Phosphorus Heterocycles

Tuning Thiophene with Phosphorus: Synthesis and Electronic Properties of Benzobisthiaphospholes

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Abstract: 1,4-Dimercapto-2,5-diphosphinobenzene and 3,6-bis(hexyloxy)-1,4-dimercapto-2,5-diphosphinobenzene were synthesized and combined with various acid chlorides to obtain a series of benzobisthiaphospholes. Electrochemical and photophysical properties of the substituted benzobisthiaphospholes have been evaluated, and the observed reductions are more facile than the related benzothiaphospholes and 2,6-diphenylbenzobisthiazole. A benzobisthiaphosphole with C_6H_4-*p*-CN substituents was reduced at $E_{1/2}=-1.08$ V (vs. saturated calomel electrode (SCE)). X-ray diffraction data for several of these phosphorus heterocycles has been obtained, and DFT calculations at the B3LYP level have been performed.

Introduction

Phosphorus has emerged as a versatile element to modulate the optoelectronic properties of conjugated organic materials.[1] In particular, phosphole-based materials have attracted a great deal of attention, because they often exhibit n-type behavior (Figure 1).[2] The phosphorus lone pair in phospholes can also be chemically manipulated to modulate the HOMO–LUMO gap and solid-state packing of conjugated architectures.[2b] However, expansion to other phosphorus-based heterocycles for organic electronics is still limited, because they are often challenging synthetic targets.[3] The 1,3-benzoxaphosphole and various derivatives are the only conjugated heterocycles investigated to date with many of these compounds being highly emissive in solution (Figure 1).[4] Studies that expand upon the chemistry of phosphorus and explore its versatility in conjugated frameworks are still in their infancy. Herein, we describe the synthesis and electronic properties of thiophene-based building blocks that incorporate P=C bonds.[5]

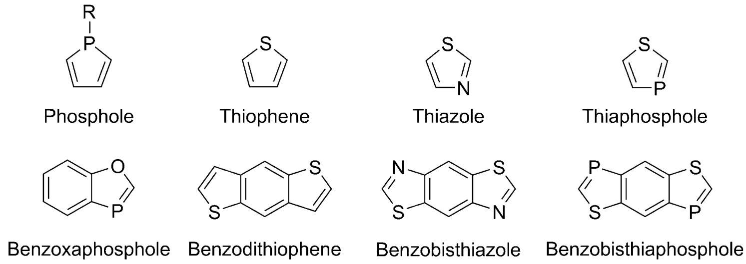

Figure 1. Conjugated building blocks for organic materials.

The facile chemical modulation and remarkable charge-transport properties of thiophene have made it the quintessential heterocyclic ring for organic electronics.[6] The incorporation of P=C bonds into a thiophene moiety should lower the LUMO of the heterocycle and afford n-type behavior for these systems (thiaphosphole, Figure 1).[7] However, investigation of such species has been limited to a few synthetic reports.[8] Herein, we describe the first synthesis of the benzobisthiaphosphole (BBTP, Figure 1). This compound is a structural mimic of benzodithiophene (BDT), a popular building block for polymeric photovoltaic materials.[9] BBTP is also isolobal with benzobisthiazole (BBT), and BBT-based materials have been synthesized for transistors,[10] photovoltaics,[11] and nonlinear optics.[12] The BBTP compounds were prepared with solubilizing hexyloxy groups and characterized by using X-ray crystallography and cyclic voltammetry.

