

# Synthesis and Photophysics of Thioindigo Diimines and Related Compounds

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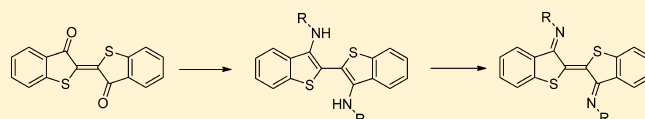
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## S Supporting Information

**ABSTRACT:** We report the synthesis and comprehensive characterization of diamine and diimine derivatives of the fluorescent compound thioindigo. Diamines **1** were obtained by metal-mediated amine condensation reaction with thioindigo. Oxidation of the products of the coupling reaction provided the diimines **2**. X-ray crystal structures, cyclic voltammetry, and spectral and photophysical data of the compounds are presented. X-ray crystal structures demonstrate a planar structure for the diimine derivatives and a twisted conformation for the diamines. The diamine compounds **1** absorb in the UV ( $\lambda_{\text{max}}$  324–328 nm), significantly blue-shifted from the absorption spectrum of thioindigo. Diamines **1** exhibit moderate fluorescence ( $\Phi_{\text{F}}$  = 0.25, 0.045). A transient triplet state is observed in laser flash photolysis (LFP) experiments of **1**, with lifetimes 1 order of magnitude longer than those of thioindigo. The diimine compounds **2** absorb at longer wavelengths ( $\lambda_{\text{max}}$  495–510 nm) than the diamines but are still slightly blue-shifted from thioindigo, with molar extinction coefficients 17–70% higher compared to thioindigo. The diimine compounds are not emissive, and LFP studies indicate transient species with microsecond lifetimes. Quenching experiments and transient absorption spectra are consistent with trans–cis isomerization.

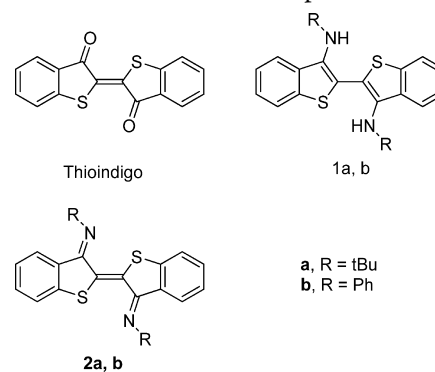


## INTRODUCTION

*trans*-Thioindigo, the sulfur analogue of the well-known dye indigo, is a highly fluorescent compound. Like indigo, thioindigo is a commercially available dye used in pigments and coatings.<sup>1</sup> The spectral and photophysical properties of the two molecules, however, differ significantly, which in the 1950s led to extensive studies of the excited-state behavior of thioindigo.<sup>2–4</sup> More recently, indigo has also become the subject of photophysical investigation.<sup>5–8</sup> Because of its intense fluorescence, thioindigo has been explored as a dye for fluorescent solar collectors.<sup>9,10</sup> Thioindigos have also been investigated as organic semiconductors and charge generation devices.<sup>11,12</sup> Additionally, thioindigo is a photochromic compound, undergoing photo-induced trans–cis isomerization. The photoinduced isomerization has been studied in solution,<sup>13–15</sup> monolayers,<sup>16</sup> and thin films<sup>17,18</sup> and on solid support.<sup>19</sup> The application of the trans–cis isomerization in liquid crystals<sup>20,21</sup> and ion transport<sup>22</sup> has also been investigated.

Research aimed at understanding and controlling the physical and photophysical properties of thioindigo has been advanced through the synthesis, characterization, and application of thioindigo derivatives. These studies have largely focused on thioindigos with substituents on the peripheral ring carbon atoms.<sup>23–27</sup> Analogues made by modification of the ketone moiety are rare; the most commonly synthesized and examined is the leuco form of thioindigo.<sup>28,29</sup> Isolated examples exist of thioether,<sup>30</sup> primary amine,<sup>31</sup> and primary imine<sup>32</sup> replacement of the thioindigo ketone.

Substituted imine derivatives represent an unexplored avenue in thioindigo chemistry. This work was undertaken with the objective of expanding the scope of thioindigo derivatives by taking advantage of the carbonyl-to-imine transformation (which has been recently used to make diimine derivatives of indigo)<sup>33</sup> and examining the properties of the products. Our synthetic efforts toward the diimines led to the isolation of several unexpected products, some of which we identified as potentially interesting. Herein the spectroscopic, electrochemical, and photophysical characteristics of some 2,2'-diimino thioindigos **2** and related diamine compounds **1** are presented.



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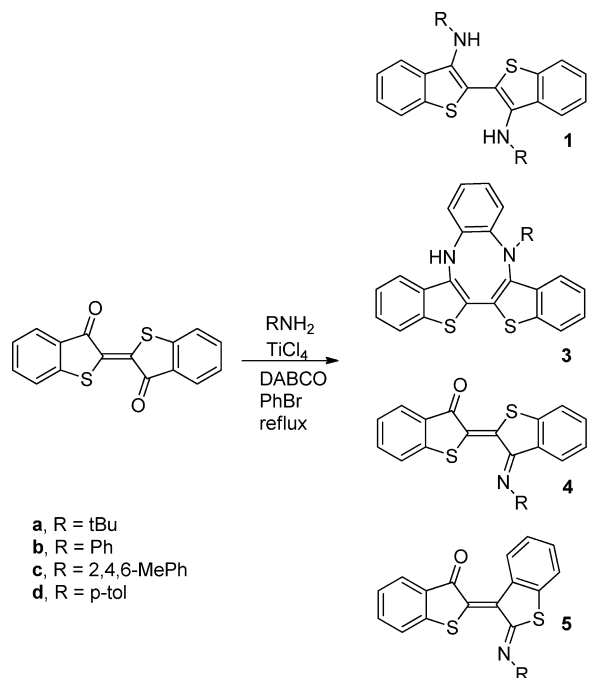
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## RESULTS AND DISCUSSION

**Synthesis.** Imines are commonly prepared by nucleophilic attack by an amine at a carbonyl carbon and subsequent elimination of water. For thioindigo, however, a survey of standard nucleophilic reaction conditions did not lead to product, instead resulting in recovery of starting material. Reaction conditions included addition of a variety of acids, both Brønsted and Lewis (to increase the nucleophilicity of the ketone), and drying agents such as molecular sieves and the use of Dean–Stark apparatus (to reduce the back-reaction involving water). Less conventional approaches, including the use of montmorillonite clay were also employed but did not result in the desired transformation. The failure of amines to react with thioindigo under nucleophilic substitution conditions is likely due to a combination of factors: the low solubility of thioindigo in most solvents and the increased electron density of the carbonyl carbon due to donation from the sulfur atom which deactivates the carbonyl to nucleophilic attack.

Procedures for making imines using a metal-mediated method in which titanium tetrachloride acts as a coordinating intermediate (not as a Lewis acid) are less common but have precedent in conjugated systems including anthraquinone and indigo.<sup>34,35</sup> In these cases a preformed titanium-imide species is refluxed in a high boiling solvent (bromobenzene) with the ketone and DABCO, affording the imine. However, when applied to thioindigo, these conditions resulted in the isolation of different products, the nature and distribution of which depend on the starting amine (Scheme 1 and Table 1). The

**Scheme 1. Products from TiCl<sub>4</sub>-Mediated Amine Condensation Reactions with Thioindigo**



reaction also appears to be sensitive to water content, with differences in product distribution observed when the solvent is dried over molecular sieves versus dried in a still. Adding a small amount of water (10–20  $\mu\text{L}$  on a 5 mM scale reaction) to molecular-sieve-dried solvent resulted in product distribution identical to still-dried solvent (which may suggest that distilled

**Table 1. Products Observed in TiCl<sub>4</sub>-Mediated Reactions**

amine	product yield, %			
	1	3	4	5
<i>t</i> BuNH <sub>2</sub>	54	0	trace	trace
PhNH <sub>2</sub>	39	35	0	0
MesNH <sub>2</sub>	0	0	9	33

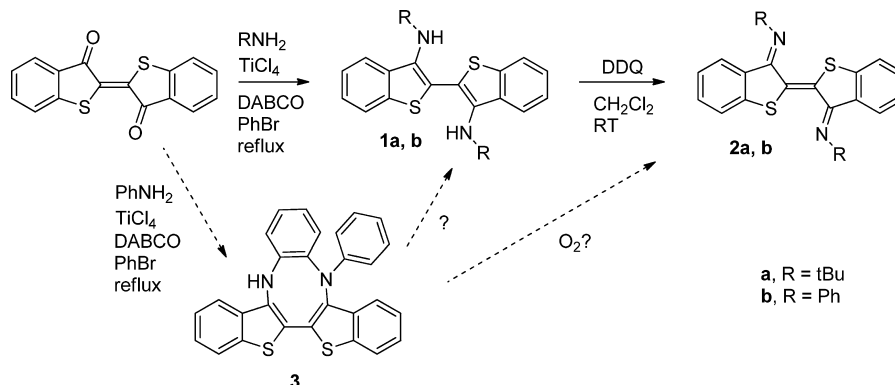
solvent is not completely dry<sup>36,37</sup>). Table 1 reports product distribution for reactions conducted in still-dried solvents.

