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Triplet-Forming Thionated Donor-Acceptor Chromophores for Electrochemically Amphoteric Photosensitization

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A series of piperidine-naphthalene monoimide, donor–acceptor (D–A) chromophores and their thionated derivatives were prepared. The physical properties of the chromophores were studied by spectroscopic and electrochemical measurements and DFT calculations. Relative to their non-thionated counterparts, the thionated D–A chromophores display enhanced visible-light absorption and ¹O₂-sensitization quantum yields and negligible fluorescence, suggesting facile triplet formation of this class of molecules. This behavior originates from the significant n–π* character in the singlet excited state, resulting in large spin-orbit coupling between the singlet/triplet manifolds regardless of the degree of D/A interactions. With the electrochemically active D/A moieties and high triplet energy, the thionated chromophores can be used as amphoteric photosensitizers to catalyze reductive and oxidative photo-reactions with efficiency comparable to Ru(bpy)₃²⁺ as the sensitizer. Our results demonstrate that thiocarbonylation can be utilized in amide/imide-containing D–A chromophores to provide a wide range of heavy-atom-free redox-active photosensitizers.

With the rapid advances in photocatalysis,^[1] photon up conversion,^[2] and photodynamic therapy,^[3] organic triplet photosensitizers have received reinvigorated attention in recent years for their atomic abundance and versatility in comparison to their inorganic counterparts.^[1a,2b,4] Long-lived triplet species, necessary for the intermolecular energy/electron transfer processes in these applications, are generated after electronic excitation followed by intersystem crossing (ISC). Conventionally, organic chromophores, especially those of polycyclic aromatic hydrocarbons, suffer from fast, spin-allowed S₁–S₀ decay that outcompetes ISC.^[5] Strategies based on heavy atoms,^[6] radical pair recombination,^[7] twisted π-conjugation,^[3a,8]

and radical-enhanced ISC^[9] have been identified to increase the rate of triplet formation. However, these methods do not always produce triplet-forming molecules with high predictability, and a careful structural design is often required to optimize the coupling and driving force factors for ISC. Incorporation of heavy atoms is a more universal approach; however, the resultant sensitizers inevitably comprise weak carbon-heavy atom bonds that are prone to degradation.^[10] Therefore, renovated molecular designs of organic triplet chromophores are continuously being explored to unlock the full potential of heavy-atom-free photosensitizers,^[3a,11] with the introduction of supramolecular interactions to enhance the bimolecular reaction kinetics and the substrate specificity being some of the latest developments.^[12]

Inspired by the prosperous use of organometallic photosensitizers, we propose a new class of organic photosensitizers based on thiocarbonyl donor–acceptor (D–A) chromophores. The n–π* excited-state character introduced by the thiocarbonyl (C=S) functionality should enable fast ISC (see below),^[3b,13] whereas intramolecular D–A interactions can permit strong light absorption that is otherwise weak for n–π* chromophores. These two features mimic the key characteristics of Ru- or Ir-based polypyridyl complexes,^[14] where the presence of heavy metals provides a reliable ISC mechanism, and the metal-to-ligand/ligand-to-ligand charge transfer (MLCT/LLCT) gives optical absorption stronger than the metal-centered transitions. Mild decoupling of the mechanisms of ISC and optical absorption allows the modification of the latter property without jeopardizing triplet formation. Incorporation of the electron D and A moieties further allows the as-formed triplet species to participate in oxidative or reductive electron transfer reactions.

Organic electron acceptors featuring amide/imide functionalities are ubiquitous in organic optoelectronic applications.^[15] Established synthetic methodologies exist for structural modification, and their carbonyl units can be thionated by Lawesson's reagent to give the corresponding thioamide/-imides,^[16] which are known to display superior stability compared to thioketo/-ester molecules.^[17] Taking these into account, we chose naphthalene monoimide (NMI) as the model acceptor in this study. Facile reduction of the parent NMI molecule takes place at ≈ –1.35 V vs. saturated calomel electrode (SCE)^[18] and its small π-system ensures the energetic triplet excited state, favorable for photosensitization, to be generated from NMI derivatives.