Results and Discussion

Synthesis of BTPs and BBTPs

Recently, we reported the preparation of benzothiaphospholes (BTPs **2a**–**e**) from 1-mercapto-2-phosphinobenzene (**1**) and var-

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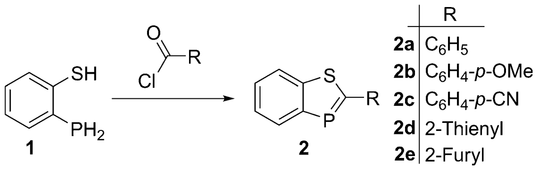
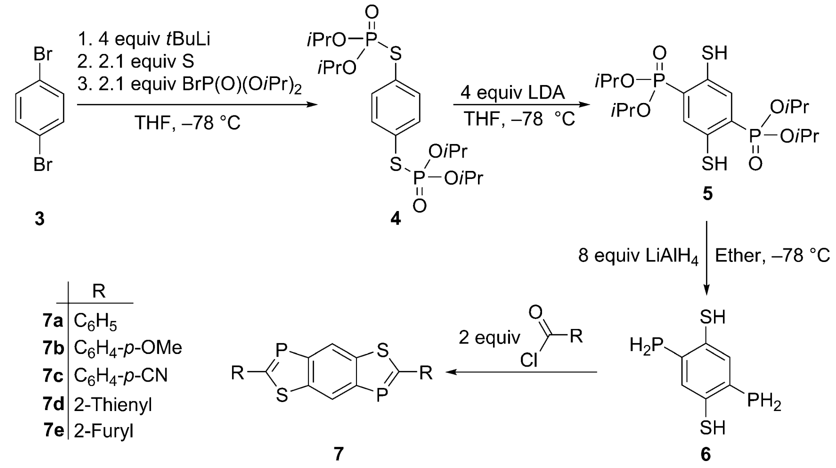


Scheme 1. Synthesis of BTPs from 1-mercapto-2-phosphinobenzene.

ious aryl acid chlorides (Scheme 1).[13] The reversible one-electron reductions observed for BTPs highlight the electron-accepting nature of the 1,3-thiaphosphole moiety.[13a] The addition of a second thiaphosphole moiety to the fused aromatic structure was achieved starting from 1,4-dibromobenzene (**3**).

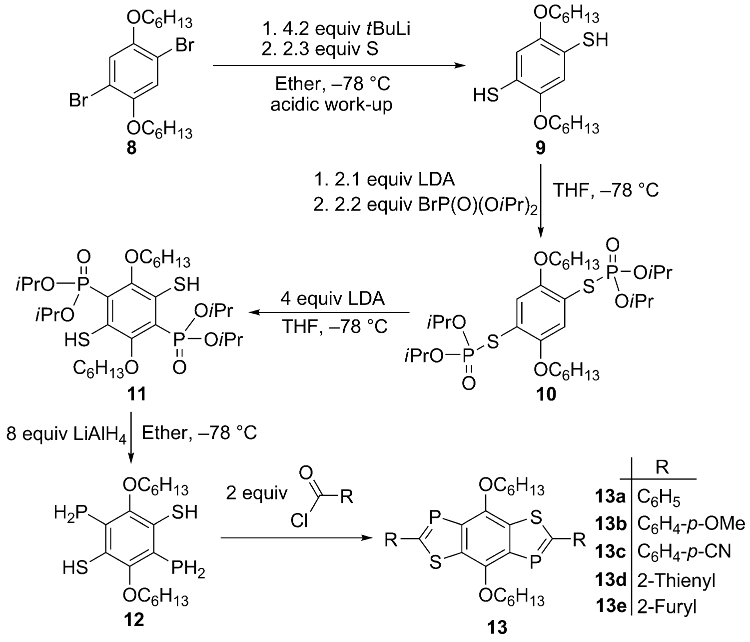
1,4-Dibromobenzene (**3**) was treated with *tert*-butyllithium to induce lithium–halogen exchange. Elemental sulfur was added to the dilithiobenzene and the resultant dithiolate was quenched with bromodiisopropylphosphate to afford **4**. Migration of the phosphate group was achieved by combination of **4** with lithium diisopropylamide (LDA) at −78 °C followed by slow warming to room temperature. An acidic work-up of the reaction mixture gave **5**, which was subsequently reduced to **6** in 81% yield. The combination of **6** with various aryl acid chlorides gave either yellow or orange solids (Scheme 2). Unfortunately, compounds **7a**–**c** are highly insoluble, precluding structural characterization via solution-phase ^{1}H and ^{31}P NMR spectroscopy. Mass-spectrometry data were obtained to confirm the formation of **7a**–**c**, but neither electrochemical nor photophysical characterization of these compounds was conducted.

