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Insights on the Design and Electron-Acceptor Properties of Conjugated Organophosphorus Materials

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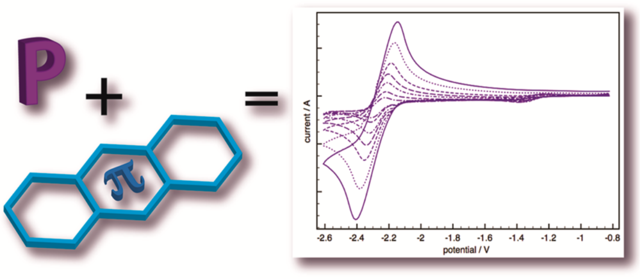

CONSPECTUS: The development of conjugated organic materials has become a rapidly evolving field of research, particularly with a view toward practical applications in so-called organic electronics that encompass a variety of device types, such as OLEDs, OPVs, and OFETs. Almost all of these devices minimally require the presence of electron-donor and -acceptor components that act as p- and n-type semiconductors, respectively. Research over the past two decades has shown that while there is an abundant resource of organic p-type materials, suitable n-type species are few and far between. To overcome this severe bottleneck for the further development of organic electronics, researchers have identified organo-main-group avenues as valuable alternatives toward organic electron-acceptor materials that may ultimately be used as n-type components in practical devices. One particular element of interest in this context is phosphorus, which at first glance may not necessarily suggest such properties.

In this Account, I provide detailed insights on the origin of the electron-acceptor properties of organophosphorus-based conjugated materials and include an overview of important molecular species that have been developed by my group and others. To this end, I explain that the electron-acceptor properties of conjugated organophosphorus materials originate from an interaction known as negative hyperconjugation. While this particular interaction creates a simply inductively withdrawing phosphoryl substituent for π-conjugated scaffolds, incorporation of a phosphorus atom as an integral part of a cyclic substructure within a π-conjugated system provides a much more complex, versatile, and consequently highly valuable tool for the tuning of the electron-acceptor properties of the materials. Notably, the degree of negative hyperconjugation can effectively be tailored in various ways via simple substitution at the phosphorus center. This is now well established for phosphole-based molecular materials, in which the electron-acceptor properties are also mirrored by the degree of antiaromaticity of the system. Particularly, fused and π-extended phosphole materials show appreciable electron-acceptor properties, evident in low reduction potentials and corresponding LUMO levels. But these features do not always translate into powerful n-type materials. My group and others have thus recently been focusing on molecular organophosphorus scaffolds that also involve incorporation of imino or carbonyl groups, next to the incorporation of low coordinate phosphorus centers, to achieve superior electron-acceptor features. This state-of-the-art research has confirmed the great potential of the organophosphorus route toward powerful electron-acceptor materials, but further work is required to also establish these species as functional n-type materials.

■ INTRODUCTION

The development of conjugated organic materials has become an ever-accelerating area of research, since it has been established that careful design of the molecular scaffolds gives rise to highly desirable optical and electronic properties.[1] The most popular applications for these materials include organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and a large variety of optical sensors. The former three rely on electronic devices that are built-up from a variety of materials, each of which fulfills a specific role for the device performance.[2] While the optical and electronic nature of the chemical components can differ significantly from one device type to another, one major common denominator is the necessity of two complementary semiconductors, p- and n-type, or in chemical terms, electron-donor and electron-acceptor species.[2] Over the past two decades, it has been established that the majority of organic conjugated materials exhibit favorable p-type character, while the number of suitable n-type species with appreciable performance is surprisingly low. This bottleneck has consequently triggered a rapidly evolving search for new electron-acceptor materials.[3]

To this end, main group element-based conjugated materials have become an attractive research area, since the unique structural and electronic properties of elements such as B, Si, P, Se, and Te create some intriguing opportunities for electronic property tuning.[4−8] These elements can induce highly tunable luminescence or supramolecular organization, and they have also provided an intriguing entry point for the development of powerful electron-acceptor materials. Due to their genuine electron deficiency (i.e., Lewis acidity), boron-based materials are "natural" electron acceptors,[4] but silicon-[5] and phosphorus-

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based[6] materials have also been found to exhibit electron-acceptor features, maybe in a less obvious fashion. In this Account, I will thus attempt to provide insights on why phosphorus-based species can be highly electron accepting and highlight important P-containing electron-acceptor materials.

THE ORIGIN OF ELECTRON-ACCEPTOR FEATURES IN ORGANOPHOSPHORUS CONJUGATED MATERIALS

Trivalent phosphorus is an electron-donor species due to the presence of its lone pair. However, oxidation to the pentavalent phosphoryl state creates a hypervalent environment, which increases the relative electronegativity of the phosphorus center and inverts its character to an electron acceptor. While phosphoryl species are commonly represented with a formal double bond between the phosphorus center and an appropriate substituent (Figure 1; e.g., E = O, S, Se, NR, or CR_2), it is important to emphasize that this bond is strongly polarized. This is borne out of the nature of the π-bonding, which should more appropriately be classified as π back-donation from a filled p-orbital (i.e., a lone pair at E) into an antibonding σ*-orbital at phosphorus, an interaction that is now established as negative hyperconjugation.[9]

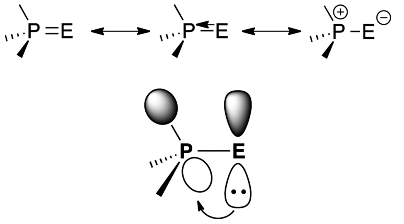


Figure 1. Nature of the phosphoryl π-bond.

The increased relative electronegativity of the P-center then creates an inductively withdrawing substituent that can, for example, lower the frontier orbitals of a π-conjugated molecular framework. This approach has successfully been employed in phosphorescent OLEDs for which a variety of phosphoryl-appended electron-acceptor species have been developed to date (Chart 1).[10,11] These materials show excellent thermal and morphological stabilities, as well as suitable triplet energies.

