# Unique Phosphorus-based Avenues for the Tuning of Functional Materials

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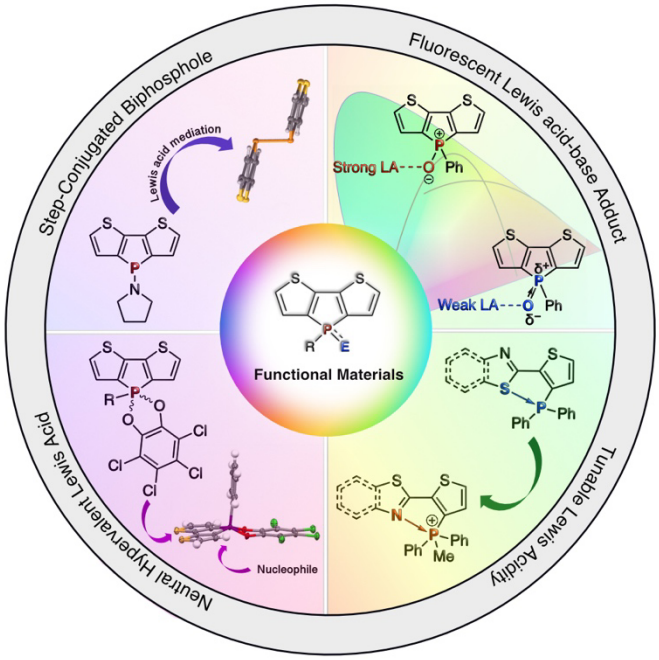
## Conspectus




Recent ground-breaking advances in synthetic chemistry have transformed main-group molecules from simple lab curiosities into powerful materials for a range of applications in all realms of life. Electron-accepting or -deficient materials in particular, have been the focus for development since their generally limited availability and stability have been a key limiting factor towards establishing new practical applications. In addition to the general requirements for the design of these materials, a deeper understanding of their inherent electronics and molecular interactions is

a requisite for the successful expansion of their utility. Previously, the incorporation of electron-deficient main-group elements, such as boron into a conjugated organic framework was considered an effective route toward the synthesis of high-performing electron-accepting materials. However, challenging conditions such as the need for bulky substituents for kinetic stabilization, air-free, and moisture-sensitive synthesis, and restricted storage abilities have led to the investigation of other elements across the periodic table to be used in a similar vein. Lately, heavier main-group elements such as Si, Ge, P, As, Sb, Bi, S, Se, and Te have also proven to be advantageous for electron-accepting materials as they exhibit polarizable molecular orbitals that are easily accessible to electrons or nucleophiles. This has laid the foundation for materials chemistry research on a variety of applications including, optoelectronic devices such as OLEDs, organic photovoltaics, energy storage such as batteries and capacitors, fluorescent sensors with both biological and physiological applications, organocatalysis and synthesis, and many more. Among the main group element-based materials, organophosphorus species are privileged as their frontier orbitals are easily altered by chemical modification or/and structural and geometrical manipulations at the phosphorus center itself, without the need for kinetic stabilization, or through electronic modification of the conjugated system. The five-membered phosphorus-based heterocycle, phosphole, is a particularly interesting motif in this context and extensive studies on the corresponding materials have uncovered the rich fundamentals of the σ*-π* interaction that imparts intriguing accepting properties, while sustaining morphological and physiological stability for utilization in real-life scenarios. Moreover, beyond the σ*-π* interaction in phospholes that is key to many of their acceptor properties as a material, the use of phosphorus also gives rise to easily accessible, low-lying antibonding orbitals. They pave the way toward Lewis acidic phosphorus species that, despite being considered as electron-rich species in general, open up

several possibilities for intriguing chemical reactivity through hypervalency. Herein, we representatively discuss some recent advancements through the various approaches that leverage the unique structures and electronics of organophosphorus species toward the design of materials with outstanding electronic, chemical, and structural properties and reactivities for the functional material world.

**Key References**


- Wang, Z.; Asok, N.; Gaffen, J.; Gottlieb, Y.; Bi, W.; Gendy, C.; Dobrovetsky, R.; Baumgartner, T. An Unexpected "Step-Conjugated" Biphosphole via Unique P–P Bond Formation. *Chem* **2018***, 4*, 2628–2643.[1] *A step-conjugated biphosphole is serendipitously synthesized via hard Lewis-acid mediated cleavage of the P-N bond of a P-amino-phosphole precursor to provide intriguing electronic communication by π-σ-π conjugation via P-P bond.*
- Gaffen, J. R.; Bentley, J. N.; Torres, L. C.; Chu, C.; Baumgartner, T.; Caputo, C. B. A Simple and Effective Method of Determining Lewis Acidity by Using Fluorescence. *Chem* **2019***, 5*, 1567−1583.[2] *The effective strength of Lewis acids can be directly measured by correlation of the red-shifted chromaticity data of corresponding Lewis-adducts with the phosphoryl group of fluorescent dithienophosphole probes on adduct formation.*
- Grenon, N.; Baumgartner, T. Exploration of Hypervalent Lewis Acid/Base Interactions in 2-(2′-Thiazolyl)-3-thienylphosphanes. *Inorg. Chem*. **2018**, *57*, 1630−1644.[3] *Conjugated organophosphorus species with a hypervalent P-center are formed via intramolecular P-N or P-S Lewis acid/base interactions, where the coordination mode is determined by the Lewis acidity of the P atom.*

- Asok, N.; Gaffen, J. R.; Pradhan, E.; Zeng, T.; Baumgartner, T. Structure- reactivity studies on hypervalent square-pyramidal dithieno[3,2-*b*:2,3'-*d*]phospholes. *Dalton Trans*. **2021**, *50*, 2243−2252.[4] *Square pyramidal geometry of supramolecular-stabilized dithienophosphole imparts Lewis acidity to the hypervalent phosphorus center and the compounds can be utilized as Lewis-acid mediators in organic transformations.*

## 1. Introduction

Organic conjugated materials can be effectively designed through structural, chemical, and electronic modifications that tailor their properties toward functional material applications. Thanks to decades of research, practical devices such as organic light-emitting diodes, organic batteries, organic photovoltaics, and optical sensors derived from these materials are now finding their way into the commercial market. With the successes of *p*-type organic systems, the development of *n*-type conjugated materials is now gaining equivalent traction. Heteroatom-incorporated conjugated materials are an attractive avenue toward electron-acceptor species as they offer unique opportunities for the tuning of optoelectronic, electrochemical, and structural properties. Moreover, heteroatom incorporation can also afford Lewis-acidic compounds with utility as reagents and catalysts for chemical transformations in organic synthesis.[5,6]

For example, boron-based materials are well known for their electron-accepting (or Lewis acidic) character that arises from the empty low-lying p orbital at boron but the heavier p-block element-containing compounds exhibit similar characteristics that evolve through less obvious interactions. Nonetheless, the mixing of the heteroatom orbitals with the π-molecular orbitals of the organic fragment is necessary in both the scenarios. Heavier p-block elements inherit atomic orbitals with a reduced tendency for hybridization, but a higher degree of polarizability. This, and the overall

lower orbital energies, potentially make antibonding orbitals of the heavier main group elements available for an interaction with a π-scaffold or a σ-donor. The case of phosphorus is an excellent representative example in this context.[5]

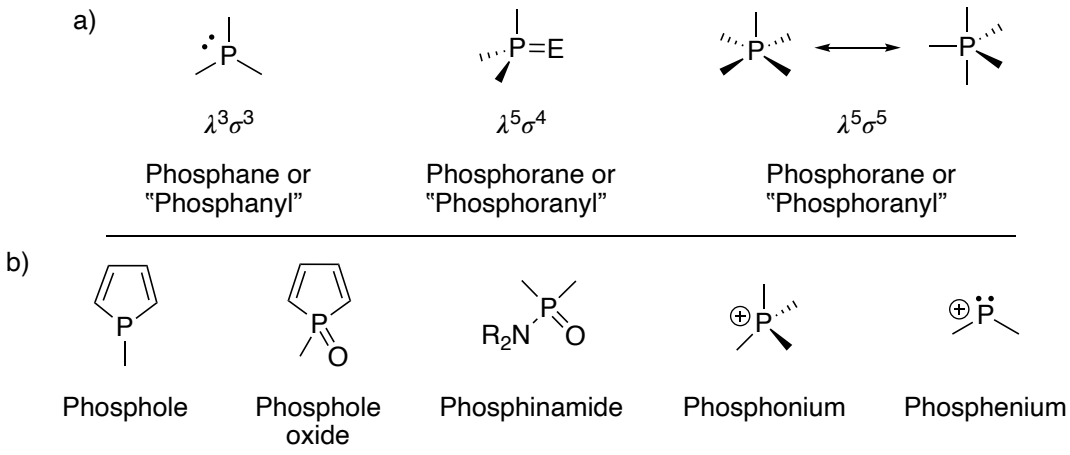



**Chart 1**. a) General P-nomenclature and b) specific building blocks used in this account.

Pentavalent ($\lambda^5$) phosphorus species that exceed the valence shell octet are a structural motif with obvious electron-accepting character as phosphoranyl groups have an increased relative electronegativity (compared to trivalent ($\lambda^3$) phosphanyl groups) that inductively withdraw electron density from the conjugated main scaffold as a function of the formal positive charge on the phosphorus atom (Chart 1). While the accepting behavior of a $\lambda^5$-phosphorus center is attributed to its hypervalency, trivalent ($\lambda^3$) phosphorus species can still acquire similar characteristics despite the inherent electron-donating nature of the lone pair at phosphorus. Trivalent $\lambda^3\sigma^3$-phosphorus generally adopts a pyramidal geometry due to its high inversion barrier arising from the strong s-character of the phosphorus lone pair, which is in stark contrast to its congener nitrogen. This is true for the five-membered phosphorus ring systems as well. Phosphole, the relative of pyrrole is considered only slightly aromatic by virtue of the pyramidal P-atom while the latter are inherently planar and have a more pronounced aromatic character.[5]