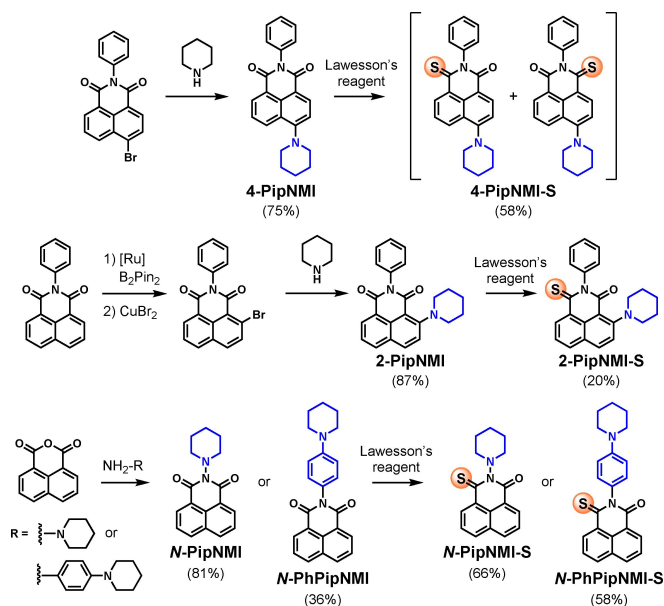
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The piperidiny donor (Pip) was introduced to the 4-, 2-, or *N*-position of NMI to vary the D–A interactions (Scheme 1, see also Supporting Information (SI) for details). The former two cases were achieved through nucleophilic aromatic substitution of the corresponding 4- and 2-bromo precursors with piperidine to give **4-PipNMI**^[19] and **2-PipNMI**, respectively. While 4-bromo NMI can be readily obtained from commercial 4-bromo-1,8-naphthalic anhydride, 2-bromo NMI was synthesized through the carbonyl-directed, Ru-catalyzed C–H borylation route



Scheme 1. Synthesis of piperidine-substituted naphthalene monoimides and their monothionated derivatives. Lawesson's reagent = $[(p\text{MeOPh})\text{PS}]_2$, $[\text{Ru}] = \text{RuH}_2(\text{CO})(\text{PPh}_3)_3$.

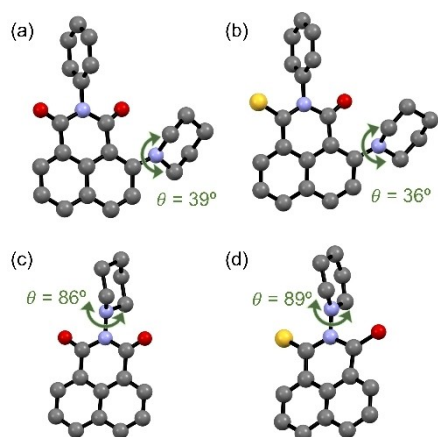


Figure 1. Single crystal X-ray molecular structure of and the dihedral angle θ between the D/A moieties in (a) **2-PipNMI** (CCDC 2088274, space group $P2_1/c$), (b) **2-PipNMI-S** (2088270, $P1$), (c) **N-PipNMI** (2088262, $P2_1/c$), and (d) **N-PhPipNMI-S** (2089607, $P2_1$). Color code: C = grey, O = red, N = blue, and S = yellow; hydrogen atoms are omitted for clarity. For **2-PipNMI** and **N-PipNMI-S**, only one of the two molecules in the asymmetric unit is presented. The (average) dihedral angle θ is defined as the angle between the respective mean planes of the piperidine and NMI rings. See SI Section 3 for the X-ray structures of all other D–A chromophores.

followed by Cu-mediated bromination.^[20] On the other hand, *N*-donor-substituted compounds (**N-PipNMI** and **N-PhPipNMI**) were prepared by imide condensation between 1,8-naphthalic anhydride and piperidin-1-amine and 4-(piperidin-1-yl)-aniline.

The extent of subsequent thionation can be controlled to some degree by the amount of reagents and reaction time to provide the mono-thionated chromophores as the major product. The fully thionated chromophores are not considered here as their triplet energies and hence the excited-state redox power are significantly lower than the mono-thionated ones.^[16a,21] Due to the molecular symmetry, only one mono-thionated product (**N-PipNMI-S** and **N-PhPipNMI-S**) is expected for *N*-donor-substituted chromophores. The piperidiny donor in asymmetric **4-PipNMI** does not provide sufficient electronic bias to distinguish the reactivity of the two carbonyl groups towards Lawesson's reagent; thionation resulted in an inseparable mixtures **4-PipNMI-S** of nearly equal amounts according to ¹H NMR. Such a regioisomeric issue was resolved for **2-PipNMI-S**, where the additional steric hindrance caused by the 2-piperidiny substituent guarantees that thionation only takes place once even in the presence of excess Lawesson's reagent. The distal-site selectivity was unambiguously confirmed by the single crystal X-ray structure of **2-PipNMI-S** (Figure 1). Despite the change in the electron-accepting power of the naphthalene imide moiety, the difference in the dihedral angle between the D and A moieties is negligible upon thionation. Since all structural parameters from the single-crystal analysis are similarly reproduced by the DFT-optimized structures at the level of $\omega\text{B97X-D/6-31G(d,p)}$, these observations indicate that the structural twisting in the present series of D–A chromophores are primarily governed by intramolecular steric factors.