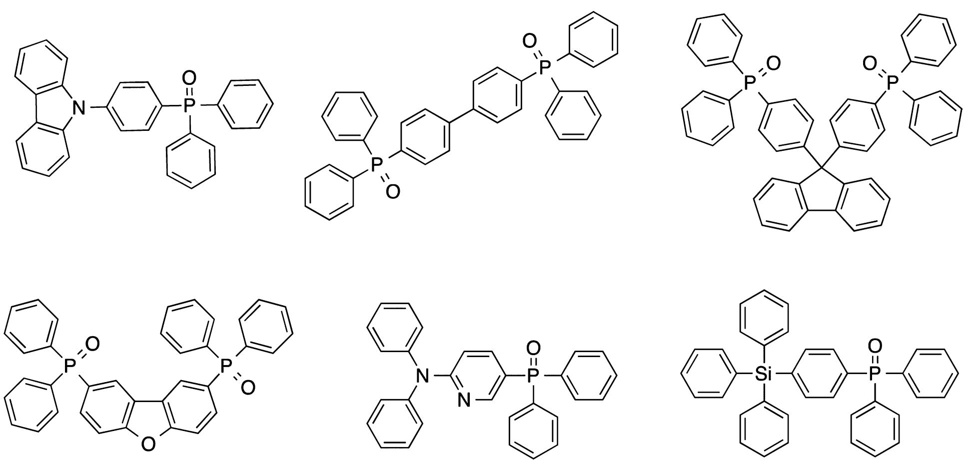
A little over a decade ago, my group and others started to investigate species with phosphorus as an integral part of a cyclic structure within the π-conjugated backbone, in order to enhance the effect of the negative hyperconjugation and to also install a high degree of tunability for the electronic properties of the scaffolds.[6] Scheme 1 summarizes some of the common synthetic approaches toward these species. In contrast to its congener nitrogen, trivalent phosphorus has a considerably higher inversion barrier, which retains its pyramidal geometry, even if the driving force were the generation of an aromatic ring system with embedded P atom. It is this pyramidal geometry that sets the stage for effective negative hyperconjugation and opens the door for pronounced electron-acceptor features.[12] Moreover, the phosphorus lone pair is accessible for further functionalization, which essentially creates an additional P-substituent with appropriately oriented σ*-orbital for a second negative hyperconjugation with the main conjugated scaffold, further enhancing the electron-acceptor character of the latter.

To illustrate this, I will highlight the classic case of phosphole electronics herein, which are now very well understood;[13,14] note that comparable features also apply to other conjugated cyclic organophosphorus materials. Phosphole, the relative of pyrrole and thiophene, is only slightly aromatic as a result of the pyramidal nature of the P-center.[6] It is now accepted that (positive) hyperconjugation of the π-system with the exocyclic σ-substituent, not the lone pair, gives rise to its “partial” aromaticity. Moreover, chemical modification of the P-center can be utilized to change its character to become slightly antiaromatic,[13] which highlights the considerable benefits of incorporating phospholes into conjugated organic materials. The electronics of phosphole and other related heteroles are usually approached by combining a butadiene fragment with the appropriate heteroatom (group), that is, “P-R” in the case of phosphole (Figure 2).[15]

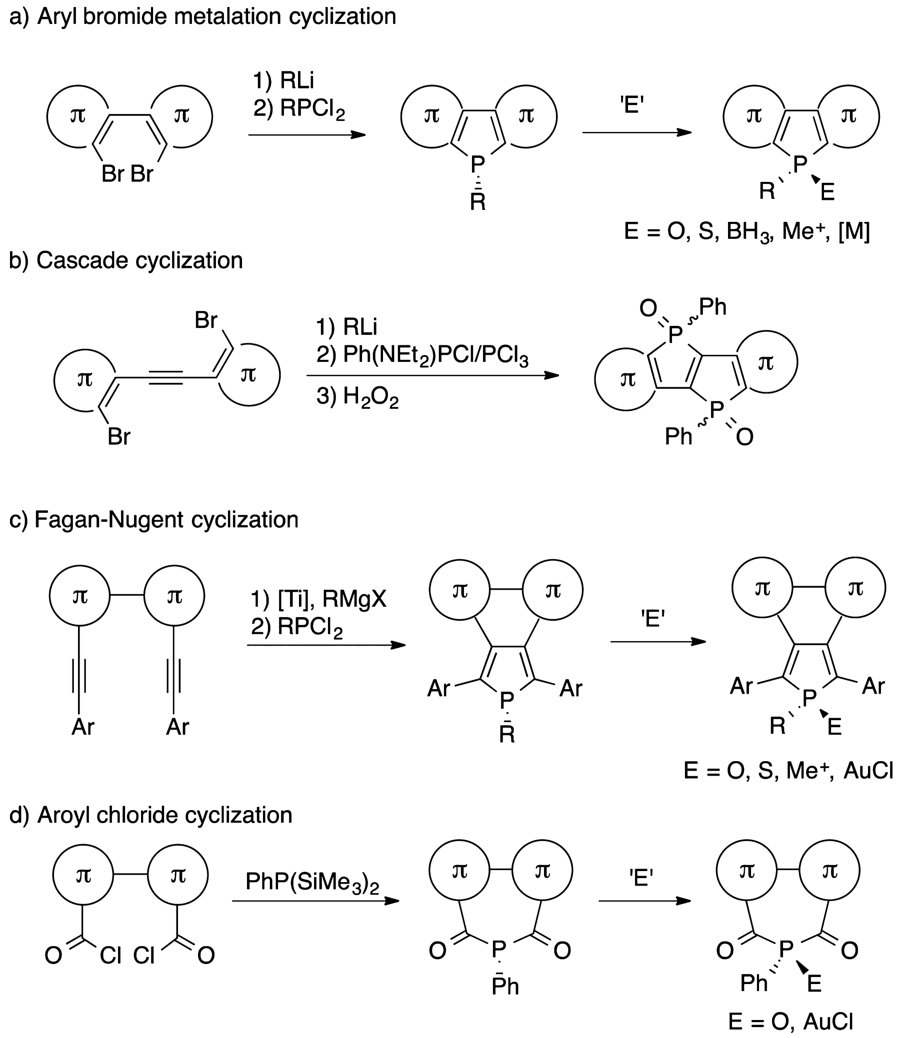
This gives rise to the orbital interactions that account for its slightly aromatic character, as well as its electron-acceptor character due to an overall lowered LUMO. The privileged hyperconjugation, positive as well as negative, in the phosphole system (that also applies to silole for that matter)[5] thus clearly sets this system apart in terms of inherent electronic tunability.

