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Synthetic Tuning of Electronic and Photophysical Properties of 2-Aryl-1,3-Benzothiaphospholes

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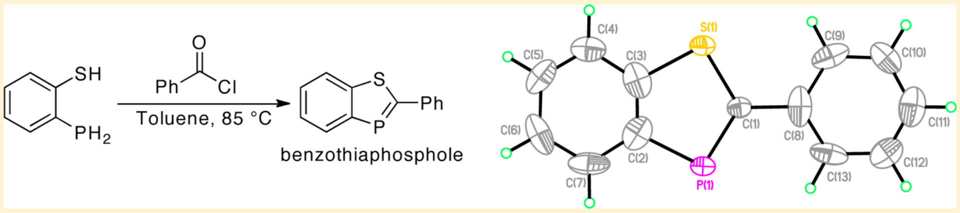
Supporting Information



ABSTRACT: A series of 2-aryl-1,3-benzothiaphospholes have been synthesized from 1-mercapto-2-phosphinobenzene and a variety of acid chlorides. The structure of 2-phenyl-1,3-benzothiaphosphole was established using X-ray diffraction. The electrochemical and photophysical properties of each benzothiaphosphole are reported and some of these molecules exhibit reversible 1-electron reductions.

INTRODUCTION

Organic π-conjugated materials have garnered enormous attention over the past 40 years as solution processable components for photovoltaics, light-emitting diodes, and field-effect transistors.[1] The incorporation of main group elements including boron,[2,3] silicon,[4] selenium,[5] tellurium,[6] and phosphorus[7] has evolved as a versatile strategy for tuning the electronic properties of π-conjugated architectures.

The use of phosphorus for this purpose is particularly intriguing due to its variable oxidation states and coordination modes. Recent reports of conjugated materials bearing phosphorus heterocycles include: dithienophospholes,[8] benzofuran-fused phospholes,[9] dibenzophosphapentaphenes,[10] biphospholes,[11] dithienodiketophosphepins,[12] and diazadibenzophosphole oxides[13] (several examples depicted in Figure 1). All of the structures shown in Figure 1 bear a 3-coordinate phosphorus atom and facile modulation of the solid-state packing and band gap can be achieved by oxidation, quaternization, or complexation of the phosphorus. Recent device fabrication with phosphole-based dopants has yielded light-emitting diodes capable of emitting white light.[14]

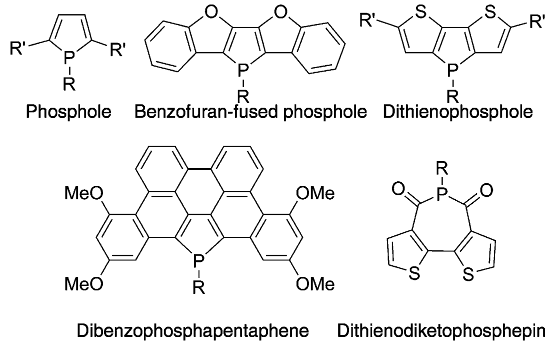


Figure 1. Several examples of π-conjugated building blocks that incorporate a 3-coordinate phosphorus atom.

The ability of phosphorus to form π-bonds[15] has led to the investigation of phosphaalkenes (P=C bonds) in extended conjugated structures. Gates[16] and Protasiewicz[17] both prepared poly(*p*-phenylene vinylene) (PPV) analogs where the vinyl unit between the phenyl groups in the polymer main chain was replaced by a P=C bond (Figure 2). Protasiewicz has also described a PPV analog with a diphosphene unit (P=P) between the aryl rings,[17a] and Ott has investigated P=C bonds in conjugation with acetylenic moieties (Figure 2).[18]

However, to our knowledge, very few reports of aromatic systems containing P=C bonds have been investigated as π-conjugated materials, though a great deal of research on aromatic heterocycles bearing phosphorus atoms has been conducted.[15,19] Protasiewicz and co-workers recently prepared a series of photoluminescent benzoxaphospholes and benzobisoxaphospholes with the P=C bond participating in the conjugated aromatic architecture (Figure 2).[20] This work provided inspiration to investigate the related benzothiaphospholes since polythiophenes are an important class of π-conjugated material. The benzothiaphosphole resembles benzothiophene except a CH moiety is replaced by a P atom. Herein, we report a new synthetic procedure to prepare 2-aryl-

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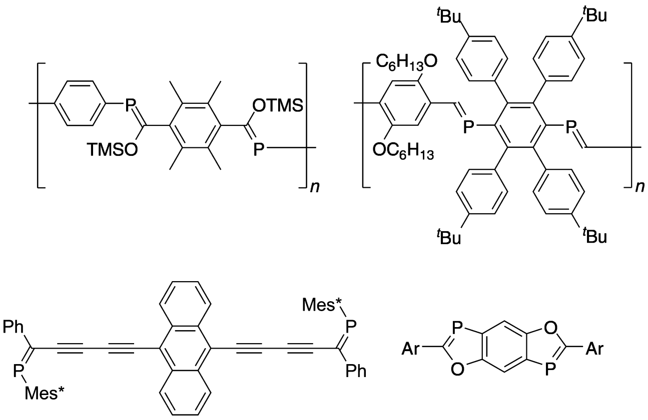


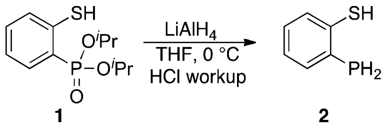
Figure 2. Extended π-conjugated materials that incorporate phosphaalkene units.