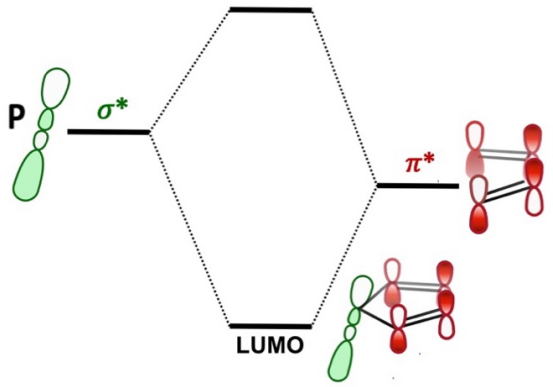



**Figure 1.** σ*-π* orbital mixing leading to favorable orientation of the σ* orbital for negative hyperconjugation with the π system of the main scaffold.

The pyramidal phosphorus atom is also the key contributing factor that gives rise to the electron-acceptor properties in conjugated phosphole materials. They are generated via a σ*-π* interaction between the σ* orbital of the exocyclic P-R bond and the π* system of the butadiene fragment of the five-membered system leading to an energetically stabilized molecular orbital (Figure 1). In most cases, this extended orbital represents the Lowest Unoccupied Molecular Orbital (LUMO) of the organophosphorus-based conjugated materials and provides a key component for the tuning of the acceptor properties by variation of the exocyclic substituent. The latter has direct implications for the energy of the σ* orbital, as a function of the polarity of the exocyclic bond. Moreover, in the $\lambda^3\sigma^3$ state, the lone pair at phosphorus is available for further chemical functionalization, such as oxidation, alkylation, or coordination to Lewis acids (E = O, S, $Me^+$, [M]). This allows installing a second exocyclic P-substituent that, with its inherent P−E σ* orbital, can engage in a second σ*-π* interaction thus further lowering the energy level of the LUMO (Figure 2).[1-5,7,8]

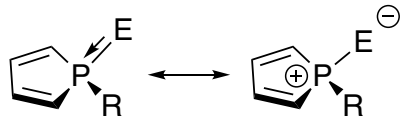



**Figure 2.** Electron-withdrawing E groups can impart a highly electrophilic P center in phosphole.

The scope of phosphole-based materials in functional applications is broad and diverse. Incorporation of the phosphole unit into a fused framework with flanking thiophenes, i.e., dithieno[3,2-*b*;2',3'-*d*]phospholes (**I**, Chart 2) leads to highly luminescent species with pronounced acceptor character. The functionalization of phosphorus with organic substituents R in **I** allows tailoring the properties for a variety of applications, including highly fluorescent sensory probes,[2,9] stimuli-responsive chromism,[10] self-assembly,[10,11] and polyelectrolytes,[12] whereas amino-functionalized dithienophospholes are precursors for materials with beneficial electron acceptor or self-assembly properties (*vide infra*).[1,11]

The related bridged bithiophene systems of the heavier group 15 heteroles also exhibit similar σ*-π* interaction but only show poor orbital overlap between the small carbon atoms and the large, diffuse heteroatomic orbitals. Nevertheless, the dithieno[3,2-*b*;2',3'-*d*]heteroles **II**-**IV** shown in Chart 2 are thermodynamically stable and exhibit phosphorescence that has not been seen for the P-containing relatives to date. The heavier pnictogens also resist oxidation due to the stronger s-character of their lone pair, while the phosphorus congener is readily oxidized, affording a new functionalization avenue for tuning the electronic properties of these systems.[5] Additionally, larger phosphorus ring systems, such as phosphepines (**V**), have similarly pronounced optical properties as their five-membered congeners, but are synthetically less accessible than dithienophospholes.[13,14]

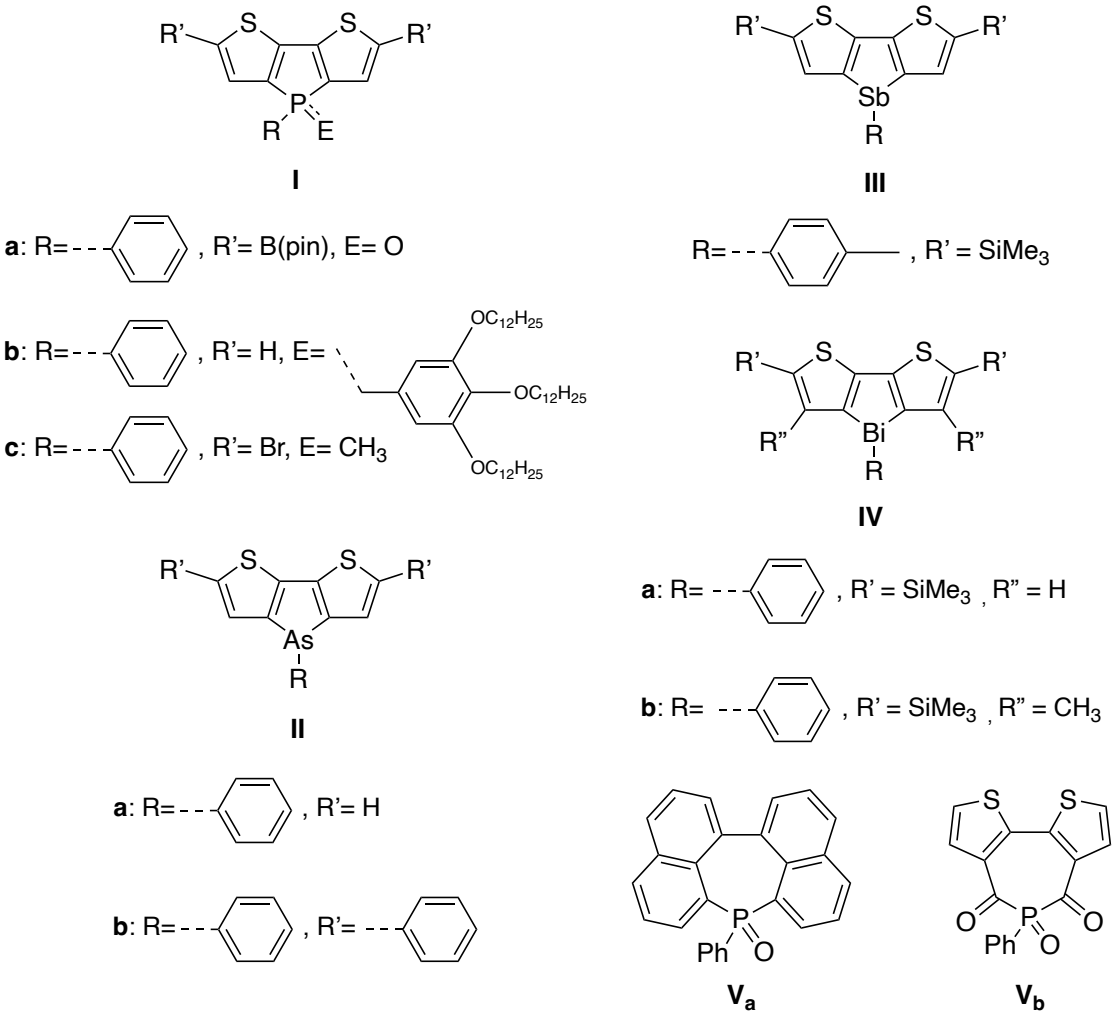
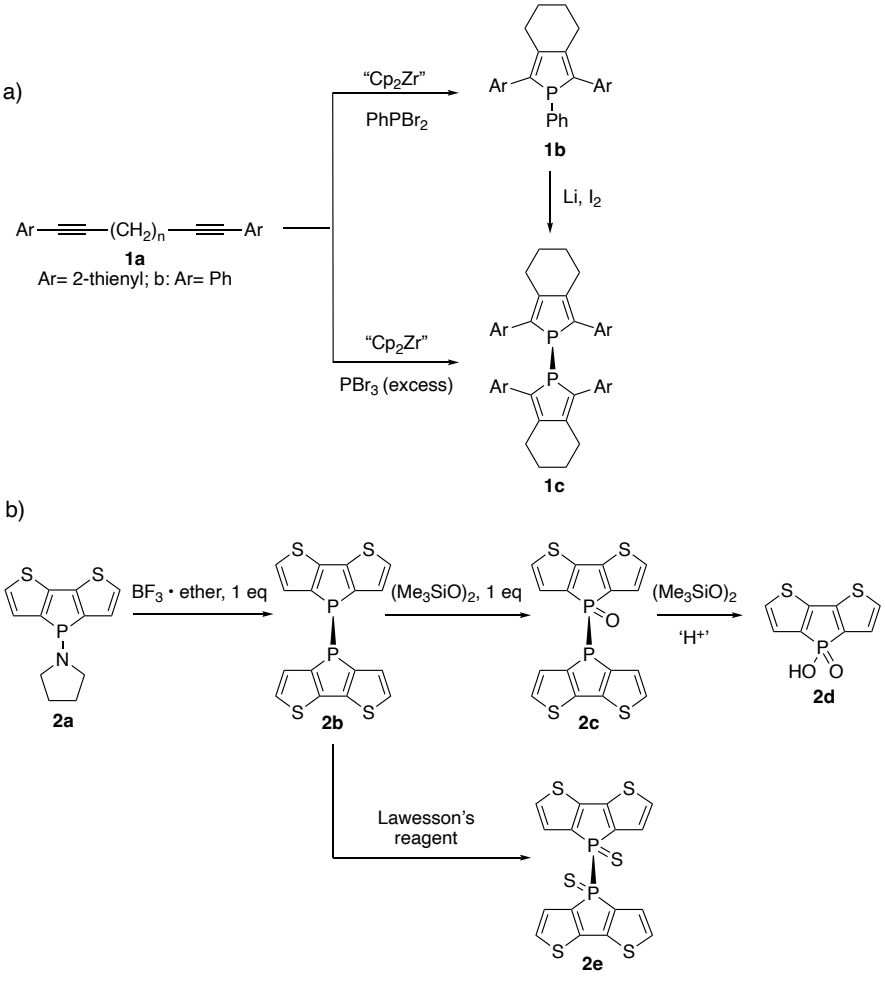