Fundamental studies on the electronics of the phosphole system have further revealed that the degree of antiaromaticity, which mirrors the electron-acceptor strength of the system, can be modulated in several ways by (i) variation of the substituent

Chart 1. Selected Phosphoryl-Based Electron Acceptors for OLEDs



Scheme 1. Common Synthetic Approaches toward Phosphacyclic Conjugated Materials



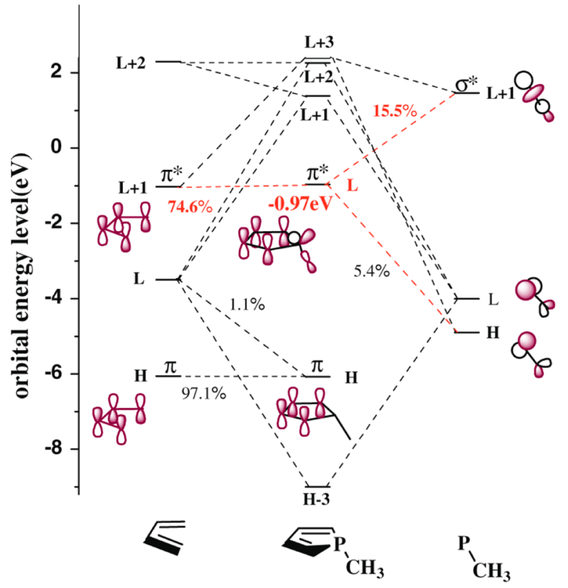


Figure 2. Molecular orbital correlation diagram for methylphosphole (B3LYP/6-31G*). Reproduced from ref 15 with kind permission from Springer Science and Business Media.

"E" that can impart a considerable degree of polarity onto the P═E bond and enhance the electrophilicity of the P-center (Figure 3) and (ii) installing an aromatic P-substituent, whose orientation can lead to conjugative stabilization of the cationic P-center (Figure 4).[14] Ultimately, both elements have a noticeable effect on the energy of the σ*-orbital(s) and consequently the strength of the negative hyperconjugation, which translates to a high degree of tunability for the LUMO energy level. In fact, theoretical studies on fused phospholes, such as dibenzo- and dithienophospholes have confirmed the strong electron affinities of these scaffolds that can be tuned by variation of the P-substituents.[15,16]

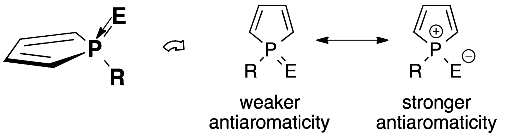


Figure 3. Effect of the P═E bond polarity on the antiaromaticity in phosphole.

Le Floch and co-workers provided the first experimental account to this end in a combined EPR and DFT study elaborating on the electron-acceptor features of phospholes.[17] Focusing on a series of conjugated and isolated neutral

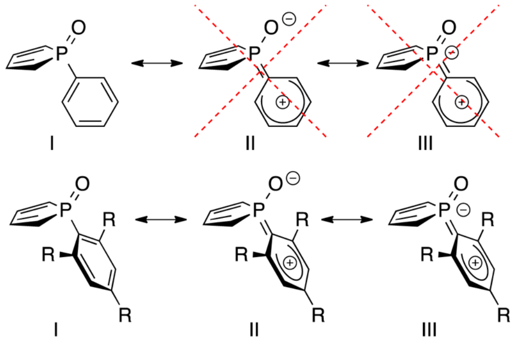


Figure 4. Conjugation potential from the orientation of the exocyclic aromatic substituent.[14]

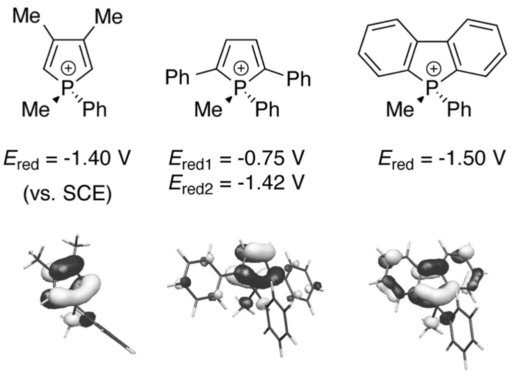


Figure 5. Phospholium species investigated by Le Floch et al. (top) and SOMOs of the corresponding reduced species (bottom). Reproduced from ref 17 with permission from the PCCP Owner Societies.

phosphole and cationic phospholium species (Figure 5), they verified that the cationic species in particular act as efficient electron acceptors at relatively low reduction potentials (E_{red} = −1.26 to −2.33 V vs Fc/Fc$^+$)[18] and that the radical obtained after the first reduction is not localized at the originally positively charged P-center; it is rather efficiently delocalized over the carbon-based framework, which ultimately enhances the stability of the reduced species. Moreover, the reduction of the phospholium species does not affect the structural integrity of the scaffold, which further emphasized their robustness and projected their high value as electron-acceptor materials. The authors also revealed that the reduction of the neutral trivalent phospholes provided much less stable systems in terms of delocalization of the radical anion, as well as structural integrity of the scaffold. This study thus confirmed that it is crucial to consider the overall substitution pattern, and the concomitant antiaromaticity of the phosphole species, when designing stable electron-acceptor species.

PHOSPHOLE-BASED ELECTRON ACCEPTORS

My group's foray into the development of organophosphorus-based electron acceptors began in 2008.[19] Our earlier work on the dithienophosphole system (**1**, Chart 2), which we introduced in 2004, almost exclusively focused on its luminescence features and tunability via modification of the P-center, the molecular scaffold, or both.[20] In a subsequent structure−property study on phosphole-based heteropentacenes **2**, we also evaluated the reduction potentials of these species, as an increasing number of reports in the literature at the time were calling for improved electron-acceptor materials.[19]

Focusing on the value of phosphorus functionalization for property tuning, we demonstrated that this avenue provides excellent tunability for not only the photophysical properties of these species (similar to earlier studies) but also their supramolecular organization in the solid state and moreover their electron-acceptor properties. The electrochemical study confirmed that the phosphole oxide **2b** exhibits the highest degree in reversibility for the reduction (E_{red} = −2.00 V), whereas the cationic phospholium **2d** has the lowest reduction potential (E_{red} = −1.80 V). In addition, DFT calculations (B3LYP/6-31+G* level) provided positive electron affinities for all derivatives, affirming the stability of the reduced species. In an attempt to further tailor the electron-acceptor properties of the dithienophosphole system, we then investigated the effect of fluorinated substituents on the frontier orbital levels of the molecular scaffold.[21] A related approach for dibenzophospholes was reported by the Tilley group in 2009.[22] Installation of a strongly electron-withdrawing perfluorophenyl substituent at phosphorus (**3**) was expected to provide an additional tool for tuning both positive and negative hyperconjugation, which was confirmed via DFT calculations (B3LYP/6-31G*) showing the HOMO and LUMO of the C_6F_5-based dithienophosphole **3a** at −5.67 and −1.54 eV, respectively (cf., −5.42 and −1.31 eV for the C_6H_5-analogue).[21] Oxidation of the P-center (**3b**) leads to a further lowered LUMO (−2.12 eV; E_{HOMO} = −5.99 eV). Although not suggested by the calculations, a decreased HOMO−LUMO gap was experimentally confirmed for **3b** via red-shifted photophysics. Expansion of the conjugated scaffold with fluorinated aryls provided an additional pathway for further lowered LUMO levels and consequently enhanced electron-acceptor features with a LUMO level as low as −2.86 eV for the bis(3,5-difluorophenyl) derivative **3c** (HOMO −6.06 eV), which was supported by red-shifted photophysics of the species. Electrochemical studies as well as theoretical calculations toward the electron affinity of the extended materials proved that they are easily reduced, with reduction potentials in the same range as