The synthesis of the *N,N'*-diphenyl diimine derivative **2b** (Scheme 2) was attempted, and a yellow compound was obtained following column chromatography. NMR spectroscopy showed lower symmetry than expected, and a single exchangeable proton was confirmed by a D<sub>2</sub>O shake. Mass spectrometry data indicated a molecular formula identical to that expected for **2b**. Single crystal X-ray analysis elucidated the structure, wherein the thioindigo diimine is reduced and substitution by one amine at the ortho position on a neighboring phenyl ring has occurred, giving rise to the polycyclic product **3**. By replacing the ortho-hydrogens of the aniline with methyl groups, we hoped to avoid the cyclization reaction. 2,4,6-Trimethylaniline was chosen as the replacement amine and was submitted to the reaction conditions. No cyclized product was observed, but neither was the desired diimine. Instead, two major products, separable by column chromatography, were found to incorporate a single amine. Proton NMR and single crystal X-ray analysis revealed one of the compounds to be a monoimine derivative of thioindigo **4c** while the other was thioindirubin derivative **5c** (Figures S1 and S2, Supporting Information). Lengthening the reaction time did not provide addition of a second amine. Another amine chosen to avoid cyclization, *tert*-butylamine, gave yet a different product, a diamine, **1a**, which was isolated in 54% yield. Minor products isolated were the monoamine and thioindirubin derivatives (identified by NMR comparison with the trimethylaniline products).

In the metal-mediated reaction, there are significant differences in reactivity between indigo and thioindigo. The titanium tetrachloride reaction with indigo consistently yields the desired diimine<sup>33,35</sup> but thioindigo products vary. Formation of cyclized product **3** was initially thought to be aided by the known photoinduced isomerization of thioindigo. However, **3** was the major product even when the reaction was run in the dark. Standard conditions for the reaction used an excess of amine (3.1 equiv) and DABCO (9 equiv), both of which could be active in reduction of the imine, and as a source of H<sup>+</sup> in the amine formation. (DABCO is used to remove the HCl generated by reaction of the amine and titanium tetrachloride). Reducing the number of equivalents of aniline to 2.2 did not prevent formation of **3** or otherwise change the outcome of the reaction. Exchanging DABCO for a base with a higher p*K*<sub>a</sub> could potentially promote formation of diimine over diamine, but the options are limited because a bridgehead nitrogen is necessary to avoid reduction of the titanium and formation of polymeric amine byproduct.<sup>34</sup>

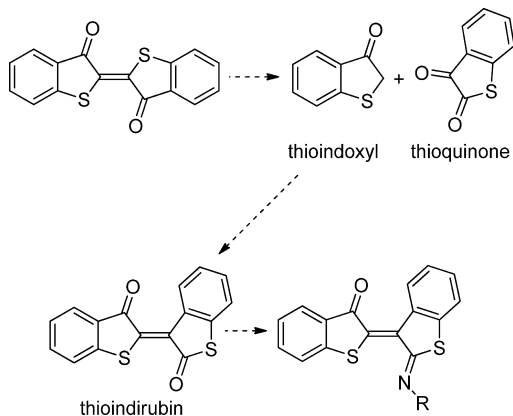
The isolation of a thioindirubin derivative **5** is striking. Its formation as a major product in the case of the sterically hindered 2,4,6-trimethylaniline, a very minor product in the case of *tert*-butylaniline, and its absence in the case of aniline, may suggest a steric component to the formation. Thioindirubins can be made by reaction of thioquinone and thioindoxyl.<sup>38</sup> One speculative scenario for the formation of **5**, albeit unlikely, given

## Scheme 2. Synthesis of Diamines 1a,b and Diimines 2a,b from Thioindigo



the air-free reaction conditions, is that thioquinone and thioindoxyl are formed and react with each other to give thioindirubin and then imine formation occurs (Scheme 3).

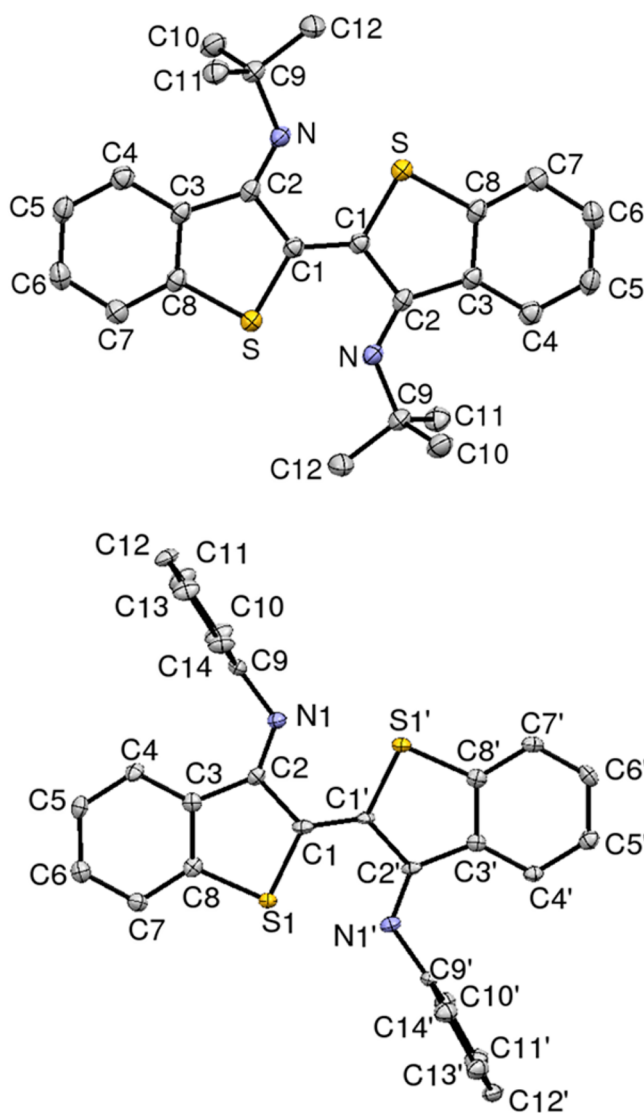
## Scheme 3. Possible Mechanism for Formation of Compounds 5



Another mechanistic possibility invokes a titanium-mediated metathesis pathway in which imine formation and cleavage of the central double bond occur simultaneously, followed by a second metathesis reaction giving the thioindirubin 5 and titanium oxide.

Formation of the diimines 2 was accomplished via two different synthetic pathways. Diamine 1a was converted to the desired diimine 2a (78% yield) by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The diimine 2b was obtained in an unorthodox manner, by subjecting the filtered reaction mixture containing cyclized product 3 to an air or oxygen atmosphere. This slowly results in formation of the diimine, and disappearance of 3, presumably through an oxidative mechanism. Diamine 1b has been isolated from this solution and may be an intermediate in the synthesis of 2b, although the formation of 1b by reduction of 3 seems unlikely given the oxidizing conditions. Diamine 1b has been subjected to oxidation with DDQ and forms 2b in high yields.