1,3-benzothiaphospholes and describe their electrochemical and photophysical behavior.

RESULTS AND DISCUSSION

Several synthetic strategies to prepare 1,3-thiaphospholes have been reported;[21] however, 1,3-benzothiaphospholes have been described only once.[22] To synthesize the desired heterocycle, we prepared diisopropyl (2-mercaptophenyl)phosphonate (**1**) according to a literature procedure.[23] Reduction of compound **1** using lithium aluminum hydride afforded the desired 1-mercapto-2-phosphinobenzene **2** (Scheme 1).

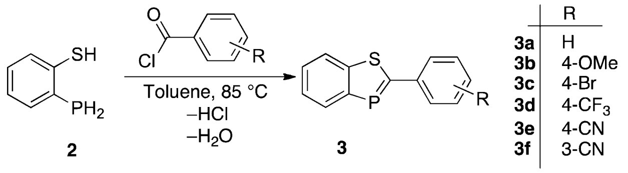
Scheme 1. Reduction of Diisopropyl (2-Mercaptophenyl)phosphonate to Prepare 1-Mercapto-2-phosphinobenzene



Benzannulated variants of 1,3-heterophospholes can be prepared from a phosphine precursor and a variety of carboxylic acid derivatives such as imidoyl chlorides, iminoester hydrochlorides, or amide acetals.[15b,24] Issleib and co-workers reported the synthesis of 2-phenyl-1,3-benzothiaphosphole from compound **2** and benzaldehyde; however, efforts to reproduce this reaction proved challenging.[22] The wide commercial availability of acid chlorides and a previous report describing 1,3-benzoxaphospholes from acid chlorides led us to investigate the reaction of **2** with benzoyl chloride.[25] The combination of **2** (^{31}P δ = −127) with benzoyl chloride proceeded smoothly in toluene at 85 °C, with nearly quantitative conversion to a single product as evidenced by ^{31}P{^{1}H} NMR spectroscopy (δ = 192). Upon cooling of the reaction mixture, yellow crystals formed and were collected by filtration to yield the desired 2-phenyl-1,3-benzothiaphosphole **3a** (Scheme 2).

The ^{31}P NMR signal of compound **3a** does not match the one previously reported (^{31}P δ = 55.3).[22] However, that report only includes ^{31}P NMR data without supporting evidence to prove the formation of the 2-phenyl-1,3-benzothiaphosphole. In this work, mass spectrometry data and X-ray analysis (Figure 3) are used to confirm the identity of the heterocycle (2-phenyl-1,3-benzothiaphosphole **3a**) which exhibits a ^{31}P{^{1}H} signal at 192 ppm.

Scheme 2. Synthesis of 1,3-Benzothiaphospholes from 1-Mercapto-2-phosphinobenzene (2) and Aryl Acid Chlorides



The P1−C1 and P1−C2 bond lengths are 1.677(9) Å and 1.789(9) Å, respectively (Figure 3). One of these bonds is slightly longer than a typical P=C bond (1.60−1.70 Å)[15a] and the observed lengths are comparable to a previously reported 1,3-thiaphosphole which exhibited bond lengths of 1.691(5) Å and 1.719(5) Å.[21e] The bond lengths for **3a** are in accord with the benzobisoxaphospholes reported recently that have phosphorus−carbon bond lengths of 1.694(1) Å and 1.782(1) Å.[20a] One of the most interesting features of the structure is that very little twisting is observed between the aryl rings. The angle between the planes of the benzothiaphosphole and phenyl group is only 3.75°. This structural feature suggests that crystalline packing in extended conjugated structures may be possible and extended delocalization could result. Following the synthesis of **3a**, a series of 1,3-benzothiaphospholes were prepared (**3b**−**3f**, Scheme 2) to investigate how electron donating and electron withdrawing groups modify the electronic and photophysical properties of the ring.

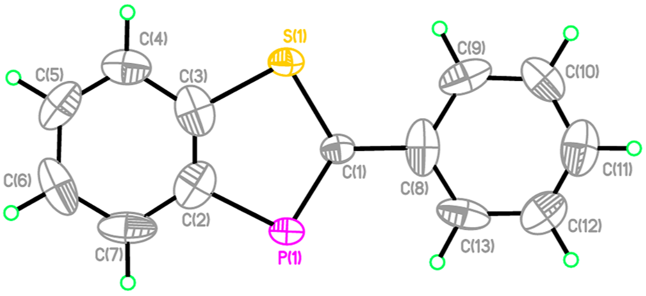


Figure 3. Solid-state molecular structure of **3a**. Thermal ellipsoids at 50%. Selected bond lengths (Å) and bond angles (deg): S1−C1 1.757(10); S1−C3 1.800(9); P1−C1 1.677(9); P1−C2 1.789(9); C1−C8 1.473(11); C1−S1−C3 92.8(5); C1−P1−C2 95.3(5); C8−C1−P1 122.8(7); C8−C1−S1 119.7(7); P1−C1−S1 117.3(6).

