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Driving high quantum yield NIR emission through proquinoidal linkage motifs in conjugated supermolecular arrays
Driving high quantum yield NIR emission through proquinoidal linkage motifs in conjugated supermolecular arrays†

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High quantum yield NIR fluorophores are rare. Factors that drive low emission quantum yields at long wavelength include the facts that radiative rate constants increase proportional to the cube of the emission energy, while nonradiative rate constants increase in an approximately exponentially with decreasing \( S_0 - S_1 \) energy gaps (in accordance with the energy gap law). This work demonstrates how the proquinoidal BTD building blocks can be utilized to minimize the extent of excited-state structural relaxation relative to the ground-state conformation in highly conjugated porphyrin oligomers, and shows that 4-ethynylbenzo[c]1,2,5-thiadiazole (E-BTD) units that terminate meso-to-meso ethynel-bridged (porphinato)zinc (PZn\(_n\)) arrays, and 4,7-diethynylbenzo[c]1,2,5-thiadiazole (E-BTD-E) spacers that are integrated into the backbone of these compositions, elucidate new classes of impressive NIR fluorophores. We report the syntheses, electronic structural properties, and emissive characteristics of neoteric PZn-(BTD-PZn)\(_n\), PZn\(_2\)-(BTD-PZn)\(_n\), and BTD-PZn\(_n\)-BTD fluorophores. Absolute fluorescence quantum yield (\( \Phi_f \)) measurements, acquired using a calibrated integrating-sphere-based measurement system, demonstrate that these supermolecules display extraordinary \( \Phi_f \) values that range from 10−25% in THF solvent, and between 28−36% in toluene solvent over the 700−900 nm window of the NIR. These studies underscore how the regulation of proquinoidal conjugation motifs can be exploited to drive excited-state dynamical properties important for high quantum yield long-wavelength fluorescence emission.

Introduction

Low band gap \( \pi \)-conjugated molecules and oligomers are central to function in electro-optic applications that span excitonic solar cells,\(^\text{1−7}\) field-effect transistors,\(^\text{8,9}\) optical power limiting (OPL),\(^\text{10}\) dye-sensitized solar cells (DSSCs),\(^\text{11,12}\) photon-upconversion (UC) technologies,\(^\text{13−17}\) long-wavelength light-emitting diodes,\(^\text{18−20}\) nonlinear optics (NLO),\(^\text{21−24}\) and biological imaging.\(^\text{25−27}\) Desirable low band gap materials for these applications typically feature singlet manifold transitions (\( S_0 \rightarrow S_1 \), \( S_0 \rightarrow S_n \), and \( S_1 \rightarrow S_n \)) that possess large absorptive oscillator strengths covering broad spectral domains that include the near-infrared (NIR).

Driving high fluorescence quantum yields is perhaps the most demanding design challenge for low band gap chromophores. Engineering augmented \( S_0 \rightarrow S_1 \) transition oscillator strength is not sufficient to realize correspondingly high \( S_1 \rightarrow S_0 \) fluorescence quantum yields (\( \Phi_f \) values), particularly as the optical band gap is diminished: while it is often the case that a large \( S_0 \rightarrow S_1 \) absorptive extinction coefficient is correlated with a correspondingly large \( S_1 \rightarrow S_0 \) radiative rate constant congruent with the Strickler–Berg relationship,\(^\text{28}\) most strongly

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absorbing NIR chromophores are not impressive emitters, due to the substantial $S_0$ state non-radiative rate constants ($k_{nr}$ values) that ensue from the energy gap law.  