**X-ray Analyses.** The structures of 2a and 2b are shown in Figure 1. The  $\pi$ -conjugated core of both derivatives is, within experimental error, planar as expected. Compounds 2a and 2b have C1–C1' bond lengths of 1.361(4) and 1.350(4) Å, C1–C2 bond lengths of 1.486(3) and 1.481(5) Å, and C2–N1 bond lengths of 1.280(2) and 1.286(5) Å, respectively, in agreement with their assignment as the diimines. The C1–S1 bond lengths

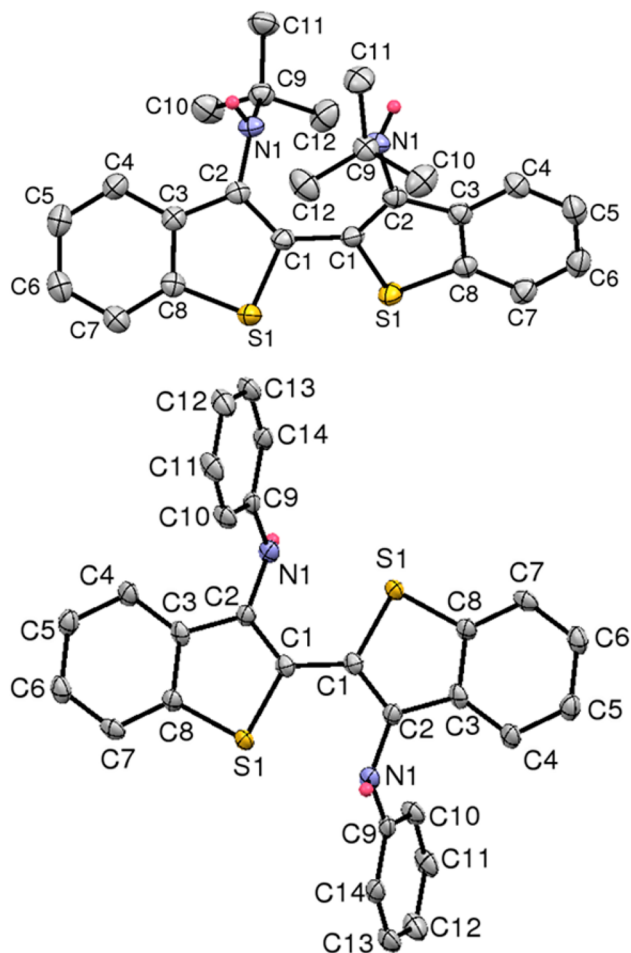


**Figure 1.** X-ray crystal structures of di-*tert*-butyl diimine 2a (top) and diphenyl diimine 2b (bottom). Hydrogen atoms have been removed for clarity. Thermal ellipsoids are presented at 50% probability.

for 2a,b are 1.743 and 1.747 Å. The C9 of the substituents is almost in plane with the core structure of the diimines; the torsion angles around C9–N1–C2–C1 are 178.75(18)° and 175.5(4)° in the *tert*-butyl and phenyl compounds. The orientation of the phenyl ring of 2b is almost perpendicular to

the core, with a torsion angle of  $88.85^\circ$  around  $C2'-N1'-C9'-C10'$ . The  $C1-C1'$ ,  $C1-C2$ , and  $C-S$  bond lengths of the diimines are comparable to those found in thioindigo derivatives.<sup>39</sup>

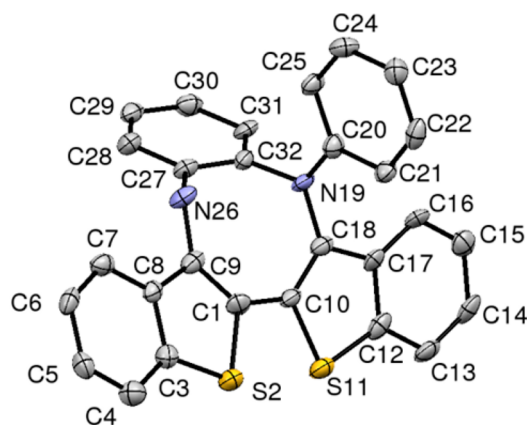
The structures of diamines **1a** and **1b** are shown in Figure 2. Diamines **1a,b** have bond lengths consistent with their canonical



**Figure 2.** X-ray structures of di-*tert*-butyl diamine **1a** (top) and diphenyl diamine **1b** (bottom). Hydrogen atoms except for the NH protons have been removed for clarity. Thermal ellipsoids are presented at 50% probability.

representations. The  $C1-C1$  bond lengths are  $1.460(3)$  and  $1.454(9)$  Å and indicate a central single bond while the  $C1-C2$  bond lengths of  $1.371(2)$  and  $1.369(7)$  Å signify double bonds. The  $C2-N1$  bond lengths  $1.416(2)$  and  $1.416(6)$  stipulate an amine. In the solid state, the diamines adopt different configurations in regard to rotation around the central  $C1-C1$  bond. In the *tert*-butyl derivative **1a**, the  $S1-C1-C1-S1$  torsion angle is  $46.5(2)^\circ$  while in the phenyl derivative **1b** the angle is  $180.0^\circ$ . The substituents in the diamines are out-of-plane with the central rings, as evidenced by the  $C9-N1-C2-C1$  torsion angles,  $91.87(19)^\circ$  for **1a** and  $-113.2(6)^\circ$  for **1b**. Additionally, the phenyl substituent in **1b** is twisted with regard to the core, with a  $C2-N1-C9-C10$  torsion angle of  $19.39^\circ$ .

The structure of compound **3** was determined (Figure 3). The structure identified the new connectivity between  $N19-C32$ , the single bond at  $C1-C10$  ( $1.453(10)$  Å), and  $C9-N26$  ( $1.408(9)$  Å). The slightly twisted conformation around the

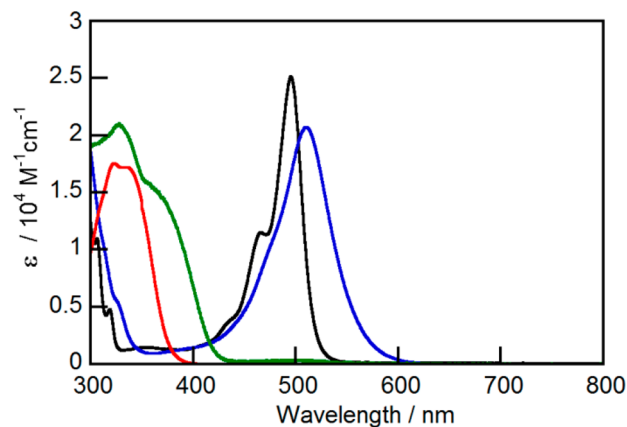


**Figure 3.** X-ray structure of cyclized product **3**. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are presented at 50% probability.

central  $C1-C10$  bond is evidenced by the  $S2-C1-C10-C18$  torsion angle of  $-159.7(7)^\circ$ .

**Photophysical Studies.** Compounds **1a,b** and **2a,b** were studied by absorption spectroscopy, fluorescence, and laser flash photolysis to determine their excited-state behavior. Comparisons of the photophysical properties of **1a,b** and **2a,b** to those of thioindigo are provided; the structural similarities between diimines **2a,b** and thioindigo are apparent and, while the structures of **1a,b** are markedly different, the juxtaposition of their properties with those of **2a,b** and thioindigo is provided as context for readers interested in potential photophysical or materials applications of these compounds.

**Diamines.** Diamine **1a** absorbs in the ultraviolet region with a maximum at 324 nm and an extinction coefficient at this wavelength of  $(1.75 \pm 0.04) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  in methanol (Figure 4 and Table 2). The compound is fluorescent and has a



**Figure 4.** Absorption spectra of **1a** (red) and **1b** (green) in methanol, and **2a** (black) and **2b** (blue) in toluene.

fluorescence maximum at 451 nm in methanol. The Stokes shift in methanol is  $8690 \text{ cm}^{-1}$  (Figure 5). The fluorescence maximum is red-shifted slightly with increasing solvent polarity, e.g., by 14 nm on changing solvents from cyclohexane to acetonitrile (Figure S3, Supporting Information). Upon cooling to 77 K, the fluorescence maximum is blue-shifted approximately 50 to 60 nm (Figure S4, Supporting Information).