For the 2-aryl-1,3-benzothiaphospholes, redox properties and frontier orbitals were probed via cyclic voltammetry (Table 1). Each compound in the series exhibited an irreversible oxidation indicative of phosphaalkenes (Figure 4). For the parent species (**3a**), the irreversibility of the process persists even at elevated scan rates (5−10 V/s) signaling that the oxidized radical cation quickly undergoes chemical reaction. High scan rates also reveal a new reduction process near 0.17 V which is too shifted to be a reversal of the oxidation and instead is consistent with redox activity of a product formed from the oxidized species.

Throughout the 2-aryl-1,3-benzothiaphosphole series, relatively high oxidation potentials (Table 1) highlight the electron-poor nature of these materials as compared to their oxaphosphole analogs[20b] and C,C-diacetylenic phosphaalkenes.[18b] DFT calculations for all variants of compound **3** indicate that the HOMO is largely concentrated on the phosphaalkene

Table 1. Photophysical and Electrochemical Properties of 2-Aryl-1,3-Benzothiaphospholes

Entry	λ_{max1} abs (nm)	ε_1 (cm^{-1} M^{-1})	λ_{max2} abs (nm)	ε_2 (cm^{-1} M^{-1})	λ_{max} emission (nm)	Φ^a (%)	E_{ox} (V vs SCE)	E_{red} (V vs SCE)	ΔE_{red} (mV)
3a	271	34300	330	36800	443	4.4	1.44^b	−1.76	81
3b	279	26800	347	60500	445	5.4	1.24^b	−1.85	82
3c	273	38900	337	49900	439	3.2	1.49^b	-1.62^b	-
3d	271	41200	331	39400	430	1.5	1.52^b	-1.54^c	85
3e	272	31800	340	32000	433	1.7	1.50^b	−1.41, −1.91	61, 94
3f	270	47200	324	43800	432	1.5	1.56^b	-1.55^c	77

[a]Quantum yields were measured according to the procedure of Abergel *et al.*[26] [b]Process is completely irreversible. [c]Process is quasi-reversible.

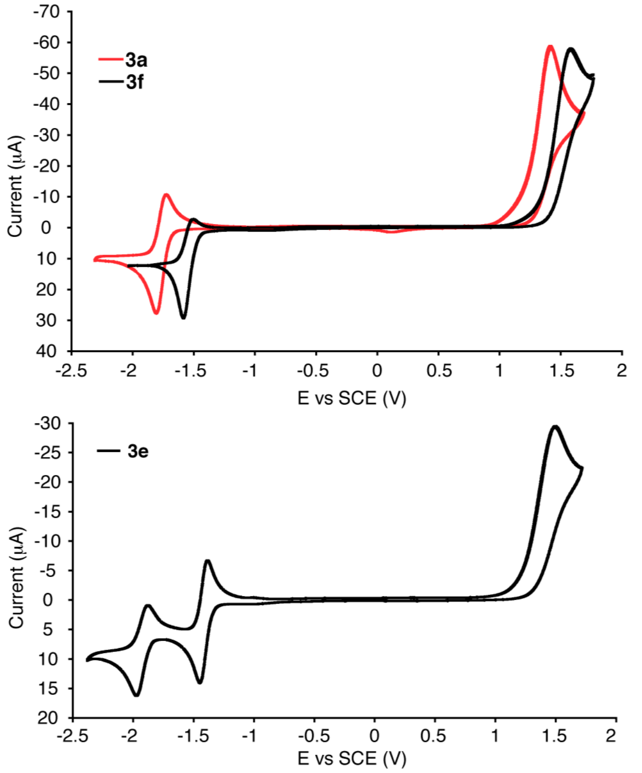


Figure 4. (Top) Cyclic voltammograms of **3a** (red) and **3f** (black). (Bottom) Cyclic voltammogram of **3e** showing the most positive first reduction of the benzothiaphosphole series and a second reduction unique to **3e**. All voltammograms were collected in 0.10 M N(*n*-Bu)$_4$PF$_6$ (MeCN) solution.

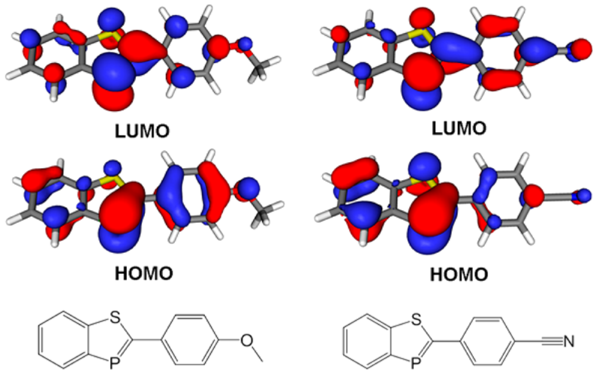


Figure 5. Frontier orbitals of compound **3b** (left) and **3e** (right) generated via DFT calculations performed with a B3LYP/6-31G (d,p) basis set.

double bond (Supporting Information). Similar HOMO assignments have been made previously with other phosphaalkene systems.[20b,27] The lowest oxidation potential is observed for compound **3b** (1.24 V) due to destabilization of its HOMO via the C$_6$H$_4$-*p*-OMe group (Figure 5). Compounds **3c**−**f** have higher oxidation potentials (1.49 V-1.56 V) as the HOMOs are stabilized by the electron withdrawing substituent (C$_6$H$_4$-*p*-Br, C$_6$H$_4$-*p*-CF$_3$, C$_6$H$_4$-*p*-CN, C$_6$H$_4$-*m*-CN). However, the oxidation potentials do not scale consistently with the electron withdrawing power of the substituent group suggesting that they exhibit limited participation in the HOMO. DFT calculations support this claim as only minor contributions to the HOMO are observed if the 2-aryl group has an electron withdrawing substituent (Figure 5 Compound **3e**).