Compounds **7d** and **e** were characterized at 65 °C by using ^{1}H and ^{31}P NMR spectroscopy (see the Supporting Information); however, the limited solubility still inhibited examination of electrochemical and photophysical properties. To circumvent this issue, solubilizing hexyloxy groups were added to the BBTP structure.



Scheme 2. Synthesis of BBTPs. Ether = diethylether.

1,4-Dibromo-2,5-bis(hexyloxy)benzene (**8**) was synthesized according to a literature procedure.[14] Compound **8** was combined with *tert*-butyllithium, quenched with elemental sulfur, and subjected to an acidic work-up to produce **9** (Scheme 3). Deprotonation of **9** to form a dithiolate was achieved by using LDA, and subsequent reaction with diisopropyl bromophosphate gave **10**. Treatment of **10** with four equivalents of LDA led to migration of the phosphate groups (**11**). Finally, reduction of **11** by using LiAlH$_4$ in diethyl ether gave the desired 3,6-bis(hexyloxy)-1,4-dimercapto-2,5-diphosphinobenzene (**12**). Several BBTPs were targeted by combining **12** with aryl acid chlorides (Scheme 3). The reaction produced the desired compounds **13a**–**e** in moderate yields (53–79%) except for compound **13c**, which was obtained in 22% yield. The compounds have colors ranging from yellow to orange and exhibit good solubility in CH$_2$Cl$_2$, THF, and toluene. The ^{31}P NMR signals observed for these derivatives ($\delta = 175$–195 ppm) are similar to the previously reported BTPs.[13a] Interestingly, these signals are significantly downfield compared to similar annelated heterophospholes, such as the 1,3-benzazaphosphole (≈70 ppm) and the 1,3-benzoxaphosphole (≈85 ppm).[3a]



Scheme 3. Synthesis of hexyloxy-substituted BBTPs. LDA = lithium diisopropylamide; ether = diethylether.

X-Ray crystallography

Crystals suitable for X-ray diffraction analysis were obtained for **13a** by slow evaporation of a toluene solution, whereas compound **13d** crystallized from a mixture of dichloromethane and diethyl ether at −40 °C (Figure 2). The P=C bond lengths for **13a** (1.713(5); 1.754(4) Å) and **13d** (1.713(4); 1.756(3) Å) are comparable to the recently reported benzobisoxaphospholes (1.694(1) and 1.782(1) Å).[4e] The S–C bond lengths for **13a** (1.721(5); 1.745(5) Å) and **13d** (1.721(4); 1.742(3) Å) are quite similar to the reported S–C(sp^2) bond lengths for benzobisthiazole **14** (1.736(2); 1.758(2) Å) confirming the aromaticity of the thiaphosphole (Scheme 4).[15]

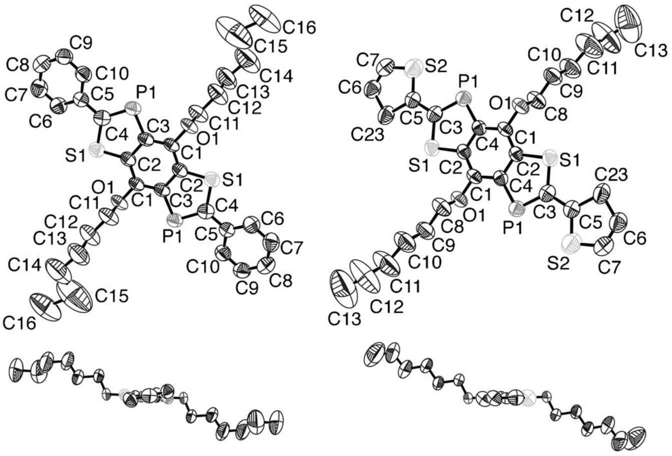
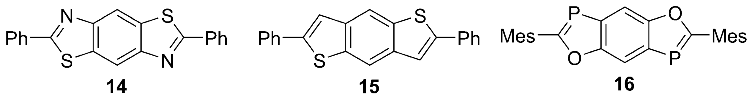