With respect to high oscillator strength NIR absorbers, meso-to-meso ethyne-bridged (porphinato)zinc (PZn$_n$) arrays (Chart 1A)\textsuperscript{17,30–46} constitute a notable exception to these generalizations. These supermolecules – conjugated structures realized from strong coupling of simple chromophoric building blocks – manifest such strong electronic and excitonic interactions between the constituent (porphinato)zinc oscillators that entirely unique photophysical entities are defined. PZn$_n$ structures, for example, possess fluorescence quantum yields comparable to the most impressive NIR laser dyes in the 750–900 nm regime,\textsuperscript{41} and rival the highest reported for organic dyes in this spectral window.\textsuperscript{47–49} Importantly, PZn$_n$ emitters do not suffer from the commonly cited drawbacks of tricarbocyanine dyes that include poor photostability and fluorescence quantum yields that drop precipitously with decreasing solvent polarity.\textsuperscript{25,50,51} PZn$_n$ chromophores feature low energy $Q$-state derived $\pi-\pi^*$ excited-states that are polarized exclusively along the long molecular axis, and lowest energy transitions that gain in intensity and progressively red-shift with increasing numbers of PZn units. Extended conjugation in these highly polarizable chromophores drives red-shifting of PZn$_n$ fluorescence spectra. Because triplet excitons are more spatially confined than singlet excitons in these systems,\textsuperscript{31,34,35,39,52,53} an unusual dependence of $\phi_f$ magnitude upon increasing emission wavelength [$\beta_{\text{max}}(S_1 \rightarrow S_0)$] is manifest that confounds that anticipated simply from the energy gap law.\textsuperscript{41} Because of this disparity in lowest energy singlet ($S_1$) and triplet ($T_1$) state delocalization, diminished $S_1$-$T_1$ intersystem crossing rate constants ($k_{isc}$ values) track with increasing conjugation in PZn$_n$ chromophores, and serve to partly counter-balance the impact of augmented Franck–Condon mediated internal conversion rate constants ($k_{ic}$ values) that typically accompany diminished $S_0$-$S_1$ energy gaps in the NIR. These impressive PZn$_n$ photophysical properties have been exploited in a wide range of fluorescence imaging applications.\textsuperscript{54–61}

The photophysical properties of PZn$_n$ chromophores may be extensively modulated via incorporation of quinoidal units into these emblematic conjugated arrays. For example, proquinoidal spacer (Sp) moieties such as 4,7-diethynylbenzo[c][1,2,5]thiadiazole (E-BTD-E), 6,13-diethylpentacene (E-PC-E), 4,9-diethynyl-6,7-dimethyl[1,2,5]thiadiazolo[3,4-g]quinoxaline (E-TDQ-E), and 4,8-diethylbenzo[1,2-c:4,5-c']bis[1,2,5]thiadiazole (E-BBTD-E) that link bis[(porphinato)zinc] units can be utilized to modulate the relative degrees of quinoidal character that characterize the ground and electronically excited singlet states in these highly conjugated supermolecules.\textsuperscript{62} Recent work highlights how electronic modulation of proquinoidal conjugation motifs can also be exploited as a powerful means to modulate independently the dynamics of excited-state relaxation pathways in these systems, enabling, for example, exceptional NIR absorbers that possess long-lived electronically excited triplet states ($\tau_{T1} > \mu$s) that are generated at unit quantum yield.\textsuperscript{63} In this contribution, we (i) show how proquinoidal BTD building blocks can be utilized to minimize the extent of excited-state structural relaxation relative to the ground-state conformation in highly conjugated porphyrin oligomers, and (ii) demonstrate that 4-ethynylbenzo[c][1,2,5]thiadiazole (E-BTD) units that terminate PZn$_n$ chromophores (Chart 1B), and E-BTD-E spacers that are integrated into the backbone of these compositions (Chart 1C), enable elucidation of new classes of impressive NIR fluorophores.

Scheme 1 Synthetic routes for PZn-(BTD-PZn)$_n$ compounds.
Results and discussion

Synthesis

Schemes 1–3 outline the synthetic strategies for the fabrication of BTD-PZnₙ-BTD, PZn-(BTD-PZn)ₙ, and PZn₂-(BTD-PZn₂)ₙ chromophores. These structures were synthesized by palladium (Pd)-mediated cross-coupling reactions involving appropriately substituted (porphinato)zinc(II) (PZn) compounds, BTD spacers, and terminal BTD units. These structures exploit [2,6-bis(3,3-dimethyl-1-butyloxy)phenyl] groups as 10- and 20-meso substituents, which facilitate solubility and straightforward assignment of $^1$H-NMR spectra. The nature of the functionalized PZn, PZnₙ, and BTD moieties used in the syntheses of these BTD-PZnₙ-BTD, PZn-(BTD-PZn)ₙ, and PZn₂-(BTD-PZn₂)ₙ arrays varied with the degree of conjugation in the precursor molecules. Synthetic details may be found in the ESI.†
Steady-state absorption and emission spectroscopy of BTD-PZnₙ-BTD, PZn-(BTD-PZn)ₙ, and PZn₂-(BTD-PZn₂)ₙ chromophores