In addition to oxidation, the benzothiaphospholes undergo reduction with varying extents of reversibility. Reduction of compound **3c** is irreversible resulting most likely from elimination of its halide after radical anion formation.[20b] Single quasi-reversible reductions are observed for **3d** and **3f** while complete reversibility is observed for the one electron reductions of compounds **3a**, **3b**, and **3e** (Figure 4). The reversibility in these compounds indicates that the anionic radicals are stable in solution on the time scale of the anodic and cathodic sweeps. Such stability suggests potential for these conjugated materials to conduct electrons and this behavior is not observed in many types of phosphaalkenes.[18b,28]

In comparison to the oxidation peaks, the reductions are roughly half as intense. Thus, while several of the reduction processes are clearly reversible, one electron processes, the oxidation may represent a two electron process facilitated by the favorability of the P(III)/P(V) redox couple. Reduction also differs from oxidation in that its potentials show a more defined pattern: they become incrementally more positive as the electron deficiency of the 2-aryl substituent increases and enhances LUMO stabilization. DFT calculations explain the more pronounced effect of electron deficient groups on reduction by showing significantly more participation of those substituents in the LUMO than in the HOMO (Figure 5). The greatest LUMO stabilization is afforded by the C$_6$H$_4$-*p*-CN group which shifts **3e**'s reduction potential by +0.35 V compared to the parent **3a** and causes observation of a second reduction within the range of the solvent window (Figure 4-bottom). In contrast to **3e**, compound **3f** does not show two reversible reductions despite its similar C$_6$H$_4$-*m*-CN group. This observed difference in reduction occurs because conjugation allows for stabilization of radicals at the P=C bond by the cyano functionality at the *para* position but not at the *meta* position. This is also reflected in the DFT calculations which illustrate that the substituent at the *para* position of the 2-aryl group of the benzothiaphospholes exhibits orbital density in the LUMO along with the phosphorus−carbon double bond while the *meta* position does not. Additionally, DFT calculations explain the facile reduction of **3e** by showing that its LUMO is stabilized by distribution across its entire C$_6$H$_4$-*p*-

CN group (Figure 5). Across the benzothiaphosphole series, each material is slightly more easily reduced than its oxaphosphole analogue likely due to facilitation of P═C reduction by the more polarizable sulfur.[20b]

The reduction potentials of the benzothiaphospholes correlate with moderate accuracy to the Hammett parameters of the employed substituents (Supporting Information). Moreover, redox properties are in agreement with the orbital energies obtained for **3a**−**3f** through DFT calculations. The LUMO energies of compounds **3a**-**3f** form a moderately linear relationship with their related reduction potentials (Figure 6).

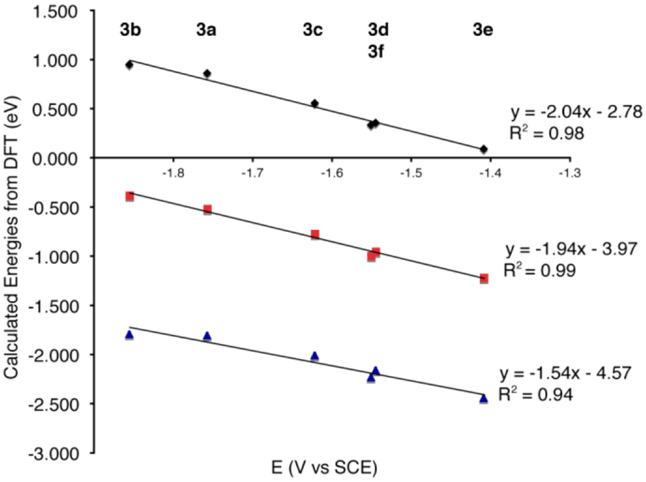


Figure 6. Linear correlation of experimental reduction potentials for **3a**−**3f** with DFT calculations. Blue triangles (▲): LUMO energies correlated to reduction potentials. Black diamonds (◆): SOMO energies of the radical anions correlated to reduction potentials. Red rectangles (■): The calculated energy difference between the radical anion and neutral benzothiaphosphole species correlated to reduction potentials.

Strong correlation is also seen between the reductions and the radical anion SOMO energies calculated to better model reduction products (Figure 6). Surprisingly, the calculated radical anions of the 2-aryl-1,3-benzothiaphospholes show lower absolute energies than the corresponding uncharged systems. This observation is likely explained by the electronegative nature of the heterocyclic phosphorus ring. Furthermore, all of the radical anions optimize to a flat geometry, which is in contrast to the 30° twisting observed in the calculated structure of the neutral species. The resulting increase in aromaticity could partially explain the observed stabilization effect for the radical anions. However, perhaps the best indicator of reduction potentials is the SCF energy difference of the radical anion and the neutral molecule. The SCF energy difference between radical anions and neutral molecules is plotted versus reduction potentials in Figure 6. The quality of the observed linearity is extraordinary, so reduction potentials of similar compounds can be predicted from DFT with great confidence. Interestingly, neither the HOMO energy nor the energy difference between the radical cation and the uncharged structure show any relationship with the measured oxidation potentials for the 2-aryl-1,3-benzothiaphospholes. The irreversible nature of the oxidation hints at the involvement of more complex processes, which are understandably problematic to evaluate by simple DFT calculations.

