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Visible-Light-Driven Triplet Sensitization of Polycyclic Aromatic Hydrocarbons Using Thionated Perinones

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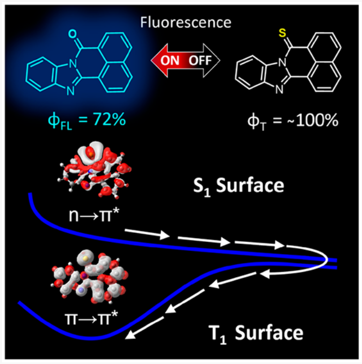

ABSTRACT: Metal-free chromophores that efficiently generate triplet excited states represent promising alternatives with respect to transition metal-containing photosensitizers, such as those featuring metal-to-ligand charge transfer excited states. However, such molecular constructs have remained underexplored due to the unclear relationship(s) between molecular structure and efficient/rapid intersystem crossing. In this regard, we present a series of three thionated perinone chromophores serving as a newly conceived class of heavy metal-free triplet photosensitizers. We demonstrate that thionation of the lone C═O substituent in each highly fluorescent perinone imparts red-shifted absorbance bands that maintain intense extinction coefficients across the visible spectrum, as well as unusually efficient triplet excited state formation as inferred from the measured singlet O_2 quantum yields at 1270 nm (Φ_Δ = 0.78–1.0). Electronic structure calculations revealed the emergence of a low energy S_1 ($n \rightarrow \pi^*$) excited state in the proximity of a slightly higher energy S_2 ($\pi \rightarrow \pi^*$) excited state. The distinct character in each of the two lowest-lying singlet state manifolds resulted in the energetic inversion of the corresponding triplet excited states due to differences in electron exchange interactions. Rapid $S_1 \rightarrow T_1$ intersystem crossing was thereby facilitated in this manner through spin–orbit coupling as predicted by the El Sayed rules. The lifetimes of the resultant triplet excited states persisted into the microsecond time regime, as measured by transient absorbance spectroscopy, enabling effective bimolecular triplet sensitization of some common polycyclic aromatic hydrocarbons. The synthetically facile interchange of a single O atom to an S atom in the investigated perinones resulted in marked changes to their photophysical properties, namely, conversion of dominant singlet state fluorescence in the former to long-lived triplet excited states in the latter. The combined results suggest a general strategy for accessing long-lived triplet excited states in organic chromophores featuring a lone C═O moiety residing within its structure, valuable for the design of metal-free triplet photosensitizers.

Polycyclic aromatic hydrocarbons (PAHs) have been intensively studied over the past several decades and are well-known for their valuable optical and electronic properties.[1] Among their applications, PAHs have recently exhibited increasing potential in photocatalysis and solar energy conversion schemes.[2−9] The triplet excited states of PAHs have become the focal point of these photoinitiated processes, where they are largely used in bimolecular chemical transformations associated with triplet–triplet annihilation upconversion[2−6] (TTA-UC) or photoredox catalysis.[7−9] In many PAHs, triplet states are inherently difficult to generate through direct excitation due to the large singlet–triplet splitting in these chromophores.[1] A limited number of PAHs are capable of singlet fission, where two triplet excited states are produced from the fission of one high-energy singlet state.[10] However, observation of this phenomenon in PAHs has been restricted to tetracene,[11] pentacene,[12] and some of their derivatives,[13,14] which feature the proper singlet/triplet energetics ($2T_1 < S_1$). Thus, most PAHs often require triplet sensitization through direct Dexter-type triplet energy transfer (TET) to efficiently access their triplet manifold.[4]

Currently, most triplet sensitizers incorporate second- and third-row transition metals to promote triplet formation because the spin–orbit coupling (SOC) constant is approximately proportional to the square of atomic number Z.[15−19] However, the simplest and most easily accessible of these molecules absorb intensely in the ultraviolet region and suffer from smaller visible absorption cross sections,[3,15,18,20,21] limiting their potential in solar-light-driven applications. Additionally, the strong SOC that results from the heavy-atom effect also drastically shortens triplet lifetimes compared to those of many organic chromophores.[15,18] Many investigations have attempted to circumvent these issues by appending organic chromophores within the ligand framework, which strategically introduces a series of energy transfer