The fluorescence quantum yield of **1a** at room temperature is  $0.25 \pm 0.01$  in methanol (three independent experiments). The



Table 2. Absorption and Emission Properties of Thioindigo Derivatives

	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$	$\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1} \text{ }^a$	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	$\Phi_f \text{ }^a$	$\tau_f/\text{ns} \text{ }^b$	solvent
1a	324	$1.75 \pm 0.04$	451	$0.25 \pm 0.01$	$1.81 \pm 0.06$	methanol
1b	328	$2.1 \pm 0.2$	449	$0.045 \pm 0.004$	$0.5 \pm 0.1$	methanol
2a	495	$2.4 \pm 0.1$	N/A	N/A	N/A	toluene
2b	510	$2.1 \pm 0.1$	N/A	N/A	N/A	toluene

<sup>a</sup>The errors in the molar extinction coefficients and fluorescence quantum yields correspond to the standard deviation of three independent experiments. <sup>b</sup>The errors in the lifetimes correspond to the average errors for two independent experiments.

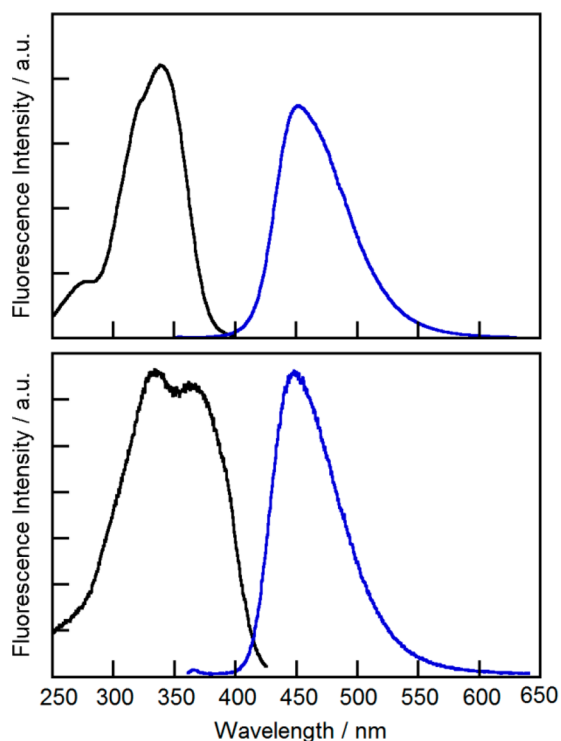


Figure 5. Top panel: Fluorescence excitation (black line) and emission (blue line) spectra of **1a** in methanol at room temperature. Bottom panel: Fluorescence excitation (black line) and emission (blue line) spectra of **1b** in methanol at room temperature.

fluorescence lifetimes in varying solvents were measured in the presence and absence of air. The decays were found to be single exponential, and the lifetimes range from 1.23 ns in cyclohexane to 2.13 ns in acetone in deaerated solvents (Table S1, Supporting Information). The fluorescence excitation spectrum and the absorption spectrum show good overlap.

Diamine **1b** has absorbance and emission profiles similar to that of **1a**. The absorbance maximum is red-shifted by 4 nm to 328 nm compared to **1a**, but a second peak is observed for **1b**. The emission maximum is almost identical, at 449 nm (versus 451 nm for **1a**). The Stokes shift is still large ( $8220 \text{ cm}^{-1}$ ), but slightly more overlap is observed between the excitation and emission spectra (Figure 5). The fluorescence lifetime was found to be 0.5 ns in methanol, and the quantum yield is correspondingly lower than **1a**:  $0.045 \pm 0.004$  at room temperature. We believe the differences in both fluorescence quantum yields and lifetimes between **1a** and **1b** can be ascribed to the different amine substituents. The phenyl substituent in **1b** leads to some additional degree of conjugation with the rest of the molecule based on the slight red shift in absorption maxima of **1b** relative to **1a**. Therefore, in the excited state the rotation of the phenyl ring can lead to an additional deactivation pathway

through internal conversion, thereby shortening the excited-state lifetime.<sup>40</sup> The roughly 3-fold increase in fluorescence intensity for **1b** at 77 K compared to room temperature (Figure S5, Supporting Information) is consistent with this argument. The 77 K emission maximum of **1b** is blue-shifted 18 nm relative to the room temperature maximum (Figure S5, Supporting Information).

The large blue shift to the UV observed in the absorption spectra for diamines **1a,b** compared to diimines **2** is consistent with the destruction of planarity coincident with diimine reduction and rotation around the resulting central single bond. The loss of planarity is also demonstrated in the crystal structure of **1a** (see above). The molar extinction coefficient for **1a** is higher than that of thioindigo but lower than the diimines. The large Stokes shift for **1a,b** reveals a substantial change in geometry between the  $S_0$  and  $S_1$  states, while the small red-shift in emission maxima found in solvents of increasing polarity suggests a relatively nonpolar excited state.

The fluorescence lifetimes of **1a** and **1b** (1.81 and 0.5 ns, respectively) are substantially shorter than that of thioindigo compared to values of  $12.3 \text{ ns}^4$  and  $13.4 \text{ ns}^3$  reported for thioindigo in toluene. Both diamines show kinetics that correspond to single exponential decays. Similarly, the quantum yield is much lower in **1a** (0.25) and **1b** (0.045) than thioindigo (0.70 to 0.73 depending on solvent).<sup>4</sup>

Transient absorption spectroscopy experiments on **1a** show a triplet excited state with an  $18 \mu\text{s}$  lifetime and a single exponential decay. The transient absorption spectrum (Figure 6) shows a ground-state bleaching at 340 nm and a positive transient absorption at 440 nm. Oxygen-quenching experiments confirm the triplet state, giving a quenching rate constant  $k_q$  of  $(3.24 \pm 0.04) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (one independent experiment; the error is from the fitting software used for eq S1, Supporting

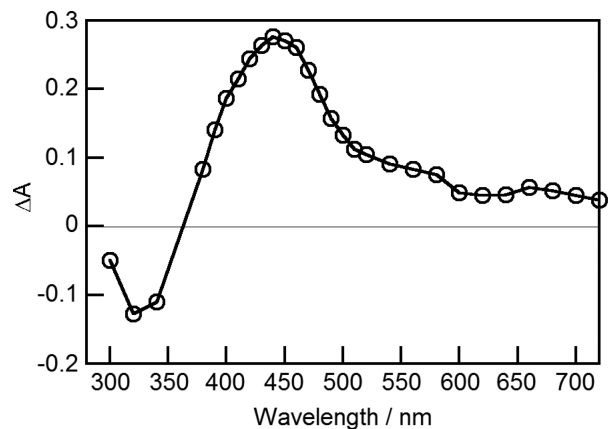
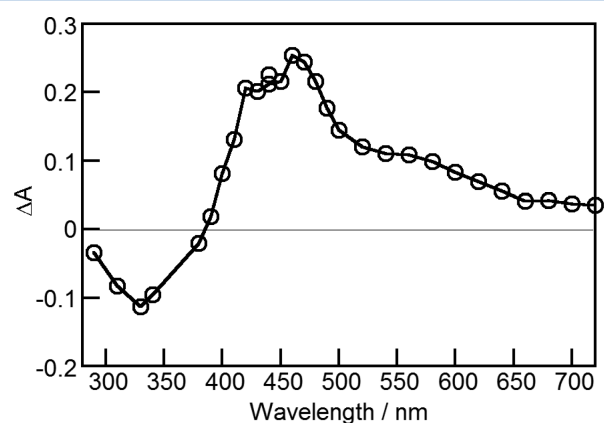


Figure 6. Transient absorption spectrum of **1a** in toluene ( $7.8 \times 10^{-5} \text{ M}$ ) integrated between 1.0 and 2.0  $\mu\text{s}$  after the laser pulse. Laser excitation at 355 nm.