Chart 2

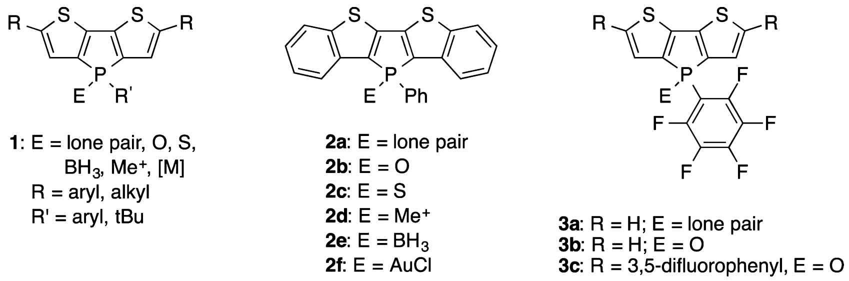
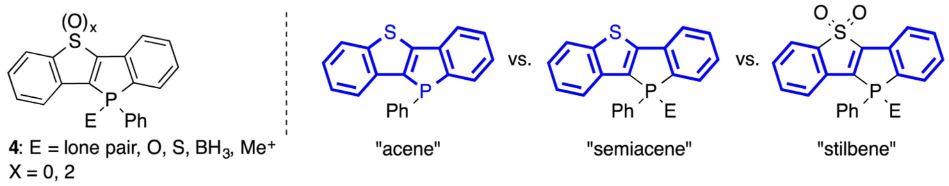


Chart 3. P,S-Tetracenes and Change of the Conjugation Path (bold blue bonds) upon P/S Functionalization

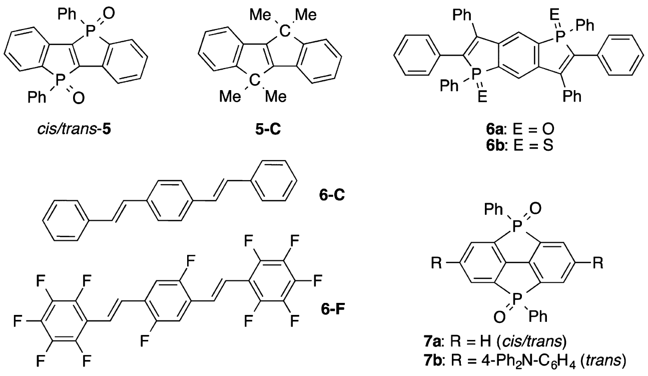


the heteropentacene species mentioned above (E_{red} = −2.07 to −2.14 V).

In 2011, we developed the tetracene-based fused molecular scaffold **4**, which can alternatively be described as P,S-bridged stilbene (Chart 3).[23] Extensive structure−property studies revealed that the optical and electronic properties of the scaffold are effectively manipulated via independent straightforward modification of the two heteroatoms. Optical spectroscopy studies showed that the oxidation of sulfur not only influences the electronic contribution of phosphorus but also alters the general conjugation pathway of the heterotetracene system (Chart 3). This dually switchable system allows for selective control of the HOMO−LUMO gap of the scaffold by the electronic nature of sulfur, while the photoluminescence quantum yield highly depends on the electronic nature of phosphorus. In terms of electron-acceptor properties, the chemical modification of the two heteroatoms allowed us to modulate the reduction potentials from E_{red} = −2.40 V (E = lone pair, $x = 2$) to as low as E_{red} = −1.66 V (E = Me^+, $x = 2$). The corresponding electron affinities were estimated to range between 2.8 and 3.2 eV, with the latter value approaching that of the well established electron-transport material PCBM (ca. 4.0 eV) and most values close to that of Alq_3 (3.2 eV), a widely used electron-transport material in OLEDs.

In three related studies, Yamaguchi and co-workers reported several ladder-type species that showcase two phosphole units within a fused framework (Chart 4).[24−26] Their first report involved *cis/trans*-isomeric bis(phosphoryl)-bridged stilbene **5**, which showed pronounced luminescence but, more importantly, considerable electron-acceptor character.[24]

Chart 4



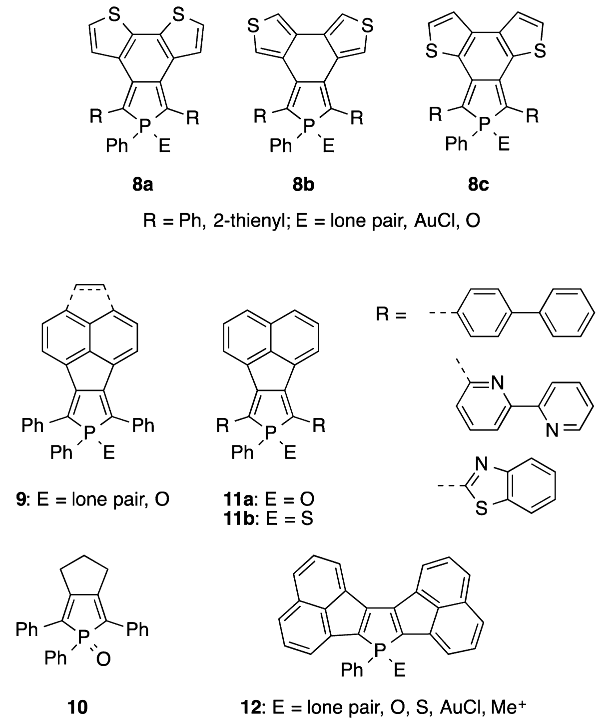
Two reduction waves were observed, of which the first at E_{red1} = −1.63/−1.67 V (*cis/trans*) was reversible and the second at E_{red2} = −2.14/−2.35 V was irreversible. Importantly, the first reductions occur at much lower potential than for the bis(carbon)-bridged analogue **5-C** (E_{red1} = −3.17 V). They later reported the "inverted" system **6** with benzodiphosphole scaffold.[25] The luminescent bis(oxophosphoryl)-species **6a** showed largely reversible reduction potentials with values at E_{red1} = −1.72/−1.74 V and E_{red2} = −2.20/−2.10 V for the two *cis/trans* isomers, respectively, at considerably lower potential than the unbridged distyrylbenzene **6-C** (cf., E_{red1} = −2.48; E_{red2} = −2.74 V), and its fluorinated congener **6-F** (cf., E_{red1} = −1.91; E_{red2} = −2.10 V). Importantly, the group also investigated the bis(thiophosphoryl)-based relative **6b**, which showed slightly shifted reduction potentials at E_{red1} = −1.76/−1.81 V and E_{red2} = −2.18/−2.13 V for the two *cis/trans* isomers, respectively, that reflect the reduced polarity in the P═S bond. In the latest paper of the series, Yamaguchi and co-workers reported the fascinating molecular system **7**, in which two phospholes were fused back-to-back in a biphenyl scaffold;[26] again, two *cis/trans* phosphoryl-bridged isomers were obtained. While they did not report the electron-acceptor features of the basic **7a**, their study included the electrochemistry of the π-extended relative **7b**. Comparison with the corresponding mono(phosphoryl)-bridged species (E_{red1} = −2.36 V) revealed that the presence of two phosphoryl groups indeed improves the overall electron-acceptor character (E_{red1} = −2.15 V).