The absorption spectra for each chromophore were measured in CH_2Cl_2 (Figure 2 and Table 1). For **4-PipNMI** and **2-PipNMI**, the low-energy, broad absorption >400 nm slightly blue shifts in toluene (Figure S1), whereas the high energy bands remain unchanged. The solvatochromism in the visible absorption reflects the mixed intramolecular charge-transfer

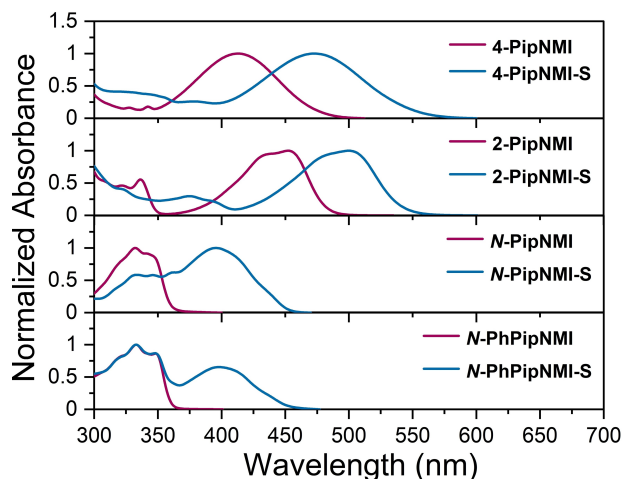


Figure 2. Normalized absorption spectra of non-thionated (red) and mono-thionated (blue) D–A chromophores in CH_2Cl_2 .

Chromophores	$\lambda_{\text{abs}}^{[a]}$ (nm)	$\epsilon^{[a]}$ ($\text{M}^{-1} \text{cm}^{-1}$)	$\Phi_{\Delta}^{[b]}$	$E_{\text{T}}^{[c]}$ (eV)	$E_{\text{RED}}^{[d]}$ (V vs. SCE)	$E_{\text{OX}}^{[d]}$ (V vs. SCE)	$E_{\text{T,RED}}^{[e]}$ (V vs. SCE)	$E_{\text{T,OX}}^{[e]}$ (V vs. SCE)
4-PipNMI	415	10 900	n.d.	2.29	−1.43	1.26 ^[f]	0.86	−1.03
2-PipNMI	450	11 900	n.d.	2.30	−1.52	1.30 ^[f]	0.78	−1.00
N-PipNMI	330	11 900	n.d.	2.90	−1.44	1.51 ^[f]	1.46	−1.39
N-PhPipNMI	335	19 800	0.23	2.47	−1.35	0.98	1.12	−1.49
4-PipNMI-S	470	16 600	0.52	1.80	−1.05	1.21 ^[f]	0.75	−0.59
2-PipNMI-S	500	17 800	0.16	1.94	−1.20	1.24 ^[f]	0.74	−0.70
N-PipNMI-S	395	16 400	0.21	1.95	−1.09	1.20 ^[f]	0.86	−0.75
N-PhPipNMI-S	400	15 200	0.18	1.78	−1.02	0.94	0.76	−0.84
Ru(bpy) ₃ Cl ₂ ^[23]	450 ^[g]	13 800 ^[g]	0.57 ^[g]	2.10	−1.33	1.29	0.77	−0.81

[a] In CH₂Cl₂; molar extinction coefficients (ϵ) determined for the lowest energy λ_{abs} ; [b] ¹O₂-generation quantum yields determined using Ru(bpy)₃Cl₂ (Φ_{Δ} = 0.57)^[23] as the standard; [c] triplet energy estimated at the level of ω B97X-D/6-31G(d,p); [d] redox potential $E = E_{1/2}$ determined by cyclic voltammetry in 0.1 M nBu₄NPF₆ in CH₂Cl₂; [e] $E_{\text{T,RED}} = E_{\text{RED}} + E_{\text{T}}$ and $E_{\text{T,OX}} = E_{\text{OX}} - E_{\text{T}}$; [f] irreversible peak potential; [g] in MeCN.