**Chart 2.** Representative dithieno[3,2-*b*;2',3'-*d*]heteroles and phosphepines.

This account will review recent work from our lab and others on leveraging σ*-π* interactions to better understand this bonding motif, and how further modification toward unique conjugated organic materials with value-added properties can be achieved through other related phosphorus-specific chemistries.

## 2. Enhancing σ*-π* interactions through P–P bond formation

An intriguing strategy to impact the frontier molecular orbitals by enhancing the σ*-π* interaction is to link two phospholes through a P–P bond. These biphospholes afford a unique avenue toward functional materials via conjugated systems mediated by σ scaffolds. While the Réau group's groundbreaking work represents a viable synthesis towards biphospholes of type **1c** from stable P-phenyl phospholes or the corresponding P-brominated species (Scheme 1), our own efforts have shown that this route cannot be extended to the dithienophosphole system, due to its distinct reactivity from that of non-ring fused phosphole systems.[1,15,16]




**Scheme 1.** A) Synthesis of Réau's biphosphole, b) synthesis of step-conjugated bi(dithienophosphole) **2b**.

Serendipitously, in the context of another project (*vide infra*), purification attempts of amino-dithienophosphole **2a** provided high-quality crystals for single-crystal X-ray diffraction after column chromatography with alumina under nitrogen. The molecular structure confirmed that the isolated species was, in fact, the elusive bidithienophosphole **2b** (Scheme 1). This observation was rather puzzling as there was no obvious reaction sequence that would lead to P–N σ-bond cleavage followed by P–P bond formation. Considering that the surface of alumina is covered with Lewis acidic sites, **2a** was treated with $BF_3$ at room temperature to observe the formation of asymmetric intermediate (**VI$_b$**, Chart 3), which upon refluxing led to biphosphole **2b**.[1]

The two phosphole subunits in **2b** are connected through an out-of-plane P–P σ bond leading to a phenomenon referred to as "step conjugation" (Figure 3a). The step-like shape of **2b** imparts electronic communication through π-σ-π conjugation between the individual dithienophosphole subunits through the P–P σ bond (via two mutual σ*-π* interactions). As the angle between the P–P σ bond and the conjugated planes is contracted to 75º, the phosphorus centers retain their pyramidal geometry. While Réau's biphosphole system adopts a twisted geometry in the solid state (Figure 3c), biphosphole **2b** exhibits a tight head-to-head conformation of the phosphole subunits (Figure 3b) suggesting potentially high charge carrier mobilities in a device setting. However, devices using **2b** as active material have not been reported to date.[1,16]

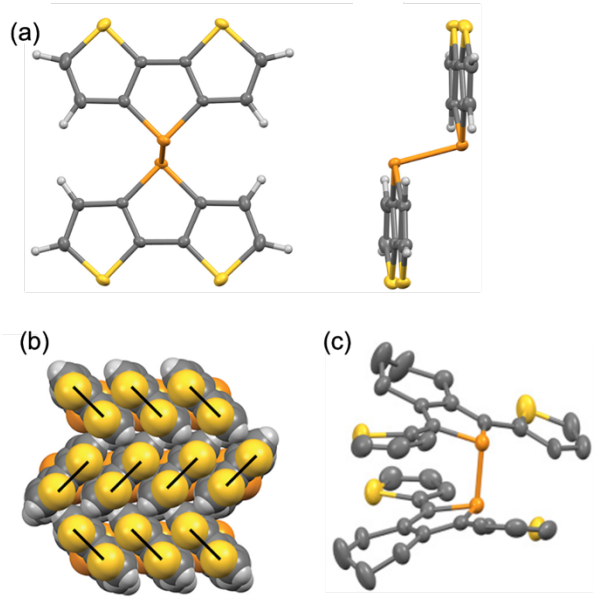



**Figure 3.** Solid-state structure of **2b** showing a) head-to-head conformation and step-like structure, b) herringbone arrangement with layer structure (intermolecular $\pi$-$\pi$ distance, 3.5 Å), c) solid-state structure of **1c**. Reproduced with permission from ref. 1. Copyright 2018 Elsevier.

To study the effect of modification of the P center on the σ*-π* interaction and the resulting electronic and optical properties, post-functionalization of the biphospholes was also investigated. Compound **2c** was synthesized by treating **2b** with one equivalent of ($(Me_3SiO)_2$) but further oxidation was found to cleave the P–P bond, resulting in the formation of **2d**. On the other hand, disulfide species **2e** was accessible without cleavage of the P–P σ bond on reacting **2b** with Lawesson's reagent (Scheme 1).[1]

The absorption onsets of the bi(dithienophosphole)s are shifted bathochromically, compared to **3**, indicating effective extension of conjugation through the P–P bond within the entire scaffold (Figure 4). Interestingly, the similarities in the absorption spectra of **2b** and **2e** suggests that optical features are dominated by the entire step-conjugated scaffold rather than the oxidation state(s) of the phosphorus atoms, which is in stark contrast to 'monomeric' dithienophospholes.[17] In mono-

oxidized **2c**, the scaffold experiences desymmetrization, leading to two distinct absorption peaks for the independent $\lambda^5$- and $\lambda^3$-P subunits respectively, instead of the broad absorption profile for the symmetric congeners **2b** and **2e**. However, all three species maintain the same absorption onset, supporting the electronic dominance of the step-conjugated scaffold overall. This is an illustrative example for how electronically modified biphospholes with distinct optoelectronic characteristics can be accessed on different levels by simple manipulation of the σ*-π* interaction.[1]

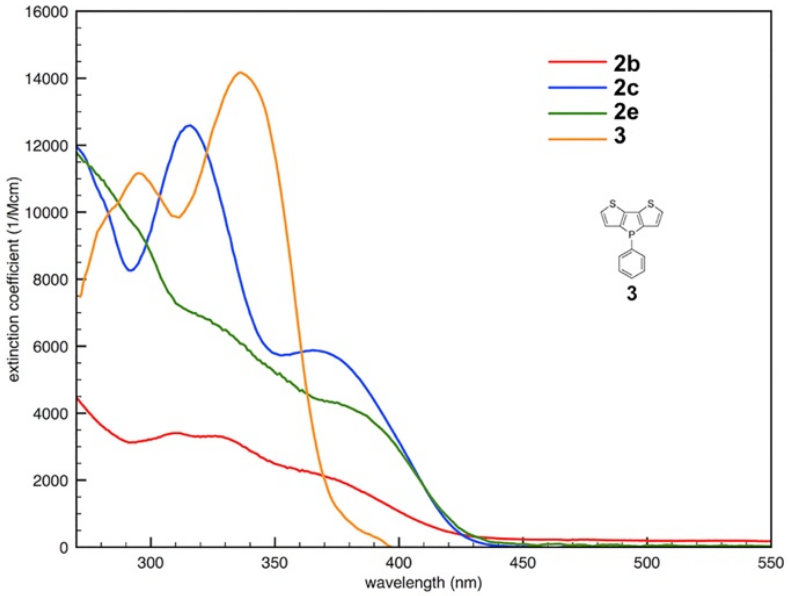



**Figure 4.** Absorption spectra of biphospholes **2b-e** compared to **3**. Adapted with permission from ref. 1. Copyright 2018 Elsevier.

