (PZn2) in THF (0.16). Φ_\text{ISC} were determined based on femtosecond transient absorption spectra, for details see ESI.

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 (Fig. 3). The S_1 state of ArPZnE-TDQ-EArPZn is dominated (~80%) by the HOMO \rightarrow LUMO configuration, whereas the ArPZnE-TDQ-EArPZn exhibits negligible CT character and substantial CI, more akin to classic porphyrin π \rightarrow π* transitions and those characteristic of PZn2 supermolecular chromophores.

These computational figures buttress the finding that the ArPZnE-TDQ-EArPZn Q_β transition has greater quinoidal character than that of ArPZnE-BTD-EArPZn, as demonstrated by analyses of the Q_α manifold FWHM and vibronic structures, fluorescence quantum yields, and the dynamic and solvent dependent Stokes shifts exhibited by these chromophores.

The contrasts outlined above regarding the S_1 state CT characters of the (porphinato)zinc(II) compounds are sustained solutions it is reduced to 140 ns (Fig. S7A and 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 (Φ_\text{ISC} \approx 51%; k_{\text{ISC}} \approx 1.67 \times 10^{7} \text{s}^{-1}) for ArPPE-TDQ-EArPPT (ESI; Table 2). The excited-state relaxation dynamics of ArPPE-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. Also note that the S_1 state lifetime of ArPPE-TDQ-EArPPT is about four times longer than that of its ArPZnE-TDQ-EArPZn analogue, whereas PPM units evince significantly diminished S_1 state lifetimes relative to the corresponding PZn2 chromophores due to ultrafast S_1 \rightarrow T_1 ISC dynamics (Scheme 2). In this regard, the longer S_1 state lifetime (Table 2) of ArPPE-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 (Fig. 1 and 2; Tables 1 and 2) demonstrate that varying the nature of the intervening quinoidal 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, have significant excited-state quinoidal character, exhibit broad long-wavelength absorptive manifolds and substantial NIR oscillator strength, negligible (Φ_\text{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 quinoidal character, exhibit narrower long-wavelength absorptive manifolds and less substantial NIR oscillator strength, long-lived (ns) S_1 states and large (Φ_\text{F} \approx 0.25) fluorescence quantum yields. (iii) ArPPP-Sp-ArPPP chromophores, characterized by ArPPE-TDQ-EArPPT and ArPPP-BTD-EArPPT, evince similar dependences of absorptive oscillator strength distribution upon the nature of the quinoidal spacer, but show an unusual dependence of the degree of electronically excited-state quinoidal character upon the magnitude of k_{\text{ISC}}: ArPPE-BTD-EArPPT, which features a modest extent of excited-state quinoidal character, features a S_1 \rightarrow T_1 ISC rate constant (k_{\text{ISC}} = 1.04 \times 10^{12} \text{s}^{-1}) three orders of magnitude greater than that for ArPPE-TDQ-EArPPT. The origins of these disparate photophysical properties modulated by these Sp units are explored below using TD-DFT calculations.
in their (porphinato)platinum(II) counterparts. A further distinction that may be drawn for these latter ArPPE-TDQ-EArPpPt and ArPPE-BTD-EArPpPt 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 ArPPE-TDQ-EArPpPt 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 ArPPE-TDQ-EArPpPt LUMO amplitude. In contrast, the ArPPE-BTD-EArPpPt 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 ArPPE-BTD-EArPpPt S1 state with its strong CI character, and smaller k ISC for the ArPPE-TDQ-EArPpPt S1 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),16,17 it is clear that the wavefunction spatial distribution of the initially prepared singlet excited state of ArPPE-BTD-EArPpPt is responsible for its considerably greater S1−T1 mixing relative to that manifested for ArPPE-TDQ-EArPpPt.