Information), Figure S6, Supporting Information. The energy of the ground state to first excited-state transition for oxygen is 94 kJ/mol.<sup>41</sup> Because this energy is low, and the ground state of oxygen is a triplet, most triplet states of organic molecules can be quenched by oxygen. The quenching rate constant of **1a** is  $(3.24 \pm 0.04) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , meaning that the quenching is close to the diffusion limit. (The diffusion rate constant for toluene is  $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .)<sup>41</sup> Together, these results indicate that the transient observed in the laser flash photolysis studies is a triplet excited state. By performing a series of quenching experiments on **1a** using triplet quenchers with sequentially higher triplet energies, the  $E_T$  of **1a** was determined to be approximately 220 kJ mol<sup>-1</sup>, with an upper bound of 240 kJ mol<sup>-1</sup> (Table S2 and Figures S6–S9, Supporting Information).

Similar to **1a**, **1b** exhibits a transient absorption spectrum with a ground-state bleaching at approximately 340 nm and a positive transient absorption at 460 nm (Figure 7). The transient species



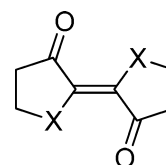
**Figure 7.** Transient absorption spectrum of **1b** in toluene ( $8 \times 10^{-5} \text{ M}$ ) integrated between 2.0 and 4.4  $\mu\text{s}$  after the laser pulse. Laser excitation at 355 nm.

has a 22  $\mu\text{s}$  lifetime and a single exponential decay (Figure S10, Supporting Information) and exhibits an oxygen-quenching rate constant consistent with a triplet state ( $(3.1 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), analogous to the transient spectroscopy of **1a**.

The triplet excited-state species observed in the transient absorption spectra of **1a** and **1b** have significantly longer lifetimes (18 and 22  $\mu\text{s}$ , respectively) than the triplet state observed for thioindigo, which is reported as 135 to 428 ns depending on the solvent.<sup>4,42–44</sup> The  $k_q$  values of  $3.24 \times 10^9$  and  $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (for **1a** and **1b**, respectively) found in oxygen-quenching experiments are on par with those found for thioindigo ( $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $2.12 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  depending on solvent).<sup>4,42</sup>

**Diimines.** Diimines **2a** and **2b** absorb in the visible region (Figure 4). The absorption maxima corresponding to the lowest energy band are 495 and 510 nm, respectively, in toluene. Molar extinction coefficients at the lowest energy absorption maxima are  $(2.4 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $(2.1 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (**2a**, **2b**). No emission is observed at room temperature or 77 K for either molecule. The spectral data are shown in Table 2.

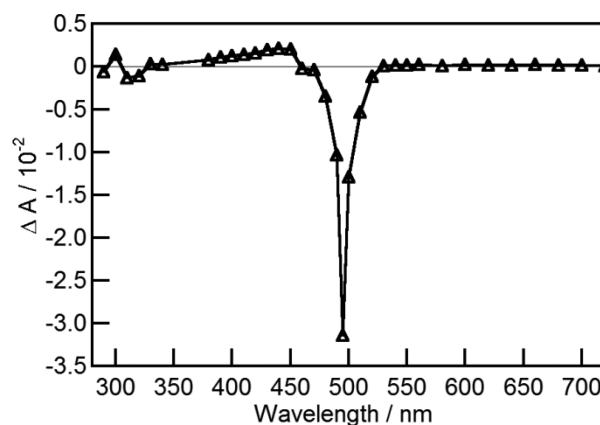
The absorbance maxima of diimines **2a,b** are blue-shifted by 47 and 32 nm from thioindigo. The relatively low energy absorption maximum of thioindigo (542 nm in toluene)<sup>4</sup> is due to the central cross-conjugated sulfur-to-oxygen structural motif, or “H-chromophore”<sup>45</sup> (Figure 8). X-ray crystal structures show that the planar structure of the central scaffold is maintained in



**Figure 8.** “H-chromophore” of thioindigo ( $X = \text{S}$ ) and indigo ( $X = \text{NH}$ ).

**2a,b**. The solid-state planarity is most likely conserved in solution, suggesting that the blue shift is caused by a disruption of the H-chromophore due to the weaker electronegativity of the imine nitrogen. The nature of the imine substituent only mildly affects the wavelength of the absorption maxima due to the out-of-plane geometry of the substituents. The  $\epsilon$  values of **2a,b** are between 17% and 70% higher than that of thioindigo, which in toluene has reported molar extinction coefficients of  $(1.4 \text{ and } 1.8) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>4,46</sup> Fine structure is observed in the absorbance spectrum of **2a**. In contrast, **2b** is broadened and lacks fine structure.

The transient absorption spectrum of **2a** (Figure 9) shows a ground-state bleaching at 495 nm and a positive transient

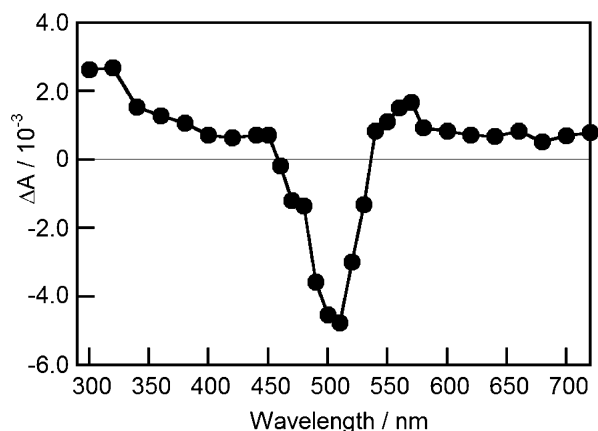


**Figure 9.** Transient absorption spectrum of **2a** in toluene ( $5.7 \times 10^{-5} \text{ M}$ ), integrated between 132 and 391 ns after the laser pulse. Laser excitation at 355 nm.

absorption at 440 nm. A 1.5  $\mu\text{s}$  transient lifetime is observed in both toluene and acetonitrile (laser excitation at 355 and 266 nm, respectively). The lifetime is unchanged when oxygen is removed from the solution. The transient absorption spectrum in acetonitrile (Figure S11, Supporting Information) has an identical shape, but the features are blue-shifted approximately 5 nm from the toluene spectrum. This is consistent with the blue shift observed in the ground-state absorption spectrum.

Because of poor solubility in acetonitrile and very low ground-state absorbance at 355 nm, LFP experiments on **2b** were performed in dichloromethane with laser excitation at 266 nm. These experiments reveal a transient species with a 29  $\mu\text{s}$  lifetime. As we observed with **2a**, the lifetime is unchanged when oxygen is removed from the solution. The transient spectrum shows a ground-state bleaching at approximately 510 nm (Figure 10).

The lack of emission from the diimines was unexpected based on the known emissive properties of thioindigo. Originally, the reformation of the central double bond (and planarization of the core structure) was hypothesized to improve fluorescence intensity compared to the diamines. Thioindigo is highly



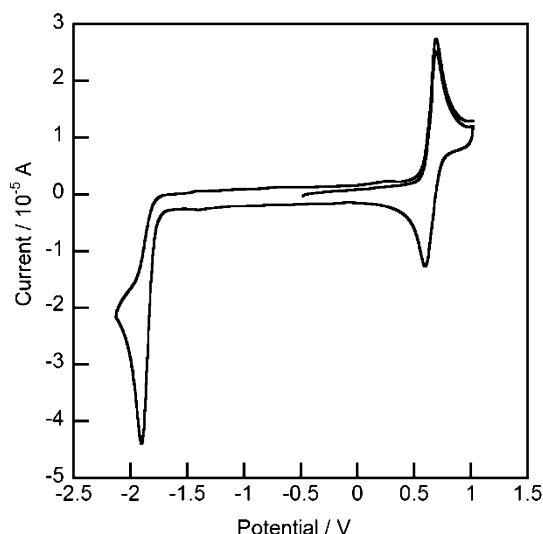
**Figure 10.** Transient absorption spectrum of **2b** in dichloromethane ( $2.2 \times 10^{-5}$  M), integrated between 852 ns and 3.70  $\mu$ s after the laser pulse. Laser excitation at 266 nm.