The above studies suggest tremendous potential for the development of electron-acceptor materials using ladder-type organophosphorus species. In fact, a recent theoretical structure−property study by Ren and co-workers not only verified these experimental values but also suggested very valuable additional features, such as desirable electron-injection and -transport abilities, for the practical application of these species.[27]

Matano and co-workers, who reported their first phosphole-based electron-acceptor materials around the same time as my group, have provided experimental proof for the latter.[28−32] One of their first reports showcased isomeric bithiophene-fused benzo[*c*]phospholes **8a−c** (Chart 5) with low and fully reversible reduction potentials for the oxide relatives (E_{red} = −1.41 to −1.80 V) supporting low-lying LUMO levels that were also confirmed via DFT.[28] In addition to these fundamental studies, the group also performed time-of-flight (TOF) measurements of simple devices that provided electron mobilities for **8a** (R = Ph; E = O) 1 order of magnitude higher than that of Alq_3 at low electric fields ($\mu_e = (2.9\text{−}3.9) \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ at $E = (5.0\text{−}6.0) \times 10^5\ \mathrm{V\ cm}^{-1}$).

In a subsequent series of papers, Matano et al. incorporated the phosphole unit into the backbone of fused acenaphthenes (Chart 5), which also enhances the electron-acceptor properties, as evidenced in lower reduction potentials of E_{red} = −1.61 to −1.89 V for **9** compared with that of nonfused phosphole **10** (E_{red} = −2.02 V).[29] Notably, the study of the electron mobilities via the TOF method revealed values as high as $\mu_e = 8 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ at $E = 1 \times 10^6\ \mathrm{V\ cm}^{-1}$. Moreover, the group reported the further π-extended acenaphtho-fused phospholes **11** that also included the corresponding P-sulfides **11b**.[30] The study confirmed that the extended species were even better electron acceptors (E_{red} = −1.24 to −1.82 V) and that the modification of the phosphorus center (i.e., E = O, S) slightly shifts the reduction potentials. TOF measurements of the extended phosphole oxide **11a** (R = 4-

Chart 5



8a **8b** **8c**

R = Ph, 2-thienyl; E = lone pair, AuCl, O

9: E = lone pair, O

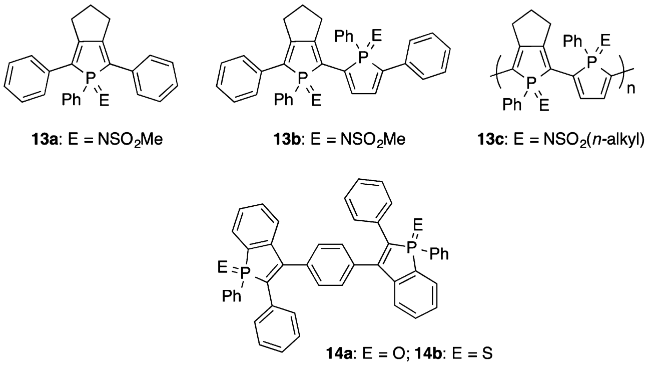
11a: E = O
11b: E = S

10

12: E = lone pair, O, S, AuCl, Me+

biphenyl) revealed electron mobilities of $\mu_e = 1 \times 10^{-5}$ cm^2 V^{-1} s^{-1} at $E = 2.5 \times 10^4$ V cm^{-1}, and these species were also successful applied as cathode buffer layer in organic photovoltaics. The fusion of a phosphole unit with two flanking acenaphtho groups (**12**) further lowers the reduction potentials of the scaffold (E_{red} = −1.00 to −1.88 V), and the group confirmed via EPR spectroscopy that the radical anions are well delocalized over the whole conjugated scaffold.[31] The electron-drift mobilities of this set of species were found to be 1−2 orders of magnitude higher (at $\mu_e = 2.4 \times 10^{-3}$ cm^2 V^{-1} s^{-1} at $E = 4.3 \times 10^5$ V cm^{-1}) than those reported for the acenaphtho-fused relatives **9** and **11**. In 2013, Matano et al. then introduced a new functionalization of the P-center via introduction of a sulfonylimine group (**13a**−**c**, Chart 6) that revealed a greater degree of polarity over the traditional oxophosphoryl group.[32] Red-shifted photophysics, as well as lowered reduction potentials (**13a**, E_{red} = −1.85 V; cf. **10**, E_{red} = −2.02 V for E = O), of a series of oligomeric and polymeric species revealed improved electron-acceptor features of the imines over the corresponding oxides. Interestingly, TOF charge-mobility measurements indicated that the new imines transport not only electrons but also holes with the same efficiency ($\mu_e = 6 \times 10^{-3}$ cm^2 V^{-1} s^{-1}; $\mu_h = 4 \times 10^{-3}$ cm^2 V^{-1} s^{-1}).