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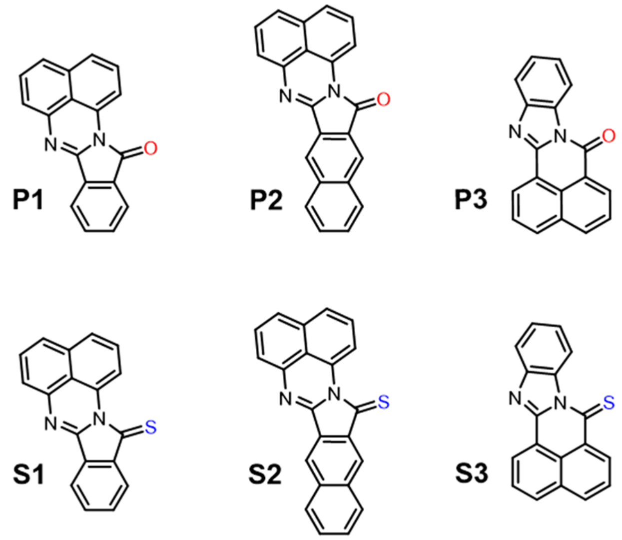
cascades and triplet state thermal equilibria to achieve enhanced visible-light harvesting and extended triplet lifetimes.[15,18,22−26] However, these bi- and polychromophoric transition metal architectures can be very cumbersome and tedious to design and synthesize, where it is also difficult to predict and control the achieved thermal equilibrium process and the resultant lifetime extension *a priori*.[23] Among the previously mentioned obstacles, the significant cost and relatively low natural abundance of the second- and third-row transition metals typically used in these constructs limit the practicality of these systems for large-scale applications. Thus, there is substantial interest in generating easily accessible organic triplet photosensitizers featuring strong visible absorbing cross sections, long excited state lifetimes, and redox properties amenable for photoredox catalysis.

Recently, Scholes and co-workers demonstrated that thionation of perylenediimides (PDIs) resulted in subpicosecond intersystem crossing (ISC) time constants, representing one of the few reported totally organic PDI derivatives with efficient access to its triplet manifold.[27] Because the rate of ISC was independent of the degree of PDI thionation, they concluded that the heavy-atom effect was not the cause of the increased SOC, but rather the energetic proximity of many of the low-lying singlet and triplet excited states. This principle has since been extended to a few thionated naphthalimide (NI) derivatives, which served as effective heavy-atom-free photosensitizers in photodynamic therapy (PDT).[28−30] Similarly, Stryland and co-workers have pioneered a new class of thionated squarine dyes that also show promise as organic photosensitizers,[31,32] resulting in their implementation in red-to-yellow upconversion schemes using rubrene as an acceptor/annihilator.[33] Thus, regardless of the core molecular framework, thionating various aromatic pendant carbonyl groups opens channels for efficient intersystem crossing to the triplet state without relying on the heavy-atom effect imparted by transition metals. While this is the case, aromatic thiones remain relatively underexplored as triplet sensitizers, with the currently available classes of molecules being restricted to the few examples discussed above.[28,32,33]

Perinones and other polycyclic benzimidazole chromophores have emerged within the past decade as promising analogues of the ubiquitous PDI chromophores, finding increasing use in the dye industry[34,35] and as organic n-type semiconductor materials.[34,36−38] This newly found interest results from their synthetic simplicity, improved visible absorption capabilities,[34,36−38] significant electron mobilities,[36,37,39] and exceptional photochemical and thermal stabilities.[34,35,40] Additionally, perinones can be easily accessed through solid state condensation and direct sublimation,[38] generating chromophores with intense visible-light absorption prepared under solvent-free "green" synthetic conditions featuring limited material and purification costs. While these properties are ideal for realizing inexpensive organic triplet photosensitizers, perinones, much like PAHs, have limited access to their triplet manifolds. Akin to the photophysics in PDIs, the excited state evolution of perinones exclusively proceeds through short-lived singlet excited states with enormous fluorescence quantum yields.[36,38]

In this investigation, we hypothesized that the photophysical tunability of perinone chromophores would echo those of PDIs and postulated that metal-free triplet photosensitizers could be generated on the basis of thionation at their lone carbonyl moiety [**S1−S3** (Chart 1)]. It is worth noting that in

Chart 1. Molecular Structures of the Parent Perinones (P1−P3) and Thioperinones (S1−S3) Investigated in This Study



comparison to the thionated PDI and NI derivatives, the presence of a single carbonyl group in perinones completely eliminates regioselectivity issues in the thionation process, whereas both PDIs and NIs produce mixtures of multi-thionated products.[27,41] Furthermore, the selected parent perinones [**P1−P3** (Chart 1)] are capable of intense light absorption across the majority of the visible spectrum (400−600 nm), which significantly red-shifted in the visible region upon thionation. Thus, flexibility was enabled in terms of the visible excitation wavelength when these sensitizers were paired with common PAH acceptors. We demonstrate that PAH acceptors with triplet energies of up to ∼1.8 eV could effectively be sensitized with diffusion-limited TET rates, which included tetracene, perylene, and 9,10-diphenylanthracene. Furthermore, we examined the nature of the electronic structure that facilitates efficient triplet formation in thionated perinones using electronic structure calculations.

