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Recent Developments in Phosphole-Containing Oligo- and Polythiophene Materials

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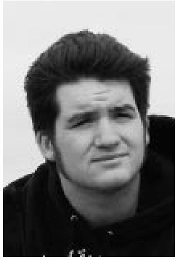
The introduction of phosphorus-containing moieties into π-conjugated thiophene materials has been found to provide materials with strongly optimized and highly tunable optoelectronic features compared to their native thiophene counterparts. 2,5-Diaryl- and 2,5-bis(heteroaryl)phospholes as well as fused tricyclic dithieno[3,2-*b*:2′,3′-*d*]phospholes represent two very valuable building blocks for organic electronics as their intriguing features can be altered systematically by several, in part unique, methodologies. The potential scope of these modifications has been determined by comprehensive investigations of their structure–property relationships via suitable molecular model compounds. On several occasions, these observations could successfully be transposed to corresponding polymers that are often difficult to characterize independently. The same is true for the first organic light-emitting diodes (OLEDs) based on a phosphole scaffold, whose properties could also be predicted successfully.

1. Introduction

Organic π-conjugated polymers and oligomers have commanded a significant amount of attention as a result of the conducting (upon doping), or semiconducting properties that they exhibit.[1] Consequently, these materials have great potential for use in electronic devices such as organic or polymer-based light-emitting diodes (OLEDs/PLEDs),[2] photovoltaic cells,[3] field-effect transistors (FETs),[4] nonlinear optical (NLO) devices and polymeric sensors.[5] The development of these systems, and the optimization of their optoelectronic properties often requires the use of model systems. Well-defined model systems allow for the elucidation of important structure–property relationships through the systematic variation of the model's chemical structure, and supramolecular organization. By taking advantage of established structure–property relationships, the properties of materials may be engineered at the molecular level to suit those required by specific applications.[1]

Varying the composition of the π-conjugated backbone in such materials has proven to be a particularly "fruitful" approach to tailoring the properties of organic π-conju-



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gated materials. Heterocyclopentadienes (pyrrole, furan, silole, and thiophene) have been used extensively to this end.[1] Poly- and oligothiophenes have proven to be particularly useful, and consequently form one of the most studied classes of π-conjugated polymers.[6] The ease with which thiophenes can be functionalized allows entire families of thiophene materials, displaying unique properties to be prepared. These families may be used to establish important structure-property relationships. Thiophene materials are often light emitting in the red-orange region of the visible spectrum, consistent with their ca. 2.0 eV bandgap.[6] This red emission is often difficult to obtain using other π-conjugated polymers, and implies that polythiophenes may be highly useful in LED applications. Unfortunately, the emission of polythiophenes is often quenched due to their tendency to form aggregates in the solid state, and the heavy-atom effect of sulfur. As a result, polythiophene materials display significantly lower emission efficiencies than those based on other more established π-conjugated scaffolds such as poly(fluorenes) (PFs), and poly(phenylenevinylenes) (PPVs).[6] The incorporation of other conjugated units into oligo- and polythiophenes has proven to be a reliable method to improve emission efficiency, and the performance of the light-emitting devices derived from these materials.[6]

Theoretical studies have implied that the phosphorus analog of pyrrole (phosphole) may be an excellent building block for the construction of π-conjugated materials.[7] Organophosphorus materials have received relatively little attention despite the fact that the incorporation of σ^3,λ^3-phosphorus centers allows for a number of facile, nearly quantitative chemical modifications to be performed. Trivalent phosphorus centers display a versatile reactivity, allowing for the preparation of entire families of materials exhibiting unique properties from a single precursor.[8] Reaction with oxidizing agents results in the formation of σ^4,λ^5-phosphorus centers, while the Lewis basicity of the σ^3,λ^3-phosphorus center allows for complexation with Lewis acids, and transition metals. The reaction of trivalent phosphorus centers with methylating agents results in the formation of a cationic λ^4-phosphorus species. Most importantly, all of these facile chemical modifications result in significant changes to the properties of the involved materials. The use of chemical modifications to tune the properties of a material is not possible in this simplicity with genuine organic systems.

The phosphole moiety **A** (Figure 1) in particular, displays a high potential for use in π-conjugated organic materials. Phosphorus centers do not readily form sp hybrids, therefore the phosphorus atom in phospholes is highly pyramidalized, and the lone pair displays a high degree of s character.[9] This prevents an efficient endocyclic interaction between the phosphorus lone pair and the phosphole's butadiene moiety. In fact, the small degree of aromaticity displayed by phospholes (an NICS value of –5.3 has been determined theoretically)[10] is actually due to a hyperconjugative overlap of the compound's butadiene system with the exocyclic P–R σ bond, and not the phosphorus lone pair.[11] This makes phosphole an ideal choice for the construction of π-conjugated materials because exocyclic delocalization along the polymer chain is favored in species exhibiting low resonance energies.[7]

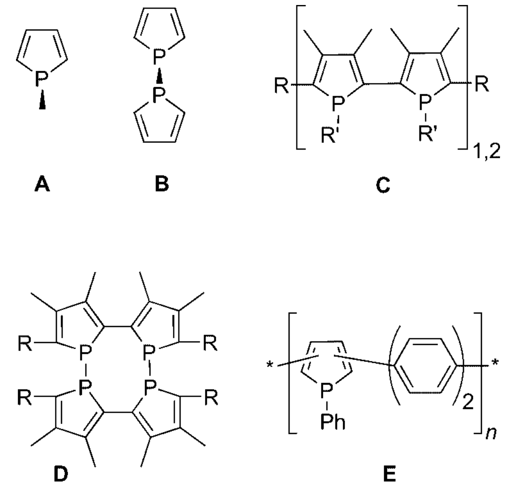


Figure 1. Phosphole-containing oligomers and polymers.

Additionally, σ–π conjugation ("through-bond" delocalization) is possible in 1,1′-biphospholes **B**, as a result of the low σ–σ* energy gap, and the high polarizability of the P–P linkage.[9] The interaction between the two phosphole π systems through the P–P σ bond in **B** may result in fascinating electronic properties that may be exploited in materials science. Although the chemistry of phospholes is well developed,[9] the incorporation of these phosphacyclopentadienes into π-conjugated materials has only been investigated quite recently. Tetrameric phosphole oligomers **C** ($n = 2$) and **D** have been prepared from α,α′-biphospholes **C** ($n = 1$),[12,13] however the first polymeric system to incorporate phosphole moieties **E**, was not reported until 1997 (Figure 1).[14,15] X-ray structural analyses revealed that the rings in compounds **C** were significantly twisted with respect to one another, preventing an effective overlap of the conjugated π system.[12,16]

Recently, phospholes have successfully been substituted for thiophene moieties in several well-defined oligo- and polythiophene systems. These systems display fascinating optoelectronic properties, and in some cases, unprecedented luminescence efficiencies. As a result, functional OLEDs and sensory materials have already been developed using these materials. Phosphaorganic materials have recently been comprehensively reviewed,[8] therefore the purpose of this microreview will be to provide a more detailed overview of the recent developments of the 2,5-dithienylphosphole, and the dithieno[3,2-*b*:2′,3′-*d*]phosphole systems. Related 2,5-diarylphosphole systems will also be discussed where relevant. The substitution at both the thiophene, and the phosphole moieties of these well-defined model systems may be altered, in addition to the possibility of facile chemical modifications involving the trivalent phosphorus center. Comparisons and contrasts between the properties of the obtained materials are highly dependant on the nature of the diarylphospholes or dithienophosphole based systems.

Consequently, structure-property relationships have been extensively investigated, and the properties of the systems have been tuned to suit potential applications.

2. 2,5-Diaryl- and 2,5-Bis(heteroaryl)phospholes

The incorporation of heteroaryl substituents at the α positions (2,5-positions) of a phosphole moiety provides materials displaying promising optoelectronic properties, as a result of exocyclic π conjugation present between the phosphole and the α-substituted aryl groups. Theoretical calculations have demonstrated this exocyclic π conjugation, by showing that the delocalization over the phosphole's 1,3-butadiene moiety increases [as determined using the Julg Index (JI)] upon introduction of heteroaryl substituents at the α positions of the phosphole ring.[17] This substitution was also shown to result in a concurrent reduction of the aromaticity (endocyclic π conjugation) of the phosphole ring (as measured by its calculated NICS values), demonstrating the fine balance between exocyclic and endocyclic delocalization in π-conjugated materials.[7] The 2,5-diarylphosphole system **1** developed by Réau and co-workers is a versatile model system for the development of π-conjugated materials (Figure 2).[18] It is possible to modify the chemical structure of **1** in a number of different manners, allowing for a full elucidation of the structure–property relationships displayed by the model system. Possible structural variations include the nature of the exocyclic phosphorus substituent, the size of the fused carbocycle present on the phosphole backbone, the aromatic groups present at the 2- and 5-positions of the phosphole moiety, and functionalization of the phosphorus center by facile chemical modifications (oxidation, complexation, methylation etc.). Structure–property relationships involving the 2,5-diarylphosphole system **1** have been established by examining the effects of these modifications on the system's interesting optoelectronic, and electrochemical properties. Where necessary, these effects have been rationalized theoretically.

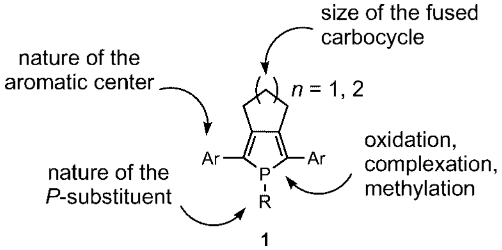
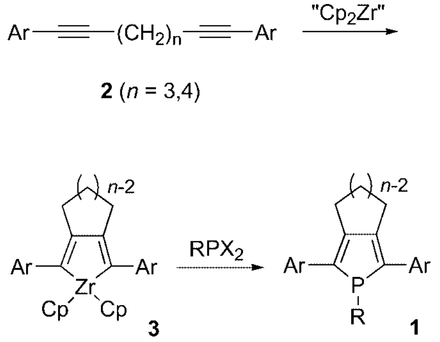


Figure 2. The π-conjugated phosphole system developed by Réau et al.

2.1 Modification of the π-Conjugated Framework

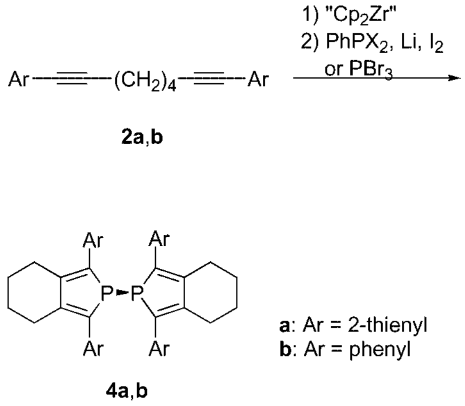
Compounds of type **1** are prepared using the Fagan–Nugent route,[18] a versatile method for the preparation of heteroles (Scheme 1).[19] They can be obtained by an intramolecular oxidative coupling between "zirconocene" and diynes in which the alkyne moieties are linked by a $(CH_2)_3$ or a $(CH_2)_4$ spacer. This spacer is required to promote the desired 2,5-substitution pattern.[18c] Subsequent reaction of the zirconacyclopentadienes **3** with dihalophosphanes produces the desired 2,5-diarylphospholes **1** in nearly quantitative yields. The use of different dihalophosphanes in the synthesis described above allows for the introduction of different substituents at the phosphorus center of 2,5-diarylphospholes **1**.[9] As a result of their stability in air, and their more favorable optoelectronic properties, *P*-phenyl-substituted phospholes dominate this family of 2,5-diarylphospholes, and the subsequent discussion of derivatives of **1** will focus on *P*-phenyl-substituted phospholes.