The investigated compounds exhibit strong light absorption in the UV which tails into the visible region of the spectrum explaining the yellow color of these materials in solution and in solid-state. Two absorption signals are observed at 271 and 330 nm for the parent compound (Table 1). The λ_{max} of the lower energy signal is influenced by substituent effects and ranges from 324 nm (**3f**) to 347 nm (**3b**). TD-DFT calculations confirm the π−π* character of this transition showing that it involves the HOMO and LUMO orbitals exclusively, with strong involvement of the P═C bond. All of the derivatives luminesce near 440 nm upon excitation at 330 nm, and the fluorescence spectrum of **3b** along with its absorption are depicted in Figure 7. The emission of **3b** is the most red-shifted in the series because of destabilization of the HOMO by the methoxy group. However, as with oxidation potentials, the emission maxima for more electron deficient derivatives do not follow a clear trend due to minimal participation of their substituents in the HOMO. Emission quantum yields vary greatly across the series (Table 1). Electron withdrawing groups diminish quantum yield while the methoxy functionality markedly increases it.

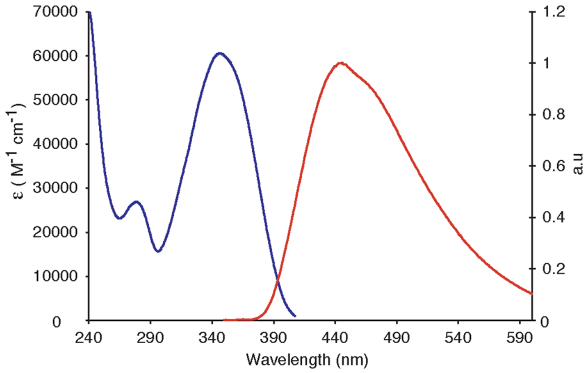


Figure 7. Absorption spectrum (blue) and luminescence spectrum (red) of **3b** collected for a 10 μM MeCN solution. Luminescence was measured following excitation at 330 nm.

■ CONCLUSION

The preparation of a series of 2-aryl-1,3-benzothiaphospholes has been reported and their redox and photophysical behavior has been evaluated. Electronic modulation of the benzothiaphosphole materials was employed as a strategy to alter the reduction and oxidation potentials of the ring system. Some of the benzothiaphosphole derivatives yielded accessible, reversible reductions highlighting the potential of these compounds as n-type charge transport systems.

■ EXPERIMENTAL SECTION

Materials and Methods. All reactions and manipulations of air or water sensitive compounds were carried out under dry nitrogen using a glovebox or standard Schlenk techniques unless otherwise specified. Diisopropyl (2-mercaptophenyl)phosphonate (**1**) was prepared according to a published procedure from thiophenol.[23] In the synthesis of **1**, diisopropyl bromophosphate (prepared from triisopropyl phosphite and bromine [(^{31}P{^{1}H} δ = −11]), was used as opposed to diisopropyl chlorophosphate. All solvents (toluene, diethyl ether, tetrahydrofuran, hexanes) were degassed with argon and dried prior to use. Acetonitrile, used for photophysical characterization and electrochemistry measurements, was degassed prior to use. $CDCl_3$ was dried using P_2O_5 and distilled prior to use. C_6D_6 was dried over 4 Å sieves prior to use. Melting points are uncorrected.

NMR Analysis. NMR spectra were recorded on either a 300 MHz or a 500 MHz Spectrometer. The ^{31}P{^{1}H} NMR spectra were referenced to an external standard (85% H_3PO_4). The ^{1}H NMR spectra are referenced to residual protio solvents (7.24 for $CHCl_3$ and 7.16 for C_6D_5H). In the ^{1}H NMR spectra of **3a**−**3f**, significant fine splittings (∼1−2 Hz) were observed from long-range coupling (^{1}H−^{1}H and ^{1}H−^{31}P) on the fused aromatic rings. Signals that are listed as broad typically exhibited fine splitting that was left unassigned. The ^{1}H NMR spectra of all compounds, except for **3a** and **3f**, have shown the typical ABCD spin systems pattern for ring A and an AA′BB′ spin system characteristic of *p*-disubstituted aromatic rings. ^{13}C NMR spectra are referenced to the solvent signal (δ 77.23 $CDCl_3$) and J_{PC} coupling is observed for most signals.

Photophysical Characterization. Photoluminescence measurements were performed at room temperature using 10 μM solutions in acetonitrile using a capped quartz cuvette (1.0 cm). UV−vis absorption spectra were measured using a dual-beam scanning spectrophotometer. Photoluminescence emission spectra were measured on a fluorimeter equipped with dual monochromators and a photomultiplier tube (PMT) at right angle geometry. The emission spectra were recorded at an excitation wavelength of 330 nm. Photoluminescent quantum yields (Φ) were measured against 100 μM quinine sulfate in 0.5 M H_2SO_4,$\Phi = (I_s/I_{ref})(A_{ref}/A_s)(\eta_s/\eta_{ref})$,[26] where Φ is the quantum yield for the sample, I_s and I_{ref} represent the points of maximum intensity in the emission spectra of the sample and reference, A_s and A_{ref} are the absorbance of the sample and the reference at the excitation wavelength, and η_{ref} and η_s are the refractive indices of the solvents of the reference and of the sample used for UV−vis absorption measurements.