Figure 2. Solid-state molecular structure of **13a** and **d**. Thermal ellipsoids at 50 % probability. Selected bond lengths [Å] and angles [°] for **13a**: S1–C4 1.721(5); S1–C2 1.745(5); P1–C3 1.754(4); P1–C4 1.713(5); C4-S1-C2 95.2(2); C3-P1-C4 95.5(2); S1-C4-P1 117.9(3). Selected bond lengths [Å] and angles [°] for **13d**: S1–C3 1.721(4); S1–C2 1.742(3); P1–C3 1.713(4); P1–C4 1.756(3); C3-S1-C2 95.15(15); C3-P1-C4 94.71(15); S1-C3-P1 118.32(19).



Scheme 4.

Figure 2 illustrates the highly symmetric BBTP structure due to the neighboring relationship of S and P in the periodic table. The endocyclic bond angles about S and P in **13a** (95.2 and 95.5°) are nearly identical, whereas in **14**, a large difference about S and N was observed (88.9 and 110.8°).[15] These differences illustrate the remarkable structural variation resulting from exchange of isolobal fragments.

The structures in Figure 2 are best described with the central benzobisthiaphosphole segment having either phenyl or 2-thienyl substituents. Remarkably, the twist angles between the fused core and the aromatic substituents differ substantially for **13a** and **d**. Compound **13a** exhibits a 16° twist from coplanarity for the central ring and its phenyl substituents while the benzobisthiaphosphole in **13d** is essentially co-planar with its thiophene substituents (1.1°). This has a direct effect on the packing of these two structures. The measured distance between the planes of the central ring for adjacent molecules is 3.74 Å in **13a**, whereas in **13d**, this distance is significantly shortened to only 3.57 Å. In fact, compound **13d** exhibits face-to-face slip stacking, which is illustrated in Figure 3.

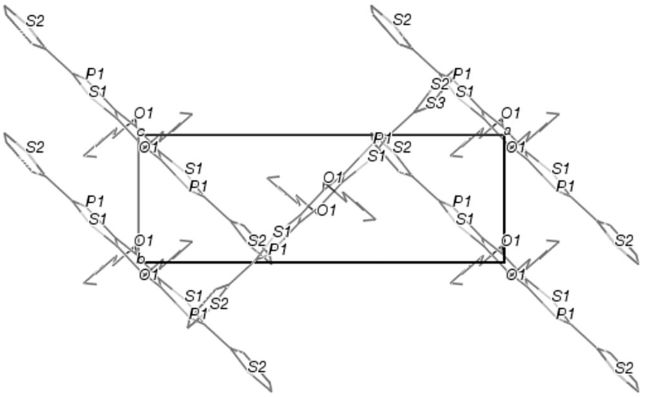


Figure 3. Packing diagram of **13d** along the *c* axis.

Photophysical properties

The absorption spectra of the BBTPs are consistent with an extended delocalized structure. Comparison with BTPs reveals that the larger heterocycle induces a redshift of approximately 100 nm in the π–π^* transition (447–471 nm for **13a–e** compared to 337–359 nm for **2a–e**) and introduces a new absorption signal (Figure 4). TD-DFT calculations were used to help assign the observed transitions (see the Supporting Information).

