

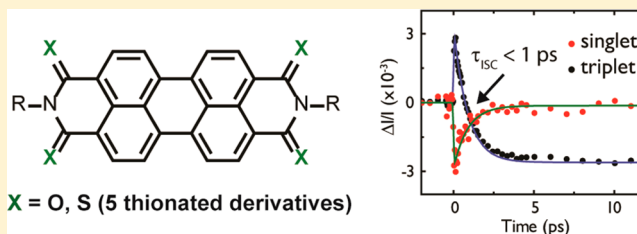
Ultrafast Triplet Formation in Thionated Perylene Diimides

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Supporting Information

ABSTRACT: Perylene diimides (PDIs) are versatile n-type materials showing great promise in a number of optoelectronic applications. While the singlet manifold of PDI can be readily populated, triplet excited states are only accessible through complex multistep energy cascades or bimolecular sensitization. In this work, we have synthesized a series of thionated PDIs that display rapid intersystem crossing to triplet states. Significantly, the thionated PDIs are synthesized in one step from the parent compound using commercially available Lawesson's reagent. Electrochemical and steady state optical absorption measurements show that the electron affinity and ionization potentials can be systematically tuned through successive sulfur atom substitution. Thin-film optical absorption measurements show how the number and regiochemistry of the thiocarbonyl groups influence π - π interactions in the solid state. Ultrafast transient absorption spectroscopy reveals rapid triplet formation that is independent of the degree of thionation, highlighting this approach as a facile means of accessing the triplet manifold of PDI.



INTRODUCTION

Second only to fullerene derivatives, perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs) are among the most promising negative charge-accepting and -transporting "n-type" materials for organic electronics due to their high molar absorptivity, excellent electron mobility and affinity, and high photochemical stability.^{1–6} An attractive feature of PDIs is that their electronic and materials properties can be tuned through synthetic modifications to the aromatic core and imide nitrogens.^{7–12} Substitution on the central aromatic rings, at the so-called bay positions, alters both electronic and materials properties, while substitution at the imide nitrogens controls only solubility and long-range molecular order.^{13–17}

Chromophores that generate triplet states are very important in a number of optoelectronic applications.^{18–23} In organic photovoltaic devices, triplet excitons can potentially improve photocurrent as their long diffusion lengths maximize the probability for charge separation to occur at a donor–acceptor interface.²⁴ Triplet-generating chromophores are also widely utilized in the production of singlet oxygen for photodynamic therapy^{25–27} and for photochemical upconversion.^{28–30} Thus, chromophores with large absorption coefficients that display efficient intersystem crossing to triplet states are highly sought after.

Presently, the only reported methods of accessing the triplet manifold of PDI are through bimolecular triplet sensitization³¹ or by appending groups to the bay and imide positions which promote intersystem crossing (ISC) via a radical pair mechanism or by the so-called "heavy atom" effect.^{32–39} However, these approaches require the synthesis of challenging molecular architectures that facilitate multiple energy cascades

(for the radical pair mechanism) or the introduction of organometallic substituents at the bay positions to enhance spin–orbit coupling. As a result, the utilization of PDI triplet states in optoelectronic applications has remained largely unexplored.

Group 16 elemental substitution is an effective means of modifying the optoelectronic properties of π -conjugated systems.^{40–43} One distinct advantage of this approach is that the frontier orbital energies can be altered without significantly perturbing the overall molecular structure. Interestingly, despite its rich chemical history, there is only one reported synthesis of group 16 substituted PDIs.⁴⁴ In this patent by Facchetti and co-workers, sulfur atom incorporation was achieved by substitution of the carboxylic oxygens using Lawesson's reagent, a commercially available reagent commonly used to thionate polyketones.^{45,46} Only trace amounts of material attributed to tri- and tetrathionated PDI were reported, likely due to challenges with solubility, and thus the photophysics and other properties of these compounds remain undetermined.

Herein we report the synthesis, characterization, and ultrafast photophysics of the first full series of thionated PDI derivatives (Figure 1). The use of a branched 3-hexylundecyl side chain allows us to prepare significant quantities of mono-, di- (both regioisomers, vide infra), tri-, and tetrathionated PDIs that we have characterized and studied using NMR, optical absorption, and fluorescence spectroscopies, electrochemistry, and ultrafast transient absorption (TA) spectroscopy. Promisingly, we show that the PDI frontier energy levels can be systematically tuned

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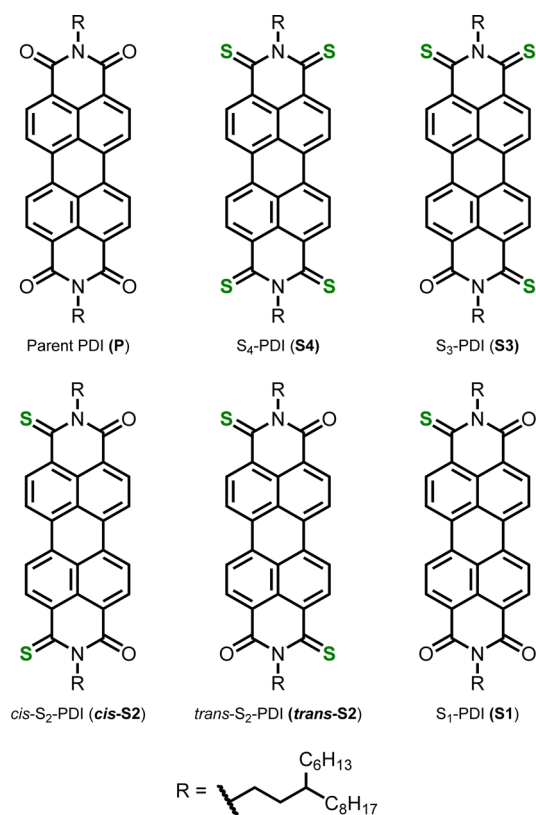


Figure 1. Thionated PDIs studied in this work.

through successive sulfur atom substitution, yet thionated PDIs undergo rapid and highly efficient ISC to triplet states that is independent of the degree of thionation. Thus, this appears to be a facile one-step means of accessing the triplet excited state of PDIs that does not require extensive syntheses or coupling to a transition metal complex.

EXPERIMENTAL SECTION

Synthesis of P–S4. *N,N'*-Di(3-hexylundecyl)-perylene-3,4:9,10-tetracarboxylic Acid Bisimide (P). A mixture of perylene-3,4:9,10-tetracarboxylic dianhydride (1.348 g, 3.436 mmol), 3-hexylundecylamine (2.661 g, 10.42 mmol) (refer to Supporting Information (SI) for synthesis), imidazole (14.00 g, 205.6 mmol), and zinc acetate (0.520 g, 2.834 mmol) was stirred at 160 °C for 24 h under argon. After 24 h the reaction mixture was allowed to cool to room temperature, diluted with CHCl_3 (200 mL), washed with H_2O (2×100 mL) and sat. aq. NaCl (1×100 mL), dried (MgSO_4), filtered, and concentrated under reduced pressure to give a purple solid. The purple solid was purified by column chromatography (100% CHCl_3) to afford the title compound as a deep red solid (2.401 g, 81%), mp 128–129 °C, λ_{max} (abs) = 526 nm. ^1H NMR (400 MHz, CDCl_3) δ 0.85–0.93 (m, 12H), 1.22–1.45 (m, 48H), 1.46–1.55 (m, 2H), 1.64–1.73 (m, 4H), 4.10–4.19 (m, 4H), 8.30 (d, J 8.3 Hz, 4H), 8.47 (d, J 7.9 Hz, 4H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.28, 14.30, 22.87, 22.91, 26.75, 26.80, 29.6, 29.9, 30.0, 30.3, 31.8, 32.1, 33.7, 36.2, 39.0, 122.5, 123.1, 125.5, 128.7, 130.6, 133.5, 162.7. FT-IR (neat, cm^{-1}) 1695 (C=O stretch), 1651 (C=O stretch). HRMS (DART) $^+ m/z$ 867.6051 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{O}_4$ [$\text{M} + \text{H}$] $^+$ requires 867.6040).