emissive, with a fluorescence quantum yield of 0.70 to 0.73 depending on solvent.<sup>3,4</sup> Trans–cis isomerization competes with fluorescence as a decay pathway in thioindigo. Photoisomerization is media dependent, with an upper limit of  $\Phi_{\text{trans} \rightarrow \text{cis}} = 0.11$  and occurs via intersystem crossing to a triplet state.<sup>3,42,44</sup> *cis*-Thioindigo exhibits a blue-shifted absorption maximum at 485 nm<sup>47</sup> and is metastable.<sup>48</sup> The lifetimes of the transient species observed for **2a,b** are unchanged in oxygen-quenching experiments, ruling out a triplet-state or radical species. The lack of sensitivity to oxygen in the quenching experiments is consistent with the formation of a *cis*-thioindigo-type (i.e., isomerism about the central C=C bond) isomer. The bleaching of the  $S_0 \rightarrow S_1$  absorption (495 nm) and blue-shifted positive absorption (440 nm) in the transient absorption spectrum supports the assignment of the transient to a *cis* isomer. Together, these features indicate that isomerism may be responsible, at least in part, for the diimines' lack of fluorescence. However, we cannot completely rule out the possibility that imine (C=N) isomerism could be occurring instead, although confirmed examples of this are quite rare due to the very fast reversion of the photoexcited *cis* form of the imine back to the *trans*.<sup>49,50</sup>

Another possible cause for the lack of emission must also be considered. Recent mechanistic studies have shown that intramolecular photoinduced electron transfer (PET) can quench fluorescence in compounds that contain imine moieties.<sup>51,52</sup> The diimines **2a,b** contain the structural motifs that make this quenching mechanism possible. However, the complete lack of emission from the diimines hinders further evaluation of this mechanism because of the requirement for the energy difference between the ground and excited states in the Rehm–Weller equation.

**Redox Behavior.** Cyclic voltammetry was used to characterize the redox behavior of the diimines **2a,b** and for comparison thioindigo was also analyzed. (Only one report on the electrochemistry of thioindigo exists in the literature; the experiments were performed in DMF).<sup>53</sup> Because of solubility considerations, the experiments were performed in dichloromethane.

The *tert*-butyl diimine **2a** exhibits a quasireversible one-electron oxidation peak at  $E_1^\circ = 0.66$  V vs ferrocene (Figure 11). An irreversible two-electron reduction peak is observed at  $-1.91$  V. Scanning to higher potentials leads to additional irreversible processes, and the 0.66 V also becomes irreversible. Like **2a**,



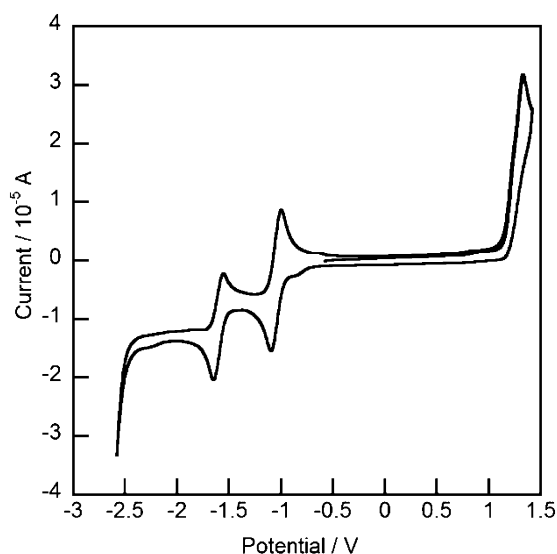
**Figure 11.** Cyclic voltammogram of diimine **2a** in dichloromethane,  $\sim 1$  mM analyte. The standard is  $\text{Fc}^+/\text{Fc}$ , the electrolyte is 0.1 M  $\text{Bu}_4\text{NBF}_4$ , and the scan rate is 100 mV/s.

diphenyl diimine **2b** has two one-electron oxidation peaks. The first is at 0.87 V vs ferrocene, and the second appears at the edge of the solvent window at approximately 1.3 V (Figure S12, Supporting Information). The oxidation peaks at the edge of the dichloromethane solvent window in **2a,b** could not be further investigated because of compound insolubility in the appropriate solvents (e.g., acetonitrile). Unlike the first oxidation in the *tert*-butyl diimine, the oxidation of **2b** at 0.87 V is irreversible, even if the switching potential is set before the onset of the second oxidation. A two-electron reduction at  $-1.55$  V is noted for diimine **2b**. The more facile nature of the reduction in **2b**, compared to that for **2a**, is accounted for by the greater ability of the phenyl substituent to delocalize the negative charge. The reduction and oxidation processes for **2b** are more closely spaced than in **2a**.

In contrast with the diimines, thioindigo has two one-electron reversible reduction processes ( $E_1^\circ = -1.1$  V;  $E_2^\circ = -1.6$  V vs  $\text{Fc}/\text{Fc}^+$ ). An irreversible two-electron oxidation process is visible at the edge of the solvent window (Figure 12). The less positive potential of the oxidation peaks in the diimines can be explained in terms of the lower electronegativity of the imine nitrogens compared to the thioindigo oxygens. Likewise, the thioindigo reduction peaks occur at more positive potentials than the diimines because of the more electronegative nature of the oxygen atoms.

## CONCLUSIONS

The first examples of substituted diimine and diamine derivatives of thioindigo have been synthesized in a two-step sequence, in good yields. The diamine compounds were found to retain some of the fluorescent nature of thioindigo, exhibiting moderate quantum yields. Surprisingly, the diimines were not fluorescent, despite the restoration of a rigid core-structure similar to that of thioindigo. Investigation into the excited-state characteristics of the diimines revealed a transient species consistent with the formation of a *cis* isomer. The trans–cis isomerization may be responsible for the absence of fluorescence; however, photoinduced electron transfer cannot be ruled out as a contributing factor. The diimine compounds were found to be redox-active. The redox-active nature of the



**Figure 12.** Cyclic voltammogram of thioindigo in dichloromethane, ~1 mM analyte. The standard is  $Fc^+/Fc$ , the electrolyte is 0.1 M  $Bu_4NBF_4$  and the scan rate is 100 mV/s.

diimines suggests that they are potential ligands for metal coordination complexes. Complexes where the diimines behave as bidentate ligands through the nitrogen and sulfur bonds may also have the dual effect of stabilizing the central C–C double bond and inhibiting PET to the imine, thereby restoring fluorescence.

## EXPERIMENTAL SECTION

**General Synthetic Methods.** The reagents used were commercially available. With the following exceptions, reagents were used without purification. Bromobenzene was dried over calcium hydride and distilled before use. Aniline, *tert*-butyl amine, and 2,4,6-trimethylaniline were purified by vacuum distillation.

$^1H$  NMR and  $^{13}C$  NMR were recorded at ambient temperature at a frequency of 360 or 300 MHz, and 90 or 75 MHz, respectively. The data are reported as follows: proton multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), coupling constants, and integration. Melting points are reported uncorrected. Flash chromatography was performed using the indicated solvent system on silica gel ( $SiO_2$ ) 60 (70–230 mesh). CV experiments were performed using a three-electrode setup consisting of a glassy carbon working electrode, platinum electrode, and silver quasireference electrode. Ferrocene was used as an internal reference. Electrolyte (tetrabutylammonium fluoride) was purified and dried prior to use.

**General Photophysical Methods.** Fluorescence measurements were made using a PTI QM-2 fluorescence spectrophotometer. Room temperature spectra were obtained using a 10 mm  $\times$  10 mm quartz fluorescence cell. Low temperature spectra were obtained using a special low-temperature fluorescence cell. The solution of compound in ethanol was placed in a 2 mm diameter quartz sample tube and frozen by immersion in a liquid-nitrogen-filled cell. The sample was inspected for homogeneity, and fluorescence measurements were taken. Control measurements (ethanol alone, and sample at room temperature) were obtained using the same apparatus. The step size was 0.5 nm, and the excitation and emission monochromator slits were set to 2 nm or 3 nm bandwidths. For emission spectra of **1a** and **1b**, the excitation wavelengths were 320 to 322 and 328 nm, respectively. For excitation spectra of **1a** and **1b**, the emission wavelengths were 440 or 450 nm and 430 or 450 nm, respectively. Fluorescence decays were recorded with an Edinburgh OB 920 single photon counter. Decays were recorded with 10 mm  $\times$  10 mm long-stem fluorescence cells. The excitation wavelength was 335 nm using a light-emitting diode (Edinburgh

Instruments EPLED-330). The emission wavelength was 450 nm unless otherwise noted. Emission slits were set to achieve 16 nm in bandwidth. The number of counts in the maximum intensity channel was 2000. The instrument response function was recorded using a Ludox solution where the emission was detected at the same wavelength as the excitation wavelength. Laser flash photolysis experiments were excited with a Nd:Yag laser at either 266 or 355 nm.<sup>54</sup> A 7 mm  $\times$  7 mm quartz cell was used for LFP experiments. Fluorescence quantum yields were measured using quinine bisulfate in 1 N sulfuric acid as the standard ( $\Phi_F = 0.546$ ).<sup>55</sup> Spectrograde or higher purity solvents were used for all photophysical experiments. 1,3-Cyclohexadiene was used in the triplet-quenching experiments and was distilled prior to use. Oxygen-free solutions were obtained by bubbling nitrogen gas through the sample solution in the cell for at least 20 min.