Steady-state electronic absorption and fluorescence spectra recorded for reference PZnₙ chromophores (PZn₂, PZn₃, and PZn₅; Fig. 1A), as well as PZn-(BTD-PZn)ₙ and PZn₂-(BTD-PZn₂)ₙ [Fig. 1B], and PZn-(BTD-PZn)ₙ [PZn₂-BTD-PZn₂ and PZn₂-(BTD-PZn₂)ₙ; Fig. 1C], and PZnₙ-(BTD-PZn-BTD), as well as PZn₂-(BTD-PZn-BTD, and BTD-PZn₂-BTD, and [BTD-PZnₙ-BTD; Fig. 1D] arrays, are shown in Fig. 1. The overall characteristics of the electronic absorption spectra for these PZn-(BTD-PZn)ₙ, PZn₂-(BTD-PZn₂)ₙ, and BTD-PZnₙ-BTD chromophores resemble those described previously for dimeric and multimeric PZn compounds that feature a meso-meso ethyne-linkage topology (PZnₙ arrays); these spectra exhibit two distinct intense absorption manifolds that are derived from the porphyrin B- (Soret, S₀ → S₁) and Q-band (S₀ → S₂) transitions.

The observed perturbations from these benchmark PZnₙ spectra trace their origin to the proquinoidal BTD units that are connected to the porphyrin macrocycle meso carbons via ethynyl moieties. Previous investigations demonstrate that the nature of proquinoidal unit conjugation to the PZn macrocycle exerts a pronounced impact on the magnitude of B- and Q-state mixing, for example, for PZn-(proquinoidal Sp)-PZn chromophores, the long axis-polarized Q state (Qₓ) absorption maxima can be modulated from 689 to 1006 nm, depending upon the extent of the quinoidal resonance contribution to the electronically excited singlet state. A combination of semiempirical electronic structure calculations and experimental data underscore the cardinal role that PZn and proquinoidal fragment orbital energy differences play in fixing the radical cation and anion state energy levels in these structures.

The principles that informed design of these PZn-(BTD-PZn)ₙ, PZn₂-(BTD-PZn₂)ₙ, and BTD-PZnₙ-BTD chromophores stem from prior work that examined the photophysics of (porphinato)metal—(proquinoidal Sp)—(porphinato)metal supermolecules. This work highlighted the central importance of the magnitude of the energy separation between the (porphinato)metal and proquinoidal Sp fragment frontier orbitals in determining whether radiative, internal conversion, or intersystem crossing decay channels dominated the relaxation dynamics of the initially prepared electronically excited states of these complexes. When the (porphinato)metal and proquinoidal Sp fragment LUMO levels featured energy separations on the order of a few tenths of an eV, as they are for the 5-ethyl-PZn, 4-ethyl-BTD, and 4,7-diethyl-BTD fragments of these PZn-(BTD-PZn)ₙ, PZn₂-(BTD-PZn₂)ₙ, and BTD-PZnₙ-BTD structures, chromophores having multiconfigurational S₁ states characterized by a modest degree of charge transfer (CT) character are anticipated; such supermolecules were shown to display large S₁ → S₀ radiative rate constants and substantial fluorescence quantum yields. Other factors that informed the blueprint of the Fig. 1B-D supermolecules included insights derived from monomeric PZn complexes in which ethynyl-BTD units were used to expand conjugation at the macrocycle meso-carbon position; these designs led to PZn chromophores characterized by enhanced transfer of B-to-x-polarized Q-state oscillator strength, intensified Qₓ absorption bands, chromophore structural rigidification, spectrally narrow fluorescence emission bands, small magnitude Stokes shifts, and enhanced radiative rate constant magnitudes relative to simple benchmark PZn complexes.

Fluorescence emission metrics of BTD-PZnₙ-BTD, PZn-(BTD-PZn)ₙ, and PZn₂-(BTD-PZn₂)ₙ chromophores

Long wavelength absorption maxima (λₛ max, S₀ → S₁), corresponding extinction coefficient measurements, fluorescence (S₁ → S₀) emission maxima, full-width at fluorescence half-

![Fig. 1](https://example-image-url.com)
maximum (FWHM), Stokes shifts, fluorescence lifetimes ($\tau_f$), radiative rate constant ($k_r$), non-radiative rate constant ($k_{nr}$), and fluorescence quantum yield ($\phi_f$) data, are tabulated in Table 1 for the PZn$_n$, PZn-(BTD-PZn)$_n$, PZn$_2$-(BTD-PZn)$_2$$_n$, and BTD-PZn$_n$-BTD supermolecules.