Scheme 1. Synthesis of 2,5-diaryl- and 2,5-diheteroarylphospholes.

The interaction between π chromophores in organic materials is not limited to assemblies connected by π-conjugated linkers. Indeed, the interaction of nearby π chromophores through σ linkers may occur with linkers that display high polarizabilities, and low σ–σ* gaps.[20] The electronic properties of materials displaying this form of σ–π hyperconjugation are often unique. The exocyclic P–R σ bond in phospholes is known to participate in a hyperconjugative interaction with the compound's butadiene moiety.[11] It has been suggested that P–P σ bonds display the requisite features (high polarizability and low σ-σ* gaps) to allow for an efficient interaction of the π-chromophores via a P–P σ bridge.[9] The 1,1′-biphospholes **B** (Figure 1) are a well-known family of compounds[9] that display the potential for an interaction of the phosphole π systems through the P–P σ link. The extended biphospholes **4a**,**b** were prepared according to the classical route for the preparation of 1,1′-biphospholes.[21] This route involves the reductive cleavage of the P–Ph bond in *P*-phenyl phospholes to generate intermediate phospholyl anions. Subsequent oxidation of the phospholyl anions results in the formation of the targeted 1,1′-biphospholes. The targeted biphospholes can also be prepared using an efficient "one-pot" synthesis starting from the 1,7-diyne precursors **2** (Scheme 2).[18f]

The structural parameters of **4a** suggest that the exocyclic conjugation observed between the composite heterocycles in the *P*-phenylphosphole precursor, remains in the 1,1′-biphosphole product, and the two π chromophores adopt a *gauche* conformation relative to one another (Figure 3).[18f] The absorption properties of the 1,1′-biphospholes, as determined by UV/Vis spectroscopy differ markedly from those of the corresponding phospholes. The individual 2,5-diarylphospholes display relatively simple ab-



Scheme 2. Preparation of conjugated P–P biphospholes.

sorption spectra with a single band in the 400 nm range due to the π–π* transition. On the other hand, the 1,1′-biphospholes **4a**,**b** display rather complex absorption spectra, with multiple bands, including one remarkably red-shifted absorption (broad shoulder between 440–560 nm for **4a**). Quantum chemical calculations revealed that an interaction of the π chromophores through the P–P linkage results in the splitting of the HOMO and LUMO levels of the parent phospholes.[18f] The optical properties, and the presence of a P–P-mediated through-bond interaction suggest that biphosphole materials, particularly those bearing thienyl substituents, may be useful in the development of novel materials. Additionally, it was demonstrated that the optical properties of the biphospholes could still be tuned by chemical functionalization (oxidation and coordination to AuCl were investigated) of the phosphorus centers.[18f]

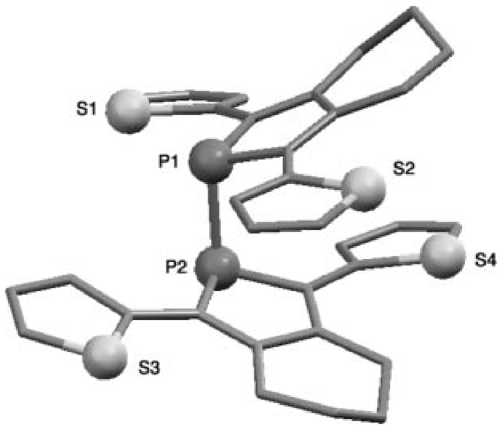


Figure 3. Molecular structure of **4a** in the solid state. Picture generated from the CSD-database file (code: BEWQAW).

Up until this point we have not been concerned with the nature of the aromatic substituents at the α positions of the phosphole moieties in Réau's 2,5-diarylphospholes **1**. In fact, a variety of aryl and heteroaryl groups have been incorporated into this system, and they display a profound influence on the optoelectronic and electrochemical properties of the system.[18] The nature of the aromatic groups can be varied by using an appropriately substituted diyne **2** in the first step of the Fagan–Nugent synthesis of the 2,5-diarylphospholes **5**–**7** (Figure 4).

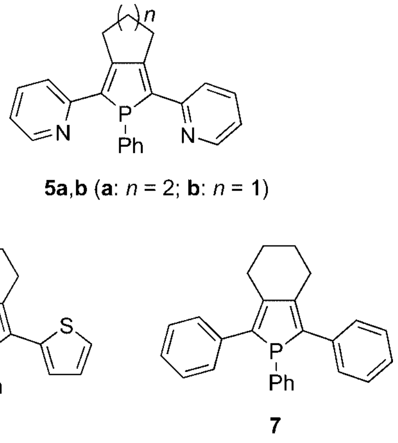


Figure 4. Variations of the aryl-/heteroaryl substituent.

2-Pyridyl groups were originally incorporated into these positions with the aim of preparing alternating electron-deficient/-rich (with the phosphole ring being considered as electron-rich heterocyclopentadiene)[22] species capable of exhibiting charge-transfer structures.[18a] It was anticipated that these charge-transfer structures would result in a more coplanar structure of the three heterocyclic rings, increasing the potential for conjugation between their π electron systems, potentially reducing the bandgaps of the corresponding materials.[23] Indeed, X-ray structural analysis of the 2,5-bis(2′-pyridyl)phosphole **5a** revealed that the twist angles between the heterocyclic rings were relatively small, and that the C–C bond lengths between the heterocyclic rings were intermediary between those expected of single and double bonds, implying an extensive π conjugation between the 2-pyridyl substituents and the central phosphole ring (Figure 5, top).[18a] Moreover, the phosphorus center in **5a** is highly pyramidalized, and the structural data indicate a rather small degree of endocyclic π conjugation, illustrating the balance between exocyclic, and endocyclic (aromatic) conjugation in these species. The oligothiophene analog **6**, in which a single thiophene ring is replaced by a phosphole ring, was prepared by Réau and co-workers shortly following their report of the preparation of **5a**.[18b] In addition to allowing for a comparison between the effects of substitution with an electron-poor heteroaromatic species (pyridine), and an electron-rich species (thiophene), the preparation of the 2,5-bis(2′-thienyl)phosphole **6** also provided an excellent model to study the effects resulting from the replacement of the central heteroatom in polythiophene with a heteroatom displaying remarkably different properties. As was observed with the 2,5-bis(2′-pyridyl)-phosphole **5a**, the structural features of **6** are consistent with an extended delocalization path incorporating the dienic moiety of the phosphole ring, and the thienyl substituents (Figure 5, bottom).[18c]

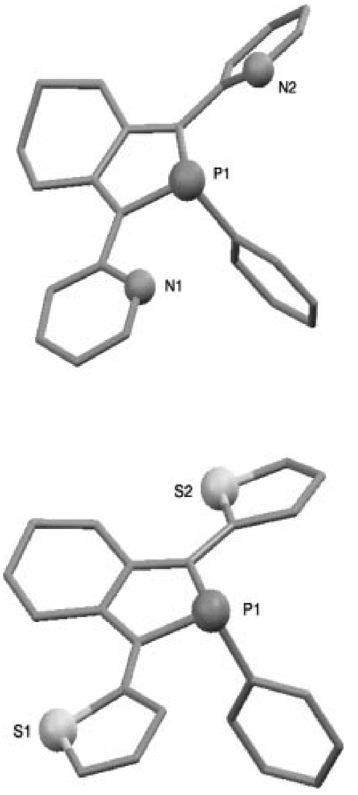


Figure 5. Molecular structures of the phospholes **5a** (top), and **6** (bottom) in the solid state. Pictures generated from the CSD-database files [codes: JOQFUQ (**5a**), MEKZEH (**6**)].

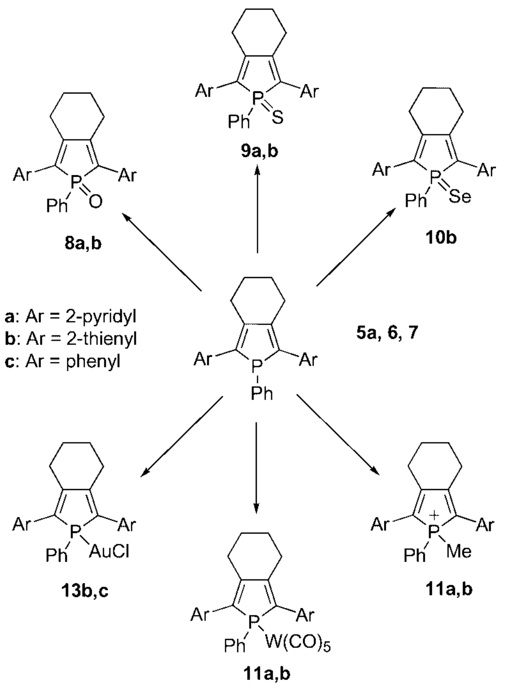
The absorbance properties of the 2,5-dithienylphosphole **6** display an even larger red shift relative to the 2,5-diphenylphosphole **7** ($\Delta\lambda_{max}$ = 58 nm, $\Delta\lambda_{onset}$ = 38 nm) than was observed with the 2,5-dipyridylphosphole **5a** ($\Delta\lambda_{max}$ = 45 nm, $\Delta\lambda_{onset}$ = 18 nm), indicating a significantly lowered HOMO–LUMO (π–π*) gap in the thienyl-substituted system. As a result, the incorporation of phosphole moieties into polythiophene materials may result in a significant optimization of the material's bandgap. Moreover, the emission of the dithienylphosphole **6** (λ_{em} = 501 nm) is also significantly red-shifted relative to that of both the diphenyl- and the dipyridylphospholes which displayed emissions at similar wavelengths (**5a**: λ_{em} = 463 nm; **7**: λ_{em} = 466 nm).[18a–18c] It is important to note that the presence of terminal thiophene units in these oligomers allows for the potential preparation of dithienylphosphole polymers by electropolymerization. Importantly, the electrochemical oxidation potential of the diarylphosphole is related directly to the electron-rich or -deficient nature of the aryl substituents.[18a–18c] In summary, the optoelectronic properties of the 2,5-diarylphospholes display increasing red shifts upon substitution of pyridyl groups for phenyl substituents, and a further red shift upon introduction of thienyl substituents.