Interestingly, the longest wavelength maximum of BBTP **13a** is significantly redshifted compared to its organic analogues **14** and **15** (Scheme 4). Compound **13a** has three well-defined absorption bands at $\lambda = 307$, 358, and 447 nm while **14** exhibits three absorption features near $\lambda = 330$, 350, and 370 nm (in $CHCl_3$).[16] Compound **15** exhibits two absorption bands at 346 and 380 nm.[17] We suspect that the observed redshifting is primarily due to the insertion of the heavy phosphorus atom as opposed to the hexyloxy substituents. Though **7a** is insoluble, the similar yellow color of **7a** and **13a** suggests little redshifting from the alkoxy groups. Moreover, DFT calculations predict only a 20 nm redshift in the π–π^* transition from **7a** to **13a**. The BBTP derivatives are also significantly redshifted compared to their phosphorus counterpart **16** (Scheme 4), which exhibits a π–π^* transition at 337 nm.[4e]

Electrochemistry

Electrochemical oxidation of the BTPs and BBTPs was observed in CH_2Cl_2, whereas reduction was probed in THF (Table 1). All of the compounds exhibited an irreversible oxidation. This pro-

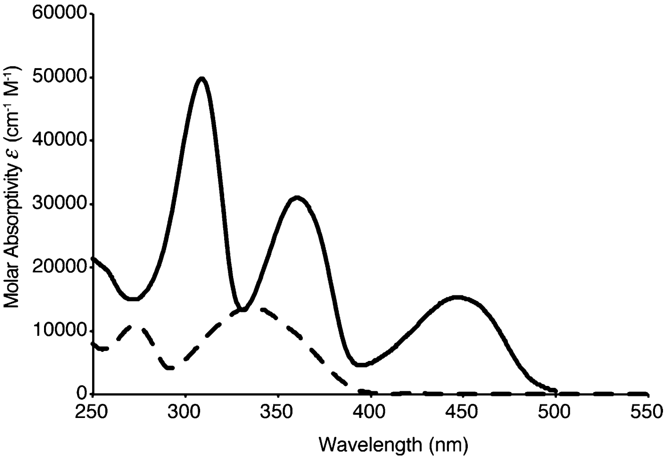


Figure 4. UV/Vis absorption spectra of compounds **13a** (black line) and **2a** (dotted line).

Table 1. Photophysical and electrochemical properties of **2a**–**e** and **13a**–**e**.

	Abs.[a] λ_{max} [nm]/ ε [cm^{-1} M^{-1}]	Em.[a] λ_{em} [nm]/ Φ [%]	Ox.[b] E_{pa} [V vs. SCE]	Red. 1[e] E_{pc} [V vs. SCE]	ΔE [mV]	Red. 2[e] E_{pc} [V vs. SCE]	ΔE [mV]
2a	337 (13500)	441 (4.3)	1.49	−1.73[f]	260	–	–
2b	347 (20500)	447 (5.4)	1.31	−1.84[f]	230	–	–
2c	344 (16400)	434 (1.0)	–[c]	−1.36[f]	200	−1.88[g]	–
2d	356 (15500)	474 (4.2)	1.43	−1.71[g]	–	–	–
2e	359 (21000)	445 (2.9)	1.41	−1.76[f]	210	–	–
13a	447 (15300)	530 (0.3)	1.05	−1.46[h]	160	−1.86[h]	180
13b	447 (21100)	500 (1.5)	1.00	−1.59[h]	130	−2.06[g]	–
13c[i]	471 (8000)	580 (0.3)	1.21	−1.08[h]	80	−1.34[h]	80
13d	462 (16700)	536 (0.8)	1.05[d]	−1.55[g]	–	−1.88[g]	–
13e	468 (24200)	520 (0.8)	1.05[d]	−1.46[h]	150	−1.86[f]	220

[a] Absorbance and emission spectra were recorded in CH_2Cl_2 under N_2, and quantum yields were determined versus quinine sulfate. [b] Irreversible, measured under argon in CH_2Cl_2 at a scan rate of 100 mV s^{-1}. [c] Process is not clearly resolved from the solvent oxidation. [d] Process does not cycle reproducibly due to interference with the working electrode. Potentials are taken from initial scans. [e] Measured under argon in THF at 100 mV s^{-1} with anodic sweeps not exceeding +0.90 V. [f] Quasi-reversible. [g] Irreversible. [h] Reversible. [i] Compound **13c** exhibited a third irreversible reduction at −2.04 V.