These fluorescence quantum yield data correspond to abso-

Table 1  Electronic absorption and emission data in THF solvent for BTD-PZn$_n$-BTD, PZn-(BTD-PZn)$_n$, and PZn$_2$-(BTD-PZn)$_2$$_n$ chromophores relative to corresponding PZn$_n$ benchmarks

| Chromophore                      | $\lambda_{\text{max}}$ (S$_0$ $\rightarrow$ S$_1$) [nm] | $\varepsilon_{\text{max}}$ (S$_0$ $\rightarrow$ S$_1$) [M$^{-1}$ cm$^{-1}$] | $\lambda_{\text{max}}$ (S$_1$ $\rightarrow$ S$_0$) [nm] | FWHM (S$_1$ $\rightarrow$ S$_0$) [cm$^{-1}$] | Stokes shift (cm$^{-1}$) | $\phi_f$ | $\tau_f$ [ns] | $k_f$ [$\times10^8$ s$^{-1}$] | $k_{nf}$ [$\times10^8$ s$^{-1}$] |
|----------------------------------|--------------------------------------------------|-------------------------------------------------|-------------------------------------------------|---------------------------------|---------------------|--------|------------|-------------------|-------------------|
| PZn-BTD-PZn                     | 689 (1194)                                      | 64 600                                          | 741                                             | 1605                           | 1018               | 0.25 (0.31) | 1.6           | 1.6               | 4.7               |
| PZn-(BTD-PZn)$_2$               | 745 (1178)                                      | 132 700                                         | 784                                             | 977                            | 543                | 0.22 (0.36) | 1.1           | 2.0               | 7.1               |
| PZn-(BTD-PZn)$_4$               | 777 (1558)                                      | 184 000                                         | 811                                             | 846                            | 490                | 0.16 (0.29) | 0.8           | 2.0               | 11                |
| PZn-BTD-(BTD-PZn)               | 674 (672)                                       | 84 000                                          | 687                                             | 727                            | 281                | 0.13 (0.13) | 1.3           | 1.0               | 6.7               |
| BTD-PZn$_n$-BTD                 | 765 (1243)                                      | 101 600                                         | 787                                             | 802                            | 365                | 0.23 (0.30) | 1.4           | 1.6               | 5.5               |
| BTD-PZn$_n$-BTD                 | 809 (1663)                                      | 157 500                                         | 846                                             | 872                            | 310                | 0.16 (0.29) | 0.8           | 2.0               | 11                |
| BTD-PZn$_n$-BTD                 | 847 (1675)                                      | 238 300                                         | 888                                             | 1008                           | 587                | 0.10 (0.28) | 0.6           | 1.7               | 15                |
| PZn$_2$-(BTD-PZn)$_2$           | 780 (1822)                                      | 145 400                                         | 822                                             | 926                            | 688                | 0.14 (0.34) | 0.6           | 2.0               | 14                |
| PZn$_2$-(BTD-PZn)$_2$           | 816 (1382)                                      | 340 000                                         | 857                                             | 1154                           | 586                | 0.12 (0.36) | 0.5           | 2.4               | 18                |
| PZn$_2$                        | 695 (1082)                                      | 51 400                                          | 711                                             | 810                            | 324                | 0.14 (0.16) | 1.0           | 1.3               | 7.9               |
| PZn$_1$                        | 770 (1386)                                      | 116 000                                         | 806                                             | 875                            | 380                | 0.19 (0.27) | 1.1           | 1.7               | 7.1               |
| PZn$_1$                        | 842 (1562)                                      | 230 000                                         | 883                                             | 955                            | 351                | 0.09 (0.11) | 0.45          | 2.0               | 20                |