and π - π^* characters of these D–A chromophores, supported by natural transition orbital (NTO) analysis (see Figure 3 and SI Section 7). As the piperidiny donor is at the imide position through which the NMI-localized LUMO nodal planes pass in *N*-PipNMI and *N*-PhPipNMI, the charge-transfer absorption is strongly forbidden,^[22] and thus only the NMI-originated absorption (< 370 nm) was observed. Thionation resulted in pronounced light absorption of all four chromophores in the visible region. The red shift has been similarly reported for other thionated rylene imides, and is often attributed to the reduction in the LUMO energy.^[13a,17] The improved visible-light absorption, especially significant for *N*-PipNMI-S and *N*-PhPipNMI-S, together with the substantial extinction coefficients of these thionated D–A chromophores (e.g., $\epsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ for 2-PipNMI-S, cf. $\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ for Ru(bpy)₃Cl₂)^[23] suggest potential solar-energy utilization of these chromophores.

While 4-PipNMI gives bright green fluorescence ($\Phi_{\text{FL}} = 0.43$), weak to no emission was observed for all other D–A chromophores ($\Phi_{\text{FL}} < 0.05$). The absence of fluorescence is indicative of fast non-radiative relaxation to the ground state or efficient formation of the triplet excited state. Using 1,3-diphenylisobenzofuran as a chemical probe, it was found that all thionated compounds sensitized triplet molecular oxygen to give singlet oxygen (¹O₂, quantum yield Φ_{Δ} 16–52%); thus, triplet formation is likely to take place efficiently. For the non-thionated molecules (except for *N*-PhPipNMI, see below), the ISC process is, however, outcompeted by radiative and non-radiative internal conversion in the singlet manifold.

Facile triplet formation of the thionated D–A chromophores can be attributed to the high spin-orbit coupling matrix elements $\langle S_n | \hat{H}_{\text{SO}} | T_m \rangle$, calculated at the level of TD- ω B97X-D/6-31G(d,p) using Gaussian 09 interfaced with PySOC (Figure 3, and SI Section 7).^[24] $\langle S_1 | \hat{H}_{\text{SO}} | T_1 \rangle$ above 100 cm^{−1} were found,

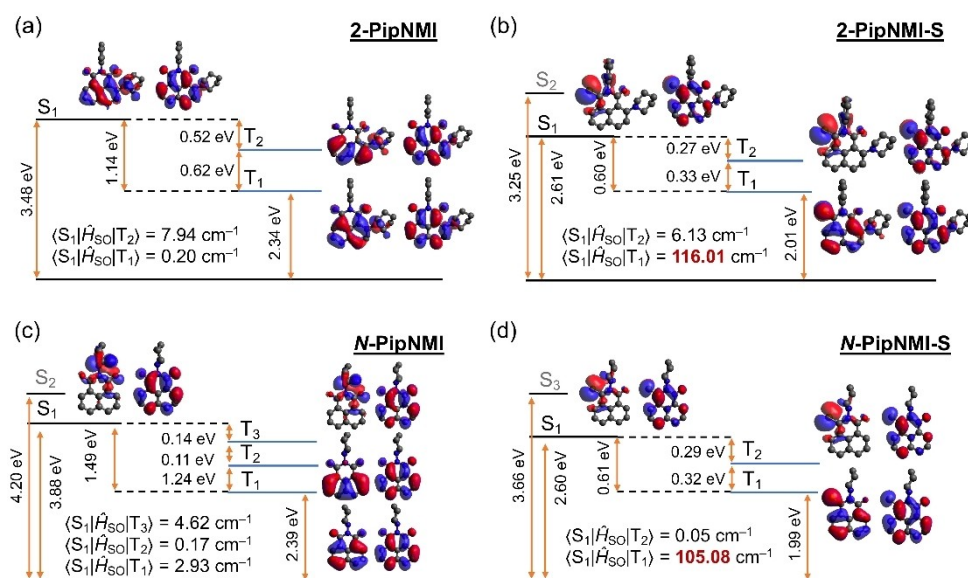


Figure 3. TD- ω B97X-D/6-31G(d,p) computed energy diagram and spin-orbit coupling matrix elements of (a) 2-PipNMI, (b) 2-PipNMI-S, (c) *N*-PipNMI, and (d) *N*-PipNMI-S. Optically bright S_n states, if not S_1 , are indicated in grey. “Hole” (left) and “particle” (right) NTO pairs are depicted next to the respective excited states to show the character of the transition. See SI Section 7 for other D–A chromophores.