S1–S3. A solution of Lawesson's reagent (0.473 g, 1.169 mmol) and P (0.507 g, 0.585 mmol) in toluene (70 mL) was

heated at reflux for 18 h under argon. The resulting blue solution was cooled to room temperature and concentrated under reduced pressure to give a crude mixture of S1–S3. Separation by column chromatography (toluene/hexanes then CHCl_3 /hexanes) gave S1–S3 in the following yields.

S1 (0.050 g, 10%), mp (decomp.) 108–110 °C, λ_{max} (abs) = 574 nm: ^1H NMR (500 MHz, CDCl_3) δ 0.86–0.94 (m, 12H), 1.24–1.43 (m, 48H), 1.46–1.55 (m, 2H), 1.65–1.80 (m, 4H), 4.13–4.21 (m, 2H), 4.65–4.72 (m, 2H), 8.28 (d, J 8.53 Hz, 1H), 8.37–8.46 (m, 3H), 8.52–8.57 (m, 3H), 8.90 (d, J 8.28 Hz, 1H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.31, 14.32, 14.35, 22.89, 22.92, 22.933, 22.934, 26.78, 26.83, 26.86, 26.91, 29.61, 29.62, 29.89, 29.92, 29.99, 30.0, 30.33, 30.35, 32.13, 32.15, 32.17, 33.72, 33.74, 36.2, 36.4, 39.2, 46.2, 122.4, 122.6, 122.8, 123.1, 123.19, 123.21, 125.32, 125.33, 126.8, 127.1, 128.8, 130.7, 130.8, 131.2, 132.7, 133.3, 133.65, 133.67, 135.8, 160.0, 162.7, 162.8, 191.9. FT-IR (neat, cm^{-1}) 1695 (sym. C=O stretch), 1682 (sym. C=O stretch), 1652 (antisym. C=O stretch), 1160 (C=S stretch), 1125 (C=S stretch). MALDI-MS m/z 883.5 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ requires 883.6).

cis-S2 (0.066 g, 13%), mp (decomp.) 118–120 °C, λ_{max} (abs) = 616 nm: ^1H NMR (400 MHz, CDCl_3) δ 0.89–0.97 (m, 12H), 1.29–1.43 (m, 48H), 1.46–1.55 (br. s, 2H), 1.66–1.77 (m, 4H), 4.47–4.58 (m, 4H), 7.73 (d, J 8.52 Hz, 2H), 7.97 (d, J 8.16 Hz, 2H), 8.22 (d, J 7.97 Hz, 2H), 8.51 (d, J 8.28 Hz, 2H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.35, 14.37, 22.94, 22.97, 26.89, 26.94, 29.7, 29.86, 29.95, 30.0, 30.4, 32.18, 32.19, 33.7, 36.4, 46.1, 121.9, 122.7, 123.0, 124.4, 126.3, 126.6, 130.8, 132.0, 132.7, 135.4, 159.5, 191.4. Partial gCOSY (500 MHz/500 MHz, CDCl_3) δ $^1\text{H}/^1\text{H}$ 8.20/7.31, 7.95/7.60.

Partial gHSQC (500 MHz/125 MHz, CDCl_3) δ $^1\text{H}/^{13}\text{C}$ 8.18/135.2, 7.93/130.6, 7.59/122.5, 7.30/121.7. Partial gHMBC (500 MHz/125 MHz, CDCl_3) δ $^1\text{H}/^{13}\text{C}$ 8.19/191.2 ($^3J_{\text{H,C}}$), 8.19/131.9 ($^3J_{\text{H,C}}$), 8.19/126.3 ($^3J_{\text{H,C}}$), 7.94/159.4 ($^3J_{\text{H,C}}$), 7.94/132.6 ($^3J_{\text{H,C}}$), 7.94/126.2 ($^3J_{\text{H,C}}$), 7.94/122.6 ($^3J_{\text{H,C}}$), 7.60/132.6 ($^2J_{\text{H,C}}$), 7.60/124.3 ($^3J_{\text{H,C}}$), 7.60/122.8 ($^3J_{\text{H,C}}$), 7.31/131.9 ($^2J_{\text{H,C}}$), 7.31/126.4 ($^3J_{\text{H,C}}$), 7.31/124.3 ($^3J_{\text{H,C}}$). Partial ROESY (500 MHz/500 MHz, CDCl_3) δ $^1\text{H}/^1\text{H}$ 8.18/7.32, 7.94/7.60. FT-IR (neat, cm^{-1}) 1682 (sym. C=O stretch), 1664 (antisym. C=O stretch), 1157 (sym. C=S stretch), 1124 (antisym. C=S stretch). MALDI-MS m/z 899.4 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{O}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$ requires 899.6).

trans-S2 (0.091 g, 17%), mp (decomp.) 152–153 °C, λ_{max} = 615 nm: ^1H NMR (400 MHz, CDCl_3) δ 0.87–0.96 (m, 12H), 1.24–1.43 (m, 48H), 1.48–1.59 (m, 2H), 1.71–1.79 (m, 4H), 4.62–4.69 (m, 4H), 8.18 (d, J 8.61 Hz, 2H), 8.27 (d, J 8.21 Hz, 2H), 8.48 (d, J 8.04 Hz, 2H), 8.79 (d, J 8.35 Hz, 2H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.35, 14.37, 22.94, 22.97, 26.9, 27.0, 29.7, 29.87, 29.95, 30.01, 30.4, 32.18, 32.19, 33.7, 36.4, 46.2, 122.2, 122.4, 122.9, 124.4, 126.3, 126.6, 130.9, 132.0, 132.7, 135.2, 159.6, 191.2. Partial gCOSY (500 MHz/500 MHz, CDCl_3) δ $^1\text{H}/^1\text{H}$ 8.13/7.37, 7.97/7.51. Partial gHSQC (500 MHz/125 MHz, CDCl_3) δ $^1\text{H}/^{13}\text{C}$ 8.13/135.2, 7.96/130.1, 7.51/122.4, 7.37/122.1. Partial gHMBC (500 MHz/125 MHz, CDCl_3) δ $^1\text{H}/^{13}\text{C}$ 8.13/191.1 ($^3J_{\text{H,C}}$), 8.13/131.8 ($^3J_{\text{H,C}}$), 8.13/126.2 ($^3J_{\text{H,C}}$), 7.96/159.5 ($^3J_{\text{H,C}}$), 7.96/132.5 ($^3J_{\text{H,C}}$), 7.96/126.2 ($^3J_{\text{H,C}}$), 7.96/122.6 ($^2J_{\text{H,C}}$), 7.51/131.8 ($^2J_{\text{H,C}}$), 7.51/124.3 ($^3J_{\text{H,C}}$), 7.51/122.8 ($^3J_{\text{H,C}}$), 7.37/132.5 ($^2J_{\text{H,C}}$), 7.37/126.4 ($^3J_{\text{H,C}}$), 7.37/124.3 ($^3J_{\text{H,C}}$). Partial ROESY (500 MHz/500 MHz, CDCl_3) δ $^1\text{H}/^1\text{H}$ 8.13/7.38, 7.97/7.52, 7.51/7.38. FT-IR (neat, cm^{-1}) 1683 (sym. C=O stretch), 1661 (antisym. C=O stretch), 1159 (sym. C=S stretch), 1122 (antisym. C=S