The valence π-MOs of these compounds are formed by a combination of the π-MOs of the constituent heterocycles (phosphole and either pyridine or thiophene).[17] The HOMO of 2,5-bis(2′-thienyl)phospholes arises from an antibonding combination of the thiophene, and the phosphole HOMOs, which have very nearly the same energies (the energy of the MOs differs by only 0.2 eV). In the case of the 2,5-dipyridylphospholes, however, the HOMO of the pyridine moiety is relatively high in energy. As a result, the HOMO of the phosphole moiety experiences a more efficient interaction with the HOMO-1 of the pyridine ring (the energies of these two MOs differ by 0.8 eV). Owing to the greater energy difference between the pyridine HOMO-1, and the phosphole HOMO, they experience a less-efficient interaction, and the resulting HOMO in the dipyridylphosphole is only moderately raised. The near match of the HOMO energies of thiophene and phosphole, on the other hand, result in a very efficient interaction. The resulting HOMO of the dithienylphosphole system is much more significantly raised in energy than that of the dipyridylphosphole. The same calculations predict that the LUMOs of the 2,5-bis(2′-thienyl)phosphole, and the 2,5-bis(2′-pyridyl)phosphole have very similar energies. Consequently, the observed red shift in the absorption (π–π* transition) spectrum of the dithienylphosphole relative to the dipyridylphospholes may be rationalized on the basis of its destabilized HOMO, and the resulting decreased HOMO–LUMO gap. Comparison of the experimentally obtained absorption values for the 2,5-bis(2′-thienyl)phosphole **6** (λ_{max} = 412 nm)[18b,18c] with that the analogous oligothiophene (λ_{max} = 353 nm)[24] reveals a significant optimization of the HOMO–LUMO gap upon substitution of the central heteroatom in the terthiophene by phosphorus.

2.2 Modification of the Phosphorus Center

As discussed earlier, the incorporation of phosphole moieties into materials is desirable because it may allow for the preparation of entire families of compounds from a single precursor, by taking advantage of the versatile reactivity displayed by the σ^3,λ^3-phosphorus center. Indeed, the phosphorus center in Réau's 2,5-dipyridylphosphole **5a**, 2,5-dithienylphosphole **6**, and 2,5-diphenylphosphole **7** has been functionalized in a number of different ways (oxidation, complexation etc.) to yield new compounds displaying significantly different optoelectronic and electrochemical properties (Scheme 3).[18,25]

The bis(heteroaryl)phosphole oxides **8** can be prepared by the quantitative reaction of the bis(heteroaryl)phosphole with trimethylsilyl peroxide. Similarly, reaction of the phosphole species with other elemental chalcogens (sulfur and selenium) results in the quantitative formation of the corresponding bis(heteroaryl)phosphole sulfides **9**, and selenides **10**.[18] This oxidative functionalization of the phosphorus center in the 2,5-bis(2-thienyl)phosphole system results in a significant red shift of both the absorption ($\Delta\lambda_{max}$ = 11–22 nm) and emission wavelengths ($\Delta\lambda_{em}$ = 46–55 nm) of these compounds.[18a–18e,18g,18h] The oxidized compounds all display a single peak in their absorption and emission spectra in both solution, and the solid state.[18g,18d] Examination of the absorption and emission data of the chalcogen series **8b**, **9b**, and **10b**, reveals that the magnitude of the



Scheme 3. Chemical modifications of the σ^3,λ^3-phosphorus center in 2,5-bis(heteroaryl)phospholes.

observed red shifts increases with the increasing electronegativity (O >> S > Se) of the chalcogen used.[18c] This trend has been rationalized formally on the basis of the stabilities of the ylide forms of the P=E bond ($\leftrightarrow P^+–E^-$).[26] The ylide forms, featuring a positively charged phosphorus center, are of course more stabilized for more electronegative chalcogens E. The introduction of a formal positive charge at the phosphorus center of a phosphole ring results in a shift in the aromaticity of the ring from slightly aromatic, to slightly antiaromatic. The increased antiaromatic character of the σ^4-phospholes results in a destabilization of the compound's bonding MOs, and a stabilization of the compound's antibonding MOs.[26] As a result the HOMO–LUMO gap is decreased in the less aromatic σ^4-phosphole species. DFT calculations[17] also revealed that oxidation of the phosphorus center results in a stabilization of the energy levels of both the HOMO and the LUMO of the oxidized bis(heteroaryl)phospholes, with the stabilization of the LUMO being more significant.[18b,18c] In summary, oxidation may prove to be a reliable method to reduce the bandgap of dithienylphosphole materials. It should be noted that the fluorescence efficiency, and the decomposition temperature of the 2,5-bis(2-thienyl)phosphole sulfide **9b** were reasonably high (ϕ_{PL} = 4.6%, T_d = 254 °C),[18c] suggesting that thioxo-2,5-dithienylphospholes may be well-suited to incorporation into functional OLEDs.

Methylation of the trivalent phosphorus center in the bis(heteroaryl)phospholes to generate phospholium salts **11** proved to be another facile, and nearly quantitative means of altering the properties of the bis(heteroaryl)phosphole system (Scheme 3).[18b,18c] The functionalization resulted in relatively small red shifts in the excitation wavelengths ($\Delta\lambda_{max}$ **11a** = 4 nm; **11b** = 30 nm), and significantly larger red shifts in the emission wavelengths ($\Delta\lambda_{em}$ **11a** = 47 nm; **11b** = 92 nm) of the phospholium products. In fact, the red shifts observed upon methylation of the dithienylphosphole system are larger than those observed as a result of any other functionalization (oxidation, coordination etc.) of the phosphole's phosphorus center.[18] As discussed earlier for the dithienylphosphole chalcogenides, the presence of a positive charge at the phosphorus center in the phosphole ring reduces the aromatic stabilization of the compound, resulting in decreased HOMO–LUMO gaps.[26] The ionic nature, and the significant reduction of the HOMO–LUMO gap of the obtained phospholium products makes this modification potentially useful towards the development of functional phospholium materials.

Trivalent σ^3,λ^3-phosphanes are among the most versatile classes of organometallic ligands. Phospholes typically display similar coordination chemistry. Consequently, a large family of complexes can be prepared from a single phosphole precursor. The coordination chemistry of the dithienylphosphole ligand, however, has to this point been limited to its inclusion in tungsten and gold complexes **12** and **13**, respectively (Scheme 3).[18c,18d,18g] Coordination to the octahedral tungsten unit seems to have relatively little effect on the properties exhibited by the dithienylphosphole ligand.[18c] In contrast, coordination to gold produces a complex displaying dramatically different properties than those reported for the free ligand.[18d,18g] Significant red shifts in the absorption ($\Delta\lambda_{max}$ = 16 nm), and the emission wavelengths ($\Delta\lambda_{em}$ = 43 nm) are observed upon coordination to AuCl, and the fluorescence efficiency of **13b** improves to 14.0% compared to 5.0% in the free ligand. The gold complex displays a relatively high thermal decomposition temperature (T_d = 218 °C), allowing thin films to be obtained upon vacuum sublimation. While the excitation properties of the complex are similar in solution and in the thin film (a small red shift of 12 nm is observed in the thin film), the emission properties of the thin film are unique,[18d,18g] displaying two broad emission bands of similar intensity. The first emission is only marginally red-shifted relative to that observed in solution ($\Delta\lambda_{em}$ = 6 nm), however the second is remarkably red-shifted ($\Delta\lambda_{em}$ = 146 nm). When the gold complexes are dispersed in a polymethacrylate matrix, the low-energy emission disappears.[18g] This observation suggests that the first emission is due to the metal-perturbed intraligand π–π^* transition, while the second, remarkably red-shifted emission, is probably due to the formation of aggregates. The above observations suggest that dithienylphosphole AuCl complexes are a promising material for incorporation into OLEDs. In particular, materials displaying broad emissions may be suitable for the development of white organic light-emitting diodes (WOLEDs).[27]

2.3 Bis(thienyl)phosphole Oligomers and Polymers

The evolution of optoelectronic and electrochemical properties with increasing chain length is of great interest in the chemistry of π-conjugated organic materials.[1] The effect of increasing chain length in the π-conjugated 2,5-dithienylphospholes has been studied through the preparation of several well-defined oligomers.[18b,18c,18e] The mixed oligomer **14** (Figure 6), containing alternating donor and acceptor units, was prepared using an appropriately substituted diyne.[18b] As with the 2,5-bis(2-pyridyl)phospholes **5b** prepared earlier, this oligomer was expected to display increased conjugation as a result of intramolecular charge transfers. Indeed, the observed wavelength of excitation (λ_{max} = 427 nm) is red-shifted relative to either the 2,5-dipyridylphosphole **5b** or the 2,5-dithienylphosphole **6**. The emission of the mixed oligomer **15** is even more significantly red-shifted ($\Delta\lambda_{em}$ = 107 nm relative to the 2,5-dipyridylphosphole **5b**).

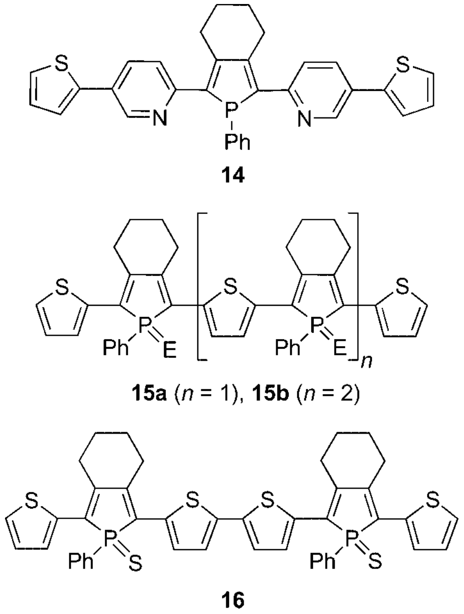
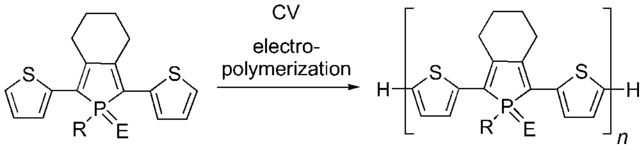


Figure 6. Well-defined 2,5-bis(heteroaryl)phosphole oligomers.

The oligo(α,α′-thiophene-phospholes) **15** (Figure 6) and their derivatives were prepared by the Fagan–Nugent route, using suitable bis- and tris(diynes).[18e] The three reported oligo(α,α′-thiophenephospholes) all display one broad band in their absorption spectra, assignable to the π–π* transitions of the thiophene-phosphole system. The excitation wavelength of the thiophene-phosphole dimer **15a** (λ_{max} = 490 nm) is significantly red-shifted relative to that of the corresponding monomeric 2,5-dithienylphosphole **6** (λ_{max} = 412 nm), demonstrating the successful extension of the conjugated π system in this oligomer. Sulfurization of the shorter oligomer leads to an additional red shift in the excitation wavelength. The magnitude of the red shift that occurs upon functionalization of the phosphorus centers with sulfur is similar for both the monomeric 2,5-dithienylphosphole **6**, and the bis(α,α′-thiophenephosphole) **15a** ($\Delta\lambda_{max} \approx$ 20 nm). Red shifts of similar magnitude are observed in the emission of both bis(α,α′-thiophenephospholes) **15a** and **15b**, resulting in emission in the red-orange region of the visible spectrum. Inspection of the UV/Vis spectrum of the larger tris(α,α′-thiophenephosphole) **15b** oligomer reveals an additional red shift relative to the bis(α,α′-thiophenephosphole) **15a** ($\Delta\lambda_{max}$ = 42 nm). This red shift reveals a further extension of the conjugated π system by the coherently smaller bandgap in the longer oligomer. The bis(α,α′-thiophenephospholes) **15** were subjected to further study by CV. This study supported the extended conjugation upon chain extension, by demonstrating that oxidation and reduction potentials were decreased, and increased respectively in the longer oligomers.[18e]