Chart 6



13a: E = NSO$_2$Me **13b**: E = NSO$_2$Me **13c**: E = NSO$_2$(n-alkyl)

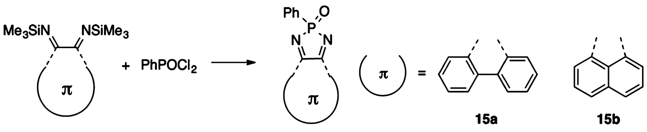
14a: E = O; **14b**: E = S

The most applied studies involving phosphole-based electron acceptors come from Nakamura and co-workers. In 2009, they reported bisbenzo[*b*]phosphole derivatives **14** with oxophosphoryl and thiophosphoryl groups (Chart 6).[33] Akin to the bisphospholes **6a**,**b** reported by Yamaguchi et al.,[25] their bisbenzo[*b*]phospholes were obtained as mixture of *cis*/*trans* isomers. Both species were tested for their electron affinities (via cyclic voltammetry), which suggested comparable features (**14a**, EA = 2.72 eV; **14b**, EA = 2.71 eV), but when applied in devices, their properties differed considerably. While the electron-drift mobility of the thio derivative showed an appreciable $\mu_e = 2 \times 10^{-3}$ cm^2 V^{-1} s^{-1} at $E = 2.5 \times 10^6$ V cm^{-1}, the oxo species only showed $\mu_e = 5 \times 10^{-6}$ cm^2 V^{-1} s^{-1} at $E = 2.5 \times 10^6$ V cm^{-1}. Similar features translated to corresponding OLED devices, with the thio-species **14b** significantly outperforming the oxo-congener **14a**. Based on these observations, the authors reasoned that the highly polarized nature of the P═O bond, in comparison to the less polar P═S unit, acts as an electron trap. In a subsequent study, Nakamura and co-workers thus reported an alternative device application for the dibenzo[*b*]phospholes **14a**,**b**, as well as the bisphospholes **6a**,**b** reported by Yamaguchi et al.[34] Due to the amorphous character of the isomeric mixtures, the two families of bis(phosphole)s were successfully employed as cathode buffer layers in organic photovoltaic cells, although the investigated structural and electronic variations only had a minor impact on the overall device performance.

■ APPROACHES TOWARD ENHANCED ACCEPTOR FEATURES

The phosphole-based conjugated materials in the preceding section have clearly established their capacity as electron-acceptor materials. However, the studies have also shown that there are limitations with regard to practical applications, which has motivated us to develop electron-acceptor materials with different molecular scaffolds. Inspired by the popularity of 2,1,3-benzothiadiazole (BTD) as electron acceptor in conjugated organic materials, we were interested in how a phosphorus analogue would compare. In 2010, we reported a direct synthetic route toward compounds **15a** and **15b**, by reacting conjugated 1,2-bissilylimines with PhPOCl$_2$ without the presence of a solvent (Scheme 2).[35] While this approach eliminated any potential for further P-functionalization, the oxo species were nevertheless found to be very good electron acceptors. For example, the phenanthrene-based diazaphosphole **15a** showed a reversible reduction at E_{red} = −0.95 V that was dramatically lower than that of BTD (E_{red} = −2.12 V). In addition, EPR spectroscopy and DFT supported a highly delocalized and stable radical anion (Figure 6), evident in the broadened EPR spectrum that also includes coupling to the nuclei of the constituent framework, as well as the spin density distribution essentially over the whole molecular scaffold.

Scheme 2. Synthesis of Diazaphosphole Oxides



Since the incorporation of imine nitrogen centers into the backbone of conjugated materials is generally known to

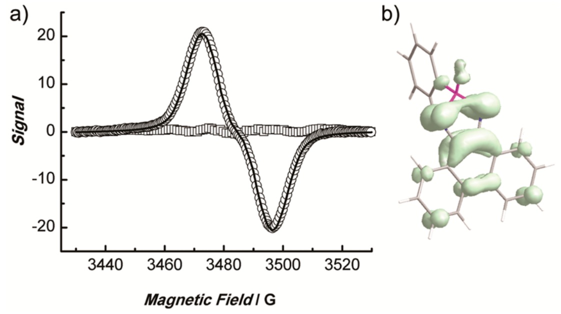
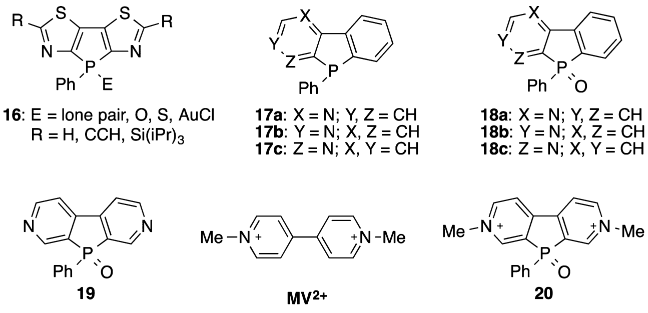


Figure 6. (a) EPR spectrum of the radical anion of **15a** in THF at room temperature (open circles, experimental; line, simulated; open squares, residuals) and (b) its spin density distribution (UB3LYP/6-31G+(d)). Reproduced with permission from ref 35. Copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

implement attractive electron-acceptor features,[3] we have started to develop several families of organophosphorus-based N-heteroacenes (Chart 7). By replacing the thiophene units in the dithienophosphole scaffold with 1,3-thiazole moieties, we were able to access a new family of derivatives whose oxides showed particularly low and reversible reduction potentials ranging from E_{red} = −1.69 to −2.07 V, compared with the dithienophosphole analogues (E_{red} < −2.0 V).[36]

Chart 7



16: E = lone pair, O, S, AuCl
R = H, CCH, Si(iPr)$_3$

17a: X = N; Y, Z = CH
17b: Y = N; X, Z = CH
17c: Z = N; X, Y = CH

18a: X = N; Y, Z = CH
18b: Y = N; X, Z = CH
18c: Z = N; X, Y = CH

19

MV^{2+}

20

In 2011, we reported a systematic structure−property study of the aza-dibenzophospholes **17** and corresponding oxides **18** with the nitrogen center at the 1-, 2-, and 4-position of the scaffold.[37] Electrochemistry of the trivalent phospholes **17**, as well as their pentavalent oxo-congeners **18**, revealed largely reversible reduction behavior. As expected, the phosphole oxide species showed the lowest reduction potentials ranging from E_{red} = −2.14 to −2.30 V, while the trivalent relatives featured reductions from E_{red} = −2.55 to −2.69 V. Importantly, both sets of values are lower than that of dibenzophosphole oxide (E_{red} = −2.33 V) and those of the dibromo-phenylpyridine precursors (E_{red} = −2.72 to −2.82 V; irreversible), supporting the improved characteristics after incorporation of a nitrogen center and the bridging phosphanyl/phosphoryl group, respectively.