The molecular structures of all the chromophores investigated in this study are presented in Chart 1, while all synthetic and characterization data are reported in the Supporting Information. We note that **P1** and **P3** have been previously synthesized and characterized,[36,38] while **P2** is a newly reported molecule. The normalized electronic absorption spectra measured in toluene of **S1−S3** and their corresponding perinone precursors (**P1−P3**) are presented in Figure 1, with other relevant measured photophysical data summarized in Table 1. The lowest energy absorption bands of **P1−P3** have previously been assigned as $^1(\pi \rightarrow \pi^*)$.[38] As presented in Figure 1, the lowest energy absorption bands of **S1−S3** have similarly structured absorption envelopes with respect to their parent chromophores but display significant bathochromic shifts. The similarity within each absorption envelope suggests that the experimentally observed lowest energy electronic transition for each thionated perinone is also $^1(\pi \rightarrow \pi^*)$ in nature, with vibronic coupling that is not significantly perturbed upon thionation. The significant red-shift observed upon thionation (>50 nm) is well-documented in the literature[27,42,43] and can be rationalized by the significant energetic lowering of the lowest unoccupied molecular orbital (LUMO), while the highest occupied molecular orbital (HOMO) remains unchanged in energy (Table S1).

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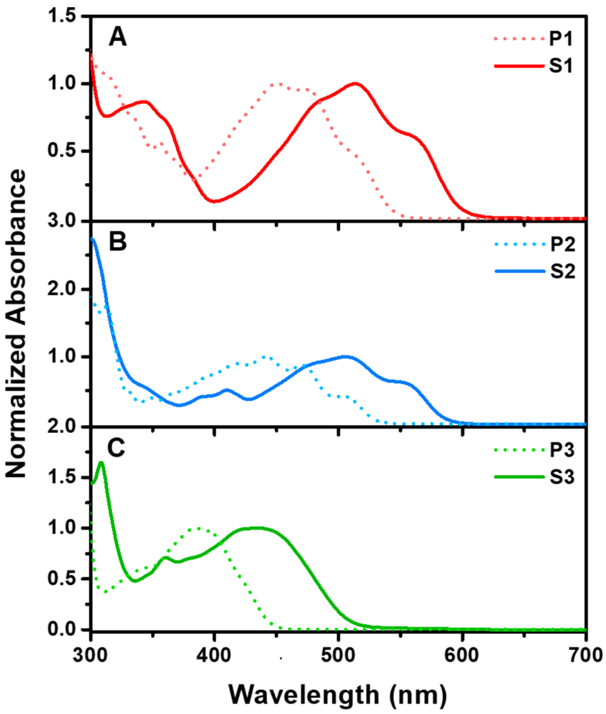

Figure 1. Normalized absorbance spectra (solid) of (A) **S1**, (B) **S2**, and (C) **S3** overlaid with the corresponding normalized absorbance spectra (dashed) of **P1−P3** in toluene.

Table 1. Absorbance and Photophysical Data of the Chromophores Used in This Study[a]

molecule	$\lambda_{abs\ max}$ (nm) [ε (M^{-1} cm^{-1})][b]	Φ_{PL} (298 K)	τ_{PL} (298 K) (ns)
P1	449 (8200)	0.046[c]	1.00[f]
S1	514 (10800)	<0.001[c,e]	–
P2	442 (11300)	0.091[c]	1.51[f]
S2	507 (8700)	<0.001[c,e]	–
P3	385 (11700)	0.72[d]	10.7[f]
S3	435 (9900)	<0.001[d,e]	–

[a]Measurements were performed in toluene. [b]Molar extinction coefficients determined for the lowest energy $\lambda_{abs\ max}$. [c]Quantum yields measured using aerated [Ru(bpy)$_3$](PF$_6$)$_2$ in acetonitrile as the standard (λ_{em} = 621 nm; Φ_{PL} = 0.018).[44] [d]Quantum yield measured using 4-aminonaphthalene-1,8-imide (ANI) in toluene as the standard (λ_{em} = 495 nm; Φ_{PL} = 0.91).[45] [e]Samples degassed using the freeze−pump−thaw technique. [f]Excited state emission lifetimes measured using time-correlated single-photon counting with pulsed laser diode excitation at 405 nm.