Electrochemical Analyses. Electrochemical potentials were determined using an electrochemical analyzer at a potential sweep rate of 100 mV/s. A 1 mm^2 platinum working electrode, a platinum coil counter electrode, and a silver wire pseudoreference electrode were employed for the measurements. Ferrocene was used as an internal standard referenced against SCE at 0.4 V ($E_{Fc/Fc+}$).[29] Solutions of the benzothiaphosphole were prepared at ∼1−2 mM and tetra-*n*-butylammonium hexafluorophosphate (electrochemical grade) served as the supporting electrolyte at a concentration of 0.1 M. The MeCN solutions with the supporting electrolyte were degassed for 5 min with bubbling Ar prior to adding the benzothiaphosphole.

Computational Studies. Hybrid density functional theory (DFT) calculations were performed for compounds **3a**−**3f** using a B3LYP/6-31G (d,p) basis set in the *Gaussian 03* suite.[30]

Mass Spectrometry. High-resolution mass spectrometry data was obtained using a double focusing sector instrument.

Synthesis of 1-Mercapto-2-phosphinobenzene (2). A 1000 mL Schlenk flask was charged with lithium aluminum hydride (14.25 g, 375 mmol) and dried *in vacuo* for 15 min. To this was added 400 mL THF and the mixture was cooled to 0 °C using an ice bath. Slow addition of **1** (33.40 g, 122 mmol) over a period of 8 min produced a vigorous reaction with significant gas evolution (the addition of **1** was conducted slowly so as to control the rate of gas evolution). Upon completion of the addition, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The mixture was quenched with 6 M HCl (100 mL) and the layers were allowed to separate. The organic layer was cannula transferred through a filter funnel containing Celite into a 1000 mL Schlenk flask containing magnesium sulfate. This extraction process was repeated using dry, degassed hexanes (4 × 75 mL). Then the dried organic layer was transferred to another 1000 mL Schlenk flask via a filter cannula. After removing volatiles *in vacuo*, the crude product was distilled using a short path column (64 °C, 0.1 Torr) to afford **2** as colorless oil. The ^{31}P{^{1}H} and ^{1}H NMR spectra were compared to a previous report.[31] Often, the ^{1}H spectrum of the distilled product contained impurities that are suspected to be aluminum isopropoxide salts. Loading the 1-mercapto-2-phosphinobenzene onto silica gel under an atmosphere of N_2 and eluting with degassed hexanes helped remove the impurity (7.51 g, 43%).

*General Procedure A: Synthesis of 2-Aryl-1,3-benzothiaphospholes **3a** and **3b**.* In a N_2 filled glovebox, a 50 mL Schlenk flask was charged with 1-mercapto-2-phosphinobenzene (0.375 g, 2.64 mmol), 5 g of dry toluene, and an aryl acid chloride (1 equiv, 2.64 mmol). The Schlenk flask was removed from the glovebox and immersed in an oil bath at 85 °C. The solution was stirred overnight and the colorless solution turned bright yellow. An aliquot of the reaction mixture was removed using a syringe and analyzed using ^{31}P NMR spectroscopy. Complete consumption of the starting material was confirmed by disappearance of the ^{31}P{^{1}H} NMR signal at −127 ppm. Formation of the desired benzothiaphosphole was confirmed by the appearance of a ^{31}P{^{1}H} NMR signal in the range of 185−203 ppm. The reaction vessel was removed form the oil bath, and cooled to room temperature. The flask was placed in a refrigerator at 4 °C for several hours and, upon removal from the fridge, yellow crystals were observed in the reaction flask. The yellow crystals were collected via filtration and washed with cold ether (3 × 10 mL).

*General Procedure B: Synthesis of 2-Aryl-1,3-benzothiaphospholes **3c** and **3d**.* In a N_2 filled glovebox, a 50 mL Schlenk flask was charged with 1-mercapto-2-phosphinobenzene (0.375 g, 2.64 mmol), 5 g of dry toluene, and an aryl acid chloride (1 equiv, 2.64 mmol). The Schlenk flask was removed from the glovebox and immersed in an oil bath at 85 °C. The solution was stirred overnight and the colorless solution turned bright yellow. An aliquot of the reaction mixture was removed using a syringe and analyzed using ^{31}P NMR spectroscopy. Complete consumption of the starting material was confirmed by disappearance of the ^{31}P{^{1}H} NMR signal at −127 ppm. Formation of the desired benzothiaphosphole was confirmed by the appearance of a ^{31}P{^{1}H} NMR signal in the range of 185−203 ppm. The volatiles of the reaction mixture were removed *in vacuo* and the crude mixture was brought into the glovebox. The residue was dissolved in a minimal amount of solvent, and placed in a 20 mL scintillation vial. The vial was stored in the freezer at −35 °C overnight. Yellow crystals were observed in the scintillation vial and they were collected by filtration. The filtrate was placed back in the freezer and a second batch of crystals was obtained. These were also collected by filtration.