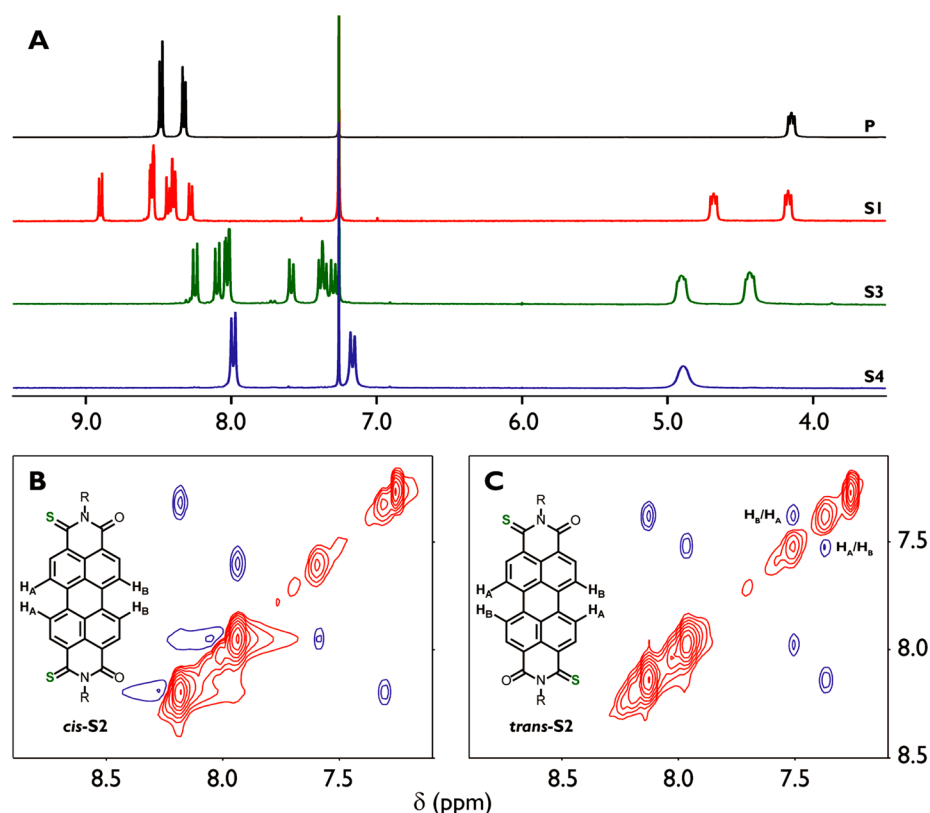


Figure 2. Partial ^1H NMR spectra of **P**, **S1**, **S3**, and **S4** (panel A) and partial ^1H – ^1H ROESY spectra of *cis*-**S2** and *trans*-**S2** (panels B and D) recorded in CDCl_3 at 25 °C. R denotes the 3-hexylundecyl side chain.

stretch). MALDI-MS m/z 899.4 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{O}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$ requires 899.6).

S3 (0.128 g, 24%), mp (decomp.) 121–123 °C, λ_{max} (abs) = 663 nm: ^1H NMR (300 MHz, CDCl_3) δ 0.89–1.00 (m, 12H), 1.31–1.42 (m, 50H), 1.63–1.79 (m, 4H), 4.37–4.50 (m, 2H), 4.84–4.96 (m, 2H), 7.30 (d, J 8.65 Hz, 1H), 7.33–7.41 (m, 2H), 7.59 (d, J 8.27 Hz, 1H), 8.00–8.05 (m, 2H), 8.10 (d, J 8.08 Hz, 1H), 8.25 (d, J 8.29 Hz, 1H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.36, 14.38, 14.39, 14.41, 22.96, 22.97, 22.98, 26.93, 26.97, 26.99, 27.04, 28.6, 29.7, 29.96, 29.99, 30.01, 30.03, 30.35, 30.38, 32.19, 32.21, 32.24, 33.65, 33.72, 36.48, 36.55, 46.2, 54.4, 122.1, 122.4, 122.6, 122.7, 122.9, 123.0, 124.15, 124.23, 126.4, 126.6, 128.23, 128.25, 131.0, 131.4, 132.1, 132.8, 135.4, 136.3, 136.4, 159.7, 187.3, 187.4, 191.3. FT-IR (neat, cm^{-1}) 1683 (sym. C=O stretch), 1662 (antisym. C=O stretch), 1154 (sym. C=S stretch), 1116 (antisym. C=S stretch). MALDI-MS m/z 915.4 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{OS}_3$ [$\text{M} + \text{H}$] $^+$ requires 915.5).

S4. Using a procedure similar to the one described above, a solution of Lawesson's reagent (2.352 g, 5.815 mmol) and **P** (1.005 g, 1.159 mmol) in toluene (150 mL) was heated at reflux for 50 h. The resulting deep blue solution was cooled to room temperature and concentrated under reduced pressure to give a blue solid. Purification by column chromatography (toluene/hexanes) gave **S4** (0.316 g, 29%) and **S3** (0.140 g, 13%) as deep blue solids. Mp (decomp.) (**S4**) 115–116 °C. λ_{max} (abs) (**S4**) = 706 nm. ^1H NMR of **S4** (300 MHz, CDCl_3) δ 0.92–1.00 (m, 12H), 1.29–1.41 (m, 50H), 1.68–1.79 (m, 4H), 4.76–5.00 (br. s, 4H), 7.17 (d, J 8.72 Hz, 4H), 7.99 (d, J 8.24 Hz, 4H). ^{13}C NMR (500 MHz, CDCl_3) δ 14.38, 14.40, 22.96, 22.97, 26.96, 27.01, 29.7, 29.96, 29.97, 30.3, 32.19, 32.20, 33.5, 36.5, 54.3, 121.9, 122.3, 123.0, 127.6, 130.6, 135.8, 186.6. FT-IR (neat, cm^{-1}) 1155 (sym. C=S stretch), 1116 (antisym.

C=S stretch). MALDI-MS m/z 931.4 ($\text{C}_{58}\text{H}_{79}\text{N}_2\text{S}_4$ [$\text{M} + \text{H}$] $^+$ requires 931.5).

RESULTS AND DISCUSSION

The nonthionated precursor PDI (**P**) was used as a control molecule throughout this study and was synthesized according to a modified literature procedure.^{47,48} Briefly, commercially available perylene-3,4,9,10-tetracarboxylic dianhydride was treated with three equivalents of 3-hexylundecylamine⁴⁹ in molten imidazole, which after chromatographic purification afforded **P** in 81% yield. To prepare the thionated PDIs, **P** was treated with Lawesson's reagent (LR), which affects thionation at the imide carboxyl positions. This reagent was recrystallized from toluene to improve the thionation yields.⁵⁰ Both the stoichiometry of LR and reaction time control the extent of thionation (see the Experimental Section).

The most intriguing aspects of the synthesis are the extent of thionation as well as the regioisomers that occur when two thionation reactions take place. When **P** was treated with 5.0 equiv of LR in toluene and heated at reflux for 50 h, tetrathionated **S4** was isolated in 29% yield (Figure S1, SI). This reaction also produces trithionated **S3** in 13% yield. These derivatives were separated by silica gel chromatography and characterized by NMR, FT-IR, and MALDI-TOF mass spectrometry. ^1H NMR spectroscopy was used to help identify **S3** and **S4** (Figure 2A).

When **P** was treated with 2.0 equiv of LR in toluene and heated at reflux for 18 h, monothionated **S1** and an isomeric mixture of dithionated PDIs (13% of *cis*-**S2** and 17% of *trans*-**S2**) are prepared. We were able to separate isomers *cis*-**S2** and *trans*-**S2** using conventional silica gel chromatography; however, structural assignment is not possible using 1D

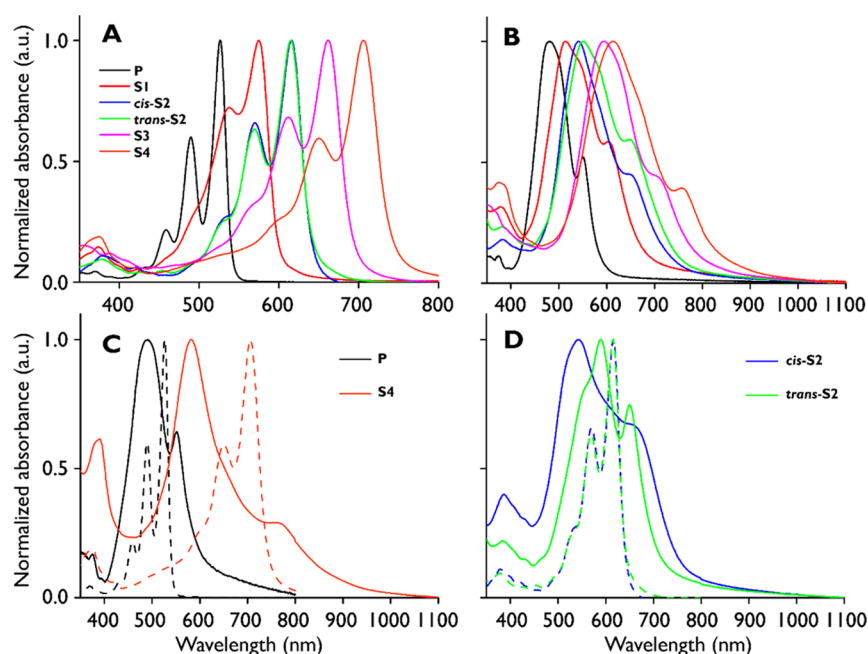


Figure 3. Optical absorption spectra of PDIs in room-temperature chloroform solution (panel A) and as-cast film (panel B). The annealed film absorption spectra (solid lines) of **P** and **S4** are shown in panel C, while *cis*-**S2** and *trans*-**S2** are compared in panel D. The corresponding solution spectra are represented by dashed lines. Films were prepared by spin-casting 10 mg/mL CHCl_3 solutions onto glass slides and were annealed until evolution of the spectral features ceased. **S4**, *cis*-**S2**, and *trans*-**S2** were annealed at 80 °C, while **P** was annealed at 100 °C. Annealed film absorption spectra for the other thionated PDIs can be found in Figure S5 (SI).