* Numbers in parentheses are spectral breadths (full-widths at half-maximum, FWHM) of the respective transitions in units of cm$^{-1}$. * Stokes shifts values correspond to the difference in energy between the low energy (Q$_f$) absorption (S$_0$ $\rightarrow$ S$_1$) and fluorescence (S$_1$ $\rightarrow$ S$_0$) band maxima. * Fluorescence quantum yields ($\phi_f$) values were determined using an integrating sphere-based absolute emission quantum yield measurement system (see ESI). * Values in parentheses represent those determined in toluene solvent. * These values were determined using S$_0$ $\rightarrow$ S$_1$ excitation (483 nm). Fluorescence lifetimes were measured via time-correlated single-photon-counting using a picosecond fluorescence lifetime measurement system. * Excited-state relaxation constants were calculated based on the following equations: $\tau_{\text{rel}} = 1/(k_r + k_{nf})$, $\phi_f = k_r \times \tau_{\text{rel}}$. * Values in parentheses represent those determined in toluene solvent. * Oscillator strengths calculated over the following wavelength domains: PZn-BTD-PZn ($\sim$360 to 600 nm); PZn-(BTD-PZn)$_2$ ($\sim$360 to 600 nm); PZn-(BTD-PZn)$_4$ ($\sim$360 to 605 nm); BTD-PZn$_n$-BTD ($\sim$360 to 560 nm); BTD-PZn$_n$-BTD ($\sim$360 to 560 nm); BTD-PZn$_n$-BTD ($\sim$360 to 560 nm); PZn$_2$-(BTD-PZn)$_2$ ($\sim$360 to 610 nm); PZn$_2$-(BTD-PZn)$_2$ ($\sim$360 to 610 nm). * Oscillator strengths calculated over the following wavelength domains: PZn$_n$-BTD-PZn ($\sim$600 to 720 nm); BTD-PZn$_n$-BTD ($\sim$600 to 820 nm); PZn$_n$-(BTD-PZn)$_2$ ($\sim$600 to 820 nm); BTD-PZn$_n$-BTD ($\sim$600 to 820 nm); BTD-PZn$_n$-BTD ($\sim$600 to 820 nm); PZn$_2$-BTD-PZn$_2$ ($\sim$610 to 860 nm); PZn$_2$-(BTD-PZn)$_2$ ($\sim$610 to 820 nm). * Ref. 41.

Table 2  Comparative integrated oscillator strengths of the B- and Q-band spectral regions of BTD-PZn$_n$-BTD, PZn$_n$-(BTD-PZn)$_n$, and PZn$_2$-(BTD-PZn)$_2$$_n$ chromophores relative to corresponding PZn$_n$ benchmarks

| Chromophore                      | Oscillator strength B-band region$^a$ | Oscillator strength Q-band region$^a$ | Total oscillator strength |
|----------------------------------|--------------------------------------|--------------------------------------|--------------------------|
| PZn-BTD-PZn                     | 2.11                                 | 0.72                                 | 3.52                     |
| PZn-(BTD-PZn)$_2$               | 4.65                                 | 1.03                                 | 5.67                     |
| PZn-(BTD-PZn)$_4$               | 5.98                                 | 1.58                                 | 7.57                     |
| BTD-PZn$_n$-BTD                 | 2.24                                 | 0.37                                 | 2.63                     |
| BTD-PZn$_n$-BTD                 | 3.54                                 | 0.89                                 | 4.42                     |
| BTD-PZn$_n$-BTD                 | 5.23                                 | 1.53                                 | 6.76                     |
| BTD-PZn$_n$-BTD                 | 7.64                                 | 2.10                                 | 9.74                     |
| PZn$_2$-(BTD-PZn)$_2$           | 6.04                                 | 1.30                                 | 7.35                     |
| PZn$_2$-(BTD-PZn)$_2$           | 10.49                                | 2.84                                 | 13.32                    |
| PZn$_3$                        | 2.134                                | 0.303                                | 2.438                    |
| PZn$_3$                        | 3.240                                | 0.716                                | 3.956                    |
| PZn$_3$                        | 5.986                                | 1.622                                | 7.608                    |