**Fluorescence Quantum Yield Measurements.** Standard and unknown solutions for quantum yield measurements were prepared to give matched ( $\pm 0.002$ ) absorbance values of approximately 0.1 at the excitation wavelength. The absorbance and fluorescence measurements were obtained with nitrogen-purged samples.

After the solutions were matched and the fluorescence spectra recorded, two matching serial dilutions (using nitrogen purged solvent) were made to obtain a minimum of three data points. The fluorescence spectra of the dilutions were also obtained.

Each experiment was independently performed three times, and each experiment yielded three quantum yield values, according to the equation<sup>56</sup>

$$\Phi_u = \left[ \frac{A_s F_u \eta_u^2}{A_u F_s \eta_s^2} \right] \Phi_s \quad (1)$$

where  $A$  is the absorbance at the excitation wavelength,  $F$  is the integrated area of the emission band,  $\eta$  is the refractive index of the solvent, and the subscript  $u$  refers to the unknown, and subscript  $s$  to the standard.

**Molar Absorptivity Measurements.** To obtain molar absorptivities for each of the compounds, a stock solution and three serial dilutions were made, and the corresponding absorbances for each major absorption band were recorded. At least four concentrations were prepared for each absorption band. The experiment was repeated at least three times on separate days. By graphing the absorbance value of the band maximum against the concentration (Beer–Lambert law), the molar absorptivity was determined from the slope of the graph.

**Synthesis.** 5-Phenyl-5,10-dihydrobenzo[b]benzo[4,5]thieno[3,2-*e*]benzo[4,5]thieno[2,3-*g*][1,4]diazocine (**3**). Bromobenzene (90 mL), aniline (1.4 mL, 15.8 mmol), and diazabicyclooctane (5.2 g, 45.9 mmol) were added to a flask. The flask was evacuated and backfilled with nitrogen three times. Titanium tetrachloride (1.0 M in toluene, 11.7 mL, 11.7 mmol) was added slowly to the clear solution. Upon addition, a brown precipitate formed and fuming occurred. After the fuming subsided, thioindigo (1.5 g, 5.1 mmol) was added in portions to ensure good mixing. The reaction was heated to reflux and aged overnight. The reaction was filtered hot, rinsing the filtercake with ethyl acetate until the filtrate ran colorless. After crystallization of **1b** (see below), the filtrate was concentrated under vacuum. The filtrate was preabsorbed on silica gel and chromatographed using, sequentially, eluent compositions of 7:1, 5:1, and 1:1 hexanes/dichloromethane. A yellow solid was obtained (0.78 g, 35%). Crystals suitable for X-ray analysis were grown by slow evaporation of a solution formed by layering dichloromethane and hexanes; mp 240–242 °C;  $^1H$  NMR (360 MHz,  $CDCl_3$ )  $\delta$  7.77 (dd,  $J = 6.1, 2.7$  Hz, 1 H), 7.72–7.65 (m, 2H), 7.55–7.50 (m, 2H), 7.38–7.29 (m, 4H), 7.20 (td,  $J = 7.7, 1.5$  Hz, 1H), 7.04 (td,  $J = 7.0, 1.8$  Hz, 2H), 6.95–6.88 (m, 2H), 6.64 (tt,  $J = 7.3, 1.0$  Hz, 1H), 6.51 (dd,  $J = 8.8, 1.0$  Hz), 5.81 (s, 1H);  $^{13}C$  NMR (90 MHz,  $CDCl_3$ )  $\delta$  147.8, 142.2, 138.4, 137.8, 136.6, 135.7, 135.1, 135.0, 134.5, 133.1, 132.7, 129.2, 129.0, 125.6, 125.1, 124.9, 124.4, 123.0, 122.9, 122.7, 122.4, 121.7, 119.4, 117.8, 113.3, 110.4; IR (thin film) 3400  $cm^{-1}$ . Anal. Calcd for  $C_{28}H_{18}N_2S_2$ : C, 75.30; H, 4.06; N, 6.27. Found: C, 74.99; H, 4.01; N, 6.29.

**3,3'-Bis(*tert*-butylamino)-2,2'-bithianaphthene (**1a**).** Bromobenzene (60 mL), *tert*-butylamine (1.1 mL, 10.4 mmol), and



diazabicyclooctane (3.4 g, 30.3 mmol) were added to a flask. The flask was evacuated and backfilled with argon three times. Titanium tetrachloride (1.0 M in toluene, 7.8 mL, 7.8 mmol) was added dropwise to the clear, colorless solution. Upon addition, a greenish-brown precipitate formed along with vigorous fuming. After the fuming subsided, thioindigo (1.0 g, 3.4 mmol) was added in portions to ensure good mixing. The reaction was heated to reflux and aged overnight. The reaction was filtered while warm, rinsing the filtercake with diethyl ether until the filtrate ran colorless. The filtrate was concentrated under vacuum. The filtrate was preabsorbed on silica gel and chromatographed using 100% dichloromethane and then switching to 1:1 ethyl acetate/hexanes. Chromatography afforded a tan solid (0.75 g, 54%). Crystals suitable for X-ray analysis were grown by slow evaporation of a solution formed by layering acetone and hexanes; mp 196–198 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (dd,  $J = 6.9, 1.2$  Hz, 2H), 7.73 (dd,  $J = 7.0, 1.3$  Hz, 2H), 7.39–7.28 (m, 4H), 4.40 (s, 2H), 1.01 (s, 18H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 139.0, 136.6, 127.5, 124.6, 123.9, 122.6, 122.4, 56.0, 30.3; IR (KBr) 3318, 3228  $\text{cm}^{-1}$ ; HRMS (ESI-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{24}\text{H}_{29}\text{N}_2\text{S}_2$  409.1767; found 409.1768.

**Thioindigo-*N,N'*-bis(*tert*-butyl)diimine (2a).** Amine **1a** (0.50 g, 1.2 mmol) was dissolved in dichloromethane (50 mL). The solution was treated with 2,3-dichloro-5,6-dicyanobenzoquinone (0.30 g, 1.3 mmol). The reaction was stirred for 3 h, diluted with dichloromethane to dissolve the orange precipitate, and washed with 1 M NaOH ( $2 \times 30$  mL) and water ( $2 \times 30$  mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to an orange solid (0.38 g, 78%). Crystals suitable for X-ray analysis were grown by slow evaporation of a solution formed by layering dichloromethane and hexanes; mp 236–239 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.1$  Hz, 2H), 7.44 (dd,  $J = 7.7, 1.5$  Hz, 2H), 7.28 (td,  $J = 7.5, 1.0$  Hz, 2H), 7.13 (td,  $J = 7.6, 1.2$  Hz, 2H), 1.67 (s, 18H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 151.4, 130.7, 130.3, 129.6, 126.9, 124.1, 124.0, 57.2, 29.9; IR (KBr) 1587, 1569  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{S}_2$ : C, 70.89; H, 6.45; N, 6.89. Found: C, 71.27; H, 6.37; N, 6.87.