Table 1. Reduction Potentials, HOMO/LUMO Energies, and Fluorescence Quantum Yields of Each PDI

| PDI | $E_{1/2}^{-1}$ (V) | $E_{1/2}^{-2}$ (V) | optical band gap (eV) ^a | HOMO (eV) ^{b,d} | LUMO (eV) ^d | Φ_f^c |
|--------------------------|--------------------|--------------------|------------------------------------|--------------------------|------------------------|------------|
| P | −0.68 | −0.91 | 2.25 | −5.92 (−6.23) | −3.67 (−3.76) | 0.97 |
| S1 | −0.55 | −0.72 | 2.06 | −5.85 (−6.15) | −3.80 (−3.88) | <0.001 |
| <i>cis</i> - S2 | −0.48 | −0.57 | 1.91 | −5.78 (−6.09) | −3.87 (−3.99) | <0.001 |
| <i>trans</i> - S2 | −0.51 | −0.61 | 1.90 | −5.74 (−6.08) | −3.84 (−3.97) | <0.001 |
| S3 | −0.36 | −0.45 | 1.78 | −5.77 (−6.04) | −3.99 (−4.07) | <0.001 |
| S4 | −0.23 | −0.33 | 1.64 | −5.76 (−5.98) | −4.12 (−4.15) | <0.001 |

^aDetermined from the onset of the solution absorption. ^bObtained by adding the optical band gap to the LUMO energy. ^cRecorded against Eosin Y ($\Phi_f = 0.60$ in MeOH). ^dCalculated HOMO/LUMO energies are shown in parentheses next to the experimentally obtained values. Calculations were performed using DFT applying the B3LYP functional and 6-31++g(d,p) basis set. Time-dependent calculations were performed from the optimized geometry at this basis set. Cyclic and differential pulse voltammograms are shown in Figure S2 (SI).

NMR. We therefore carried out ^1H – ^1H ROESY 2D NMR to assign the *cis*-**S2** and *trans*-**S2** isomers. The ROESY spectrum of the *cis*-**S2** isomer contains four cross peaks, attributed to through-space correlations between *ortho* aromatic protons (at 8.18/7.32 and 7.94/7.60 ppm; Figure 2B). On the other hand, the ROESY spectrum of *trans*-**S2** contains the same four cross peaks and also two additional cross peaks (at 7.38/7.51 and 7.51/7.38 ppm). These cross peaks, labeled $\text{H}_\text{B}/\text{H}_\text{A}$ (7.38/7.51 ppm) and $\text{H}_\text{A}/\text{H}_\text{B}$ (7.51/7.38 ppm) in Figure 2C, arise from a strong rotatory nuclear Overhauser effect (ROE) across the bridgehead of the perylene core. In the ROESY spectrum of the *cis*-**S2** isomer (Figure 2B), cross peaks between bridgehead protons H_A and H_B are not observed due to their large interatomic distance (6.778 Å on the basis of the optimized geometry, see SI for computational details), thus allowing for structural assignment of the two **S2** isomers.

The third **S2** isomer (*gem*-**S2**–PDI) was also present in very minor amounts, but we were unable to isolate it. The weak signals at 4.0 and 4.9 ppm in the ^1H NMR spectra of *cis*-**S2** and *trans*-**S2** (attributed to the $\text{N}-\text{CH}_2$ protons; see Figures S14 and S16, SI) coupled with additional low intensity peaks in the

aromatic region are consistent with the structure of *gem*-**S2**–PDI. It is likely that it is unfavorable for thionation to occur at two adjacent carbonyl positions, which explains why this isomer is the least abundant component. The mixture also contained 24% (molar yield) of **S3**, which was separated by chromatography and had the identical ^1H NMR spectra of **S3** prepared in the previous reaction with a larger amount of LR.

Whereas parent PDI is a deep red solid, thionated PDIs are brilliant purple-blue compounds. Optical absorption and electrochemical measurements in dilute chloroform solutions were thus used to understand the changes in electronic structure that occur with successive PDI thionation. The absorption maximum of **P** shifts steadily from 526 nm to a maximum of 706 nm upon full thionation (Figure 3). Experimental HOMO/LUMO energies and those calculated from density functional theory (DFT) using the 6-31++g(d,p) basis set (see Table 1) confirm that the LUMO energies decrease with increasing thionation (increased electron affinity), while the HOMO energies raise, which causes the observed red shift in optical absorption.

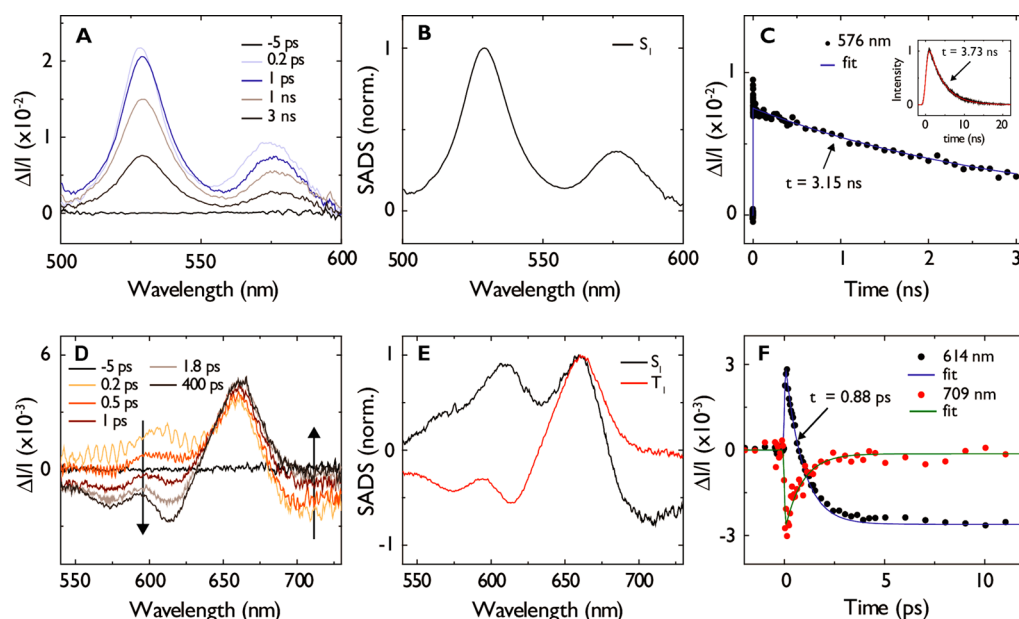


Figure 4. TA spectra, SADS, and time evolution at specific wavelengths with corresponding fits from global target analysis overlaid for **P** (panels A–C) and **S3** (panels D–F). Time delays for the transient spectra in panels A and D are indicated in the legend. The SADS plotted in panels B and E were obtained from a single- and two-component model to the transient data, respectively, as discussed in the main text. The inset in panel C displays a TCSPC measurement of **P** in chloroform solution with an optical density of ~ 0.05 . The sample was excited at 494 nm and the emission detected at 535 nm in these measurements. These data are fit with a single exponential decay convoluted with the 1.25 ns instrument response function.