*General Procedure C: Synthesis of 2-Aryl-1,3-benzothiaphospholes **3e** and **3f**.* In a N_2 filled glovebox, a 50 mL Schlenk flask was charged with 1-mercapto-2-phosphinobenzene (0.375 g, 2.64 mmol), 5 g of dry toluene, and an aryl acid chloride (1 equiv, 2.64 mmol). The Schlenk flask was removed from the glovebox and immersed in an oil bath at 85 °C. After stirring overnight, the colorless solution had turned bright yellow and some precipitate was observed. The hot reaction mixture was separated from the precipitate by a hot gravity filtration. The yellow filtrate was collected and immediately transferred to a 20 mL scintillation vial. The vial was allowed to cool to room temperature and placed in a refrigerator at 4 °C for several hours and, upon removal from the fridge, yellow crystals were observed in the reaction flask. The yellow crystals were collected via filtration and washed with cold ether (3 × 10 mL).

*2-Phenyl-1,3-benzothiaphosphole (**3a**).* was prepared following general procedure A. The combination of compound **2** (0.375 g, 2.64 mmol) and benzoyl chloride (0.370 g, 2.64 mmol) afforded **3a** as yellow crystals (0.234 g, 39%). Mp 142−145 °C dec ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 191.9. ^{1}H NMR (500 MHz, C_6D_6): δ 8.06 – 8.00 (m, 1H), 7.89 – 7.84 (m, 2H), 7.63 (br d, J = 7.8 Hz, 1H), 7.11 – 6.98 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.1 (d, J_{PC} = 52.8 Hz), 153.8 (d, J_{PC} = 39.8 Hz), 148.4 (d, J_{PC} = 10.2 Hz), 137.0 (d, J_{PC} = 16.1 Hz), 130.9 (d, J_{PC} = 27.5 Hz), 129.4 (d, J_{PC} = 3.5 Hz), 129.3, 126.9 (d, J_{PC} = 14.6 Hz), 126.7 (d, J_{PC} = 3.5 Hz), 124.1 (d, J_{PC} = 13.4 Hz), 123.4. HR-EIMS (m/z): $[M]^+$ calculated for $C_{13}H_9PS$: 228.0163; found 228.0153.

*2-(4-Methoxyphenyl)-1,3-benzothiaphosphole (**3b**).* was prepared following general procedure A. The combination of compound **2** (0.375 g, 2.64 mmol) and 4-methoxybenzoyl chloride (0.450 g, 2.64 mmol) afforded **3b** as yellow crystals (0.170, 25%). Mp 164−165 °C dec ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 184.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (br t, J = 7.0 Hz, 1H), 8.02 (br d, J = 8.1 Hz, 1H), 7.83 – 7.78 (AA′BB′ system, A centered on 7.82, A′ centered on 7.80, 2H), 7.42 (br t, J = 7.6 Hz, 1H), 7.36 (br t, J = 7.5 Hz, 1H), 6.94 – 6.90 (AA′BB′ system, B centered on 6.94, B′ centered on 6.92, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.2 (d, J_{PC} = 53.1 Hz), 160.9 (d, J_{PC} = 3.7 Hz), 153.8 (d, J_{PC} = 39.7 Hz), 148.0 (d, J_{PC} = 10.1 Hz), 130.7 (d, J_{PC} = 27.6 Hz), 130.0 (d, J_{PC} = 16.2 Hz), 128.1 (d, J_{PC} = 14.7 Hz), 126.3 (d, J_{PC} = 3.4 Hz), 124.1 (d, J_{PC} = 13.2 Hz), 123.2, 114.6, 55.6. HR-EIMS (*m*/*z*): [M]$^+$ calculated for $C_{14}H_{11}OPS$: 258.0268; found 258.0260. Anal. Calcd for $C_{14}H_{11}OPS$: C, 65.10; H, 4.29. Found: C, 64.84; H, 4.15.

*2-(4-Bromophenyl)-1,3-benzothiaphosphole (**3c**).* was prepared following general procedure B using compound **2** (0.375 g, 2.64 mmol) and 4-bromobenzoyl chloride (0.579 g, 2.64 mmol). **3c** was obtained as a yellow powder (0.246 g, 30%) after recrystallization from Toluene/THF (10:1). Mp 176−177 °C dec $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 194.0. ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (br t, *J* = 7.1 Hz, 1H), 8.04 (br d, *J* = 8.1 Hz, 1H), 7.73 − 7.69 (AA′BB′ system, A centered on 7.72, A′ centered on 7.70, 2H), 7.53 − 7.49 (AA′BB′ system, B centered on 7.52, B′ centered on 7.51, 2H), 7.46 (br t, *J* = 7.6 Hz, 1H), 7.38 (br t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1 (d, J_{PC} = 52.6 Hz), 153.7 (d, J_{PC} = 39.7 Hz), 148.4 (d, J_{PC} = 10.4 Hz), 136.0 (d, J_{PC} = 16.6 Hz), 132.3, 131.0 (d, J_{PC} = 27.6 Hz), 128.2 (d, J_{PC} = 14.8 Hz), 126.9 (d, J_{PC} = 3.5 Hz), 124.3 (d, J_{PC} = 13.5 Hz), 123.5, 123.4. HR-EIMS (*m*/*z*): [M]$^+$ calculated for $C_{13}H_8BrPS$: 305.9268; found 305.9267. Anal. Calcd for $C_{13}H_8BrPS$: C, 50.84; H, 2.63. Found: C, 50.58; H, 2.38.