Considering that typical second- and third-row transition metal sensitizers exhibit only modest light absorption in the visible region,[3,15,18,20,21] it is worth noting that **S1−S3** are capable of light absorption across the majority of the visible spectrum (400−600 nm), with maxima at 514, 507, and 435 nm for **S1−S3**, respectively. The extinction coefficients at these respective maxima are on the order of 10^4 M^{-1} cm^{-1}, which are similar to the intensities of the MLCT absorptions in transition metal complexes but can be readily tuned with facile structural modifications and can achieve significantly red-shifted absorption bands by comparison. Consequently, the total integrated intensity of the absorption spectra across the visible region is much larger for **S1−S3**, suggesting an advantage of using these chromophores over traditional metal-containing photosensitizers.

Chromophores **P1−P3** exhibit intense fluorescence arising from the initially populated $^1(\pi \rightarrow \pi^*)$ excited state that decays within the early nanosecond time regime (Table 1). In addition to inducing significant bathochromic shifts to the electronic absorption spectra, **S1−S3** also resulted in quantitative quenching of this prompt singlet fluorescence. Additionally, no photoluminescence was observed for any of the thionated perinone chromophores even at 77 K in 2-methyl-tetrahydrofuran, indicating the presence of substantial nonradiative deactivation channels. The observation of quantitatively quenched fluorescence was anticipated given the prediction of efficient triplet formation in these chromophores;[27−29,31] however, the lack of phosphorescence even at 77 K encouraged us to measure singlet oxygen quantum yields to confirm triplet state formation as the dominant driver in excited state decay. The observation of singlet oxygen phosphorescence at ∼1270 nm in aerated solutions of **S1−S3** (Figure S21) confirmed the process of triplet formation.[46] To the best of our knowledge, this is the first report of accessing the triplet manifold in perinone chromophores without incorporating a third-row transition metal into the molecular architecture.[47] Furthermore, the singlet oxygen quantum yields [Φ_Δ (Table 2)] were measured

Table 2. Triplet-Based Photophysical Properties of Chromophores S1−S3[a]

molecule	τ_T (298 K)[b,c] (μs)	Φ_Δ (298 K)[d]	E_T (eV)[e]
S1	0.664	0.78	1.53−1.77
S2	1.90	0.85	1.53−1.77
S3	12.9[f]	1.0	1.77−2.00

[a]Measurements were performed in toluene. [b]Excited state TA lifetimes taken with an Edinburgh LP920 laser flash photolysis spectrometer. [c]Samples degassed using the freeze−pump−thaw technique. [d]Singlet oxygen quantum yields measured using aerated ZnTPP in toluene as the standard (Φ_Δ = 0.93).[46] [e]Triplet energies estimated using energy transfer quenching with a series of triplet acceptors (see the Supporting Information). [f]Excited state lifetime determined in the absence of self-quenching (theoretical infinite dilution) from concentration dependence (Figure S28).

as 0.78 for **S1**, 0.85 for **S2**, and 1.0 for **S3**, suggesting large triplet quantum yields (Φ_T) that rival those featured in transition metal complexes; the quantum yield of triplet state formation of **S3** must be unity. The singlet oxygen phosphorescence signal was completely absent in aerated solutions of **P1−P3**, signifying that triplet state generation in **S1−S3** was a direct consequence of a single thionation (Figures S22−S24). To glean more insight into the potential of **S1−S3** as triplet photosensitizers, their triplet lifetimes were determined using nanosecond transient absorption spectroscopy, with the associated difference spectra presented in Figure 2A−C. The resultant single-exponential triplet lifetimes were measured as 0.664, 1.90, and 12.9 μs for **S1**, **S2**, and **S3**, respectively (Table 2).

In each case, the lifetimes of the thioperinones persisted into the microsecond time domain, which is sufficient to engage in bimolecular triplet sensitization. This process has yet to be demonstrated using perinone chromophores and is significantly underexplored using aromatic thiones in general. Therefore, we used **S1−S3** to sensitize a series of pertinent PAH acceptors through TET under selective visible excitation (480 or 560 nm) of the thioperinone. Initially, a range of PAH acceptors were chosen for each thionated perinone to establish