In addition to the structural, chemical, and optoelectronic characteristics, the unprecedented mechanism that leads to the formation of the **2b,** further makes this system intriguing. Evidence suggests that the hard Lewis acid $BF_3$ interacts with the hard Lewis basic nitrogen center **($VI_a$)** (Chart 3).[18] This weakens the P–N bond and leads to the formation of the asymmetric intermediate (**$VI_b$**), which was also confirmed spectroscopically in solution. Subsequently, the α-carbon of the

pyrrolidinyl substituent is deprotonated by a second pyrrolidinide as shown in the transition state (**VI$_c$**) and lost as imine, ultimately providing the symmetric biphosphole **2b**.[1,19]

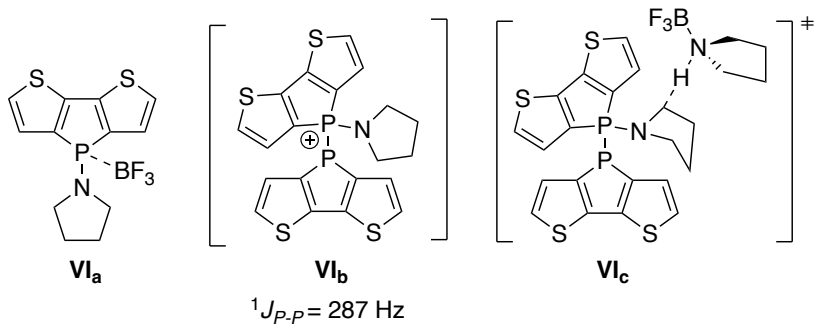
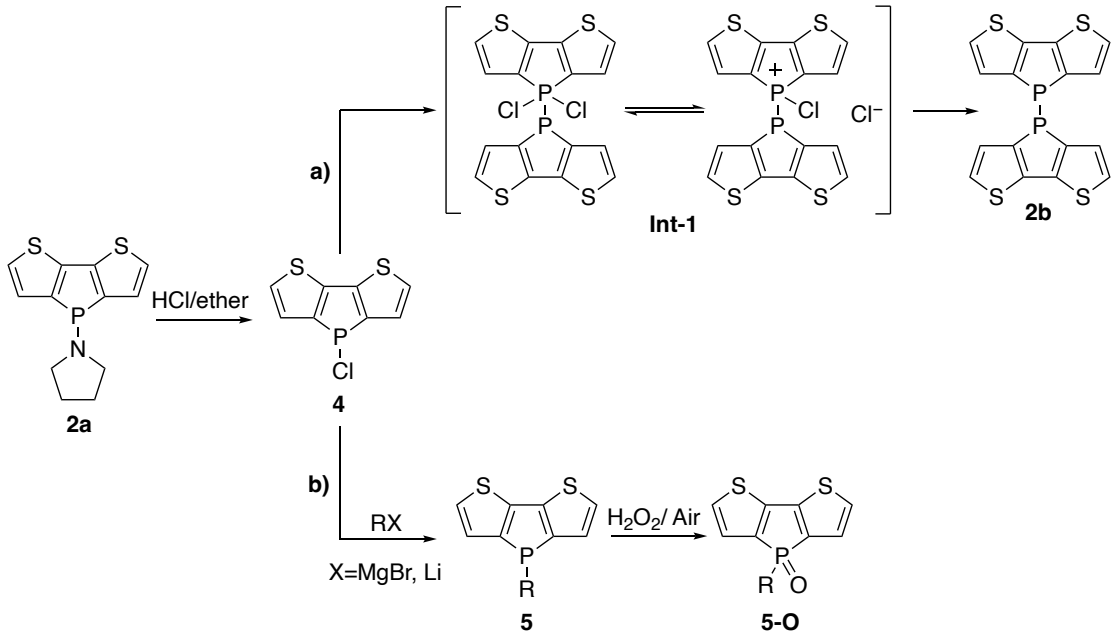
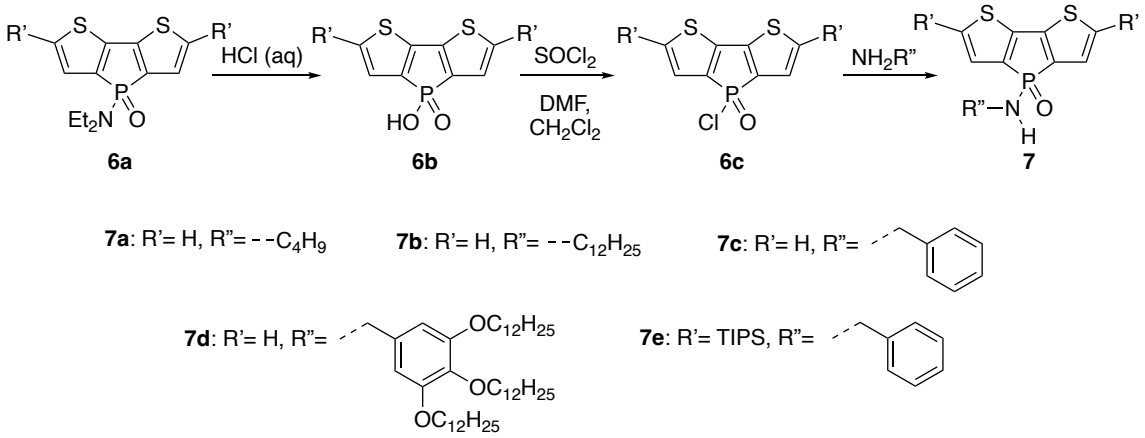



**Chart 3.** Reaction intermediates and transition state for Lewis-acid promoted synthesis of biphosphole.

In addition to the pyrrolidine-functionalized dithienophosphole **2a**, trivalent P-chloro-dithienophosphole **4** also serves as a precursor for biphosphole **2b** (Scheme 2). This compound reacts *in-situ* at room temperature to generate an asymmetric intermediate **(Int-1)** that reductively eliminates molecular chlorine to form **2b**. However, considering the highly reactive and transient nature of **4**, this method is not very practical for the synthesis of **2b**. Nonetheless, its reactivity can be leveraged for the synthesis of various P-substituted dithienophosphole and corresponding oxides that are inaccessible otherwise. For example, compound **4** can be treated with organometallic reagents, such as Grignard and organolithium species to afford dithienophospholes with a variety of P−R groups (**5**, **5-O**) (Scheme 2).[20,21,22]




**Scheme 2.** a) Alternate route towards the synthesis of biphosphole, b) synthesis of various P-functionalized dithienophosphole from P-chloro-dithienophosphole.




**Scheme 3.** Synthesis of self-organizing phosphinamides.

Amino-dithienophospholes **(6a)** are also robust precursors for the generation of a series of phosphinamides **(7a-e)** with unique hydrogen-bond self-organization properties (Scheme 3). Notably, the central PO−NH fragments in **7** give rise to a much richer set of secondary bonding

and structures when compared to the CO−NH-based carbamide congeners.[23,24] While the latter are strictly limited to two bonding motifs, *syn*/head-to-head (i.e., 0°) and *anti*/head-to-tail (i.e., 180°), the P-based system essentially provides a highly adjustable dial that easily adapts to any given secondary/tertiary structure dictated by other intermolecular interaction types.[25] To this end, the combination of intermolecular π-π interactions and H-bonding in **7a** causes the molecules to π-stack in unusual H-aggregate type 1D columnar arrangement (Figure 5a), with head-to-tail linked PO−NH units at an angle of 131° between the PO and the NH groups. By contrast, the π-conjugated backbones in **7c** align in a *syn*-type, parallel fashion favoring a zigzag pathway for H-bonding with PO−NH at an intermediate angle of 47° between the PO and the NH groups. The bulky TIPS groups in **7e** suppress π-stacking and the compound only adopts H-bonding in a "head-to-head" dimer with a PO−NH angle of 17° (Figure 5c). The mesogenic versions, **7b** and **7d** exhibit soft-crystalline and liquid-crystalline features respectively at elevated temperatures, where **7d** is also able to form an organogel with n-heptane (Figure 6). While these phosphinamides enforce the functional application of the dithienophospholes, it is an illustrative account on how manipulation through flexible nitrogen substituents at the P-center can influence the aggregation properties in highly organized self-assembled materials.