*2-(4-(Trifluoromethyl)phenyl)-1,3-benzothiaphosphole (**3d**).* Following the general procedure B using compound **2** (0.375 g, 2.64 mmol) and 4-(trifluoromethyl)benzoyl chloride (0.550 g, 2.64 mmol) afforded **3d** as yellow crystals (0.256 g, 33%) after recrystallization from THF. Mp 215−217 °C dec $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 199.5. ^1H NMR (500 MHz, C_6D_6) δ 8.02 (br t, *J* = 6.8 Hz, 1H), 7.63 (br d, *J* = 7.9 Hz, 1H), 7.60 (br d, *J* = 7.3 Hz, 2H), 7.24 (br d, *J* = 8.2 Hz, 2H), 7.08 − 6.99 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4 (d, J_{PC} = 52.7 Hz), 153.9 (d, J_{PC} = 40.1 Hz), 148.8 (d, J_{PC} = 10.5 Hz), 140.5 (d, J_{PC} = 16.8 Hz), 131.2 (d, J_{PC} = 27.7 Hz), 127.3 (d, J_{PC} = 3.6 Hz), 127.1 (d, J_{PC} = 14.7 Hz), 126.3 and 126.2 (overlapping doublets), 124.5 (d, J_{PC} = 13.6 Hz), 124.3, (q, J_{FC} = 271.5 Hz), 123.5. HR-EIMS (*m*/*z*): [M]$^+$ calculated for $C_{14}H_8F_3PS$: 296.0036; found 296.0031. Anal. Calcd for $C_{14}H_8F_3PS$: C, 56.76; H, 2.72. Found: C, 56.48; H, 2.49.

*2-(4-Cyanophenyl)-1,3-benzothiaphosphole (**3e**).* was prepared following general procedure C. The combination of **2** (0.375 g, 2.64 mmol) and 4-cyanobenzoyl chloride (0.437 g, 2.64 mmol) afforded a crude yield of 0.254 g of **3e** as yellow crystals. Recrystallization from toluene yielded analytically pure **3e** (0.139 g, 21%). Mp 178 °C dec $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 202.7. ^1H NMR (500 MHz, C_6D_6) δ 7.98 (br t, *J* = 6.9 Hz, 1H), 7.60 (br d, *J* = 7.8 Hz, 1H), 7.44 − 7.39 (AA′BB′ system, A centered on 7.43, A′ centered on 7.41, 2H), 7.07 − 6.97 (m, 2H), 6.94 − 6.89 (AA′BB′ system, B centered on 6.92, B′ centered on 6.91, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.2 (d, J_{PC} = 52.7 Hz), 153.7 (d, J_{PC} = 39.7 Hz), 148.7 (d, J_{PC} = 10.5 Hz), 141.3 (d, J_{PC} = 16.8 Hz), 133.0, 131.3 (d, J_{PC} = 27.6 Hz), 127.5 (d, J_{PC} = 3.7 Hz), 127.1 (d, J_{PC} = 15.4 Hz), 124.5 (d, J_{PC} = 13.8 Hz), 123.6, 118.8, 112.4 (d, J_{PC} = 4.2 Hz). HR-EIMS (*m*/*z*): [M]$^+$ calculated for $C_{14}H_8NPS$: 253.0115; found 253.0111. Anal. Calcd for $C_{14}H_8NPS$: C, 66.39; H, 3.18; N, 5.53. Found: C, 66.09; H, 2.91; N, 5.29.

*2-(3-Cyanophenyl)-1,3-benzothiaphosphole (**3f**).* was prepared following general procedure C. The combination of **2** (0.375 g, 2.64 mmol) and 3-cyanobenzoyl chloride (0.437 g, 2.64 mmol) afforded **3f** as yellow crystals (0.131 g, 20%). Mp 178 °C dec $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 198.5. ^1H NMR (300 MHz, C_6D_6) δ 7.98 (br td, *J* = 6.7, 1.9 Hz, 1H), 7.80 (br d, *J* = 1.8 Hz, 1H), 7.65 − 7.57 (m, 2H), 7.09 − 6.97 (m, 2H), 6.87 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.60 (br t, *J* = 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0 (d, J_{PC} = 52.4 Hz), 153.6 (d, J_{PC} = 39.8 Hz), 148.5 (d, J_{PC} = 10.5 Hz), 138.2 (d, J_{PC} = 17.3 Hz), 132.2 (d, J_{PC} = 3.4 Hz), 131.2 (d, J_{PC} = 27.6 Hz), 130.9 (d, J_{PC} = 14.7 Hz), 130.1, 130.0 (d, J_{PC} = 14.9 Hz), 127.4 (d, J_{PC} = 3.7 Hz), 124.5 (d, J_{PC} = 13.7 Hz), 123.6, 118.5, 113.6. HR-EIMS (*m*/*z*): [M]$^+$ calculated for $C_{14}H_8NPS$: 253.0115; found 253.0119.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, cyclic voltammograms, absorption and emission spectra, crystallographic data, calculated energies, coordinates, and orbitals images. This material is available free of charge via the Internet http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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