Schematic potential energy surfaces summarizing the spectroscopic and dynamical data, and computed electronic structures for ArPM-Sp-EArPM chromophores

The spectroscopic, dynamical, and computational results for these ArPM-Sp-EArPM structures can be schematically illustrated using a series of qualitative potential energy surfaces as displayed in Scheme 3. In these schematic illustrations, the free energies of 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 play a prominent role in determining the excited-state relaxation pathways. TD-DFT calculations show that the ArPME-TDQ-EArPpPt S1 states feature stronger quinoid contributions and greater CT character than those of ArPME-BTD-EArPM analogues (Fig. 3). The CT character of the 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 S1 state, funnelling excited-state energy through S1 → S0 nonradiative conversion that competes with S1 → T1 ISC (Scheme 3A). In this regard, note that the 1 ps characteristic solvent relaxation timescale (marked on potential energy surfaces for ArPME-TDQ-EArPM, Scheme 3A and C) corresponds to the timescale of the potential energy curve displacement (∆q) dynamics between S0 and S1 states that are driven along the solvaton coordinate. The S0 → S1 vertical transition of ArPpPE-TDQ-EArPpPt manifests a lower degree of CI relative to that for ArPpPE-BTD-EArPpPt (vide supra), and the major single-excitation configuration involves virtual FOs featuring spacer-dominant (~77%) electron density, resulting in diminished S1−T1 mixing (Scheme 3C), and hence the experimentally observed slow ISC rate constant (1.67 × 105 s−1). In contrast, the low-energy transition for ArPpPE-BTD-EArPpPt exhibits a higher degree of CI, and (porphinato)platinum(II)-derived electron density makes prominent (>50%) contributions to the

Fig. 3 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.
Relative frontier orbital energies of ArPM and spacers, and implications for new chromophore designs

The disparate CT characters of the ArPME-TDQ-EArPM and ArPPtE-BTD-EArPPt 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 (Fig. 4). 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.

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 e-electron withdrawing effect exploits meso-perfluoroalkyl substitution.22 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 (Fig. 4).23 Furthermore, as the computed Rf3PZnArPPtE LUMO is energetically close to that of Rf3PZnE (Fig. 4), the Rf3PZnArPPtE-TDQ-EArPPtF3PZn compound was designed with the expectation that it would display attenuated electronically excited-state quinoidal character compared to ArPPtE-TDQ-EArPPt, and thus an ISC rate constant substantially larger than that of the parent chromophore ArPPtE-TDQ-EArPPt. Likewise, Rf3PZnE-TDQ-ERf3PZn was designed with the expectation that this electronic structural engineering would provide a NIR fluorophore, and contrast those photophysics delineated above for ArPZnE-TDQ-EArPZn.

To that end, Rf3PZnE-TDQ-ERf3PZn and Rf3PZnArPPtE-TDQ-EArPPtF3PZn 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 (Fig. 5A, Table 1). Rf3PZnE-TDQ-ERf3PZn spectroscopic highlights include a narrow lowest-energy absorption manifold (Q_x(FWHM) = 1163 cm⁻¹), a modest Stokes shift (Δυ = 851 cm⁻¹), and a substantial fluorescence...
quantum yield ($\Phi_F = 0.12$) in THF solvent. Likewise, $\text{Rf}_3\text{PZnArPPtE-TDQ-EArPPtRf}_3\text{PZn}$ manifests spectral signatures that reflect attenuated $S_1$ state CT character relative to the parent chromophore $\text{ArPPtE-TDQ-EArPPt}$, and features a low-energy transition having a reduced Q(x/FWHM) (1738 cm$^{-1}$) and a smaller Stokes shift ($\Delta\nu = 945$ cm$^{-1}$) relative to that evinced by
**ArPPE-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 $\Delta E_L$, $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ and $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ possess globally delocalized $S_1$ states having reduced CT character relative to those of $\text{ArPME-TDQ-EArPM}$.