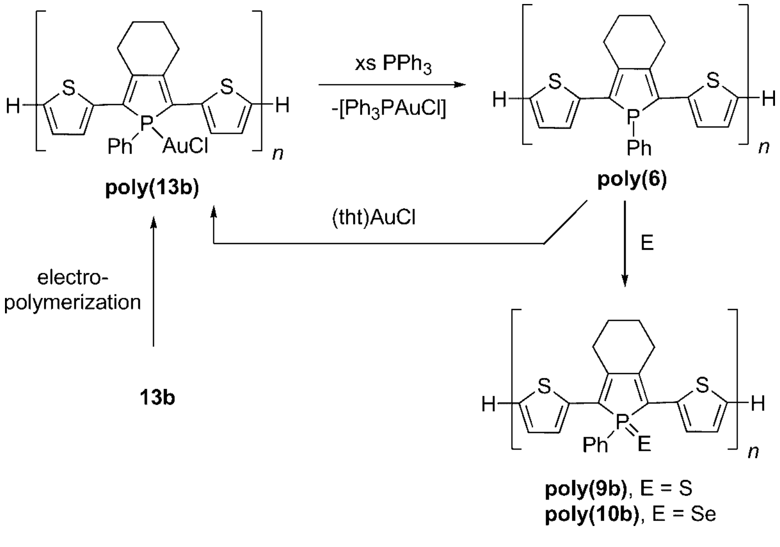
Polythiophenes are often prepared by electropolymerization of thiophene monomers and oligomers.[6] The presence of terminal thiophene functionalities in the 2,5-dithienylphospholes, and their derivatives is thus interesting, because they may allow for the preparation of polymers from this well-developed family of π-conjugated oligomers. It is well known that α,α′ coupling is the major route involved in the electropolymerization of thiophenes,[6,28] therefore the "dimer" **16** (Figure 6), the product of one such coupling was prepared to examine the effects of α,α′ coupling in the 2,5-dithienylphosphole system **6**. The "dimer" was prepared using the Fagan–Nugent method with an appropriately substituted bis(diyne),[29] and was isolated as the sulfurized phosphole derivative.[18c] Absorption spectroscopy of **16** revealed significant red shifts in the excitation wavelengths relative to those displayed by the corresponding monomer **9b** ($\Delta\lambda_{max}$ = 100 nm, $\Delta\lambda_{onset}$ = 132 nm). These bathochromic shifts suggest an effective extension of the conjugated system, and imply that polymers generated electrochemically from 2,5-dithienylphosphole derivatives may display highly favorable properties, particularly with respect to bandgap.

During the electrochemical CV analyses of many of the 2,5-bis(2-thienyl)phosphole derivatives, the deposition of insoluble films was observed on the working electrode surfaces (Scheme 4).[18b,18c,18f] Repeated cycling resulted in a regular increase of the oxidation and reduction peak currents, consistent with the formation of an electroactive material on the surface of the electrode. By this method, polymeric films were obtained for the parent σ^3-dithienylphosphole **6** (E = lone pair),[18c] the σ^3-dithienyl-1,1′-biphosphole **4a**,[18f] and a large number of σ^4-dithienylphospholes,[18b,18c] including oxidized (**8**, E = O), methylated (**11**, E = Me^+), and transition-metal-coordinated species **13** (E = AuCl). The poor solubility of these films prevented the full characterization of most of the obtained polymers, however the optical properties of all the polymers were probed through their thin-film absorption spectra. The film obtained from the parent 2,5-bis(2-thienyl)phosphole **poly(6)** (E = lone pair) displayed two unresolved absorptions, both red-shifted relative to the corresponding monomer **6** ($\Delta\lambda_{max}$ = 51 nm, 155 nm). The absorption spectra of the functionalized dithienylphospholes all displayed red shifts relative to the appropriate monomers as well, illustrating the extension of the conjugated π system upon polymerization. The functionalized nature of the phosphorus centers in these polymers often resulted in an additional red shift in their λ_{max} values relative to that of the parent σ^3-dithienylphosphole polymer **poly(6)**. The general trends observed for the monomers with respect to the red shift resulting from a specific functionalization of the phosphorus center were preserved in the polymers. For example, the largest red shift in both the polymer and the monomer series is observed upon methylation of the phosphorus center. Comparison between the properties displayed by the well-defined α,α′-coupled dimer **16**, and the analogous polymer suggest that the polymers obtained are in fact, longer α,α′-coupled oligomers.[18c] In summary, these results demonstrate the utility of incorporating a reactive heteroatom such as phosphorus into electroactive polythiophene materials. In addition to allowing the bandgaps of the resulting polythiophene-like materials to be tuned via facile chemical modifications of the monomeric precursors, the incorporation of the phosphorus center may result in a bandgap that is already optimized relative to that displayed by analogous, purely thiophene-containing oligomers.[17]



Scheme 4. Electropolymerization of 2,5-dithienylphospholes.

The presence of reactive, Lewis basic σ^3,λ^3-phosphorus centers in polythiophene materials such as those described above should allow for a variety of postfunctionalizations to be performed with the polymeric materials such as **poly(6)**. Functionalized dithienylphosphole polymers have been shown to display different properties than their nonfunctionalized analogs, therefore postfunctionalization of trivalent phosphorus-containing polythiophenes should allow them to be used as effective chemosensors.[5] In order to investigate the utility of the phosphole-modified polythiophenes as molecular sensors, the preparation of a corresponding 2,5-dithienyl-σ^3,λ^3-phosphole polymer film was required. This non-protonated polymer film[30] **poly(6)** was obtained using a *P*-protection/electropolymerization/deprotection sequence (Scheme 5).[18h] Protection of the phosphorus center by coordination to AuCl (**13b**), followed by electropolymerization resulted in the formation of the insoluble AuCl-coordinated dithienylphosphole polymer film **poly(13b)**. Deprotection was achieved in the presence of excess triphenylphosphane, affording [AuCl(PPh$_3$)] and the deprotected polymer **poly(6)**. The σ^3-phosphole-containing polymer displayed a blue shift in its absorption band ($\Delta\lambda_{\text{onset}}$ = 41 nm), and a significant negative shift in its oxidation current offset (ΔE_{pa} = 0.26 V), consistent with the shifts observed at the molecular level for this system.[18d,18g] The polymer **poly(6)** could be treated with a AuCl solution to regenerate the protected polymer **poly(13b)**. This result effectively demonstrated that the chemistry displayed by phospholes at the molecular level could be extended to the macromolecular level, a prerequisite for the development of chemosensors from the phosphorus-modified polythiophenes. The possibility that further postfunctionalizations of the deprotected polymer might result in property shifts similar to those displayed at the molecular level, led to the investigation of the σ^3-phosphorus-containing polythiophene's reactions with chalcogens. Immersion of Pt electrode, modified with a film of the deprotected polymer **poly(6)** into a solution containing elemental sulfur resulted in the nearly quantitative sulfurization of the polymer.[18h] The polymer **poly(9b)** displayed a red shift in its absorption ($\Delta\lambda_{\text{onset}}$ = 38 nm), and an anodic shift in its oxidation current (ΔE_{pa} = 0.23 V) upon exposure to elemental sulfur. The σ^3-phosphole-modified polythiophene also displayed an anodic shift (ΔE_{pa} = 0.11 V) in the presence of elemental selenium. When the anodic shifts of the σ^3-phosphole-modified polythiophene **poly(6)** were monitored as a function of time in a sulfur-containing solution, a collective response was observed, and the degree of sulfurization could be monitored by observing the gradual shifts in the electro-



Scheme 5. Postfunctionalization of poly(2,5-thienylphospholes).

chemical properties of the material. This σ^3,λ^3-phosphorus-containing polythiophene is the first reported conjugated polymer capable of detecting chalcogens.

2.4 Phosphole-Based OLEDs

The development of functional OLEDs requires materials displaying several requisite features.[2] The materials must display high thermal stabilities, so that homogeneous thin films may be deposited upon vacuum sublimation. Good luminescence efficiencies are also required if a material is to be incorporated into OLEDs. Additionally, it is essential that the materials display favorable hole and electron injection, and transportation properties. It has been demonstrated that materials based on the 2,5-bis(2′-thienyl)phosphole **6** and its derivatives display remarkable properties, with the potential for tuning by simple chemical modifications of the material's phosphorus center.[18] It is possible to tune the emission properties, the ionization potentials, and the electron affinities of these materials, allowing the color of the emission to be varied, and a good match to be obtained between the HOMO and LUMO levels of the material, and the cathode and anode (respectively) of the device. Moreover, a number of dithienylphosphole derivatives display high thermal stabilities (the thioxo- and AuCl-coordinated species **9b** and **13b** for example). These characteristics suggest that dithienylphosphole materials may be particularly well suited for incorporation into functional OLEDs. Indeed the incorporation of thioxo-dithienylphosphole, and AuCl-coordinated dithienylphosphole into functional OLEDs represented the first examples of OLEDs based on organophosphorus materials.[18d,18g] These compounds were both incorporated into single-layer OLEDs having an ITO/PEDOT:PSS/**phosphole**/Mg:Al/Ag configuration [ITO = indium-tin oxide; PEDOT = poly(3,4-ethylenedioxythiophene); PSS = polystyrene sulfonate]. The OLEDs incorporating the AuCl-functionalized phospholes displayed unique emission properties, similar to those observed for the same materials in the solid state.[18g] The long-wavelength emission of the AuCl-functionalized 2,5-diphenylphosphole **13c** was dominant, resulting in a saturated red emission from the device. This is of interest because non-doped red-emitting OLEDs are relatively rare.[31] The emission of the AuCl-coordinated dithienylphosphole **13b** on the other hand, uniformly covers a broad range (λ_{EL} = 500–800 nm), suggesting its potential for use in WOLED applications. The performance of a number of other single-layer devices having the same configuration but incorporating other diarylphospholes were also evaluated.[18g] Importantly, the electroluminescence of these devices matched those displayed by the emissive materials in the solid state, suggesting that the luminescence mechanisms involved are similar. This result implies that the structure–property relationships established for the diarylphosphole materials, can be extended to luminescent devices, offering a predictable means of tuning the emission color of the devices. The device based on the thioxo-2,5-dithienylphosphole **9b** outshone the other devices (including those based on the AuCl-coordinated diarylphospholes **13b**) in all respects.[18g] This device displayed the lowest turn-on voltage (2.0 V), the greatest brightness (3613 cd m^{-2}), and the best external electroluminescence quantum efficiency (EEQE) (0.16%). Unfortunately, the EEQE values of the single-layer devices, including that based on the thioxo-dithienylphosphole **9b** were rather modest. This often occurs in single-layer devices as a result of unbalanced charge carrier injection and transport. With the aim of improving device performances, multilayer devices were prepared for all the emissive phosphole materials examined, by sandwiching the emissive layer between a hole-transporting layer (HTL), *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-biphenyl-4,4"-diamine (α-NPD), and an electron-transporting layer (ETL), tris(8-hydroxyquinoline)aluminum (Alq_3). The resulting devices displayed turn-on voltages, and emissions similar to those observed in the corresponding single-layer devices. It was therefore concluded that the diarylphospholes remained the source of emission, and not the newly introduced ETL or HTLs. The performance of the multi-layer devices were dramatically improved with respect to brightness, and EEQE, often displaying improvements of over one order of magnitude. Once again, the best performance in all aspects was obtained with the thioxo-2,5-bis(2-thienyl)phosphole **9b** based device. This device displayed a low turn-on voltage (2.2 V), and dramatically improved brightness (37830 cd m^{-2}), and EEQE (0.80%). As a result of the outstanding performance of the thioxo-, and the intriguing emission of the AuCl-functionalized dithienylphospholes **9b** and **13b**, these materials were evaluated as potential hosts for dopant fluorescent dyes. The problem of obtaining red emission is often solved by incorporation of a dopant such as 2-*tert*-butyl-4-(dicyanomethylene)-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) into an emissive host matrix.[31] Both doped multilayer devices displayed red emission arising from the DCJTB dopant (λ_{EL} = 617–623 nm), and not the dithienylphosphole host. Moreover, the performance of both devices was similarly exceptional. Low turn-on voltages (2.2–2.4 V), and exceptional brightness (36538 cd m^{-2}), and EEQEs (1.22 and 1.83%) were observed for the doped devices. These observations suggest an efficient resonant energy transfer from the dithienylphosphole emissive matrices to the DCJTB dopant. These results demonstrate that efficient luminescent devices can be prepared from phosphole-containing oligothiophenes, offering the additional ability to fine-tune the properties of the system by taking advantage of the reactive phosphorus heteroatom.