One of the hallmarks of the characteristic PDI absorption spectra is the four peaks from perylene C=C stretching modes (0–0, 0–1, 0–2, and 0–3) coupled to the π – π^* electronic transition.⁵² These four vibronic bands are present in all of the thionated derivatives with peak spacings that range from 0.14 to 0.19 eV (see Figure 3A, Table S1, SI) and are thus not greatly perturbed by thionation. The intensities of the 0–0, 0–1, and 0–2 vibronic bands are roughly consistent throughout the series. The spectral similarity of the two **S₂** isomers implies that their singlet electronic manifold is independent of the regiochemistry of the thiocarbonyl groups.

Another interesting characteristic of PDIs is their strong crystallochromic behavior, where small displacements along the short (transverse) molecular axis and twisting of the perylene backbone can significantly affect electronic transition energies and band intensities in the solid state.^{12,53} This twisting can occur due to the greater single bond character of the C–C bonds connecting the two naphthalene subunits of the perylene core (see Figure S3, SI) and leads to reduced π – π overlap in the solid state. Given the strong crystallochromic behavior of PDI and the structural diversity afforded by thionation, we employed solid state absorption spectroscopy to illuminate differences in molecular packing and crystallinity in the series.

Thin-film linear optical absorption spectra of **P–S4** are shown in Figure 3B. In each case, a pronounced change in line shape and band maximum is observed in the as-cast films compared with solution. For each derivative the absorption maximum is assigned to the 0–2 vibronic transition, with the 0–1 transition present as a broad shoulder. This causes an apparent blue shift that is indicative of H-aggregate formation.⁵⁴ The two **S₂** isomers have slightly different absorption maxima (541 nm for *cis*-**S2** and 550 nm for *trans*-**S2**) in the as-cast films, which is in contrast to their nearly identical solution spectra and suggests differences in their solid state packing. The spectral profiles of the thionated derivatives closely resemble

the parent (**P**), which suggests that large-scale molecular order in these films is primarily governed by the sterically bulky 3-hexylundecyl side chains.

To investigate how the degree of thionation influences molecular packing in the solid state, thin-film spectra of **P** and **S4** are compared following thermal annealing (Figure 3C). After thermal treatment, the absorption maximum of **S4** is blue-shifted 3018 cm^{-1} from the solution maximum, while **P** displays a much smaller blue shift of 1355 cm^{-1} , which suggests tetrathionation enhances π – π stacking interactions (H-aggregate formation) in the annealed films (vide supra). This hypothesis is supported by temperature-dependent ^1H NMR measurements on equimolar solutions of **P** and **S4**, showing a much stronger temperature-dependent chemical shift for perylene protons in **S4**, consistent with a greater degree of π – π overlap (see Figure S4, SI).⁵⁵ The enhanced interchromophore coupling observed is possibly due to strong attractive van der Waals interactions between sulfur atoms of adjacent chromophores. Annealed film spectra of the other thionated derivatives can be found in Figure S5 (SI) and also display spectral features characteristic of enhanced π – π interactions in the solid state.

To investigate the regioisomeric influence of the thiocarbonyl groups, the annealed thin-film spectra of *cis*-**S2** and *trans*-**S2** are compared (Figure 3D). The band profiles and absorption maxima are noticeably different. The absorption maximum (0–1) of *cis*-**S2** is blue-shifted by 2182 cm^{-1} from the solution 0–1 band, while *trans*-**S2** has a smaller spectral blue shift of 699 cm^{-1} . *Cis*-**S2** also has a more intense 0–2 transition (apparent as a shoulder at 526 nm), both of which could suggest stronger π – π interactions (H-aggregation) in this isomer. This preliminary result shows that the regiochemistry of the thiocarbonyl groups influences solid state packing in thionated PDIs and highlights thionation as a means of varying

morphology beyond modifications to *N*-alkyl side chains and bay substituents.

Although S1–S4 are deeply colored, we are unable to observe fluorescence from any of the thionated PDIs ($\Phi_f < 0.001$). This is somewhat unexpected given the high fluorescence quantum yield of **P** ($\Phi_f = 0.97$) as well as the large number of known emissive sulfur-containing fluorophores and shows that the presence of one C=S functional group is enough to completely quench PDI emission. To investigate the cause of the quenched fluorescence, we employed ultrafast TA spectroscopy.

We first describe the features of the emissive parent PDI to highlight the differences between known PDIs and those reported here. The TA spectrum of **P** consists of features at 530 and 578 nm (Figure 4A). The feature at 530 nm arises from a combination of a ground state bleach (GSB) and stimulated emission (SE) process. The feature at 578 nm arises from the 0–1 transition of the solution emission spectrum (see Figure S6, SI), and is attributed to only SE. A global target analysis of these data employing a single-component kinetic scheme yields the species-associated difference spectrum (SADS) representative of the excited-singlet state (S_1) (see Figure 4B) with a decay rate constant of $3.1 \times 10^8 \text{ s}^{-1}$ (corresponding to a time constant of 3.2 ns). This is in good agreement with the 3.7 ns fluorescence lifetime obtained by time-correlated single photon counting (see inset of Figure 4C).

We next describe S3, a heavily thionated PDI that has negligible emission and is spectroscopically well resolved from **P**. S3 has a GSB feature at 660 nm that persists without decaying throughout the time scale of the experiment (~ 400 ps) (see Figure 4D). The spectrum also contains two overlapping photoinduced absorption (PIA) features at 574 and 614 nm and a broad red-shifted feature at 709 nm. The long-lived spectral features at 574 and 614 nm are assigned to a triplet PIA on the basis of triplet sensitization experiments on *N,N'*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenebis(dicarboximide) by Ford and Kamat³¹ and transient absorption measurements on a platinum-acetylide disubstituted PDI by Llewellyn and co-workers.³⁷ A global target analysis of the data employing a two-component, sequential kinetic scheme yields two SADS representative of the singlet and triplet excited states (Figure 4E). Rate constants of $1.14 \times 10^{-12} \text{ s}^{-1}$ and $8.6 \times 10^{-19} \text{ s}^{-1}$ (corresponding to time constants of 0.88 ps and $\gg 400$ ps) for the interconversion of these species along with the return to the ground state are determined for these SADS (see Figure 4F). The subpicosecond time constant suggests highly efficient conversion between the singlet and triplet manifold, while the lack of a decay on the time scale of the experiment provides further support for our assignment of the long-lived transient species to a triplet state.

The transient spectral features of S3 are observed in all other thionated derivatives and appear to be general for this series of compounds (see Figure S7, SI). Accordingly, we assign the long-lived PIA feature to a T_1-T_n transition and the short-lived, red-shifted PIA feature to an S_1-S_n transition and conclude that each thionated PDI undergoes ISC following excitation into S_1 . Interestingly, time constants for ISC are relatively constant across the series (see Table 2), and thus the rate of ISC appears independent of the degree of thionation.

An important distinction between this work and previous work is that the so-called heavy atom effect does not explain the photophysics that are at play here. In many molecular systems, ISC is facilitated by the spin–orbit coupling that occurs when a

Table 2. Time Constants (τ_{ISC}) and Corresponding Rate Constants (k_{ISC}) for ISC in Thionated PDIs as Determined from a Global Target Analysis of Their Respective TA Spectra

| PDI | τ_{ISC} (ps) | k_{ISC} ($\times 10^{12} \text{ s}^{-1}$) |
|------------------|--------------------------|--|
| S1 | 0.59 | 1.69 |
| <i>cis</i> -S2 | 0.97 | 1.03 |
| <i>trans</i> -S2 | 0.81 | 1.23 |
| S3 | 0.88 | 1.14 |
| S4 | 0.94 | 1.06 |

heavy atom is situated in close proximity to the delocalized π -system.^{56–58} This phenomenon is observed in a number of systems including those that employ group 16 elements.^{59–61} For example, Detty has shown that ISC rates in chalcogenapyrylium dyes are enhanced by 4 orders of magnitude from oxygen to tellurium and depend on the degree of substitution.⁶² In the present work, however, the rate of ISC is independent of the number of attached heavy atoms. Furthermore, the relatively small spin–orbit coupling constant of sulfur (365 cm^{-1})⁶³ is not sufficient to promote the subpicosecond ISC observed here.