* Integrated oscillator strengths ($f$) were calculated based on the following expression: $f = 4.3 \times 10^{-8} \int \varepsilon dV$, where $\varepsilon$ is the experimental extinction coefficient, and $\int$ is the energy (in wave numbers) of the absorption. Values noted derive from electronic absorption spectra recorded in THF solvent.
Table 1 highlights that E-BTD units that terminate Pznn chromophores (Fig. 1A) give rise to BTD-Pznn-BTD supermolecules (Fig. 1D) in which λ_{max} (S_1 → S_0) for BTD-Pznn-BTD, BTD-Pznn2-BTD, BTD-Pznn3-BTD, and BTD-Pznn4-BTD redshift by 1358, 587, and 64 cm\(^{-1}\), respectively, relative to their Pznn, Pznn2, and Pznn3 benchmarks. Note that as a function of the number of Pznn units in these arrays, BTD-PznnBTD and Pznn supermolecules display similarly narrow fluorescence FWHM values as well as modest Stokes shifts; these energy differences between the low energy (Q_x) absorption (S_0 → S_1) and fluorescence (S_1 → S_0) band maxima of these chromophores range from 325–585 cm\(^{-1}\). A key spectroscopic ramification of terminal ethynyl-BTD conjugation to these Pznn frameworks is highlighted in the data chronicled in Table 2, which contrasts the integrated oscillator strengths of the B- and Q-band regions of the electronic absorption spectra of these chromophores. Note that the integrated Q-state oscillator strengths of these BTD-Pznn-BTD chromophores are augmented by more than 50% relative to their respective Pznn benchmark. These factors, coupled with a diminished nonradiative rate constant, play important roles in driving the substantial, long-wavelength emission quantum yield manifest by BTD-PznnBTD (ϕ_f = 0.28) relative to that for the parent Pznn chromophore (ϕ_f = 0.11) in low dielectric toluene solvent (Table 1).

Pznn(BTD-Pznn)_m chromophores (Fig. 1B) contrast the electronic spectral properties of BTD-Pznn-BTD supermolecules; Pznn(BTD-Pznn), Pznn(BTD-Pznn)\(_2\), and Pznn(BTD-Pznn)\(_4\) display Q_x state absorption maxima that are blue-shifted 126, 436, and 994 cm\(^{-1}\) with respect to the λ_{max}(S_0 → S_1) transitions of their respective Pznn, Pznn2, and Pznn3 benchmarks (Table 1, Fig. 1); this effect derives from the fact that 4,7-diethynylbenzo[c][1,2,5]thiadiazole provides diminished Pznn-Pznn electronic coupling relative to the ethynyl linker. While Pznn(BTD-Pznn) displays an augmented Stokes shift (1018 cm\(^{-1}\)) relative to Pznn (324 cm\(^{-1}\)) due to the greater cumulenic character in its relaxed electronically excited S_0 state,\(^6\) the Stokes shifts manifest for Pznn(BTD-Pznn)\(_2\), Pznn(BTD-Pznn)\(_4\), Pznn3, and Pznn5 are similar in magnitude (~560 cm\(^{-1}\)), congruent with more modest structural differences between the relaxed S_0 and S_1 states for these supermolecules (vide infra).

Pznn(BTD-Pznn), Pznn(BTD-Pznn)\(_2\), and Pznn(BTD-Pznn)\(_4\) display fluorescence emission maxima centered at 741, 784, and 811 nm, respectively, and substantial fluorescence quantum yields in THF solvent [ϕ_f(Pznn(BTD-Pznn)) = 0.25; ϕ_f(Pznn(BTD-Pznn)\(_2\)) = 0.22; ϕ_f(Pznn(BTD-Pznn)\(_4\)) = 0.16]. Similar to that observed for BTD-Pznn-BTD chromophores, fluorescence quantum yields are significantly enhanced in nonpolar solvent; note in this regard that ϕ_f(Pznn(BTD-Pznn)\(_4\)) is amplified to 29% in toluene (Table 1).

Fig. 1C highlights the absorptive and emissive spectral properties that ensue when Pznn chromophores are linked by 4,7-diethynylbenzo[c][1,2,5]thiadiazole units. These Pznn(BTD-Pznn)\(_n\) chromophores display dramatic Q_x absorption band intensification with increasing conjugation (Tables 1 and 2); note in this regard that Pznn2(BTD-Pznn)\(_n\) is an exceptional long-wavelength absorber (ε(816 nm) = 340 000 M\(^{-1}\) cm\(^{-1}\); Table 1). Pznn2(BTD-Pznn) and Pznn2(BTD-Pznn)\(_2\) emit respectively at 822 and 857 nm in THF solvent, with corresponding quantum yields of 14 and 12%. As demonstrated for both Pznn(BTD-Pznn)\(_n\) and BTD-Pznn_BTD chromophores, these fluorescence quantum yields are dramatically enhanced in toluene solvent [ϕ_f(Pznn(BTD-Pznn)\(_n\)) = 0.34; ϕ_f(Pznn2(BTD-Pznn)\(_2\)) = 0.36]. These data acquired for Pznn2(BTD-Pznn)\(_n\) designs suggest additional approaches to realize related frameworks that make possible high quantum yield NIR emission that include electronic modulation of the proquinoidal units that both terminate supermolecules that utilize Pznn building blocks, as well as those that are integrated into the conjugated backbones of these compositions.