3. Fused Tricyclic Dithieno[3,2-*b*:2′,3′-*d*]-phospholes

Open-chain organic π-conjugated materials consisting of aromatic, or heteroaromatic rings often display a significant degree of twisting between adjacent subunits in the solid state. Because the orbital overlap of the conjugated π system varies approximately with the cosine of the twist angle, this rotational disorder in open-chain systems results in a significant decrease in the degree of π conjugation displayed by oligomers and polymers of this type.[6] Annelated ring systems have the advantage of forcing the constituent rings to adopt a coplanar geometry, maximizing the overlap of the π systems of the constituent subunits. Moreover, the fused nature of the ring system in annelated materials limits the possibility of non-radiative decay processes, potentially allowing for extremely efficient emission from materials of this type. Theoretical calculations have suggested that fused polythiophene materials may display favorable bandgaps relative to their open-chain analogs.[32] Moreover, fused dithienothiophenes have recently been shown to display remarkably efficient emission.[33] Because emission is favored relative to internal conversion in the fused polythiophene system, the observed emissions of an annelated system were found to be blue-shifted relative to those of its α-coupled, open-chain polythiophene analogs. The 2,5-dithienylphospholes **1** developed by Réau et al., demonstrated that the incorporation of a phosphole moiety into the backbone of an oligothiophene results in the formation of materials displaying a number of highly favorable optoelectronic properties. Furthermore, the presence of a reactive heteroatom in these systems allows their properties to be tuned in a predictable manner following the establishment of structure–property relationships.[18,25] These results prompted Baumgartner and co-workers to develop the dithieno[3,2-*b*:2′,3′-*d*]phosphole system **17**.[34] As was seen in the 2,5-dithienylphosphole system **1**, it is possible to systematically modify the structure of **17** in a number of different ways, allowing for the establishment of structure–property relationships (Figure 7).[34] Modification of the substitution at both the phosphorus center, and the 2- and 6-positions of the dithieno unit generates a wide variety of dithienophospholes with unique properties. Moreover, the versatile reactivity of the σ^3,λ^3-phosphorus center allows for a number of chemically facile functionalizations (oxidation, complexation etc.) to be performed. Specific attention will be paid to the dithienophosphole's optoelectronic properties since their extraordinary nature makes this system a promising candidate for the development of materials to be used in optoelectronic applications (e.g. OLEDs, PLEDs, OFETs as well as photovoltaic cells).

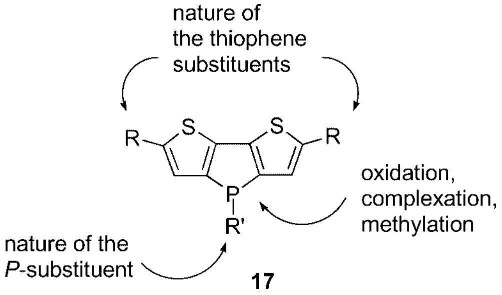


Figure 7. The dithieno[3,2-*b*:2′,3′-*d*]phosphole system developed by Baumgartner et al.

Many of the intriguing properties displayed by the dithieno[3,2-*b*:2′,3′-*d*]phosphole system can be rationalized by examining the molecule's frontier orbitals. Quantum chemical calculations revealed that both the HOMO and the LUMO of the parent dithieno[3,2-*b*:2′,3′-*d*]phosphole **17** can be easily derived from the frontier orbitals of the individual composite heterocycles, providing evidence that the π system is well-delocalized over the entire molecule (Figure 8).[34b] The HOMO of **17** is an antibonding combination of the HOMOs of the individual thiophene rings, resembling the phosphole's HOMO. The LUMO of **17** also resembles the phosphole ring's LUMO, and is comprised mainly of a bonding combination of the thiophene rings' LUMOs. It is important to note that the HOMO contains a nodal plane at the phosphorus center, while the LUMO contains a contribution from the $\sigma^*_{P\text{–}R}$ MO. As a result, chemical modifications of the phosphorus center will significantly affect the compound's LUMO. This feature will prove essential to the eventual tuning of the optoelectronic properties of dithienophosphole materials through modifications of the compound's phosphorus center.

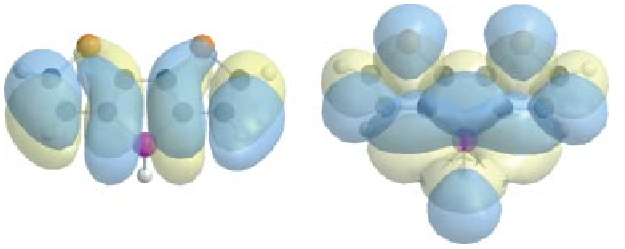
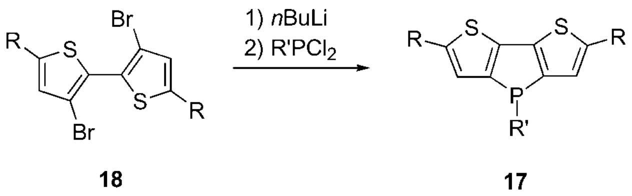


Figure 8. Frontier orbitals of the dithieno[3,2-*b*:2′,3′-*d*]phosphole (B3LYP/6-31G* level): HOMO (left), LUMO (right); P (purple), S (orange), C (black).

The dithieno[3,2-*b*:2′,3′-*d*]phospholes **17** can be accessed synthetically by lithiation of 3,3′-dibromo-2,2′-bithiophenes **18**, followed by reaction with an appropriately substituted dichlorophosphane (Scheme 6).[34] The resulting dithienophospholes display strong photoluminescence, typically in the blue region of the visible spectrum. The photoluminescence quantum yields are unprecedentedly high, ranging from 47 to 88 %,[34] providing evidence that emission in these annelated systems is indeed favored relative to internal conversion.



Scheme 6. Synthesis of dithieno[3,2-*b*:2′,3′-*d*]phospholes **17**.

The rigid tricyclic system of the *P*-phenyl compound **19a** is planar, and displays a high degree of π conjugation, as evidenced by the shortened C–C single bonds, and the elongated C=C double bonds present in the fused ring system (Figure 9).[34a] The observed bond shortening/elongation is significantly more pronounced in the fused tricyclic system than in Réau's 2,5-dithienylphospholes. The phosphorus center is significantly pyramidalized, and the endocyclic P–C bonds are similar in length to the exocyclic P–C bond, implying a minimal involvement of the phosphorus lone pair in the molecule's delocalized π system. These observations support the reduced aromatic character of the phosphole moiety in **19a**, and the resulting increased exocyclic π conjugation within the molecule, once again illustrating the balance between endocyclic (aromaticity), and exocyclic conjugation. As a result of this feature, materials derived from the dithieno[3,2-*b*:2′,3′-*d*]phosphole scaffold display highly desirable optoelectronic properties.[34]

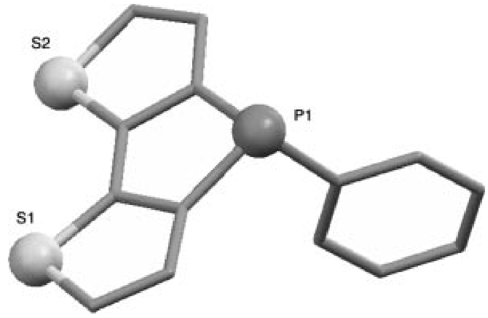
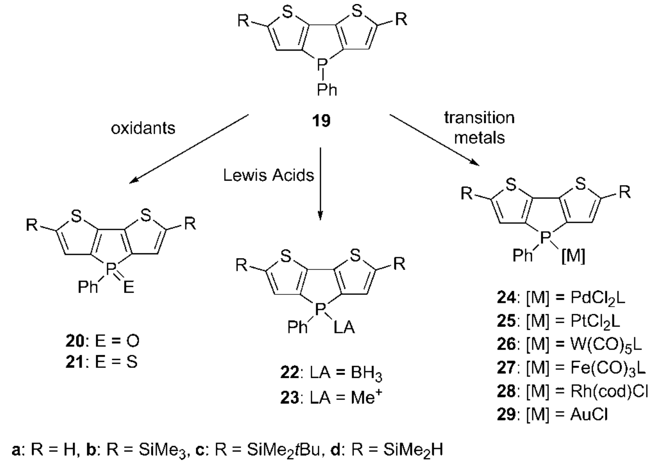


Figure 9. Molecular structure of **19a** in the solid state. Picture generated from the CSD-database file (code: FEHQAL).

3.1 Modification of the Phosphorus Center

The use of different dichlorophosphanes allows for the introduction of different substituents at the phosphorus center. Aromatic substituents at the phosphorus center typically result in more stable compounds than alkyl substituents due to the propensity for oxidation displayed by the latter.[9,34a] The subsequent discussion of derivatives of **17** will therefore focus on *P*-phenyl-substituted phospholes. The presence of a reactive phosphorus heteroatom in the dithieno[3,2-*b*:2′,3′-*d*]phosphole system allows the system to be tuned by taking advantage of these synthetically facile chemical modifications (Scheme 7).[34] The optoelectronic properties of the dithienophospholes **19** are particularly sensitive to such modifications as a result of the phosphorus center's contribution to the molecule's LUMO. Reaction of the Lewis basic phosphorus center in the dithieno[3,2-*b*:2′,3′-*d*]phosphole system with a Lewis acidic borane results in the formation of the phosphane–borane adducts **22** in almost quantitative yield.[34a,34b,34e]

As observed with Réau's system **1**, the phosphorus center in the dithieno[3,2-*b*:2′,3′-*d*]phosphole system may also be oxidized using a variety of oxidizing agents. The reactions are very general, and proceed in almost quantitative yields regardless of differences in the substitution at the thiophene rings. Reaction with peroxides (H_2O_2 or *t*BuOOH) results in the formation of σ^4,λ^5-dithienophosphole oxides **20**, while σ^4,λ^5-dithienophosphole sulfides **21** may be prepared by reaction with elemental sulfur.[34a,34b,34d,34e] Both the borane adducts, and the oxidized σ^4-dithienophospholes **22** and **20** display red-shifted excitation and emission wavelengths. The magnitude of this red shift is greater for the oxidized species than for the dithienophosphole–borane adducts ($\Delta\lambda_{max}$ = 8 nm, $\Delta\lambda_{em}$ = 9 nm). The phosphole oxides **20** and sulfides **21** display identical red shifts as a result of their similar nature, however the intensity in the observed fluorescence is significantly stronger for the dithienophosphole oxide than for the sulfide as a result of sulfur's increased quenching ability.[34b] These red shifts are larger in both the excitation ($\Delta\lambda_{max}$ = 28 nm) and emission wavelengths ($\Delta\lambda_{em}$ = 38 nm) than those observed for the corresponding borane adducts **22** as a result of the oxidized phosphorus center's increased electron-accepting ability. It should be noted that in the presence of electron-withdrawing substituents on the thiophene rings (vide infra), a cumulative effect is observed in both the excitation and emission wavelengths, resulting in larger red shifts for both the borane adducts **22**, and the oxidized σ^4,λ^5-dithienophospholes **20**, **21**. Quantum chemical calculations show that the oxidation of the phosphorus center in the dithieno[3,2-*b*:2′,3′-*d*]phosphole system results in a significant lowering of the LUMO energy level.[34b] Because the HOMO of the dithienophospholes **17** contains no contribution from the phosphorus center, this lowering of the LUMO's energy accounts for the observed red shifts. The experimentally observed band maxima are in good agreement with those calculated by TD-DFT means, implying that such computations may be helpful in predicting the optoelectronic properties of yet unknown dithienophospholes.[34b]



Scheme 7. Functionalization of the σ^3,λ^3-phosphorus center in dithienophospholes **19**.