Later that year, the 2,7-diazadibenzophosphole analogue **19** (Chart 7) was introduced by us as an extension of this study.[38] The diaza species exhibits two reversible reduction waves at E_{red1} = −1.85 V and E_{red2} = −2.47 V that reflect enhanced acceptor features due to the cumulative effect of the two nitrogen centers. Moreover, there is an obvious relation of this scaffold to that of 4,4′-bipyridine, which sparked us to investigate its utility toward a phosphorus-bridged viologen. Viologens, the dialkylated cations of 4,4′-bipyridine, have long been known as exceptionally powerful redox probes due to their two fully reversible reduction processes that are accompanied by color changes, effectively visualizing the redox steps. Methylviologen (MV^{2+}), also known as paraquat, shows two reduction steps at E_{red1} = −1.09 V and E_{red2} = −1.52 V, accompanied by color changes from colorless (MV^{2+}) to deep purple (MV^{+}) and to orange (MV), respectively. N,N-Dimethylation of the 2,7-diazadibenzophosphole oxide was easily achieved with methyl triflate and the phosphaviologen **20** also showed two fully reversible reduction steps at an impressive E_{red1} = −0.51 V and E_{red2} = −1.00 V, respectively. In addition, we have also shown via spectroelectrochemistry, as well as chemical reduction, that our phosphaviologen indeed exhibits similar color changes between the various redox states (Figure 7).

Another successful approach toward lowered frontier orbitals of conjugated materials is the incorporation of carbonyl groups as inductively withdrawing substituents. Along these lines, we have reported two new fused six- and seven-membered ring systems that involve the incorporation of one and two carbonyl groups, respectively, next to a phosphorus center (Chart 8).[39−41] Both the dithieno[2,3-*b*:3′,2′-*e*]-4-keto-1,4-dihydrophosphinine (**21**) and the dithieno[3,2-*c*:2′,3′-*e*]-2,7-diketophosphepin (**22**) systems show appreciable electron-acceptor features. In the context of these studies, we have confirmed that modification of the P-substituent has considerable impact on the redox potentials. For the dithienophosphinine system, one reversible reduction is observed for the oxo-species **21a** (E_{red} = −1.53 V), while the alkylated cationic relative **21b** exhibits two reversible reduction waves at E_{red1} = −1.12 V and E_{red2} = −1.75 V. Notably, in case of the phosphepin-based system **22**, two reduction steps can be observed for all derivatives, even the trivalent species, that range between E_{red1} = −1.15 V (**22a**; E = AuCl) and −1.66 V (**22a**; E = lone pair) for the first and E_{red2} = −1.59 V (**22a**; E = AuCl) and −1.95 V (**22a**; E = lone pair) for the second reduction. These potentials translate to low LUMO energy levels of E_{LUMO} = −3.65 eV to −3.14 eV, again approaching that of PCBM (ca. −3.7 eV).

Notably, we were unable to methylate the trivalent P-center of the dithienodiketophosphepin **22**, likely due to the inductive effect of the two adjacent keto groups. However, in an extension of our initial study, we succeeded in methylating appended triazole units (**23**), which we obtained via click chemistry from the alkynylated relative.[41] To our surprise, this quite remote methylation had a dramatic effect of the photophysics and electron-acceptor properties of the main scaffold. Next to a pronounced blue shift of the absorption and emission, two considerably lower and perfectly reversible reduction waves (E_{red1} = −1.12 V and E_{red1} = −1.39 V; cf., E_{red1} = −1.53 V and E_{red1} = −1.84 V for the nonmethylated triazole species **24**) were observed (Figure 8).

■ LOW COORDINATE SPECIES

To round out the discussion of state-of-the-art organophosphorus-based electron acceptor materials, it is important to also touch on low-coordinate species. Low-coordinate phosphorus species with P═C and P═P π-bonds have long been a focus in the context of conjugated materials, but their overall optical and electronic properties had remained largely unimpressive.[6] However, this has changed with the introduction of 1,3-benzoxaphospholes **25** by Protasiewicz and co-workers (Chart 9).[42] Not only does incorporation of the P═C double bond into a rigid cyclic framework considerably enhance their luminescence properties, the compounds also show stable reduction behavior. In extensive structure−property studies, the group uncovered reversible one-electron reduction waves

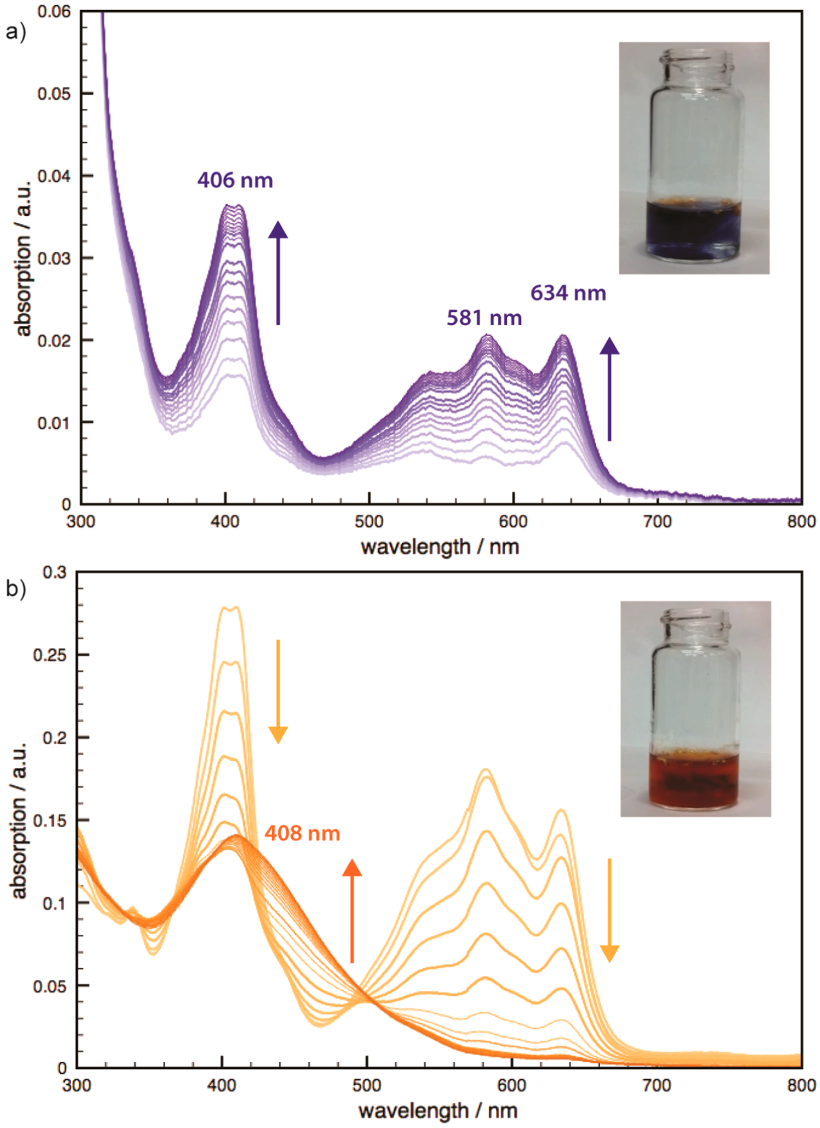
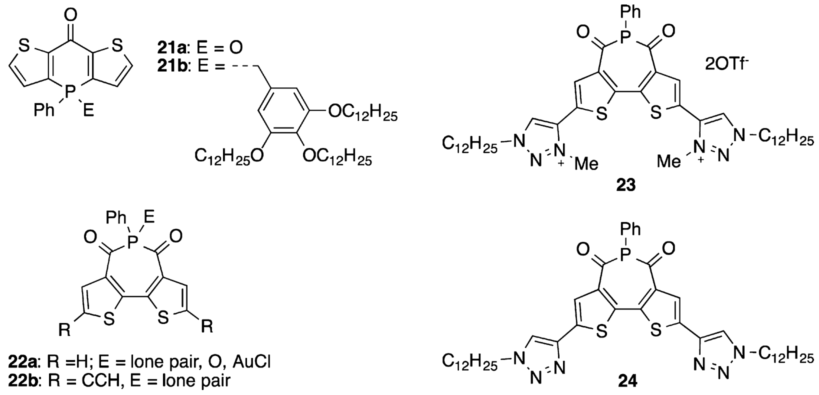