**Computed electronic structures of BTD-Pznn-BTD, Pznn(BTD-Pznn)\(_m\), and Pznn2(BTD-Pznn)\(_m\) chromophores**

The natures of the low energy S_1 states of Pznn(BTD-Pznn)\(_m\), and Pznn2(BTD-Pznn)\(_m\) chromophores were probed through frontier orbital (FO) population and transition matrix
eigenvector analyses derived using TD-DFT methods. Fig. 2–4 show FO diagrams for BTD-PZn₃-BTD and PZn-(BTD-PZn)₂, along with those for the PZn₃ benchmark, and highlight the prominent one-electron configurations that contribute to their respective lowest energy Qₓ transitions; related data for the PZn₁₋₃(BTD-PZn)₂ chromophore is presented in the ESL†.

The natures and energy separations between the PZn₃, BTD-PZn₃-BTD, and PZn-(BTD-PZn)₂ FOs underscore the x-polarized nature of the lowest energy excited state for these supermolecules, and the globally delocalized character of their respective S₁ excited states. The low-lying excited states of these supermolecules are described by extensive configuration interaction (CI). The S₀ → S₁ transitions of PZn₃, BTD-PZn₃-BTD, and PZn-(BTD-PZn)₂ have large contributions (~55%) from the one electron HOMO → LUMO (H → L) configuration, and highlight the importance of quinoidal resonance contributions to this low-lying excited state; this resonance contribution plays a key role in the solvent-dielectric dependent fluorescence quantum yields evidenced in THF and toluene solvent.

For PZn₃ (Fig. 2), seven single excitation configurations describe the transition matrix eigenvector; in contrast, nine and six single excitation configurations describe respectively the transition matrix eigenvectors for BTD-PZn₃-BTD and PZn-(BTD-PZn)₂. For PZn₃, the transition eigenvector is dominated by configurations (representing an ~82% weighting in the CI expansion) that do not redistribute to a significant degree electron density. For BTD-PZn₃-BTD and PZn-(BTD-PZn)₂, the relative importance of such single excitation configurations that do not redistribute significantly electron density drops respectively to 74 and 22%, highlighting the increased importance of single-excitation configurations that redistribute electron density in the CI expansions that describe the S₀ → S₁ transition eigenvectors for these supermolecules. While the bandgap represented by ΔE_HOMO-LUMO varies to a minor degree and spans ~4.5 to 4.8 eV, note that the FO bandwidth in these Fig. 2–4 fluorophores varies significantly: ΔH → L+5 for PZn₃ is 9.77 eV but only 7.76 eV for PZn-(BTD-PZn)₂, a decrease of 2.01 eV.

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**Fig. 3** Calculated frontier molecular orbitals, energy levels, and relative one-electron configurations that contribute to the lowest energy (Qₓ) transition for BTD-PZn₃-BTD. Calculations were performed at the M11/6-311g(d) theory level.

**Fig. 4** Calculated frontier molecular orbitals, energy levels, and relative one-electron configurations that contribute to the lowest energy (Qₓ) transition for PZn-(BTD-PZn)₂. Calculations were performed at the M11/6-311g(d) theory level.
Note that as supramolecular conjugation evolves from PZn₃ to BTD-PZnₓ-BTD and PZn-(BTD-PZn)ₓ, an increased degeneracy of energy eigenvalues is manifest in the Fig. 2–4 FOs. This increased density of states (DOS) evident in BTD-PZnₓ-BTD and PZn-(BTD-PZn)ₓ differs from the mixing of BTD and PZn frontier orbitals. Congruent with Fermi’s Golden Rule, transition probability correlates with increased DOS. This larger DOS near the HOMO and LUMO levels serve to increase the multi-reference nature of the S₁ state wave function; S₁ configurations that involve these delocalized and mixed frontier orbitals will thus exhibit enhanced S₁ state wave function spatial delocalization. This computational trend is in line with the experimentally determined transition moments, wherein Qₓ transition oscillator strengths for PZn-(BTD-PZn)ₓ exceed that of PZnₓ. Note also that this dispersion of FO energies, which decreases progressively from PZnₓ to BTD-PZnₓ-BTD to PZn-(BTD-PZn)ₓ (Fig. 2–4), is correlated with increased π conjugation which is reflected in the computed electronic delocalization range function for these fluorophores (ESI†); due to the nature of these orbitals and their diminished energy gaps within the filled and empty regimes of the FO manifold, a greater weighted fraction of single excitation configurations having charge resonance character is manifest, congruent with the augmented Qₓ absorption oscillator strengths observed for BTD-PZnₓ-BTD and PZn-(BTD-PZn)ₓ relative to PZnₓ (Fig. 1, Tables 1 and 2).