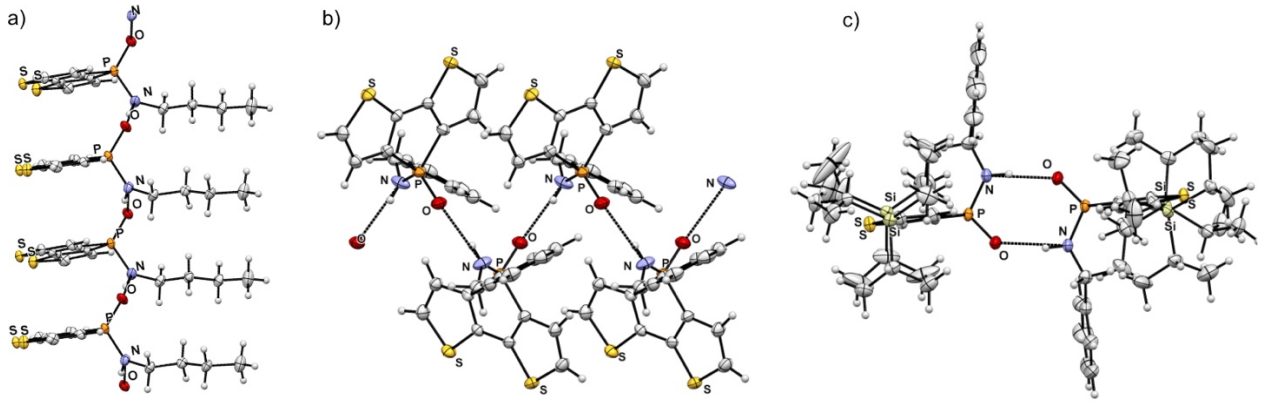



**Figure 5.** Solid-state structures of a) **7a** showing parallel alignment and columnar H-bonding, b) **7c** showing zigzag packing, and c) **7e** showing H-bonded dimers. Adapted with permission from ref. 11. Copyright 2016 John Wiley and Sons.

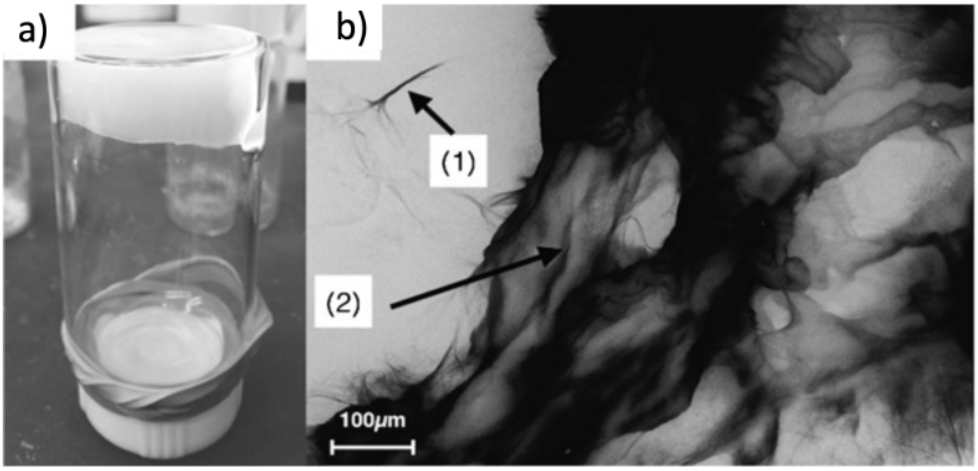



**Figure 6.** a) Organogel of **7d**, b) xerogel of **7d** visualized via SEM showing fiber bundles (1) and a sheet-like microstructure (2). Reproduced with permission from ref. 11. Copyright 2016 John Wiley and Sons.

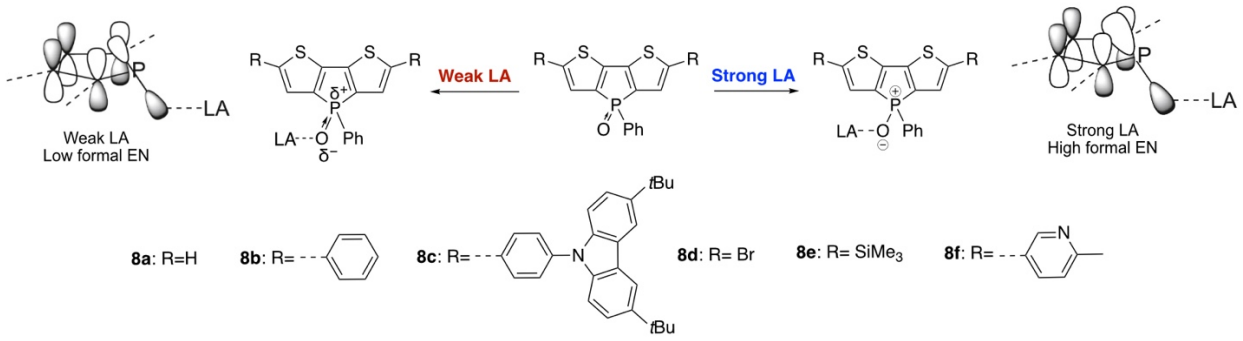
## 3. σ*-π* Tuning through polarization of the P=O bond

While the hydrogen-bonding ability of the P=O bond is beneficial for generating self-assembled materials as discussed above, its Lewis basic donor character has proven quite advantageous for the determination of Lewis acidity. Lewis acids (LAs) in general have been established as catalysts, anion sensors, and are increasingly used in materials science as well.[5,26-28] For these reasons, several methodologies currently exist that measure Lewis acidity through a variety of select parameters. Of the more prolific ones, the Gutmann-Beckett (GB) method correlates Lewis-acid strength to the charge separation of the P=O bond as measured by $^{31}$P NMR spectroscopy.[29] Other methods similarly correlate to spectroscopic or computational parameters, such as the Childs method,[30] fluoride ion affinity (FIA),[31] or the global electrophilicity index.[32] But a comprehensive study on Lewis acidity has not yet been accomplished due to the difficulty for correlative parameters to accurately account for the complexity of Lewis acidity. One reason for this is the hard-soft acid-base theory (HSAB)[18] and the propensity for these methods to rely on a single Lewis base, potentially influencing the measured parameter.

In this context, we showed that dithienophosphole oxides provide access to a simple and effective method for the determination of Lewis acidity via fluorescent Lewis acid-base adducts (FLAs). Generally, fluorescent probes allow detection of very low concentrations of LA while exhibiting a high degree of analyte specificity and they often provide easily detectable and visible color changes. Considering the highly sensitive nature of LAs, the FLA method allows for safe and air free testing condition for a wide range of Lewis acids across the periodic table.[2]

It is well established that P=O bonds are polar and better described with the canonical structure $P^{+}$–$O^{-}$ (Figure 2), which inherently creates the possibility for the oxide species to interact with electrophiles; this scenario also applies to the highly fluorescent dithienophosphole oxides.[8]

Correspondingly, upon adduct formation, the polarization of the P=O bond is enhanced by the coordinated Lewis acid, which in turn strengthens the σ*-π* interaction and lowers the energy of the LUMO. The polarization effect that is used to correlate Lewis acidity with the GB method also applies to the Lewis-adduct formation with a dithienophosphole oxide, but a photophysical alteration will also be established through FLA formation. Here, a stronger LA will considerably increase the polarity of the P=O bond, which leads to a much stronger contribution of the phosphorus atom to the σ* orbital that then enhances the interaction with the π* fragment and lowers the LUMO correspondingly. The extent of emission redshift directly correlates to the strength of LA, where the most prominent difference is observed for strong Lewis acids and not so much for weak ones (Scheme 4).[2,33,34]




**Scheme 4.** Impact of weak and strong LAs on the polarization of the P=O bond via change in σ*-π* interaction.

For example, parent dithienophosphole oxide **8a**[17] shows a visibly distinct, immediate shift in emission color from sky blue ($\lambda_{em}$ 446 nm) to aquamarine ($\lambda_{em}$ 509 nm) on adduct formation with the strong LA $B(C_6F_5)_3$. Here, the fluorescent parameter correlates Lewis acid strength to the frontier molecular orbitals, i.e., via the σ*-π* interaction, instead of the core shell electrons, allowing for much higher sensitivity of the parameter to small changes in Lewis acidity. Notably,

the FLA method relies on combined data sets from three to four dithienophosphole probes with different emission colors and the method thus minimizes potential bias from the Lewis base itself. It is also important to note that the FLA method measures the chromaticity of the corresponding adducts, rather than relying on simple emission (maxima). The chromaticity values of the three FLAs from a single Lewis acid, e.g., $B(C_6F_5)_3$ or 'BCF', and that of free phosphole oxide probes can be fit well with a parabolic function. Similarly, a well-defined parabolic function can also be used to compare the emission of all the free probes. These parabolas intersect at the point which corresponds to the chromaticity of an ideal adduct (cf.: HSAB) of a theoretical dithienophosphole oxide that can generate FLA with a given LA in 1:1 mole ratio at saturation (Figure 7). The Commission Internationale de l'clairage (CIE) coordinates[35] at this point correlate precisely with the strength of the Lewis acids and the FLA method successfully determines the Lewis acidity of different compound classes, such as neutral boranes, heavy group 13 elements, cationic, and metallic species, including rare-earth metal triflates ($RE(OTf)_3$).[2,33,34] The latter is quite intriguing considering they usually display similar physicochemical properties with minimal detectable changes.