cess is indicative of phospha-alkenes and occurs more readily in the BBTPs than in their BTP analogues. The E_{pa} values observed for **13a**–**e** range from 1.00–1.21 V (vs. SCE in CH_2Cl_2) so oxidation is more facile than in benzobisoxaphosphole **16** (E_{pa} = 1.52 V vs. SCE in CH_2Cl_2).[4d] For BBTP derivatives **13d** and **e**, observation of the oxidation is complicated by significant shifting and loss of intensity in consecutive potential cycles (see the Supporting Information). To reproduce the oxidation signal for those derivatives, the working electrode must be polished in between cycles, which suggests that application of highly positive potentials causes decomposition or other processes creating deposits on the electrode. Oxidation can be consecutively repeated at least four times without significant change in all other derivatives. It is possible that electropolymerization of **13d** and **e** is occurring with the formation of an electrochemically inactive polymer. However, we currently have no conclusive evidence for this process, and follow-up studies are necessary to develop a better understanding of the oxidative behavior of these compounds.

Upon scanning negative potentials, all of the benzothiaphospholes undergo a quasi-reversible or irreversible first reduction, whereas **2c** also exhibits a second reduction process. Addition of hexyloxy groups and a second thiaphosphole moiety resulted in facilitation of the first reduction process and observation of a second reduction for all benzobisthiaphospholes. Furthermore, the reversibility of the first reduction is typically increased in **13a**–**e**. Reductions cycle reproducibly for all compounds when the anodic sweep does not exceed +0.9 V.

Reduction potentials of the compounds are not significantly altered by using heterocyclic substituents (e.g., thiophene and furan) instead of phenyl groups. However, as was previously demonstrated for BTPs,[13a] reductions of phenyl substituted BBTPs are readily tuned by modifying the phenyl ring. Compound **13b** displays the most negative reduction potentials in its series due to the electron donating nature of its C_6H_4-*p*-OMe substituents. The C_6H_4-*p*-CN group meanwhile has the opposite effect causing **13c** to exhibit the most positive reduction potentials, as well as a third reduction process (Figure 5). The feasibility of using phosphorus to tune frontier orbitals in heterocycles is also evident from the BBTPs. Comparison of the electrochemical behavior of **13a** with benzobisthiazole **14** reveals the expected effect of heavy heteroatom insertion. The two reversible reductions observed for **14** in THF (−1.62 and

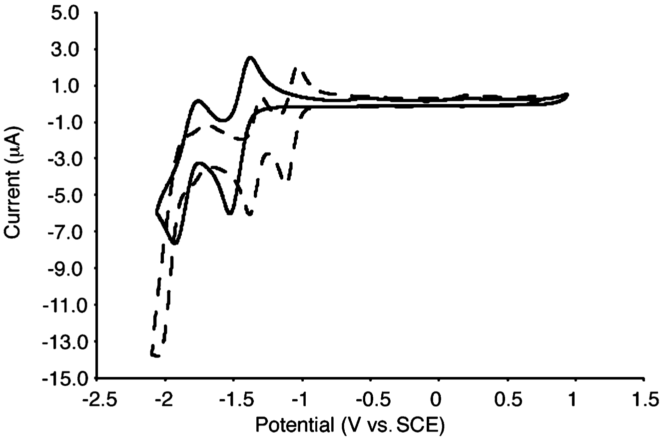


Figure 5. Cyclic voltammograms of **13a** (black line) and **13c** (dotted line) measured in THF. Voltammograms were collected using 0.10 M $[N(nBu)_4][PF_6]$ as the supporting electrolyte.