Recently, cationic phospholium compounds **23**, based on the dithieno[3,2-*b*:2′,3′-*d*]phosphole system have been prepared by methylation of the phosphorus center (Figure 10).[34f] Treatment of the dithienophosphole with methyl triflate resulted in the formation of the cationic phospholium salt **23a** (Scheme 7). The fluorescence of the cationic dithienophosphole exhibits a pronounced red shift, emitting in the green region of the visible spectrum [λ_{max}(π–π*) = 376 nm, λ_{em} = 467 nm].[34f] This is the largest red shift observed, due exclusively to the functionalization of the phosphorus center, and not due to a cumulative effect resulting from functionalization of both the phosphorus and the thiophene rings in the dithieno[3,2-*b*:2′,3′-*d*]phosphole system (vide infra). The magnitude of this red shift highlights the potential utility of this simple chemical modification in terms of significantly tuning the optoelectronic properties of dithienophospholes. It should be noted in this context that the methylation of the phosphorus center provides access to species that are also water soluble.[34f]

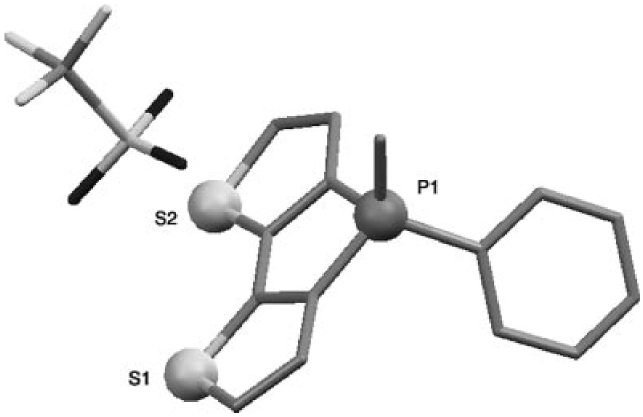
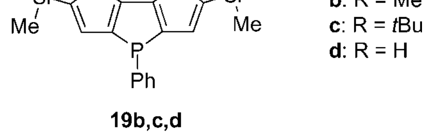


Figure 10. Molecular structure of **23a(OTf⁻)** in the solid state. Picture generated from the CIF-file.[34f]

Dibenzophospholes are known to coordinate to a variety of metal centers, behaving similarly to diphenylphosphanes.[9] The rigid tricyclic dithieno[3,2-*b*:2′,3′-*d*]phospholes **19** behave in a similar manner (Scheme 7).[34b,34c] The coordination of the dithieno-phospholes to transition metals results in an increase in the acceptor character of the dithienophosphole's phosphorus center. X-ray structure analyses of several complexes based on Pd, Pt, W, and Au revealed that the structural properties of the coordinated dithienophosphole ligands are similar to those of the free ligands. This result is in line with the poor delocalization of the phosphorus lone pair in the dithienophosphole system **17**.[9] Similarly to the free ligands, the fluorescence observed in the transition-metal complexes is due to intra-ligand π–π^* transitions. As a result of the increased acceptor capacity of the phosphorus center however, red shifts in the absorption and emission wavelengths of the dithienophosphole–metal complexes relative to the free ligands are typically observed. The magnitude of these shifts is dependant on a number of factors that are not always predictable, including the nature of the metal, the substitution of the dithienophosphole ligand, and the geometry of the resulting complexes.[34c] The earlier work of Réau and co-workers had demonstrated that phosphole AuCl complexes display very promising optoelectronic properties. In fact, the complexes have been incorporated into functional OLEDs.[18d,18g] Consequently, the gold(I) complexes **29** of the dithieno[3,2-*b*:2′,3′-*d*]phosphole system were also prepared (Scheme 7). Reaction of the dithienophospholes **19** with AuCl(tht) (tht = tetrahydrothiophene) resulted in quantitative formation of the desired AuCl complexes **29**. The gold center displays a linear geometry, and shows no evidence of aurophilic interactions in the solid state (closest Au–Au distance ca. 5.639 Å) as determined by X-ray crystallography.[34c] While the optoelectronic properties of the transition metal–dithienophosphole complexes examined earlier were relatively insensitive to the nature of the metal (emission at ca. 460 nm for Pt, W, Fe, and Rh complexes **25**, **26**, **27**, and **28**), the AuCl complexes **29** display intriguing optoelectronic properties, including unique absorption and emission wavelengths.[34c] The gold complexes display two absorptions. The red-shifted absorptions have been assigned to the intraligand π–π^* transition, whereas the blue-shifted absorptions observed (λ_{max} **29b**: 375 nm; **29c**: 405 nm) are likely due to σ_{AuP}–π^* transitions, although a ligand-to-metal charge transfer (LMCT) process cannot be ruled out. Typically bands in the absorption spectra of dithienophospholes are broad and poorly resolved. This is indeed the case with gold complex **29b**.[34c] The absorption spectrum of complex **29c** however, displays relatively narrow, well-resolved bands. This feature may arise as a result of poorer intermolecular interactions between the complexes in solution due to the added steric bulk of the *tert*-butyl group present in the silyl substituents on the thiophene rings of **29c**. The AuCl complex **29c** also displays a strong emission at 445 nm in the solid state, identical to that observed in solution, providing evidence that the complex does not aggregate in the solid state. The unique absorbance properties displayed by **29c** suggest that variation of the silyl functionality may allow the selective optoelectronic properties displayed by this system to be controlled. As a result, AuCl-coordinated dithienophosholes may be well-suited for the development of functional materials and devices.

3.2 Modification of the Dithieno-Framework

A number of different substituents may also be introduced at the 2- and 6-positions of the thiophene rings in dithieno[3,2-*b*:2′,3′-*d*]phospholes. The introduction of electron-accepting groups on the thiophene rings results in red shifts for both the excitation and emission wavelengths relative to those observed for the non-functionalized dithienophosphole **19a**.[34] This observation is in line with the further extension of the delocalized π system, and concurrent reduction in the molecule's optical HOMO–LUMO gap induced by the electron-accepting centers. This extension of the delocalized π system is further supported by spectroscopic data. Silyl groups have been used extensively to this end,[34a,34b,34c,34e] including trimethylsilyl (**19b**), *tert*-butyldimethylsilyl (**19c**), and dimethylsilyl (**19d**) groups that have been investigated systematically (Figure 11).

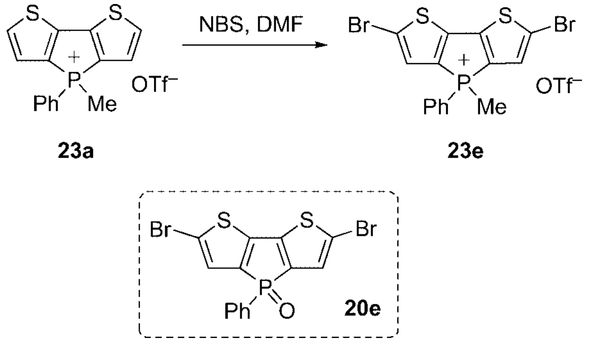


19b,c,d

Figure 11. Silyl-functionalized dithienophospholes.

All of these silyl-substituted dithienophospholes display similar emission wavelengths (λ_{em} = 420–422 nm), however the nature of the silyl groups has a significant effect on the excitation wavelengths.[34b,34e] The red shifts observed (R = tBu: $\Delta\lambda_{max}$ = 20 nm; R = H: $\Delta\lambda_{max}$ = 22 nm) are consistent with the relative inductive effects expected for methyl, *tert*-butyl, and hydrogen (Me < tBu < H) substituents at the silyl centers. The fact that the emission wavelength in these molecules is not significantly affected by the changes to the silyl centers, while the excitation wavelength is sensitive to them, allows the Stokes shifts of these dithienophospholes to be tuned in a predictable manner. Additionally, the use of the dimethylsilyl-substituted dithieno[3,2-*b*:2′,3′-*d*]phospholes **19d** allowed access to polymeric systems through hydrosilation and dehydrogenative coupling reactions (vide infra).

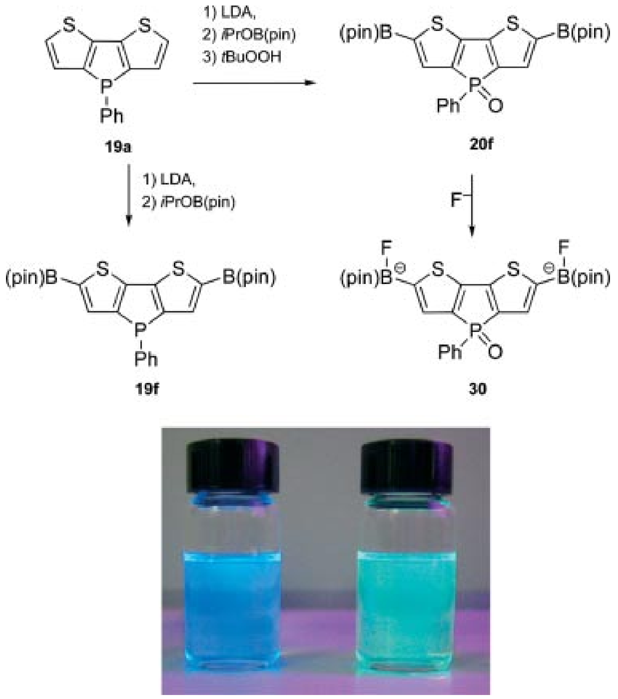
The introduction of bromo substituents at the 2- and 6-positions, to provide the dithienophospholium salt **23e**, can be achieved by treatment of the dithienophospholium salt **23a** with NBS in DMF (Scheme 8).[34f] As with other electron-accepting substituents, the presence of the bromo substituents results in a decrease in the compound's optical HOMO–LUMO gap. This feature becomes obvious when examining the extraordinarily red-shifted values obtained for both the absorption [$\lambda_{max}(\pi-\pi^*)$ = 411 nm] and the emission (λ_{em} = 495 nm) wavelengths of the dibrominated dithienophosphole **23e**.