which is 2–3 orders of magnitude larger than that of non-thionated precursors and notably larger than that of Ru(bpy)₃²⁺ ($\langle S_1 | \hat{H}_{50} | T_1 \rangle = 39 \text{ cm}^{-1}$).^[25] By NTO analysis, it is clear that the S₁ and T₁ states of all thionated D–A chromophores feature n-π* and π-π* transitions, respectively; the change in orbital spatial orientation facilitates ISC, in accordance with the El-Sayed rule (Figure 3b and Figure 3d).

In the absence of the C=S unit, both the S₁ and T_n states are dominated by the π-π* character and thus small spin-orbit coupling (< 1 cm⁻¹). ISC is comparatively less efficient given such a low value and the sizable energy difference between the singlet and triplet states (ΔE_{ST}) in these molecules. However, it is worth noting that due to the orientation of the N lone-pair in **N-PipNMI** or the aniline ring in **N-PhPipNMI**, these energetically high-lying orbitals can mix well with the in-plane p orbitals of C=O oxygen, giving the n-π* character to the S₁ state of these two non-thionated molecules (Figure 3c). This unusual scenario provides $\langle S_1 | \hat{H}_{50} | T_n \rangle \approx 3 \text{ cm}^{-1}$ for **N-PipNMI** and **N-PhPipNMI** that are noticeably higher than that of common π-π* chromophores. Efficient triplet formation ($\Phi_A = 72\%$) of organic chromophores with $\langle S_1 | \hat{H}_{50} | T_1 \rangle \approx 2 \text{ cm}^{-1}$ has been reported.^[26] Additionally, the orthogonal orientation of the D/A π systems in **N-PhPipNMI** may facilitate ISC through the spin-orbit charge transfer (SOCT) mechanism, where charge recombination is accompanied with a molecular orbital angular momentum change due to the large twist in structure.^[7a,27] These factors seem contribute to the triplet formation and ¹O₂ sensitization of **N-PhPipNMI**, and may explain the unusual, delayed fluorescence observed from the crystals of analogous *N*-[4-(dimethylamino)phenyl]-NMI.^[22] However, as this molecule only absorbs in the UV region, we will focus on the triplet-forming, visible-light absorbing thionated chromophores.

High triplet energy ($E_{T_1} = 1.78\text{--}1.95 \text{ eV}$) estimated computationally for the thionated D–A chromophores supports the energetic driving force required for triplet energy transfer to sensitize ¹O₂ as mentioned above. These values further suggest ample excited-state redox power in the triplet chromophores. Due to the presence of both the electron donor and acceptor in the same molecule, these electrochemically amphoteric chromophores are reduced at $E_{\text{RED}} = -1.20$ to -1.02 V and oxidized at $E_{\text{OX}} = +0.94$ to $+1.24 \text{ V}$ vs. SCE, offering excited-state redox power of $E_{T,\text{RED}} \approx +0.74$ to $+0.86 \text{ V}$ and $E_{T,\text{OX}} \approx -0.84$ to -0.66 V .

To assess the amphoteric photoredox capacity of the thionated D–A chromophores, photooxidative aza-Henry^[23b] and photoreductive dehalogenation^[28] reactions were chosen (Table 2). The reactions were conducted in the presence of 1–5 mol% thionated D–A chromophores as the photocatalyst under anaerobic conditions. The photo aza-Henry reaction involves the generation of the amino radical cation of *N*-phenyltetrahydroisoquinoline (**A**) at $E_{\text{OX}} = +0.78 \text{ V}$,^[23b] close to the minimal $E_{T,\text{RED}}$ available from the thionated D–A chromophores. On the other hand, reduction of α-bromoacetophenone at $E_{\text{RED}} \approx -0.5 \text{ V}$,^[29] more positive than $E_{T,\text{OX}}$ of the present chromophores, is required to provide the key radical intermediate (**B**) in the debromination reaction. Additionally, the thionated D–A chromophores were also tested as energy transfer (EnT) photocatalysts using a [2+2] cycloaddition