To explain the rapid ISC rates in thionated PDIs, the effect of sulfur atom substitution on the electronic structure needs to be considered. A general characteristic of conjugated thiocarbonyl compounds (thiones) is that their S_1-T_1 energetic splitting is very small ($<2000 \text{ cm}^{-1}$), resulting from a lowering of the $^1(n, \pi^*)$ state such that it becomes the lowest-lying S_1 state (see Figure 5).^{64,65} Reordering of the S_1 and S_2 states facilitates rapid ISC as a $^1(n, \pi^*)-^3(\pi, \pi^*)$ (S_1-T_1) transition involves a change in orbital angular momentum (El-Sayed rule).⁶⁶ This effect is observed in aromatic thiones, such as xanthenethione, where ISC occurs within 1 ps,⁶⁷ and also explains the rapid ISC observed in thionated squaraine dyes.⁶⁸ While detailed spectroscopic and theoretical investigations are required to fully elucidate the singlet and triplet manifolds of these complex systems, the absence of a noticeable heavy atom effect coupled with the equivalency of the ISC rates leads us to conclude that reordering of the molecular electronic structure is the primary cause of rapid ISC in thionated PDIs.

CONCLUSION

A series of five distinctly substituted thionated PDIs were synthesized and characterized and their optoelectronic properties studied. Through use of the 3-hexylundecyl side chain, we were able to synthesize five thionated derivatives from the parent compound using commercially available Lawesson's reagent. Optical absorption experiments show that sulfur atom substitution does not perturb electronic–vibrational coupling but causes a spectral red-shift that is proportional to the degree of thionation, leading to PDIs that are among the most red light absorbers of those previously reported. Solution electrochemistry reveals that this spectral red-shift is mostly attributable to an increased electron affinity, in agreement with theoretical calculations. Remarkably, any degree of thionation renders PDIs nonemissive. Ultrafast TA experiments show that rapid and highly efficient intersystem crossing (ISC) to triplet states is the cause of the quenched emission. The rate of ISC is found to be independent of the degree of thionation, such that S1 and S4 display equally rapid ISC, which is attributed to a reordering of the molecular electronic structure. The high triplet yield of thionated PDIs makes them potential

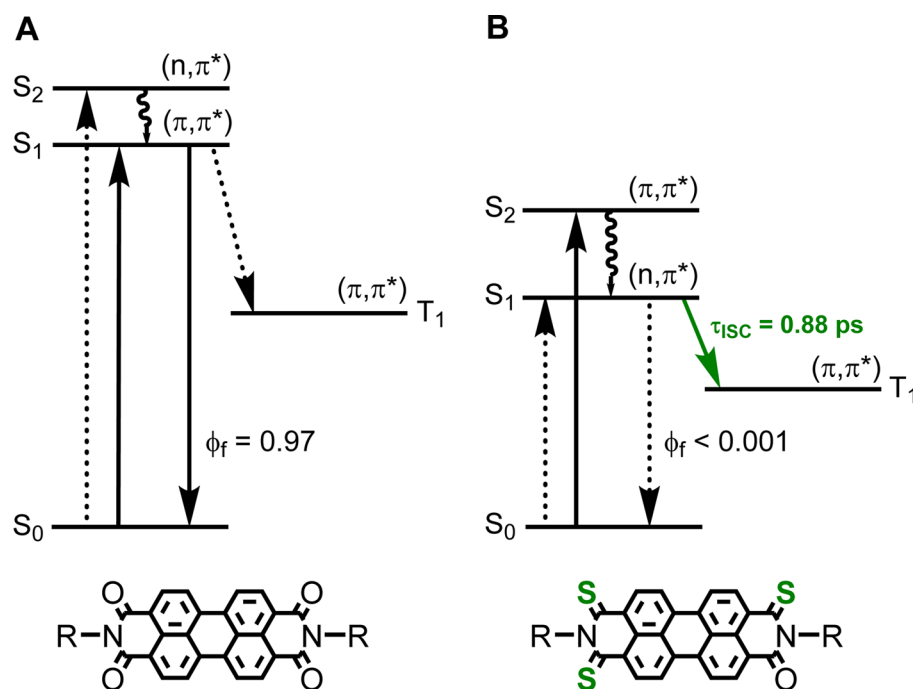


Figure 5. Proposed energy level schematic of P (panel A) and S3 (panel B). Solid arrows represent probable electronic transitions, while less probable transitions are represented by dashed arrows. R denotes the 3-hexylundecyl side chain. Note that mixing of the $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states is possible in thiones such that S_2 – S_1 internal conversion is rapid.⁶⁴ The T_1 – S_0 radiative transition has been omitted for clarity.

triplet sensitizers and candidates for optoelectronic applications that involve triplet energy harvesting.

■ ASSOCIATED CONTENT

Supporting Information

Details of precursor syntheses, compound stability, computational methods, electrochemistry, transient absorption spectroscopy, and global target analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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■ REFERENCES

- (1) Kozma, E.; Catellani, M. Perylene Diimides Based Materials for Organic Solar Cells. *Dyes Pigm.* **2013**, *98*, 160–179.
- (2) Finlayson, C. E.; Friend, R. H.; Otten, M. B. J.; Schwartz, E.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; Rowan, A. E.; Samorì, P.; Palermo, V.; Liscio, A.; et al. Electronic Transport Properties of Ensembles of Perylene-Substituted Poly-Isocyanopeptide Arrays. *Adv. Funct. Mater.* **2008**, *18*, 3947–3955.

- (3) Kamm, V.; Battagliarin, G.; Howard, I. A.; Pisula, W.; Mavrinskiy, A.; Li, C.; Müllen, K.; Laquai, F. Polythiophene:Perylene Diimide Solar Cells – the Impact of Alkyl-Substitution on the Photovoltaic Performance. *Adv. Energy Mater.* **2011**, *1*, 297–302.
- (4) Kaiser, T. E.; Stepanenko, V.; Würthner, F. Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure–Property Relationship, Nucleation–Elongation Mechanism, and Sergeants-and-Soldiers Principle. *J. Am. Chem. Soc.* **2009**, *131*, 6719–6732.
- (5) Hains, A. W.; Chen, H.-Y.; Reilly, T. H.; Gregg, B. A. Cross-Linked Perylene Diimide-Based N-Type Interfacial Layer for Inverted Organic Photovoltaic Devices. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4381–4387.
- (6) Müller, G. R. J.; Meiners, C.; Enkelmann, V.; Geerts, Y.; Müllen, K. Liquid Crystalline Perylene-3,4-Dicarboximide Derivatives with High Thermal and Photochemical Stability. *J. Mater. Chem.* **1998**, *8*, 61–64.
- (7) Würthner, F.; Thalacker, C.; Sautter, A.; Schärfl, W.; Ibach, W.; Hollricher, O. Hierarchical Self-Organization of Perylene Bisimide–Melamine Assemblies to Fluorescent Mesoscopic Superstructures. *Chem.—Eur. J.* **2000**, *6*, 3871–3886.
- (8) Yagai, S.; Seki, T.; Karatsu, T.; Kitamura, A.; Würthner, F. Transformation from H- to J-Aggregated Perylene Bisimide Dyes by Complexation with Cyanurates. *Angew. Chem., Int. Ed.* **2008**, *47*, 3367–3371.
- (9) Schmidt, K.; Brovelli, S.; Coropceanu, V.; Beljonne, D.; Cornil, J.; Bazzini, C.; Caronna, T.; Tubino, R.; Meinardi, F.; Shuai, Z.; et al. Intersystem Crossing Processes in Nonplanar Aromatic Heterocyclic Molecules. *J. Phys. Chem. A* **2007**, *111*, 10490–10499.
- (10) Cormier, R. A.; Gregg, B. A. Synthesis and Characterization of Liquid Crystalline Perylene Diimides. *Chem. Mater.* **1998**, *10*, 1309–1319.
- (11) Liu, S.-G.; Sui, G.; Cormier, R. A.; Leblanc, R. M.; Gregg, B. A. Self-Organizing Liquid Crystal Perylene Diimide Thin Films: Spectroscopy, Crystallinity, and Molecular Orientation. *J. Phys. Chem. B* **2002**, *106*, 1307–1315.
- (12) Würthner, F. Perylene Bisimide Dyes as Versatile Building Blocks for Functional Supramolecular Architectures. *Chem. Commun.* **2004**, 1564–1579.