Scheme 8. Introduction of bromo functionalities to the dithienophosphole.

It should be noted that the large magnitude of the observed red shift in this compound arises as the result of the cumulative effect of the electron-accepting cationic phosphorus center, and the electron-accepting substituents on the thiophene moieties. This observation highlights the fact that considerable optimizations of the dithienophosphole system's optoelectronic properties are possible through these simple chemical modifications, or combinations of simple chemical modifications. This method has recently been extended to provide access to 2,6-dibromo-dithienophospholes oxides **20e** (Scheme 8) as well.[34g] Most importantly, in terms of the potential for the use of this system in future optoelectronic materials, is the fact that the bromo functionalities allowed for the incorporation of the dithieno-phosphole system into polymeric materials,[34f] and well-defined oligomers through palladium-catalyzed cross-coupling reactions (vide infra).[34g]

The introduction of Lewis acidic boron centers to the thiophene rings of the dithienophosphole system was possible using a different strategy. Lithiation of the 2- and 6-positions of the unsubstituted dithienophosphole **19a** with LDA, followed by addition of two equivalents of isopropoxy(pinacol)borane resulted in the formation of the boryl-functionalized dithienophosphole **19f** (Scheme 9).[34d] Similarly to other dithienophospholes, boryl-substituted compound **19f** displays blue luminescence, and the emission wavelength (λ_{em} = 419 nm) is not significantly different from those displayed by dithienophospholes bearing electron-accepting silyl groups on the thiophene rings (λ_{em} = 420–422 nm).[34a,34b,34e]



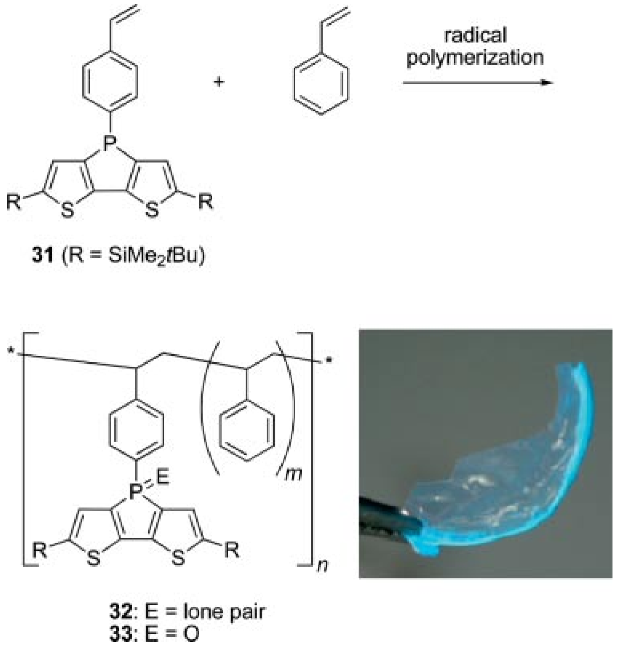
Scheme 9. Boryl-functionalized dithienophospholes – sensory materials (bottom left: **20f** - without fluoride, bottom right: **30** - with fluoride).

As a result of the high affinity of Lewis acidic boron centers for fluoride anions, the development of an effective sensory material based on the dithienophosphole system was possible.[34d] The fluorescence spectrum of the oxidized, air and moisture stable compound **20f** displays the expected red shifts in both the absorption and emission wavelengths ($\Delta\lambda_{max}$ = 22 nm, $\Delta\lambda_{em}$ = 33 nm) consistent with the increased electron-acceptor character of the phosphorus center upon oxidation. Treatment of **20f** with Bu_4NF results in the formation of the ionic borate-functionalized dithienophosphole **30** (Scheme 9).[34d] The ionic borate species **30** displays significantly red-shifted absorption (λ_{max} = 415 nm) and emission wavelengths (λ_{em} = 485 nm) relative to its neutral borane-functionalized precursor **20f**. In fact, the emission of the compound now occurs in the blue-green region of the visible spectrum, allowing for naked-eye detection of fluoride ions under UV light. These changes in the fluorescence spectrum upon addition of fluoride can be detected at the ppm scale. Addition of Bu_4NCl, Bu_4NBr, or Bu_4NI however, results in no change to the fluorescence properties of the borane-functionalized dithienophosphole **20f**, consistent with the high selectivity of the boron centers for fluoride ions. As a result, the borane-functionalized dithienophospholes **19f** and **20f** function as useful, selective, and potentially quantitative sensory materials for fluoride ions.[34d]

3.3 Dithienophosphole Polymers

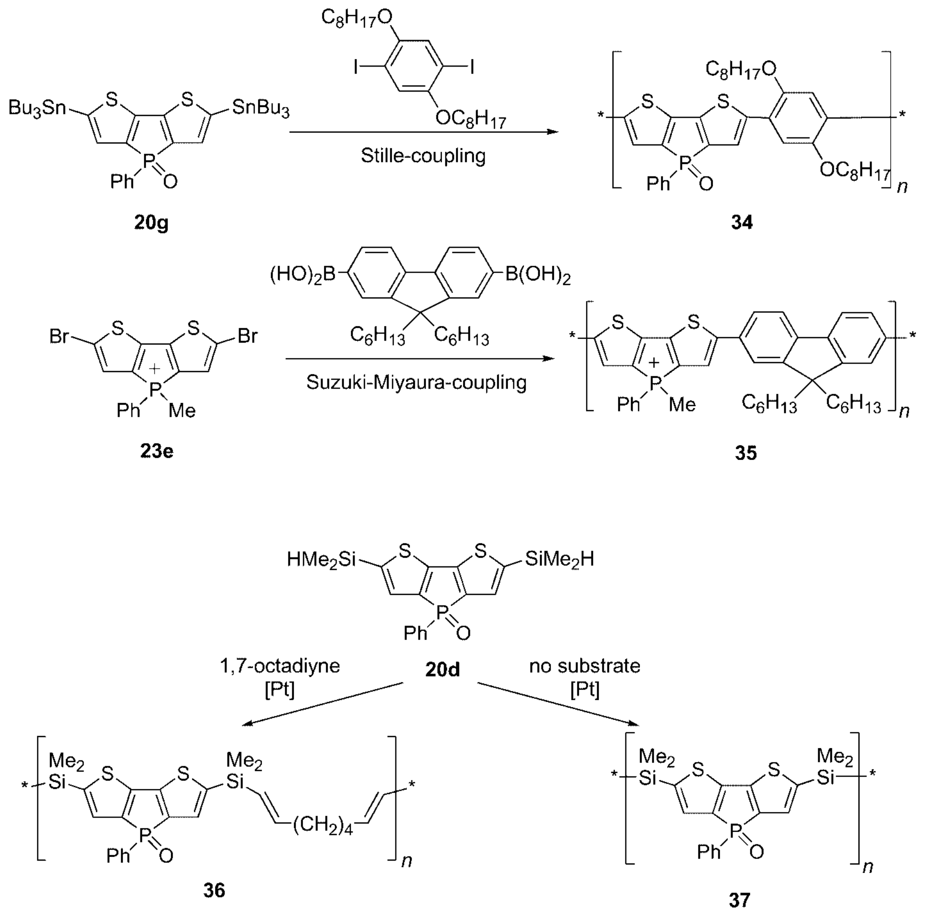
Polymeric materials based on the dithieno[3,2-*b*:2′,3′-*d*]phosphole scaffold have been prepared with the aim of combining the favorable optoelectronic properties displayed by the monomers, with the desirable properties, such as processability (e.g. as thin films) displayed by macromolecular systems.[1] Additionally, oligomers and polymers incorporating the dithienophosphole moiety directly into the conjugated backbone may display additional delocalization between π-conjugated subunits, resulting in optimization of the material's bandgap and further tuning of the material's optoelectronic properties.

The introduction of a 4-vinylphenyl substituent at the phosphorus center of **31** allowed for the incorporation of the dithienophosphole scaffold into a polymeric system as a side-chain functionality.[34a] Radical polymerization of **31** in the presence of styrene in varying ratios provided polymers such as **32** as white amorphous solids (Scheme 10). Gel permeation chromatography (GPC) revealed a high molecular weight of M_n = 147650 g mol^{-1}, and a polydispersity (PDI) of 2.46 for a copolymer with a 1:30 (**31**/styrene) ratio. Differential scanning calorimetry (DSC) analysis of the copolymer **32** revealed other favorable properties of the material, such as a glass transition temperature T_g = 114.2 °C superior to that of polystyrene, and a high thermal decomposition temperature of T_d = 428.2 °C. As expected the favorable optoelectronic properties of the dithienophosphole monomers were preserved in the copolymer **33**, which displayed absorption and emission wavelengths (λ_{max} = 352 nm, λ_{em} = 424 nm) nearly identical to those of the monomeric dithienophosphole **31** (λ_{max} = 352 nm, λ_{em} = 422 nm). Additionally, the exceptional photoluminescence efficiency of the monomers was preserved with the copolymer displaying a high photoluminescence quantum yield (ϕ_{PL} = 74.3 %). Oxidation of the phosphorus centers is accomplished by reaction of **32** with H_2O_2. As was observed with the dithienophosphole monomers, oxidation of the phosphorus center results in a significant red shift in the optical spectra of the air-stable oxidized polymer **33** ($\Delta\lambda_{max}$ = 22 nm, $\Delta\lambda_{em}$ = 34 nm) relative to their σ^3-phosphole-containing analogs **32**. In order to probe the potential of the obtained copolymers as PLED materials, thin films of the copolymers were prepared. The thin film of the σ^3,λ^3-dithienophosphole copolymer **32** displayed red shifts in both its excitation and emission wavelengths (λ_{max} = 374 nm, λ_{em} = 452 nm), while surprisingly the σ^4,λ^5-dithienophosphole copolymer **33** displayed a slightly blue-shifted absorption ($\Delta\lambda_{max}$ = –2 nm), and a significantly blue-shifted emission ($\Delta\lambda_{max}$ = –22 nm). Both the oxidized and the non-oxidized copolymers displayed good light stability, with decreases in emission intensity of less than 5 % following two hours irradiation. As a result of these favorable properties, the incorporation of the obtained copolymer into functional optoelectronic devices may be possible.



Scheme 10. Incorporation of the dithienophosphole system into polystyrene as a side-chain functionalization; right: thin film of the polymer **32**.