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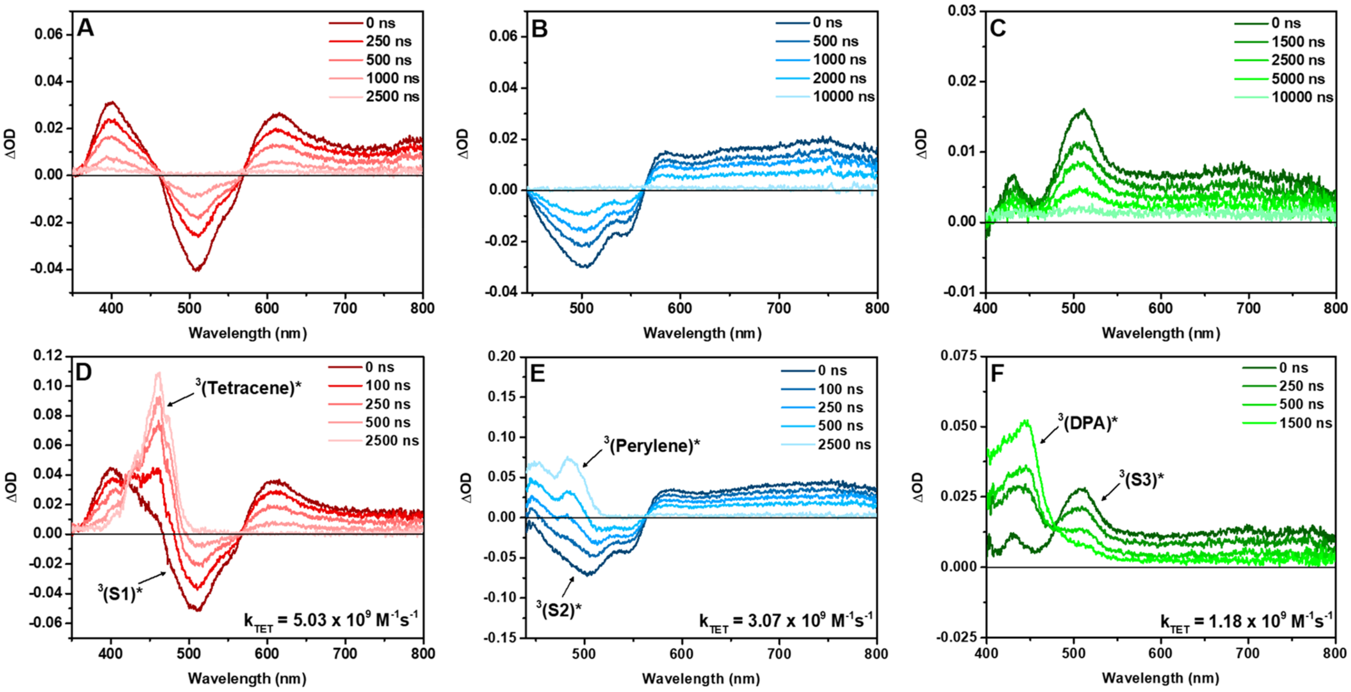

Figure 2. Nanosecond transient absorption difference spectra of (A) **S1** (70 μM), (B) **S2** (90 μM), and (C) **S3** (50 μM) without a quencher. Nanosecond transient absorption difference spectra of (D) **S1** (70 μM), (E) **S2** (90 μM), and (F) **S3** (50 μM) with tetracene (0.60 mM), perylene (0.40 mM), and DPA (1.30 mM) as quenchers, respectively. Transient spectra were recorded using 480 nm (**S3**) or 560 nm (**S1** and **S2**) pulsed excitation (~1.3−1.6 mJ/pulse, 7 ns full width at half-maximum) in deaerated toluene. The samples were deaerated using the freeze−pump−thaw method.

an estimate of their triplet energies because **S1**−**S3** are not phosphorescent at 77 K, even when the glass-forming solvent was doped with an external heavy atom.[48] The resultant triplet energies are listed in Table 2 as 1.53−1.77 eV for **S1** and **S2** and 1.77−2.0 eV for **S3**. A discussion of the experimental details and the triplet energy estimation procedure are reported in the Supporting Information.

The sensitized PAH triplets manifested in the TA difference spectra (Figure 2D−F) as characteristic peaks at 465 nm (tetracene), 480 nm (perylene), and 435 nm (DPA). The prompt signals in these transient spectra were dominated by contributions from each triplet ^{3}(thioperinone)*, which then give rise to the ^{3}(PAH)* signal at longer delay times. The TET dynamics were monitored using Stern−Volmer quenching of the nanosecond TA kinetics (see the Supporting Information), with the resultant energy transfer rate constants (k_{TET}) reported in Table 3. Comparison of TET dynamics across all three sensitizers indicated that the PAH acceptors with triplet energies of up to ~1.8 eV could be sensitized at the diffusion limit. Chromophore **S3** was the only molecule that could effectively sensitize DPA (Figure 2F; k_{TET} = 1.18 × 10^9 M^{-1} s^{-1}), while the lower triplet energies of **S1** and **S2** prevented a sufficient energetic driving force to facilitate the same process (k_{TET} < 10^7 M^{-1} s^{-1}). Thus, **S1** and **S2** served as ideal sensitizers for tetracene (Figure 2D; k_{TET} = 5.03 × 10^9 M^{-1} s^{-1}) and perylene (Figure 2E; k_{TET} = 3.07 × 10^9 M^{-1} s^{-1}), respectively, due to the lower triplet energies of these PAHs.