- (13) Huang, D. M.; Mauger, S. A.; Friedrich, S.; George, S. J.; Dumitriu-LaGrange, D.; Yoon, S.; Moulé, A. J. The Consequences of Interface Mixing on Organic Photovoltaic Device Characteristics. *Adv. Funct. Mater.* **2011**, *21*, 1657–1665.
- (14) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Perylene and Related Diimides for Organic Electronics. *Adv. Mater.* **2011**, *23*, 268–284.
- (15) Briseno, A. L.; Mannsfeld, S. C. B.; Reese, C.; Hancock, J. M.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. Perylenediimide Nanowires and Their Use in Fabricating Field-Effect Transistors and Complementary Inverters. *Nano Lett.* **2007**, *7*, 2847–2853.
- (16) Kaiser, T. E.; Stepanenko, V.; Würthner, F. Fluorescent J-Aggregates of Core-Substituted Perylene Bisimides: Studies on Structure–Property Relationship, Nucleation–Elongation Mechanism, and Sergeants-and-Soldiers Principle. *J. Am. Chem. Soc.* **2009**, *131*, 6719–6732.
- (17) An, Z.; Yu, J.; Jones, S. C.; Barlow, S.; Yoo, S.; Domercq, B.; Prins, P.; Siebbeles, L. D. A.; Kippelen, B.; Marder, S. R. High Electron Mobility in Room-Temperature Discotic Liquid-Crystalline Perylene Diimides. *Adv. Mater.* **2005**, *17*, 2580–2583.
- (18) Difley, S.; Beljonne, D.; Van Voorhis, T. On the Singlet-Triplet Splitting of Geminate Electron-Hole Pairs in Organic Semiconductors. *J. Am. Chem. Soc.* **2008**, *130*, 3420–3427.
- (19) Van Dijken, A.; Bastiaansen, J. J. A. M.; Kikken, N. M. M.; Langeveld, B. M. W.; Rothe, C.; Monkman, A.; Bach, I.; Stössel, P.; Brunner, K. Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Polymer Hosts for High-Efficiency Light-Emitting Diodes. *J. Am. Chem. Soc.* **2004**, *126*, 7718–7727.
- (20) Shao, Y.; Yang, Y. Efficient Organic Heterojunction Photovoltaic Cells Based on Triplet Materials. *Adv. Mater.* **2005**, *17*, 2841–2844.
- (21) Singh-Rachford, T. N.; Castellano, F. N. Triplet Sensitized Red-to-Blue Photon Upconversion. *J. Phys. Chem. Lett.* **2010**, *1*, 195–200.
- (22) Singh-Rachford, T. N.; Castellano, F. N. Photon Upconversion Based on Sensitized Triplet – Triplet Annihilation. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
- (23) Hudson, Z. M.; Ko, S.-B.; Yamaguchi, S.; Wang, S. Modulating the Photoisomerization of N,C-Chelate Organoboranes with Triplet Acceptors. *Org. Lett.* **2012**, *14*, 5610–5613.
- (24) Yost, S. R.; Hontz, E.; Yeganeh, S.; Van Voorhis, T. Triplet vs Singlet Energy Transfer in Organic Semiconductors: The Tortoise and the Hare. *J. Phys. Chem. C* **2012**, *116*, 17369–17377.
- (25) Bonnett, R. Photosensitizers of the Porphyrin and Phthalocyanine Series for Photodynamic Therapy. *Chem. Soc. Rev.* **1995**, *24*, 19–33.
- (26) Spikes, J. D.; van Lier, J. E.; Bommer, J. C. A Comparison of the Photoproperties of Zinc Phthalocyanine and Zinc Naphthalocyanine Tetrasulfonates: Model Sensitizers for the Photodynamic Therapy of Tumors. *J. Photochem. Photobiol. A: Chem.* **1995**, *91*, 193–198.
- (27) Griffiths, J.; Schofield, J.; Wainwright, M.; Brown, S. B. Some Observations on the Synthesis of Polysubstituted Zinc Phthalocyanine Sensitizers for Photodynamic Therapy. *Dyes Pigm.* **1997**, *33*, 65–78.
- (28) Islangulov, R. R.; Castellano, F. N. Photochemical Upconversion: Anthracene Dimerization Sensitized to Visible Light by a RuII Chromophore. *Angew. Chem., Int. Ed.* **2006**, *45*, 5957–5959.
- (29) Cheng, Y. Y.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. On the Efficiency Limit of Triplet-Triplet Annihilation for Photochemical Upconversion. *Phys. Chem. Chem. Phys.* **2010**, *12*, 66–71.
- (30) Cheng, Y. Y.; Fückel, B.; Khoury, T.; Clady, R. G. C. R.; Tayebjee, M. J. Y.; Ekins-Daukes, N. J.; Crossley, M. J.; Schmidt, T. W. Kinetic Analysis of Photochemical Upconversion by Triplet–Triplet Annihilation: Beyond Any Spin Statistical Limit. *J. Phys. Chem. Lett.* **2010**, *1*, 1795–1799.
- (31) Ford, W. E.; Kamat, P. V. Photochemistry of 3,4,9,10-Perylenetetracarboxylic Dianhydride Dyes 3. Singlet and Triplet Excited-State Properties of the Bis(2,5-di-*tert*-butylphenyl)imide Derivative. *J. Chem. Phys.* **1987**, *91*, 6373–6380.
- (32) Jiménez, Á. J.; Späning, F.; Rodríguez-Morgade, M. S.; Ohkubo, K.; Fukuzumi, S.; Guldi, D. M.; Torres, T. A. Tightly Coupled Bis(zinc(II) phthalocyanine)–Perylenediimide Ensemble To Yield Long-Lived Radical Ion Pair States. *Org. Lett.* **2007**, *9*, 2481–2484.
- (33) Prodi, A.; Chiorboli, C.; Scandola, F.; Iengo, E.; Alessio, E.; Dobrawa, R.; Würthner, F. Wavelength-Dependent Electron and Energy Transfer Pathways in a Side-to-Face Ruthenium Porphyrin/ perylene Bisimide Assembly. *J. Am. Chem. Soc.* **2005**, *127*, 1454–1462.
- (34) Wasielewski, M. R. Energy, Charge, and Spin Transport in Molecules and Self-Assembled Nanostructures Inspired by Photosynthesis. *J. Org. Chem.* **2006**, *71*, S051–S066.
- (35) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. Making a Molecular Wire: Charge and Spin Transport through. *J. Am. Chem. Soc.* **2004**, *126*, 5577–5584.
- (36) Rachford, A. A.; Goeb, S.; Castellano, F. N. Accessing the Triplet Excited State in Perylenediimides. *J. Am. Chem. Soc.* **2008**, *130*, 2766–2767.
- (37) Llewellyn, B. A.; Slater, A. G.; Goretzki, G.; Easun, T. L.; Sun, X.-Z.; Davies, E. S.; Argent, S. P.; Lewis, W.; Beeby, A.; George, M. W.; Champness, N. R. Photophysics and Electrochemistry of a Platinum-Acetylide Disubstituted Perylenediimide. *Dalton Trans.* **2014**, *43*, 85–94.
- (38) Suzuki, S.; Kozaki, M.; Nozaki, K.; Okada, K. Recent Progress in Controlling Photophysical Processes of Donor–acceptor Arrays Involving Perylene Diimides and Boron-Dipyrromethenes. *J. Photochem. Photobiol. C: Photochem. Rev.* **2011**, *12*, 269–292.
- (39) Danilov, E. O.; Rachford, A. A.; Goeb, S.; Castellano, F. N. Evolution of the Triplet Excited State in Pt(II) Perylenediimides. *J. Phys. Chem. A* **2009**, *113*, 5763–5768.
- (40) Pensack, R. D.; Song, Y.; McCormick, T. M.; Jahnke, A. A.; Hollinger, J.; Seferos, D. S.; Scholes, G. D. Evidence for the Rapid Conversion of Primary Photoexcitations to Triplet States in Seleno- and Telluro- Analogues of Poly(3-Hexylthiophene). *J. Phys. Chem. B* **2014**, *118*, 2589–2597.
- (41) Gibson, G. L.; McCormick, T. M.; Seferos, D. S. Effect of Group-14 and Group-16 Substitution on the Photophysics of Structurally Related Donor–Acceptor Polymers. *J. Phys. Chem. C* **2013**, *117*, 16606–16615.
- (42) Chattopadhyaya, M.; Sen, S.; Alam, M. M.; Chakrabarti, S. The Role of Relativity and Dispersion Controlled Inter-Chain Interaction on the Band Gap of Thiophene, Selenophene, and Tellurophene Oligomers. *J. Chem. Phys.* **2012**, *136*, 094904.
- (43) Lévesque, S.; Gendron, D.; Bérubé, N.; Grenier, F.; Leclerc, M.; Côté, M. Thiocarbonyl Substitution in 1,4-Dithioketopyrrolopyrrole and Thienopyrroledithione Derivatives: An Experimental and Theoretical Study. *J. Phys. Chem. C* **2014**, *118*, 3953–3959.
- (44) Quinn, J.; Zheng, Y.; Chen, Z.; Usta, H.; Newman, C.; Yan, H.; Facchetti, A. (Polyera Corporation) Organic Semiconductors and Devices Incorporating Same. WO2011/82234 A1, 2011.
- (45) Jesberger, M.; Davis, T. P.; Barner, L. Applications of Lawesson’s Reagent in Organic and Organometallic Syntheses. *Synthesis* **2003**, *13*, 1929–1958.
- (46) Taylor, P.; Polshettiwar, V.; Kaushik, M. P. Recent Advances in Thionating Reagents for the Synthesis of Organosulfur Compounds. *J. Sulfur Chem.* **2006**, *27*, 353–386.
- (47) Van Herrikhuyzen, J.; Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. Synthesis of N-Type Perylene Bisimide Derivatives and Their Orthogonal Self-Assembly with P-Type Oligo(p-Phenylene Vinylene)s. *J. Am. Chem. Soc.* **2004**, *126*, 10021–10027.
- (48) Liu, Y.; Zhao, J. Visible Light-Harvesting Perylenebisimide-Fullerene (C60) Dyads with Bidirectional “Ping-Pong” Energy Transfer as Triplet Photosensitizers for Photooxidation of 1,5-Dihydroxynaphthalene. *Chem. Commun.* **2012**, *48*, 3751–3753.
- (49) Hurd, R. N.; De La Mater, G.; McElheny, G. C.; Turner, R. J.; Wallingford, V. H. Preparation of Dithiooxamide Derivatives. *J. Org. Chem.* **1961**, *26*, 3980–3987.
- (50) John Foreman, M., St.; Woollins, J. D. Organo-P–S and P–Se Heterocycles. *J. Chem. Soc., Dalton Trans.* **2000**, 1533–1543.