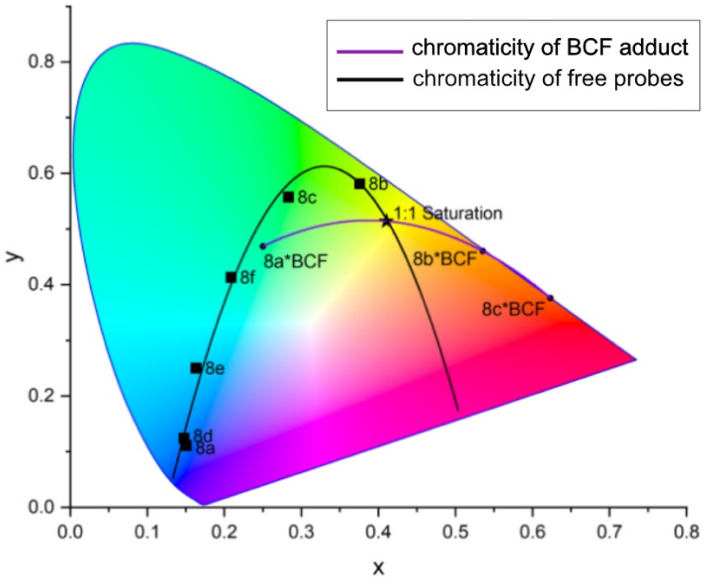


**Figure 7.** Critical point used to determine LA strength from the CIE space of free probes and their corresponding BCF adducts. Reproduced with permission from ref. 2. Copyright 2019 Elsevier.

The complexity of measuring and comparing Lewis acids in solution is not strictly overcome by the choice of parameter being measured, but by the design of the experiment itself. The use of a reliable metric, such as the polarization of the P=O bond by coordination to a Lewis acid, with the added sensitivity of the influence on the frontier molecular orbitals via the σ*-π* interaction, allows for a much more sensitive measure. However, an additional metric by which the complexity of Lewis acids in solution can be addressed is still necessary, as evidenced by the difference in emission maxima across the individual probes. As chromaticity is a linear combination of all emissions from solution, all available emissive adducts, regardless of the nature of the acid-base adduct or the specifics of the Lewis acid in solution can be summarized in one measure. As such, the use of dithienophosphole oxides for measuring Lewis-acid strength allows for both a highly sensitive measure and one that more appropriately represents the solution-state or *effective nature* of the Lewis acid.[2,33,34]

## 4. Lewis-acidity through $\lambda^5\sigma^5$ hypervalency

A more traditional route to manipulating the σ* and π* contributions to the HOMO and LUMO (or more generally, the frontier molecular orbitals) of phosphorus-based molecular species is via $\lambda^5\sigma^5$ hypervalency. A sufficiently strong acceptor σ* orbital on phosphorus, especially arising from an electronegative substituent, can allow for a highly Lewis acidic phosphorus center. For example, the electronically saturated P center in **VII** (Chart 4) is sterically shielded by a

pseudotetrahedral arrangement of substituents that can directly activate C–F bonds for catalytic hydrodefluorination (HDF) of fluoroalkanes.[36]

Similarly, the phosphanyl group in 2-(2′-thiazolyl)-3-thienylphosphanes **9a,b** can serve as soft Lewis acid in its trivalent state, but upon functionalization of the phosphorus center is converted into a relatively hard Lewis acidic species, as defined by the HSAB theory (Scheme 5).[18] The phosphorus centers in **9a,b** are capable of engaging in weak intramolecular LA/LB interactions through S→P coordination with a P−Ph σ* orbital acting as the acceptor for the sulfur lone pair. This interaction provides a covalent, albeit weak, 3c−4e bond type involving the now hypervalent phosphorus center (Figure 8a,b). Upon methylation of phosphorus (**9c,d**), the coordination switches to N→P as evident from their solid-state structures (Figure 8c,d). The N→P interaction is better described as σ-hole bond type involving the hypervalent P center through a strong electrostatic contribution that lies more closely at the ionic end of the spectrum for hypervalent bonding.[3]

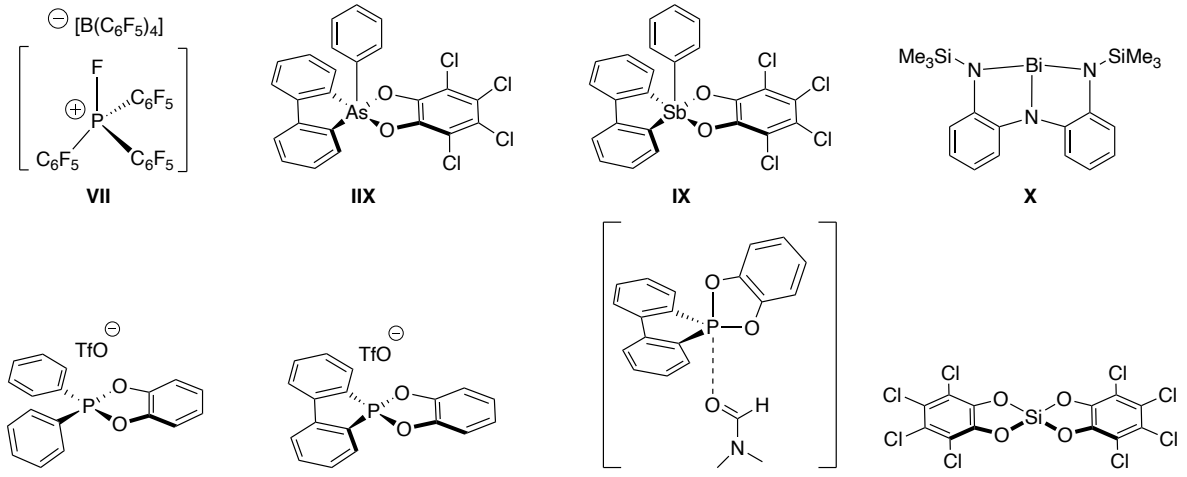
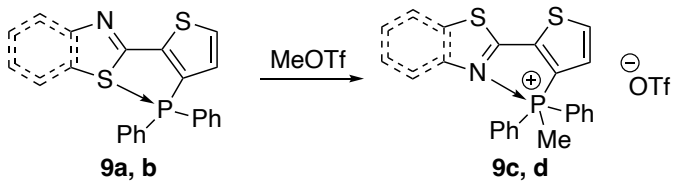