Because thionation was demonstrated to be an effective means for accessing the triplet manifold in perinones, we sought to elucidate the details of their electronic structures using DFT and TD-DFT calculations (M06-D3/Def-2-TZVP).[49−53] The frontier molecular orbitals obtained from the ground state geometry optimizations of **S1**−**S3** are shown

Table 3. TET Quenching of Chromophores S1−S3 as a Function of PAH Acceptor[a]

sensitizer	acceptor	acceptor triplet energy (eV)[b]	k_{TET} (M^{-1} s^{-1})
S1	tetracene	1.27	5.03 × 10^9
	perylene	1.53	1.89 × 10^8
	DPA	1.77	<10^7
S2	tetracene	1.27	4.74 × 10^9
	perylene	1.53	3.07 × 10^9
	DPA	1.77	<10^7
S3	perylene	1.53	7.48 × 10^9
	DPA	1.77	1.18 × 10^9
	pyrene	2.00	2.70 × 10^6

[a]Measurements were performed in deaerated toluene. Additional experimental details and kinetic data can be found in the Supporting Information. [b]Acceptor energies obtained from ref 1.

in Figure 3. For the low-lying singlet−singlet transitions, the HOMO, HOMO−1, and LUMO are the diagnostic orbitals for these chromophores. Throughout the series, the frontier orbitals feature HOMO and LUMO as π and π^* in character, respectively, and the HOMO−1 to be nonbonding in character, with most of the electron density centered on the sulfur atom. This is in stark contrast to **P1**−**P3**, which do not exhibit frontier molecular orbitals with any significant non-bonding character (Figure S38). Using TD-DFT, the transitions between the frontier orbitals of **S1**−**S3** were calculated and are reported for the two lowest-lying singlet−singlet transitions (Table S2). For each chromophore, TD-DFT predicts the lowest energy singlet−singlet transition (S_0 → S_1) to be an optically forbidden n → π^* transition, which was confirmed by the electron density difference surfaces generated from the optimized S_1 structures (Figure S43). The

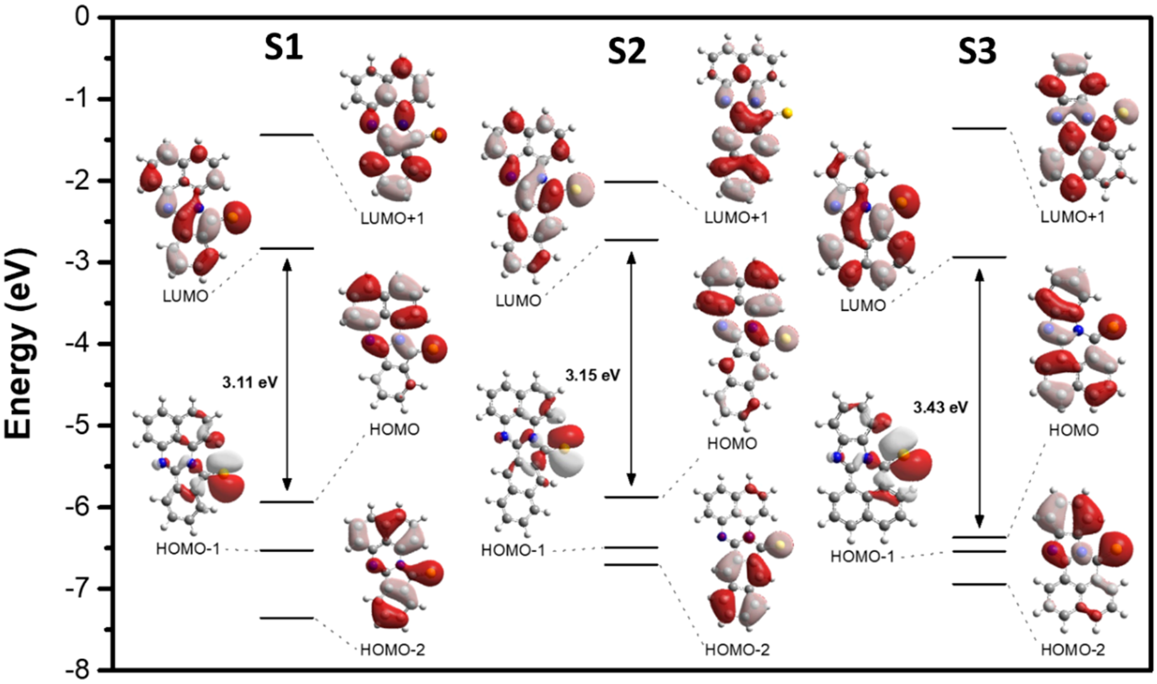

Figure 3. Frontier molecular orbital diagram of chromophores **S1−S3**. Calculations reveal the emergence of a nonbonding molecular orbital (HOMO−1) upon thionation when compared to the perinone models.