Table 2. Photoredox Reaction Yields (%) for the Aza-Henry Reaction, Debromination, and [2+2] Cycloaddition.^[a]

Photocatalyst	Aza-Henry ^[b]	Debromination ^[c]	[2+2] Cycloaddition ^[d]
4-PipNMI-S ^[e]	43.4	13.5	19.1
2-PipNMI-S ^[e]	68.1	9.8	75.8
N-PipNMI-S ^[f]	5.8	16.0	10.7
N-PhPipNMI-S ^[f]	0.7	4.3	19.7
Ru(bpy)₃Cl₂ ^[e]	53.6	17.4	69.1

[a] The yield was calculated by quantitative ¹H NMR using 2,5-dimethylfurfuran as the internal standard (See SI Section 6); [b] 2-phenyl-1,2,3,4-tetrahydroisoquinoline (60 mg), photocatalyst (0.01 eq) and CH₃NO₂ (3 mL); the reaction was irradiated for 4 h; [c] α-bromoacetophenone (80 mg), photocatalyst (0.05 eq), *i*-PrNEt₂ (8 eq) and MeCN (4 mL); the reaction was irradiated for 24 h; [d] ethyl (*E*)-2-(2-oxoindolin-3-ylidene)acetate (80 mg), photocatalyst (0.01 eq) and MeOH (4 mL); irradiated for 24 h; [e] λ_{irrad} 434–541 nm; [f] λ_{irrad} 375–425 nm.

reaction (Table 2).^[30] The yields of the photo products catalyzed by the thionated D–A chromophores were found comparable to those obtained using Ru(bpy)₃Cl₂ as the sensitizer. It is also notable that each thionated D–A chromophore could be recovered after the reaction by chromatography. Although the yields display no apparent correlation with the ¹O₂-generation quantum yield or the photoredox driving force, these results provide clear evidence that the photoexcited thionated D–A chromophores can engage in reductive/oxidative single electron transfer (SET) and EnT photocatalytic processes. Among these chromophores, the strong visible-light absorption and high triplet energy and excited-state redox power of **2-PipNMI-S** make it a highly promising SET and EnT photocatalyst. Rate-constant characterization of the excited-state physical and chemical processes will provide more quantitative insights into the photocatalytic behaviors of these sensitizers in future study.

In summary, we synthesized, characterized, and tested the photo-reactivity of a series of thionated D–A chromophores. In comparison with the non-thionated precursors, these chromophores display strong visible-light absorption, negligible fluorescence, redox amphoteric activity, and moderate ¹O₂ sensitization. The combination of the latter two enables the application of these thionated chromophores in both reductive and oxidative photocatalytic reactions. This proof-of-concept study demonstrates the generality of thionating D–A chromophores to provide heavy-atom-free organic triplet photosensi-

tizers. The effective design can be attributed to the decoupling of molecular optical/electrochemical properties from their triplet formation mechanism. The involvement of the $n-\pi^*$ excited state promotes ISC regardless of the detailed D–A interactions. Since many commercial pigments or high-performance organic LED and photovoltaics materials contain amide/imide functionalities, thionation of these chromophores can provide a wide range of photosensitizers with bespoke photo-redox activity. As hinted by the comparison between *N*-PhPipNMI and *N*-PhPipNMI-S, additional ISC channels may exist due to charge separation and/or the twisting between D/A moieties. Our future study will unravel the interplay between different ISC mechanisms for triplet formation and evaluate this complex scenario for sensitizer design, in addition to the quantitative rate-constant characterization.

Single Crystal X-Ray Data

Deposition Numbers 2088261 (for 4-PipNMI), 2088277 (for 4-PipNMI-S₂), 2088266 (for 2-BrNMI), 2088356 (for 2,7-BrNMI), 2088264 (for 2,7-PipNMI), 2088274 (for 2-PipNMI), 2088270 (for 2-PipNMI-S), 2088262 (for N-PipNMI), 2089607 (for N-PipNMI-S), 2088267 (for N-PipNMI-S₂), 2088263 (for N-PhPipNMI), 2089008 (for N-PhPipNMI-S), and 2089061 (for N-PhPipNMI-S₂) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Donor-acceptor systems • Intersystem crossing • Photocatalysts • Sensitizers • Thiocarbonyl

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