Representative transient absorption spectra recorded at selected time delays for $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ and $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ are displayed in Fig. 5C and D; key spectral data are highlighted in Table 2. $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ evinces no dynamic Stokes shift in the femtosecond transient absorption spectra, indicating modest CT character of the Franck-Condon state congruent with the minimal $\Delta E_L$ calculated for this chromophore. As a result, $S_1 \rightarrow S_0$ internal conversion along the solvation coordinate is greatly diminished, and the $S_1$ state lifetime of $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ reaches $\sim 0.8$ ns, comparable to that of $\text{ArPznE-BTD-EArPzn}$. For $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$, because of the low $\Delta E_L$ between the $\text{Rf}_3\text{PznArPPtE}$ wings and the central TDQ unit, the $S_0 \rightarrow S_1$ vertical transition involves less electron density redistribution than that of $\text{ArPPE-TDQ-EArPPt}$. As a result, $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ manifests an ISC rate constant about four times as large as that of the parent chromophore $\text{ArPPE-TDQ-EArPt}$ (6.76 $\times 10^{12}$ s$^{-1}$ vs. 1.67 $\times 10^{12}$ s$^{-1}$), and now displays photophysics that approach those of $\text{ArPPE-BTD-EArPt}$. Note that these changes of ISC rate constant reflected in the evolution of supermolecular structure from $\text{ArPPE-TDQ-EArPPt}$ to $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ strikingly contrast the corresponding photophysics evinced in classic $\text{Pzn}_n$ (Scheme 2) multimeric species, where ISC rate constants decrease dramatically with increasing $\text{Pzn}_n$ conjugation length.$^{49}$ The spectroscopic features displayed by $\text{ArPPE-TDQ-EArPPt}$ and $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ highlight the cardinal role of $S_1$ state proquinoidal character in tuning the NIR ground-state absorption, fluorescence quantum yield, and ISC rate constant for long-wavelength absorbing (porphinato)metal(ii) species.

**Conclusion**

While the influence of proquinoidal character upon the linear absorption spectrum of low optical bandgap $\pi$-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, RfP), the central metal ion is Zn(u) or Pt(u), and the proquinoidal Sp is either 4,7-diethylbenzo[c]1,2,5 thiadiazole (E-BTD-E) or 4,9-diethylbenzo[c]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) points 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 $\text{ArPznE-BTD-EArPzn}$, 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, $\text{ArPznE-TDQ-EArPzn}$, 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 $\text{ArPPE-BTD-EArPt}$ 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 $\text{ArPPE-TDQ-EArPpt}$ demonstrates an unusually fluorescent Pt(u) 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 $S_1$-state wavefunction density proximal to the heavy Pt nuclei, thus realizing a rare if not unique example of a fluorescent (porphinato)platinum(u) chromophore at ambient temperature having ISC dynamics on the ns timescale.$^{13,19,18}$

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, $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ and $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$ were synthesized: the $\pi$-electron withdrawing effect of $\text{Rf}_3\text{PznE}$ *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. $\text{Rf}_3\text{PznE-TDQ-ERf}_3\text{Pzn}$ thus contrasts $\text{ArPznE-TDQ-EArPzn}$ in that NIR fluorescence dominates its photophysics. Likewise, $\text{Rf}_3\text{PznArPPtE-TDQ-EArPPtRf}_3\text{Pzn}$, because of the low $\Delta E_L$ between the $\text{Rf}_3\text{PznArPPtE}$ 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 the modest degree of CI that characterizes 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 the S_{1}–T_{1} ISC rate constant from 10^{-6} to 10^{12} s^{-1} and (iv) realize T_{1}-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.

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.

**Experimental section**

**Synthesis and characterization**

The synthetic procedures and corresponding characterization data of all new compounds, complete with the reaction schemes, are given in the ESI†.

**Instrumentation**

Electronic absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Steady-state emission spectra were recorded on a FLS920 spectrometer that utilized a xenon lamp (Xe900) as excitation light source and an extended red sensitive PMT (Hamamatsu R2658P side window photomultiplier, spectral range: 200–1010 nm) or NIR-PMT (Hamamatsu H10330-75, spectral range: 950–1700 nm) for detection. Emission spectra were corrected using a calibration curve supplied with the instrument.

**Picosecond fluorescence lifetime measurement system (streak-scope)**

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.

**Femtosecond and nanosecond transient absorption experiments**

The transient optical system utilized in this work has been discussed previously. All the samples for pump-probe experiments were deoxygenated via three successive freeze–pump–thaw cycles prior to measurement.

**Time-dependent density functional theory calculations**

All electronic structure calculations were performed upon model compounds in which aliphatic chains were truncated to methyl groups (ESI†). Structure optimization and linear response calculations were performed with density functional theory (DFT) using Gaussian 09, revision C.1. The M11 (ref. 22) 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. Selected frontier orbital wave functions were plotted as isosurfaces (iso = 0.02) using Gaussview 5.24 TD-DFT result files were post-processed using the GaussSum package; this software partitions the wave function amplitudes onto atomic components using Mulliken population analysis and parses the electronic configurations contributing to each excitation.

**Conflict of interest**

No competing financial interests have been declared.

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