calculated $S_0 \rightarrow S_2$ transitions in chromophores **S1−S3** reveal these excitations to be intense $\pi \rightarrow \pi^*$ transitions, which correspond well with the experimentally observed $\lambda_{abs\ max}$ for the lowest energy absorbance bands (Figure S39). This result was expected given the similar appearance of the absorbance envelopes of chromophores **S1−S3** to their nonthionated parent chromophores **P1−P3**.

The assignment of S_1 as $n \rightarrow \pi^*$ and S_2 as $\pi \rightarrow \pi^*$ is widely established for numerous aromatic thioketones.[27,42,43,54−58] However, whereas the $S_1 - S_2$ energy gap is large in most of these cases, the energetic proximity of the S_1 and S_2 excited states in **S1−S3** was revealed through electronic structure calculations (Table S2). Consequently, we anticipated that the much larger singlet−triplet splitting energy (ΔE_{ST}) of the $\pi \rightarrow \pi^*$ configuration may cause inversion of the corresponding $^3(n \rightarrow \pi^*)$ and $^3(\pi \rightarrow \pi^*)$ excited states, similar to what has been proposed for thionated PDIs[27] and squarine dyes.[32] Thus, we were motivated to perform natural transition orbital (NTO) analysis on the low-lying triplet manifold of chromophores **S1−S3** (Figures S40−S42). The $S_0 \rightarrow T_1$ NTOs display that the hole and electron reside mainly in the π system in chromophores **S1−S3** (i.e., T_1 can be described as $\pi \rightarrow \pi^*$ in all cases). The $S_0 \rightarrow T_2$ NTOs show that the hole resides in the nonbonding orbital centered on the sulfur atom, while the electron resides mainly in the π system in chromophores **S1−S3** (i.e., T_2 can be described as $n \rightarrow \pi^*$ in all cases). These results are supported by the triplet spin densities from the optimized T_1 states (Figure S43), confirming the suspected energetic inversion of the two lowest energy triplet excited states with respect to their corresponding singlet excited states.

As a result of triplet state inversion, the difference in ISC efficiencies between the thionated and nonthionated perinones can be rationalized according to the El Sayed selection rules.[59] These ISC selection rules state that an $S_1(n{-}\pi^*) \rightarrow T_1(\pi{-}\pi^*)$ transition is allowed because the change in multiplicity is coupled with a change in symmetry, thus conserving the total angular momentum of the interacting excited states. Similar observations of this $S_1(n{-}\pi^*) \rightarrow T_1(\pi{-}\pi^*)$ transition have also been established for the thionated squarine dyes discussed previously.[32] Note that ISC to upper $^3(\pi \rightarrow \pi^*)$ excited states (T_3 and above) has been ruled out because they are significantly higher in energy with respect to S_1, preventing an adequate driving force to enable efficient triplet state formation. While the nature and alignment of the singlet and triplet manifolds facilitate enhanced SOC in **S1−S3** via the El Sayed rules, the presence of solely $\pi \rightarrow \pi^*$ transitions in the low-lying singlet manifolds (Figure S38 and Table S3) of chromophores **P1−P3** illustrates why the model perinones exhibit comparatively inefficient ISC dynamics. Thus, the two main design criteria that allow efficient triplet formation in **S1−S3** can be generalized from these results: (1) these systems contain two lowest-lying singlet excited states in energetic proximity, where the higher energy configuration allows a larger exchange interaction due to the superior overlap density of participating orbitals, and (2) these singlet states possess different symmetries, facilitating SOC via the El Sayed rules. A representative summary of these criteria as they apply to **S3** is shown in Figure 4, along with the associated photophysical properties.