Figure 7. Spectroelectrochemistry of the phosphaviologen **20**. The spectra show the absorption changes upon formation of the radical cation (a) and the neutral species (b). The insets show vials of the corresponding species upon chemical reduction with Zn (a) or Na (b), respectively.

Chart 8



between E_{red} = −2.41 and −2.72 V as a function of the substituents at the 2-, and 6-position of the scaffold that were comparable to other noncyclic phosphalkenes in the literature.

Notably, when the substituent at the 2-position was switched from aryl to alkyl, the reduction waves became irreversible, which was attributed to higher LUMO energy levels ($E_{LUMO} > -1.3$ eV). These results were also mirrored by the study of the corresponding benzobis(oxaphosphole)s **26**, which showed reduction waves between E_{red1} = −2.46 and −2.87 V and, in the case of 2-aryl substituents, a second irreversible reduction

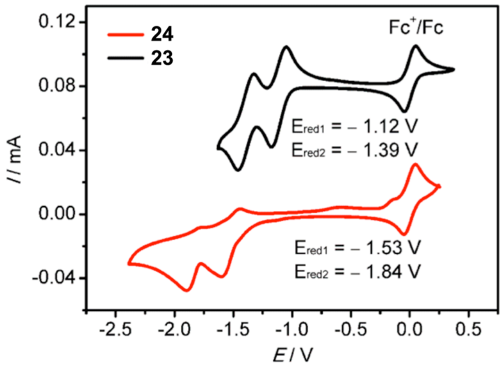
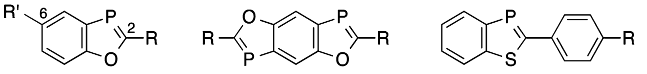


Figure 8. Cyclic voltammograms of **23** and its nonmethylated congener **24** with added Fc/Fc$^+$ as internal standard. Adapted with permission from ref 41. Copyright 2013 American Chemical Society.

Chart 9



25: R = alkyl, aryl
R' = H, i-Pr

26: R = alkyl, aryl

27: R = H, OMe, Br, CF_3, CN

around $E_{red2} = -2.9$ V. In 2013, Noonan and co-workers followed up with an analogous series of benzothiaphospholes **27**, whose reduction potentials range between $E_{red} = -1.92$ and -2.36 V as a function of the Hammett parameter of the phenyl substituent and with varying extent of reversibility, considerably lower than those of the oxa-congeners.[43]

CONCLUSIONS AND FUTURE PROSPECTS

Based on the research highlighted in this Account, it is clear that the organophosphorus approach has considerable potential for the generation of powerful electron-acceptor materials. Rigid, π-extended molecular scaffolds with phosphorus-containing heterocycles, in particular, hold the key in a valuable tool set for the electronic tuning toward desirable properties. Notably, this provides an almost infinite pool of possibilities for the synthesis of novel P-based molecular scaffolds. However, it should also be pointed out that while easy reduction (i.e., low LUMO levels) and stability of the reduced species make good electron-acceptor materials, this does not necessarily translate into suitable n-type materials for practical devices (e.g., see mobilities). Nevertheless, potential pitfalls but also potential solutions and alternative application arenas have been identified by the work highlighted herein. We have now reached a point that allows us to more deeply venture into the transformation of organophosphorus-based electron-acceptor materials toward practical n-type semiconductor materials. Next to avoiding the generation of inherent electron traps such as in phosphole oxides (which can be addressed through different P-functionalization), it is equally important to consider the supramolecular organization of the species in the solid state, that is, the bulk phase, for providing suitable conduits for n-type electron transport. A particularly intriguing avenue to this end, in which my group is now also deeply invested, is the formation of self-assembled supramolecular materials.

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Notes

The authors declare no competing financial interest.

Biography

Thomas Baumgartner was born in Bad Neuenahr, Germany, in 1968. He received his Dr. rer. nat. degree from the University of Bonn, Germany, and he was a postdoctoral fellow at the University of Toronto, Canada. In 2002, he started his independent career at the Johannes Gutenberg-University in Mainz and later at the RWTH-Aachen University, both in Germany. He joined the University of Calgary, Canada, in 2006, where he is now Full Professor. His research interests involve molecular and supramolecular organophosphorus π-conjugated materials with a focus on sustainable energy applications. He has been recognized with several awards including a Liebig fellowship from the German chemical industry association, an Alberta Ingenuity New Faculty Award, a JSPS invitation fellowship, and a Friedrich Wilhelm Bessel Research Award from the Alexander von Humboldt Foundation.

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