**Chart 4.** Select main-group element-centered Lewis acids.




**9a, b** **9c, d**

**Scheme 5.** P-Methylation of 2-(2'-thiazolyl)-3-thienylphosphanes changes coordination mode.

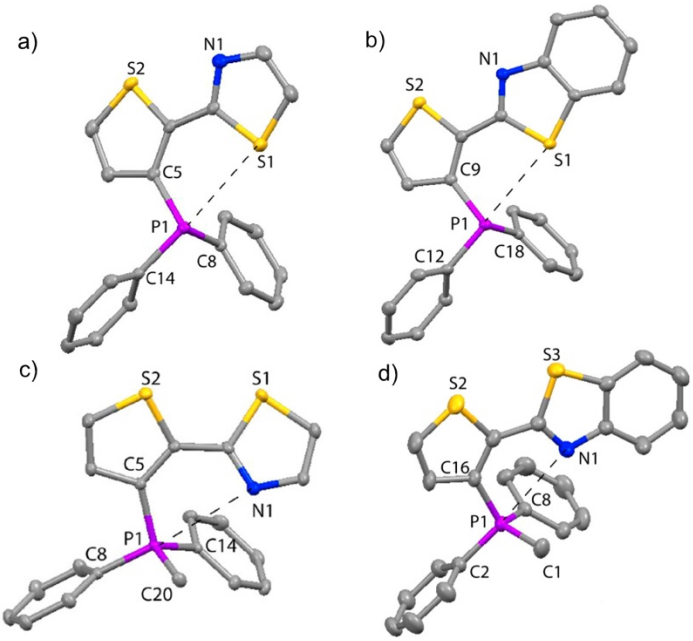


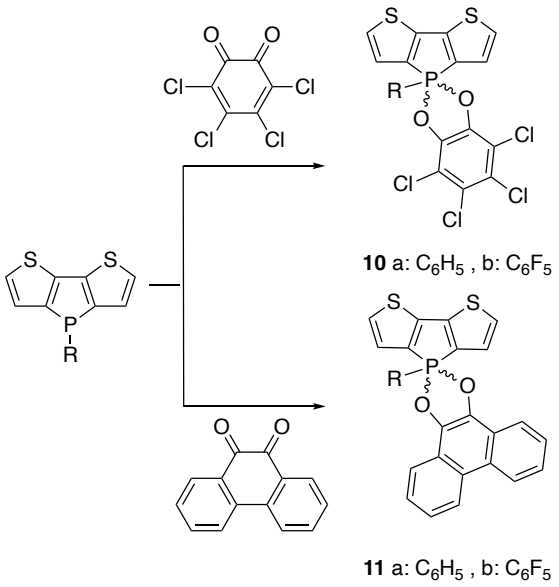

**Figure 8.** Solid-state structure of a) **9a**, b) **9b**, c) **9c**, and d) **9d**. Counter anion in **9c,d** omitted for clarity. Reproduced with permission from ref. 3. Copyright 2018 American Chemical Society.

The heavier analogues of phosphorus also exhibit intriguing Lewis acidic character through hypervalency. For example, neutral $\lambda^5\sigma^5$ As **(IIX)** and Sb **(IX)** species (Chart 4) adopt distorted square pyramidal geometries that project out a $\sigma^*$ orbital to serve as an electron-acceptor site. The Lewis acidity arising from Sb/As−$C_{Ph}$ $\sigma^*$ orbital in these species is enhanced by stabilization of the π-system and/or electron-withdrawing substituents.[5,37,38] While hypervalency is a prominent route towards Lewis acidity, a recent study shows that geometrical constrains of trivalent pnictogen centers can also serve as effective design strategy towards neutral LAs. Recently, trivalent bismuthanes **X** with a constrained planar geometry around Bi, were found to be borderline

hard/soft acids. The Bi center engages lone pairs conventionally through vacant p orbitals, rather than a low-lying antibonding orbital, thus behaving analogous to electrophilic triaryl boranes. The tethered ligand imposes rigidity to the Bi center to retain planarity upon ligand binding allowing the addition of a second ligand (L) to form nearly linear L−Bi−L arrangement.[39,40]

## 5. Altering the σ*-π* interaction through hypervalency

More generally, main group centers can exhibit σ-hole type Lewis acidity in a variety of ways, such as by altering the coordination number,[3] as discussed above, but also geometry,[37,38] charge,[36,41-43] or less commonly, by generating open-shell species. One such example are phosphonium cations bearing mono- or bicyclic structures **(XI$_{a,b}$)** to generate an active pentavalent species (**XI$_c$**) that catalyzes Diels-Alder reactions (Chart 4). Even though these species reveal the importance of five-membered 1,3,2-dioxaphosphacyclic structure in achieving high catalytic efficiency, the phosphonium cations are transient and decompose immediately in protic environments.[41] This underscores the strong interest in neutral main group species, specifically pnictogen-based Lewis acids, to combine similar catalytic potential with ambient stability. The hypervalent pnictogen-based LAs derive their Lewis acidity from vacant p orbitals[39,40] or a sterically and energetically accessible σ* orbital via a trigonal pyramidal geometry with three covalent bonds and a lone pair (LP) of electrons on the central atom.[36,,44] Such geometrical manipulations can also be achieved with $\lambda^3\sigma^3$-phospholes as an effective design towards neutral P-based LAs.[36,45,46]




**Scheme 6.** Synthesis of hypervalent dithienophospholes.

One way to introduce this structural modification to trivalent dithienophospholes is by exploiting the reactivity of the lone pair to undergo [4+1] cycloaddition with *o*-quinones.[47] This generates neutral and air-stable pentavalent molecules (Scheme 6). There are many advantages to these pentavalent derivatives but the most impactful is the potential to fine-tune the electronics of the system by altering the *o*-quinone component. For example, **10** contains an electron-withdrawing catecholate that specifically hosts the LUMO in the hypervalent species, while the electron-rich phenanthrene quinone in **11** predominantly host the HOMO. This allows efficient tuning of the Lewis-acid strength through reactions with various *o*-quinones, but the overall electronics can be further tuned with an electron-withdrawing perfluorophenyl group, as in **10b** and **11b**.[4]

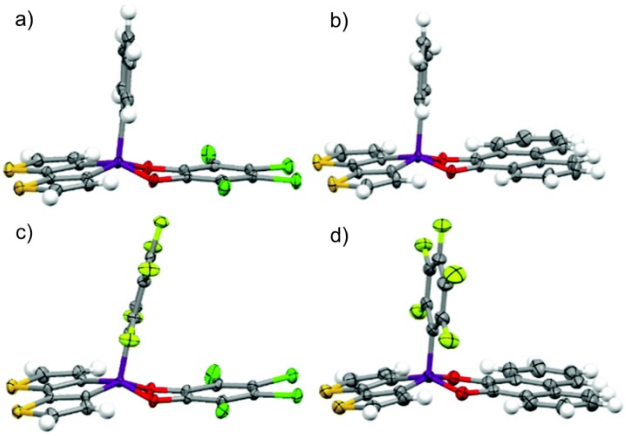



**Figure 9.** Solid state structures for a) **10a**, b) **11a**, c) **10b**, and d) **11b** (50% probability). Reproduced with permission from ref. 4. Copyright 2021 Royal Society of Chemistry.

However, considering the VSEPR-predicted triagonal bipyramidal geometry (3BP), these molecules surprisingly adopt an unexpected, though not unprecedented,[37,38] square pyramidal (4SQ) geometry (Figure 9). The geometry enhances the Lewis acidity of the P center, which is now much more sterically accessible for nucleophiles than in the 3BP geometry. Notably, the 4SQ geometry persists irrespective of the nature of the substituents at the phosphorus center. Generally, strong electron-withdrawing and/or sterically bulky ligands impart geometric constraints that in turn generate reactive 4SQ sites for use in main-group catalysis.[6,45,46] However, the Lewis acidity of these hypervalent phosphorus centers arises from the preferred formation of two 3c–4e bonds with moderate strength in 4SQ over a single, strong 3c-4e bond in the corresponding 3BP geometry. While the 4SQ geometry is slightly energetically favored over 3BP, these compounds dynamically exchange between these two geometries in solution, not unlike the Berry pseudo rotation mechanism invoked for other pentacoordinate main group species.[7,47,48] The 4SQ geometry appears desirable in the solid state as this allows for a parallel arrangement between the extended conjugated scaffolds of adjacent molecules to enhance their intermolecular π–π

interactions, which in turn mutually protect the neighboring phosphorus centers from exposure to nucleophiles (Figure 10, inset). It is noteworthy that this interaction persists not only in the solid state but also in solution at very low concentrations. The fluorescence spectra of these compounds show excimer-type emissions that originate from the supramolecular dimerization, only resolving into vibronic structures at low concentrations. Notably, two highly electron-withdrawing substituents form a significantly stronger supramolecular interaction, such as in **10b**, maintain the excimer even at concentrations as low as $10^{-13}$ M (Figure 10).[4]