As mentioned previously, sensitization of various PAH acceptors has pivotal implications in TTA-UC and photoredox catalysis, where costly second- and third-row transition metal complexes currently dominate as triplet sensitizers. Sensitization of DPA and other anthracene derivatives by **S3** is particularly attractive for sensitization-initiated electron transfer (SenI-ET) in photoredox catalysis.[7] Sensitized $^3(DPA)^*$ can be reduced by sacrificial electron donors to generate highly reductive radical anions (−1.94 vs SCE),[1] which are capable of activating various stable substrates for the construction of challenging carbon−carbon and carbon−heteroatom bonds.[7] Thus, replacement of archetypal photoredox catalysts such as $Ru(bpy)_3^{2+}$ or *fac*-$Ir(ppy)_3$ with **S3**/DPA can substantially

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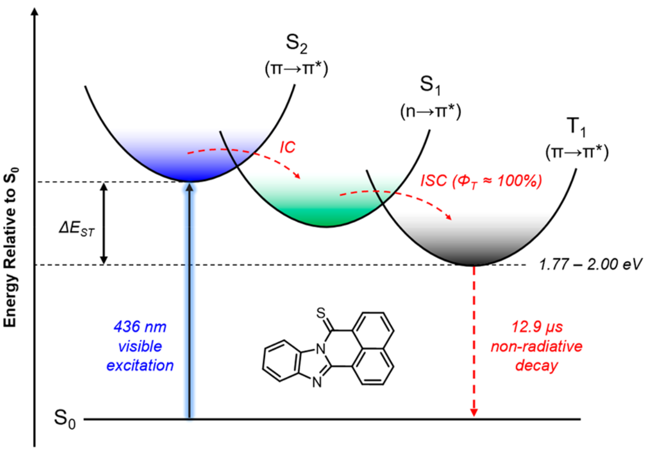

Figure 4. Proposed mechanism for excited state decay through the triplet manifold for chromophore **S3** and associated photophysical data. Only the most probable electronic transitions are shown.

alleviate scalability barriers in the catalytic activation of many organic molecules.[60] SenI-ET using **S3**/DPA is also an attractive replacement for many totally organic photoredox catalysts, which often absorb strongly only in the ultraviolet.[61] As an alternative to photoredox catalysis, chromophores **S1** and **S2** can readily serve as candidates for green-to-blue upconversion schemes using perylene as an acceptor/annihilator.[62] In these cases, excitation over a range of green wavelengths (500−580 nm) can potentially facilitate upconverted blue fluorescence and an anti-Stokes shift of up to ∼0.6 eV, which is typically achieved using expensive Pt(II)-porphyrin or polypyridyl complexes as photosensitizers.[4,6] Upconversion schemes such as this may have further implications in energy conversion processes allowing sub-band gap harnessing of solar photons in photovoltaics, a crucial step toward breaching the Shockley−Queisser efficiency limit.[63] Clearly, PAHs are used pervasively throughout the literature as molecular acceptors, which is why these molecules were chosen to emphasize the applicability of **S1**−**S3** as photosensitizers. However, other acceptors, such as common BODIPY dyes used in TTA-UC schemes,[6] represent viable candidates to pair with **S1**−**S3** as sensitizers. Furthermore, the notably high singlet oxygen quantum yields of **S1**−**S3** make them promising sensitizers for photodynamic therapy, particularly when visible-light excitation is required.[28]

In summary, we have demonstrated the first comprehensive design and implementation of metal-free triplet photosensitizers using the perinone molecular framework. Highly desirable red-shifted absorbance bands that maintain intense molar extinction coefficients across the visible region were achieved through a one-step thionation, which were also accompanied by efficient population of the triplet manifold inferred from the quantum yields for singlet oxygen formation (Φ_Δ = 0.78−1.0). Consequently, the excited state lifetimes of the perinone chromophores were extended into the microsecond time domain, allowing effective bimolecular triplet sensitization of PAH acceptors with triplet energies of up to ∼1.8 eV. Finally, we characterized the nature of the electronic structure that facilitates efficient triplet formation in thionated perinones and generalized an emerging design approach for metal-free triplet photosensitizers. As emphasized above, using totally organic triplet photosenzitizers can substantially reduce the cost of many bimolecular photochemical and physical transformations that currently utilize transition metal photosensitizers. This is particularly evident when considering species such as platinum porphyrins and benchmark ruthenium(II) polypyridine complexes, which have been commonly used as sensitizers for solar-based TTA-UC[2,4,19] or photochemical reactions.[3,7] Because of the transition from small laboratory investigations to industrial processes required to serve the general public, scalability costs become a primary issue. Additionally, most transition metal-based sensitizers rely on selective excitation into MLCT states with fairly weak absorption in the visible region,[3,15,18,20,21] which implies that excess material is required for maximum photon absorption at visible wavelengths. Thus, we believe that the tailored design of thionated perinone chromophores enables them to serve as potential replacements for precious transition metal photosensitizers in applications where energy is extracted from the triplet state under visible-light excitation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01634.

Experimental methods, structural characterization data, additional static and time-resolved spectra, additional electronic structure calculation details, and the three-dimensional structures (XYZ) of **S1**−**S3** (PDF)

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Notes

The authors declare no competing financial interest.

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