**3,3'-Dianilino-2,2'-bithianaphthene (1b).** Bromobenzene (90 mL), aniline (1.4 mL, 15.8 mmol), and diazabicyclooctane (5.2 g, 45.9 mmol) were added to a flask. The flask was evacuated and backfilled with nitrogen three times. Titanium tetrachloride (1.0 M in toluene, 11.7 mL, 11.7 mmol) was added slowly to the clear solution. Upon addition, a brown precipitate formed and fuming occurred. After the fuming subsided, thioindigo (1.5 g, 5.1 mmol) was added in portions to ensure good mixing. The reaction was heated to reflux and aged overnight. The reaction was filtered hot, rinsing the filtercake with ethyl acetate until the filtrate ran colorless. The filtrate was concentrated on a rotary evaporator until the volume remained constant. Dichloromethane (100 mL) was added to the solution via addition funnel. After aging for 10 min, a fine precipitate was observed, the mixture was filtered, and the solid was collected and washed with dichloromethane, affording an off-white solid (0.46 g). The filtrate was then concentrated to dryness on a high vacuum rotavap. The residue was slurried in dichloromethane (50 mL). The resulting solid was filtered and washed with dichloromethane to give a second batch off-white solid (0.43 g). A combined yield of 0.89 g, 39% was obtained. Off-white solid; mp (turns red and then melts) 266–268 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 7.3$  Hz, 2H), 7.49 (d,  $J = 7.9$  Hz, 2H), 7.34 (td,  $J = 7.5, 1.3$  Hz, 2H), 7.29–7.24 (m, 2H), 7.18 (td,  $J = 7.0, 1.6$  Hz, 4H), 6.85 (tt,  $J = 7.4, 1.0$  Hz, 2H), 6.67 (dd,  $J = 8.6, 1.0$  Hz, 4H), 5.76 (s, 2H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  145.0, 138.4, 135.8, 131.6, 129.3, 126.2, 125.3, 124.3, 122.59, 122.57, 119.6, 114.9; IR (KBr) 3353  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{28}\text{H}_{20}\text{N}_2\text{S}_2$  448.1068; found 448.1071.

**Thioindigo-*N,N'*-diphenyldiimine (2b).** Method 1. Bromobenzene (30 mL), aniline (0.47 mL, 5.2 mmol), and diazabicyclooctane (1.70 g, 15.1 mmol) were added to a flask. The flask was evacuated and backfilled with argon three times. Titanium tetrachloride (1.0 M in toluene, 3.9 mL, 3.9 mmol) was added dropwise to the clear, colorless solution. After fuming subsided, thioindigo (1.0 g, 3.4 mmol) was added in portions to the brown, heterogeneous mixture. The reaction was heated to reflux and aged overnight. The reaction was filtered hot,

and the filtercake was washed with diethyl ether until the filtrate ran colorless. The filtrate was allowed to stand open to air for 4 weeks, after which time dichloromethane (42 mL) was added, followed by hexanes (40 mL). Aged overnight with stirring and filtered to give a red solid (0.44 g, 58%). **Method 2.** Bithianaphthene **1b** (1.0 g, 2.3 mmol) was dissolved in dichloromethane and treated with 2,3-dichloro-5,6-dicyanobenzoquinone (0.57 g, 2.5 mmol). The reaction was stirred for 1 h and then concentrated to a volume of approximately 30 mL by rotary evaporation. The reaction was filtered to give a red solid (0.83 g, 82%); mp 269–271 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.42 (m, 6H), 7.30 (td,  $J = 7.4, 1.4$  Hz, 2H), 7.21 (tt,  $J = 7.4, 1.2$  Hz, 2H), 7.02 (dd,  $J = 8.3, 1.1$  Hz, 4H), 6.94–6.83 (m, 4H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 150.1, 148.3, 131.4, 129.6, 127.3, 127.1, 124.7, 124.1, 123.7, 118.2; IR (KBr) 1588  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{18}\text{N}_2\text{S}_2$ : C, 75.31; H, 4.06; N, 6.27. Found: C, 75.50; H, 4.14; N, 6.24.

**Thioindigo-*N*-(2,4,6-trimethylphenyl)imine (4c).** Bromobenzene (60 mL), 2,4,6-trimethylaniline (1.4 mL, 10.4 mmol), and diazabicyclooctane (3.4 g, 30.3 mmol) were added to a flask under argon. Titanium tetrachloride (1.0 M in toluene, 7.8 mL, 7.8 mmol) was added dropwise to the clear, colorless solution. Upon addition, a green-black precipitate formed and fuming occurred. After the fuming subsided (approximately 10 min), thioindigo (1.0 g, 3.4 mmol) was added in portions to ensure good mixing. The reaction was heated to reflux and aged overnight. The reaction was then filtered hot, rinsing the filtercake with diethyl ether until the filtrate ran colorless. The filtrate was concentrated under vacuum. The resulting reddish-black solid was preabsorbed on silica gel and chromatographed using 1:2 dichloromethane/hexanes. A dark reddish-purple solid was isolated (0.12 g, 9%). Crystals suitable for X-ray analysis were grown by slow evaporation from deuterated chloroform; mp 178–181 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.6$  Hz, 1H), 7.59–7.49 (m, 3H), 7.41 (td,  $J = 7.6, 1.1$  Hz, 1H), 7.32 (td,  $J = 7.4, 1.0$  Hz, 1H), 7.01 (s, 2H), 6.98 (dd,  $J = 7.2, 0.9$  Hz, 1H), 6.88 (d,  $J = 7.6$  Hz, 1H), 2.39 (s, 3H), 2.05 (s, 6H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  189.3, 162.8, 150.3, 145.4, 145.2, 138.6, 134.7, 133.5, 132.7, 130.0, 129.1, 127.4, 127.3, 126.4, 126.1, 126.0, 125.6, 124.2, 124.0, 123.8, 20.9, 18.0; IR (KBr) 1660, 1587  $\text{cm}^{-1}$ ; HRMS (EI)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{NOS}_2$  413.0908; found 413.0911.

**Thioindirubin-*N*-(2,4,6-trimethylphenyl)imine (5c).** Bromobenzene (60 mL), 2,4,6-trimethylaniline (1.4 mL, 10.4 mmol), and diazabicyclooctane (3.4 g, 30.3 mmol) were added to a flask under argon. Titanium tetrachloride (1.0 M in toluene, 7.8 mL, 7.8 mmol) was added dropwise to the clear, colorless solution. Upon addition, a green-black precipitate formed and fuming occurred. After the fuming subsided (approximately 10 min), thioindigo (1.0 g, 3.4 mmol) was added in portions to ensure good mixing. The reaction was heated to reflux and aged overnight. The reaction was then filtered hot, rinsing the filtercake with diethyl ether until the filtrate ran colorless. The filtrate was concentrated under vacuum. The resulting reddish-black solid was preabsorbed on silica gel and chromatographed using 1:2 dichloromethane/hexanes. A reddish-black solid was isolated (0.45 g, 33%). Crystals suitable for X-ray analysis were grown by slow evaporation of a solution formed by layering dichloromethane and hexanes; mp 192–194 °C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  9.59 (dd,  $J = 8.2, 1.0$  Hz, 1H), 7.92 (dd,  $J = 7.6, 0.4$  Hz, 1H), 7.57 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.44–7.28 (m, 5H), 6.98 (s, 2H), 2.35 (s, 3H), 2.14 (s, 6H);  $^{13}\text{C}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  189.8, 166.6, 148.6, 146.7, 138.5, 137.7, 136.9, 135.3, 134.4, 132.8, 131.4, 130.2, 129.0, 128.8, 126.8, 126.0, 125.9, 125.5, 123.7, 122.8, 20.9, 17.8; IR (KBr) 1671, 1588  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{NOS}_2$ : C, 72.61; H, 4.63; N, 3.39. Found: C, 72.48; H, 4.86; N, 3.42.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details, X-ray structures for compounds **4c** and **5c**, low temperature fluorescence for compounds **1a** and **1b** and absorbance spectra of **1a** in various solvents, transient spectra for compound **2a**, transient decay trace of **1b**, singlet lifetimes of **1a** in varied solvents, determination of  $E_T$  and oxygen-quenching

rate constants for **1a**, cyclic voltammogram of **2b**,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for compounds **1a,b**, **2a,b**, **3**, **4c**, **5c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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