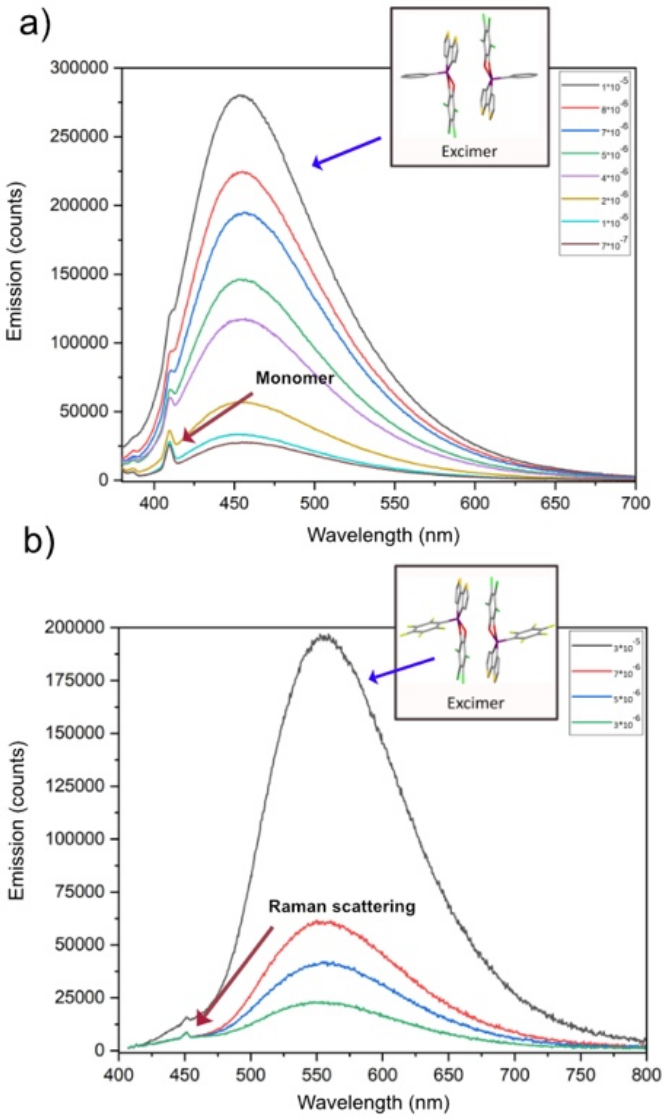


**Figure 10.** Emission spectra for a) **10a** (excitation at 365 nm) and b) **10b** (excitation at 397 nm). Reproduced with permission from ref. 4. Copyright 2021 Royal Society of Chemistry.

Computations revealed an area of positive electrostatic potential on the phosphorus center in these structures, consistent with a σ-hole (Figure 11). It serves as potential coordination site for nucleophiles, such as $OH^-$ or $F^-$. The calculated FIAs for the hypervalent phosphorus species indicate moderate Lewis acidity (300–380 KJ $mol^{-1}$), that is lower than the super Lewis-acidic bis(perchlorocatecholato)silane, **XII** (507 KJ $mol^{-1}$).[49] Fluoride abstraction of the hypervalent dithienophospholes with a dry fluoride source generates the corresponding fluoride adducts **(Int-2)** that, despite anaerobic conditions, continue to react within an hour. Surprisingly, next to the formation of the dithienophosphole oxide **8a**, the corresponding dioxin **12** was also detected, suggesting a double deoxyaryloxylation to occur (Scheme 7a). Similarly, the high susceptibility of **10a** to even trace amount of water facilitates a transformation to the dithienophosphole oxide **8a** and catechol **13**, respectively, even in the crystalline state (Scheme 7b).[4]

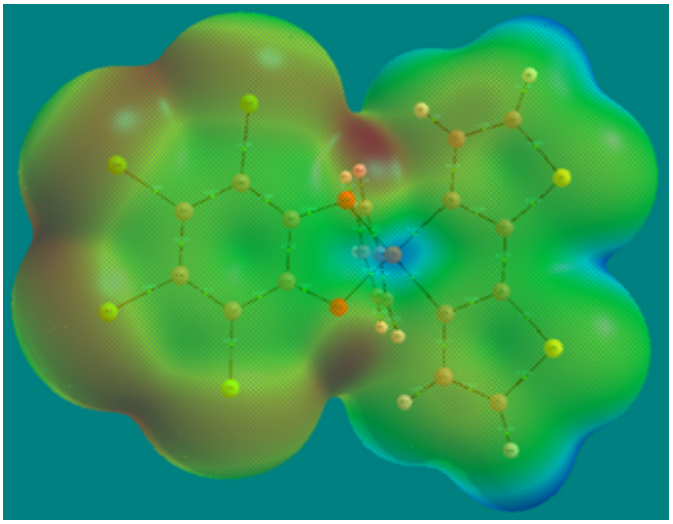
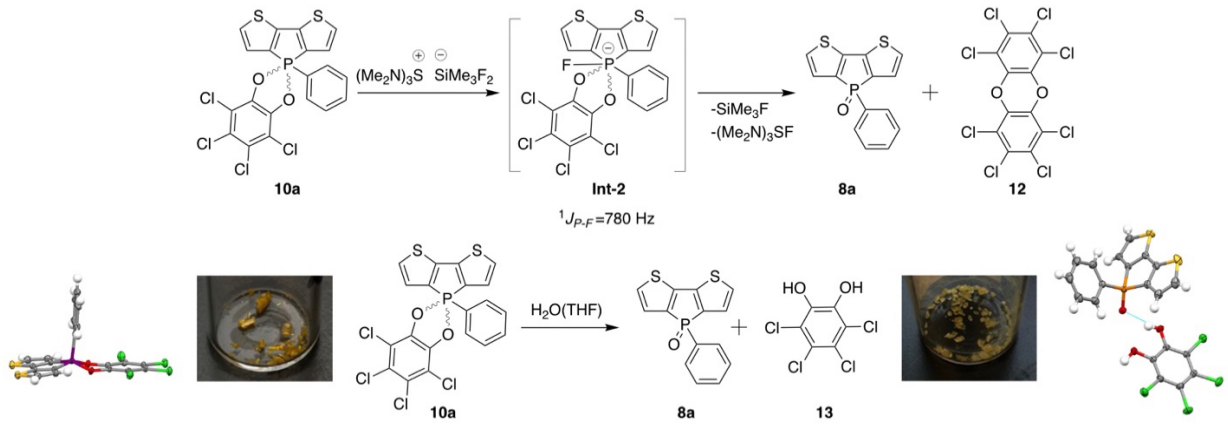


**Figure 11.** Electrostatic potential mapping for **10a**. Red to blue represent electron-rich to electron-poor. Reproduced with permission from ref. 4. Copyright 2021 Royal Society of Chemistry.




**Scheme 7.** Deoxyaryloxylation initiated by fluoride (top); hydrolysis under ambient conditions showing crystal-to-crystal transformation (bottom). Adapted with permission from ref. 4. Copyright 2021 Royal Society of Chemistry.

Notably, the Lewis acidity of these pentavalent species is outwardly accounted to their hypervalent nature, but it is interesting to note that not all are similarly acidic; their reactivity can thus be fine-tuned through the electronic nature of the *o*-quinone employed in the P-oxidation. The distinctive reactivities exhibited by these derivatives support their inherent potential for development toward effective mediators in other chemical transformations involving different nucleophiles that could be used to access otherwise arduous organic target species.[6,36,42,45,46,50]

## 6. Conclusion

The σ*-π* interaction in dithienophospholes can be easily altered through chemical modification of the P center or the dithienophosphole scaffold, thereby enhancing their n-type character. We are pursuing alternative strategies that can lead to improvement in the optoelectronic features of

dithienophospholes. In this context, we have found that amino-functionalized dithienophospholes serve as excellent precursors towards step-conjugated biphospholes with intriguing photophysical properties, reactive P-chlorodithienophospholes, and phosphinamides with unique self-assembly characteristics. While these dithienophospholes offer unique avenues for structurally and chemically diverse materials, the Lewis basicity of dithienophosphole oxides is equally intriguing. The photophysical changes on adduct formation of dithienophosphole oxide with LAs is an innovative, yet robust analytical platform to measure the real-time strength of LAs. On the contrary, the deliberate implementation of $\lambda^5\sigma^5$ hypervalency introduces a low-lying $\sigma^*$ orbital in dithienophosphole with Lewis acidic character that is easily tuned from soft to hard by chemical modification of the P center. Nevertheless, the sigma-hole-type Lewis acidity in hypervalent dithienophospholes, which is achieved on geometrical constraints of the P center, enables the development of neutral and stable LAs with potential to mediate otherwise arduous organic transformations.

We believe that the representative examples for various strategies discussed in this account, by which dithienophospholes in particular, and organophosphorus materials more broadly, can be effectively modified are an intriguing platform for materials design. We hope that the exemplary qualities and functional applications that have been achieved to date will motivate others in their research pursuits along these lines.

**Biographical Sketches**

**Nayanthara Asok** received her MSc in Chemistry from Vellore Institute of Technology (VIT), India in 2016. She joined Thomas Baumgartner's research group at York University for PhD

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**Joshua Gaffen** received his PhD from Case Western Reserve Univeristy in Cleveland, OH in 2018, working in the lab of John Protasiewicz. He worked with Thomas Baumgartner at York University as a postdoctoral researcher between 2018 and 2022 focusing on exploring the electronic properties of organo-main group compounds in unique environments, conditions, and geometries.

**Thomas Baumgartner** received his PhD degree in 1998 from the University of Bonn, Germany, working in the group of Edgar Niecke. From 1999 to 2002 he was a postdoctoral fellow at the University of Toronto with Ian Manners. He started his independent career as habilitand at the University of Mainz and RWTH Aachen University, Germany under the mentorship of Jun Okuda before moving to the University of Calgary, Canada in 2006. Since 2017, he is a Full Professor and Canada Research Chair at York University, Toronto, Canada. His research interests are focused on molecular organophosphorus π-conjugated materials and supramolecules for sustainable energy applications.

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