- (51) Fleming, G. R.; Knight, A. W. E.; Morris, J. M.; Morrison, R. J. S.; Robinson, G. W. Picosecond Fluorescence Studies of Xanthene Dyes. *J. Am. Chem. Soc.* **1977**, *99*, 4306–4311.
- (52) Clark, A. E.; Qin, C.; Li, A. D. Q. Beyond Exciton Theory: A Time-Dependent DFT and Franck-Condon Study of Perylene Diimide and Its Chromophoric Dimer. *J. Am. Chem. Soc.* **2007**, *129*, 7586–7595.
- (53) Zugenmaier, P.; Duff, J.; Bluhm, T. L. Crystal and Molecular Structures of Six Differently with Halogen Substituted Bis (benzylimido) Perylene. *Cryst. Res. Technol.* **2000**, *35*, 1095–1115.
- (54) Gómez, R.; Veldman, D.; Blanco, R.; Seoane, C.; Segura, J. L.; Janssen, R. A. J. Energy and Electron Transfer in a Poly(fluorene-Alt-Phenylene) Bearing Perylenediimides as Pendant Electron Acceptor Groups. *Macromolecules* **2007**, *40*, 2760–2772.
- (55) Wang, W.; Han, J. J.; Wang, L.-Q.; Li, L.-S.; Shaw, W. J.; Li, A. D. Q. Dynamic Π - π Stacked Molecular Assemblies Emit from Green to Red Colors. *Nano Lett.* **2003**, *3*, 455–458.
- (56) Cui, G.; Fang, W. State-Specific Heavy-Atom Effect on Intersystem Crossing Processes in 2-Thiothymine: A Potential Photodynamic Therapy Photosensitizer. *J. Chem. Phys.* **2013**, *138*, 044315.
- (57) Miskoski, S.; Soltermann, A. T.; Molina, P. G.; Gunthe, G.; Zanolco, A. L.; Garcia, N. A. Sensitized Photooxidation of Thyroidal Hormones. Evidence for Heavy Atom Effect on Singlet Molecular Oxygen [$O_2(^1\Delta_g)$]-mediated Photoreactions. *Photochem. Photobiol.* **2005**, *81*, 325–332.
- (58) Nag, M.; Jenks, W. S. Photochemistry and Photophysics of Halogen-Substituted Dibenzothiophene Oxides. *J. Org. Chem.* **2004**, *69*, 8177–8182.
- (59) Detty, M. R.; Merkel, P. B.; Michael, R. Chalcogenapyrylium Dyes As Potential Photochemotherapeutic Agents. Solution Studies of Heavy Atom Effects on Triplet Yields, Quantum Efficiencies of Singlet Oxygen Generation, Rates of Reaction with Singlet Oxygen, And Emission Quantum Yields. *J. Am. Chem. Soc.* **1990**, *112*, 3845–3855.
- (60) Xu, H.-J.; Mack, J.; Wu, D.; Xue, Z.-L.; Descalzo, A. B.; Rurack, K.; Kobayashi, N.; Shen, Z. Synthesis and Properties of Fused-Ring-Expanded Porphyrins That Were Core-Modified with Group 16 Heteroatoms. *Chem.—Eur. J.* **2012**, *18*, 16844–16867.
- (61) Ohulchanskyy, T. Y.; Donnelly, D. J.; Detty, M. R.; Prasad, P. N. Heteroatom Substitution Induced Changes in Excited-State Photophysics and Singlet Oxygen Generation in Chalcogenoxanthylum Dyes: Effect of Sulfur and Selenium Substitutions. *J. Phys. Chem. B* **2004**, *108*, 8668–8672.
- (62) Detty, M. R. Singlet Oxygen with Organometallic Compounds. Oxophilicity and Rates of Intersystem Crossing in Organochalcogen Compounds. *Organometallics* **1992**, *11*, 2310–2312.
- (63) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; CRC Press: Boca Raton, FL, 2006.
- (64) Maciejewski, A.; Steer, R. P. The Photophysics, Physical Photochemistry, and Related Spectroscopy of Thiocarbonyls. *Chem. Rev.* **1993**, *93*, 67–98.
- (65) Szymanski, M.; Maciejewski, A.; Steer, R. P. Concerning Apparent Intersystem Crossing Efficiencies in Molecules with Small S1-T1 Energy Gaps. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 405–418.
- (66) El-Sayed, M. A. Spin—Orbit Coupling and the Radiationless Processes in Nitrogen Heterocyclics. *J. Chem. Phys.* **1963**, *38*, 2834.
- (67) Anderson, R. W., Jr.; Hochstrasser, R. M.; Pownall, H. J. Picosecond Absorption Spectra of the Second Excited Singlet State of a Molecule in the Condensed Phase: Xanthione. *Chem. Phys. Lett.* **1976**, *43*, 4–7.
- (68) Webster, S.; Peceli, D.; Hu, H.; Padilha, L. A.; Przhonska, O. V.; Masunov, A. E.; Gerasov, A. O.; Kachkovski, A. D.; Slominsky, Y. L.; Tolmachev, A. I.; et al. Near-Unity Quantum Yields for Intersystem Crossing and Singlet Oxygen Generation in Polymethine-like Molecules: Design and Experimental Realization. *J. Phys. Chem. Lett.* **2010**, *1*, 2354–2360.