Recently, several copolymers containing the dithieno[3,2-*b*:2′,3′-*d*]phosphole moiety in the polymer backbone have also been prepared (Scheme 11).[34b,34e,34f] Consequently, conjugation between monomers, or comonomers may be possible, resulting in further optimization of the optoelectronic properties of the resulting dithienophosphole materials. The ability to introduce a variety of functionalities at the 2- and 6-positions of the thiophene rings of the dithienophosphole system has allowed for the preparation of a variety of copolymers using different coupling protocols. The incorporation of stannyl groups on the thiophene rings allowed for the preparation of a copolymer using Stille cross-coupling methods.[34b] Stille coupling of the oxidized stannyl-substituted dithienophosphole **20g** with 1,4-diiodo-2,5-bis(octyloxy)benzene as the aryl halide component resulted in the formation of a reddish-brown, poorly soluble material **34**. Suzuki–Miyaura coupling was used to obtain a copolymer from dithienophospholium monomers bearing bromo functionalities (**23e**) and a suitable fluorene-bis(boronic) acid.[34f] The obtained yellow copolymer was sufficiently soluble to allow for its analysis using GPC. This analysis revealed a molecular weight M_w = 9800 g mol^{-1}, and a *PDI* of 1.70. A dibromo-functionalized dithienophosphole oxide has recently been subjected to similar reaction conditions, resulting in the formation of an insoluble dithienophosphole-fluorene copolymer.[34g] The insolubility of this material prevented a full characterization, however, the red shifts observed in its optoelectronic properties relative



Scheme 11. Preparation of polymers containing the dithienophosphole system in the polymer backbone.

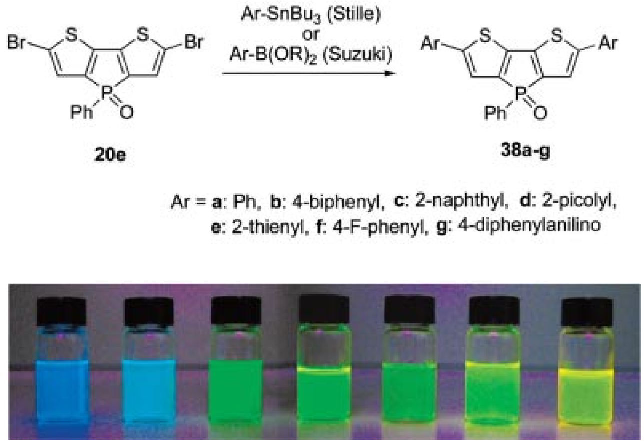
to those of the dibrominated precursor supported the successful copolymerization. The introduction of borane ester substituents in dithienophosphole **20f** should also allow for the copolymerization of this compound using Suzuki–Miyaura protocols, however to date, attempts to do so have resulted in the regeneration of the parent dithienophosphole **20a**.[34g]

Platinum-catalyzed hydrosilation has also been used to obtain copolymers from an α,ω-bis(alkyne) (1,7-octadiyne) and oxidized dimethylsilyl-substituted dithienophospholes **20d**.[34e] The use of PtDVDS ("Karstedt catalyst") resulted in conversion to the polymeric material **36**. GPC analysis of the obtained oily **36** revealed molecular weights up to M_w = 8000 g mol^{-1}. When a similar hydrosilation reaction was attempted using an alkene (cf. alkyne) substrate with the same catalyst system, a surprising result was obtained. Instead of the expected 1,2-addition of silicon and hydrogen to the alkene, dehydrogenative homocoupling of the dimethylsilyl groups was observed, producing a polymer **37** in which the dithienophosphole moieties are linked directly by disilanylene groups.[34e] The formation of this product was also observed in the absence of alkene substrates confirming that the alkenes were not involved in its generation. The disappearance of the Si–H signal and the presence of two sets of ^{29}Si satellites in the methyl proton signal ($^{2}J_{\text{Si–H}}$ = 25.4 Hz, $^{3}J_{\text{Si–H}}$ = 17.2 Hz) of the product's ^{1}H NMR spectrum were particularly supportive of such a dehydrogenative Si–Si homocoupling. GPC analysis of the obtained polymer **37** revealed molecular weights up to M_w = 10000 g mol^{-1}. This quantitative dehydrocoupling of a tertiary silane is unprecedented to date. The optoelectronic properties of the copolymer **36** ($\lambda_{\max}$ = 378 nm, λ_{em} = 460 nm) are not significantly different from those displayed by the corresponding monomer **20d** ($\lambda_{\max}$ = 383 nm, λ_{em} = 457 nm), indicating that the conjugated π system of the dithienophosphole is not significantly extended as a result of copolymerization. Similarly, the emission of the homopolymer **37** (λ_{em} = 459 nm) is almost identical to that of the monomer, while the absorption experiences a slight red shift ($\Delta\lambda$ = 10 nm) relative to the dithienophosphole monomer **20d**. These observations are in line with the earlier observation that modification of the silyl substituents in dithienophospholes results in slight changes to the compound's absorption properties, but not to its emission wavelength.[34b] Both silicon-containing dithienophosphole polymers **36** and **37** display good emission intensities, and photoluminescence quantum yields of ca. 56 %,[34e] in line with the preservation of the favorable optoelectronic properties of the monomers in the macromolecular systems.

In contrast to the silicon-containing dithienophosphole polymers **36** and **37**, those obtained through coupling reactions of the dithienophospholes and suitable aryl copolymers **34** and **35** display optoelectronic properties, with emissions and absorptions that are significantly different from those of the corresponding monomers.[34b,34f] These polymers contain an exclusively π-conjugated backbone, containing the dithienophosphole moiety. As a result, narrowing of the polymer's optical HOMO–LUMO gap and a corresponding red shift in the absorption and emission wavelengths of the macromolecular systems relative to the monomeric compounds was anticipated. Indeed, the emission of the polymer **35** obtained by Suzuki–Miyaura coupling with a fluorene copolymer displays a visibly red-shifted emission, now appearing in the yellow-green region (λ_{em} = 509 nm) of the visible spectrum (cf. the blue emission at λ_{em} = 467 nm of the corresponding monomer **23e**).[34f] The absorption wavelength of the polymer (λ_{max} = 485 nm) is also significantly red-shifted relative to that of the monomer (λ_{max} = 376 nm). The photoluminescence quantum yield of polymer **35** (ϕ_{PL} = 47.0%) is in the same range as those reported for the dithienophosphole monomers.[34f] Although poor solubility prevented a full characterization of the copolymer **34** obtained by Stille coupling of the stannyl-functionalized dithienophosphole **20g** with an aryl halide,[34b] the obtained product displayed significantly red-shifted optoelectronic properties. The yellow emission of compound **34** at λ_{em} = 555 nm is the most strongly red-shifted emission reported to date for polymeric materials derived from the dithieno[3,2-*b*:2,3-*d*]phosphole system. A red shift of similar magnitude is also observed in the excitation wavelength of polymer **34** ($\Delta\lambda_{max}$ = 123 nm). These results are indicative of a strongly extended π conjugation in both of the polymers discussed. As a result, dithienophosphole polymers **34** and **35**, containing exclusively π-conjugated backbones display highly intriguing optoelectronic properties, making them promising materials for future optoelectronic applications. The ionic nature of the methylated dithienophosphole fluorene copolymer **35** in particular, makes this material appealing for potential applications as a conjugated polyelectrolyte (CPE).[1]

3.4 Extended Dithienophosphole Molecules

To date, the emission of molecular dithieno[3,2-*b*:2′,3′-*d*]phosphole systems has been largely limited to the blue region of the visible spectrum (λ_{em} = 408–495 nm).[34] As was seen with Réau's system, the extension of the conjugated π system in well-defined oligomers, allows for further optimization of the bandgaps in the resulting materials. In principle, this strategy should allow access to well-defined species capable of displaying emission over a much larger range, depending on the π-conjugated system's degree of extension. Very recently, the use of 2,6-dibromodithienophosphole oxide **20e**, allowed for the incorporation of a wide variety of aryl substituents at the 2- and 6-positions of the dithienophosphole via palladium-catalyzed C–C coupling processes (Scheme 12).[34g] Stille and Suzuki–Miyaura cross-coupling protocols allowed for the preparation of a number of 2,6-diaryl-substituted dithienophospholes **38a**–**g**, displaying significantly extended π-conjugated systems (Scheme 12). Indeed the visible shift from blue-green to yellow-orange fluorescence emission could be observed in the cross-coupling reaction mixtures over the course of the reactions. The complete results of this study will be presented in a forthcoming publication.[34g] The effect of extended π conjugation on the optoelectronic properties of the resulting materials was investigated by incorporating aryl substituents displaying increasing conjugated paths. In line with the conclusion that extension of the conjugated path results in decreased HOMO–LUMO gaps, increasing red shifts in the optoelectronic properties of the products were observed with increasing conjugated path length in the aryl substituents. The effect of electron-rich, and electron-deficient aryl and heteroaryl substitution was also examined. The incorporation of thienyl groups (**38e**) was once again demonstrated to result in more favorable optoelectronic properties in the resulting materials, in line with the prediction that thienyl substituents are subject to a more favorable orbital interaction with phosphole moieties, resulting in decreased HOMO–LUMO gaps in the corresponding materials.[17]



Scheme 12. Synthesis of well-defined, extended dithienophospholes with different emission colors.

The most significant red shift in the optoelectronic properties of the dithieno[3,2-*b*:2′,3′-*d*]phosphole system observed to date arises as a result of the incorporation of 4-diphenylanilino substituents at the 2- and 6-positions of the thiophene rings (**38g**). This compound displays a bright orange emission (λ_{em} = 566 nm), and a remarkably red-shifted absorption (λ_{max} = 527 nm). When compared with the blue emission of the parent dithienophosphole **19a** (λ_{em} = 415 nm), this observation illustrates the versatile nature of the dithienophosphole system, and as a result the wide range of properties accessible through this system.

4. Conclusions

The incorporation of phosphole moieties into π-conjugated oligo- and polythiophenes has resulted in the development of new materials displaying fascinating properties. Both the 2,5-bis(2′-thienyl)phosphole, and the dithieno[3,2-

b:2′,3′-*d*]phosphole systems have proven to be versatile scaffolds as a result of the various manners in which their frameworks may be modified. Firstly, the nature of the exocyclic phosphorus substituents has profound effects on the stabilities of the obtained materials in both scaffolds. The properties of the obtained materials were also shown to be highly dependant on the nature of the 2,5-aryl substituents in Réau's diarylphosphole system, and the nature of the substituents at the 2- and 6-positions of Baumgartner's dithienophosphole system. In many respects diarylphospholes bearing thienyl substituents displayed superior properties relative to phospholes bearing alternative aryl, or heteroaryl substituents. Well-defined oligomers displaying additional π conjugation relative to the corresponding monomers have been prepared for both systems, potentially serving as useful models for larger macromolecular systems. Both families of compounds have been incorporated into such macromolecular systems, either as side-chain functionalities, or as subunits within the conjugated path. Of paramount importance in both scaffolds, the presence of a reactive trivalent phosphorus center allows for a variety of facile, quantitative chemical modifications (oxidation, complexation, methylation) to be performed. These modifications often result in significant changes to the properties of the obtained materials. As a result, large families of compounds, displaying novel properties may be prepared from single precursors. These modifications have been extended from the molecular level to the macromolecular level, allowing for a variety of postfunctionalizations of the obtained polymeric materials. Due to their intriguing properties, both phosphole-containing oligothiophene systems serve various functions in different applications: chemosensors for fluoride anions have been prepared using molecular dithienophospholes, while polymeric 2,5-dithienylphospholes were used in the development of the first polymeric chalcogen sensor. Recently, the fascinating emissive properties of the 2,5-dithienylphosphole system allowed for its incorporation in the first functional OLEDs based on organophosphorus materials. Although it is acknowledged that the study of organophosphorus π-conjugated materials such as the 2,5-diarylphosphole, and the dithieno-phosphole systems examined remains in its infancy, these promising systems represent key developments towards maturity in this field, and the development of new functional devices based on organophosphorus π-conjugated materials.

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