Conclusions

We describe a design strategy for (porphinato)zinc-based supermolecules that possess large NIR fluorescence quantum yields. These PZnₓ-(BTD-PZn)ₓ, PZnₓ-(BTD-PZn)ₓ, and BTD-PZnₓ-BTD fluorophores feature either 4-ethylbenzo[c][1,2,5]thiadiazole (E-BTD) units that terminate meso-to-meso ethyne-bridged (porphinato)zinc (PZnₓ) arrays, or 4,7-diethylbenzo[c][1,2,5]thiadiazole (E-BTD-E) spacers that are integrated into the backbone of these compositions. PZnₓ-(BTD-PZn)ₓ, PZnₓ-(BTD-PZn)ₓ, and BTD-PZnₓ-BTD chromophores are characterized by enhanced transfer of B-to-x-polarized Q-state oscillator strength relative to their corresponding PZnₓ benchmarks, intensified Qₓ absorption bands, supermolecule structural rigidity, spectrally narrow fluorescence emission bands, small magnitude Stokes shifts, and large radiative rate constant magnitudes. TD-DFT calculations point to the importance of a greater weighted fraction of single excitation configurations having charge resonance character that describe the S₀ → S₁ transition matrix eigenvector in PZnₓ-(BTD-PZn)ₓ, PZnₓ-(BTD-PZn)ₓ, and BTD-PZnₓ-BTD emitters relative to PZnₓ oscillators in driving these spectroscopic and dynamical properties. Collectively, these systems define an unusual family of intensely absorbing vis-NIR absorbers that display strikingly high fluorescence quantum yields (φₑ values) over the 700–900 nm regime of the NIR. These THF φₑ values for PZnₓ-(BTD-PZn)ₓ, PZnₓ-(BTD-PZn)ₓ, and BTD-PZnₓ-BTD supermolecules, perhaps without peer in a solvent of this dielectric strength over this spectral window, range from 10–25%; notably these φₑ values are dramatically amplified in hydrophobic media and thus contrast the behavior of classic tricarbocyanine NIR dyes, displaying fluorescence quantum yields ranging from 28–36% in toluene solvent. Because these BTD-PZnₓ-BTD, PZnₓ-(BTD-PZn)ₓ, and PZnₓ-(BTD-PZn)ₓ supermolecules display extraordinarily large NIR fluorescence quantum yields in hydrophobic solvent, these designs underscore new opportunities to evolve NIR-emissive nano- and mesoscale vesicles for fluorescence imaging applications in which the emissive irradiance exceeds the impressive metrics already established for such structures that membrane-disperse PZnₓ fluorophores.54–61,63

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 the excitation light source and an extended red sensitive PMT (Hamamatsu R2658P side window photomultiplier, spectral range: 200–1010 nm) for detection. Emission spectra were corrected using a calibration curve supplied with the instrument.

Fluorescence lifetime measurements

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. Fluorescence lifetimes were acquired in single-photon-counting mode using Hamamatsu HPD-TA software and analyzed using the Hamamatsu fitting module.

Quantum yield measurements

A Hamamatsu C9920-03 Absolute Quantum Yield Measurement System was employed to make the quantum yield measurements. Excitation initiates from a Xe-lamp, where the wavelength is selected by a monochromator, and passed through a 1 mm optical excitation filter. The inside of the sphere is coated with Spectralon (Labsphere, Inc.) that has at least 99% reflectance over the 350–1650 nm spectral window. Added detail regarding these measurements is provided in the ESI†.

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 16, revision C.01.57 The M11 64
functional was employed for all calculations. Optimizations were performed with minimal symmetry constraints using tight optimization criteria with the 6-311g(d) basis set implemented. Selected frontier orbital wave functions were plotted as iso-
surfaces (iso = 0.02) using Avogadro.™ 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.

Conflicts of interest
No competing financial interests have been declared.

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