−2.01 V vs. SCE)[18] are more negative than the related reductions of **13 a** (−1.46, −1.86 V vs. SCE) reflecting a decrease in LUMO energy for the phosphole structure.

To date, there are a very limited number of reports describing electrochemical studies of heterocyclic architectures bearing more than one P=C bond. The benzobisoxaphosphole **16** has been characterized electrochemically and exhibits two reduction waves with the first one being reversible ($E_{1/2}=$ −2.01 V vs. SCE in THF). The exchange of O for S results in a significantly more facile first reduction ($E_{1/2}$ for **13 a**–**e** between −1.08 V and −1.59 V vs. SCE in THF). These data suggest a significant decrease in the LUMO energy upon going from the oxaphosphole to thiaphosphole moiety. Comparison of the BBTP (**13 a**–**e**) reduction potentials to the 2,2′-biphosphinine (−1.85 and −2.42 V vs. SCE in DMF) also illustrates the ease of reduction for the sulfur–phosphorus heterocycles.[7]

Conclusion

The synthesis and electrochemical properties of a series of fused heterocycles (BBTPs: **13 a**–**e**) that incorporate P=C bonds directly into the conjugation pathway have been reported. The participation of the P=C bond in the delocalized π-electron structure is indicated by substantial redshifts relative to their BTP counterparts (**2 a**–**e**) and to the analogous benzobisthiazole system (**14**). A potential advantage of these heterocycles for materials applications is the more facile reduction. The reduction potentials of **13 a** are approximately 150 mV more facile than their nitrogen counterpart **14**. The results indicate that insertion of phosphorus within the butadiene fragment of thiophene can be used to alter both the electronic and physical structure of conjugated π-electron frameworks. Future work will focus on incorporating the BBTP moiety into polymer architectures.

Experimental Section

General procedure for the synthesis of BBTPs 13 a, b, d, and e

In a nitrogen-filled glovebox, a Schlenk flask (100 mL) was charged with compound **12** (0.3 g, 0.74 mmol), dry toluene (30 mL), and an aryl acid chloride (2.1 equiv, 1.55 mmol). The Schlenk flask was removed from the glovebox, and triethylamine (4 equiv, 2.95 mmol) was added. Then, the reaction vessel was immersed in an oil bath at 110 °C. The solution was stirred overnight and turned bright yellow. After 17 h, the reaction mixture was cooled to RT, and NaOH solution (20 mL, 1 M) was added, and the mixture was stirred for 2 min before the aqueous layer was removed by syringe. This process was repeated once, and then $MgSO_4$ was added to remove residual water. The mixture was then transferred by cannula filtration into another 100 mL Schlenk flask. The solvent was removed in vacuo and the resultant product was washed with degassed diethyl ether (5 mL) under a N_2 atmosphere.

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Keywords: fused-ring systems · heterocycles · n-type acceptors · organic electronics · phosphorus heterocycles

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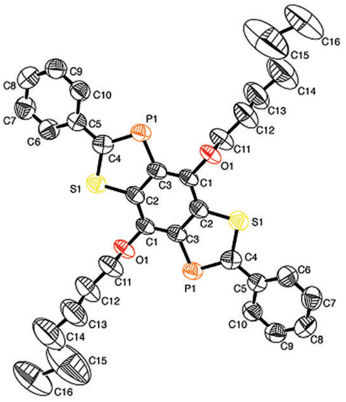
FULL PAPER

Fused-ring systems: Energetic tuning of conjugated building blocks can be achieved by atomic modulation of aromatic architectures. A phosphorus mimic of benzodithiophene and benzobisthiazole has been synthesized and structurally characterized (see figure). The UV/Vis spectrum of the phosphorus heterocycle is significantly redshifted compared to its organic counterparts. The redox properties of the benzobisthiaphospholes have been probed and revealed reversible reductions in THF.



Phosphorus Heterocycles

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Tuning Thiophene with Phosphorus: Synthesis and Electronic Properties of Benzobisthiaphospholes