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# Phosphinine Lipids: A Successful Marriage between Electron-Acceptor and Self-Assembly Features**

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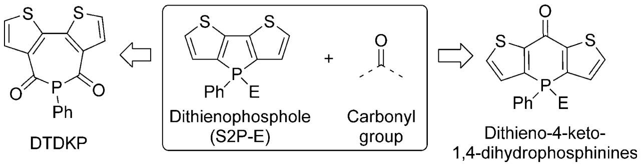
Organophosphorus chemistry has made a great impact on the advances in inorganic/organometallic chemistry and life sciences in the last century.[1] Moreover, as a result of their unique optical and electronic features, organophosphorus species have very recently also attracted much attention in the field of organic electronics, as well as sensory and self-assembled materials.[1] Phosphole-based conjugated systems, in particular, exhibit extraordinary photophysical properties that can be easily tuned through the versatile reactivity of phosphorus. In addition, a peculiar $\sigma^*$–$\pi^*$ orbital coupling, made possible through the pyramidal geometry of the P center in these materials, stabilizes the LUMO energies and thus provides a very promising alternative approach toward electron-acceptor (n-type) materials.[1d]

In the field of organic electronics, the number of suitable n-type materials is actually quite limited compared to that of p-type materials, and thus impedes any significant improvement in the performance of organic electronics; conventional strategies toward n-type materials usually rely on the introduction of electron-withdrawing moieties, such as carbonyl, cyano, $C_6F_5$, $CF_3$, or imide groups into an organic framework.[2] In this context, we have recently reported a novel electron-accepting building block, dithieno[3,2-*c*:2′,3′-*e*]-2,7-diketophosphepin (DTDKP), by the introduction of two electron-withdrawing carbonyl groups into the dithienophosphole framework (Scheme 1).[3] DTDKP exhibits improved electron-accepting character over its nitrogen analogue, thus highlighting the unique contributions phosphorus can provide for organic electronics.[4]



***Scheme 1.*** Design strategy for electron-accepting organophosphorus materials by introducing carbonyl groups.

Combining organic electronic species with self-assembly features that generate well-ordered micro-/nanostructures has been recognized as highly desirable for the development of efficient optoelectronic devices, such as solar cells and field-effect transistors, but also electroactive liquid crystals.[5] Most of these materials are based on neutral polycyclic aromatic hydrocarbons (PAHs)[5] or cationic imidazole-based materials.[6] However, the combination of systems based on inorganic main group elements (B, Si, P) with self-assembly properties remains fairly underexplored to date, mainly because of the synthetic challenges involved. In this regard, organophosphorus materials offer excellent advantages over other main-group elements. Inspired by the amphiphilic phospholipid cell membranes with unique self-assembled bilayer structures, the research groups of Weiss and Kato pioneered the study of the self-assembly of ionic phosphonium compounds, by focusing on nonconjugated systems.[7,8] Very recently, we reported a family of conjugated "phosphole-lipid" systems with $\pi$-conjugated head groups that exhibited self-assembly features as well as intriguing stimuli-responsive behavior. These systems combined the amphiphilic features of lipids and the valuable photophysical features of conjugated phospholes.[9]

Herein, we report on a novel electron-accepting organophosphorus system, dithieno[2,3-*b*;3′,2′-*e*]-4-keto-1,4-dihydrophosphinine, obtained by introducing an electron-withdrawing carbonyl group at the *para* position of the six-membered phosphinine ring. This design is not expected to affect the desirable reactivity of the phosphorus center, such as oxidation or quaternization, which has limited the versatility of the DTDKP system to some extent.[4] Further functionalization of this building block with self-assembly groups provides novel amphiphilic phosphonium materials that combine the electronic character of the $\pi$-conjugated phosphinine core with the amphiphilic character of phospholipids, similar to our earlier studies on the phosphole-lipid system,[9] and for a deeper understanding of conjugated organophosphorus lipid systems in general.

The synthetic route is shown in Scheme 2 and the procedures are described in detail in the Supporting Information. Notably, the trivalent phosphorus center in **1** is easily modified by oxidation and quaternization to form **2** and **3**, respectively. Transformation of the 1,3-dioxolane-protected **3** to ketone **4** was carried out with HBr to retain the Br$^-$ counterion in the final product. The identity and purity of all new compounds was confirmed by conventional spectroscopic methods. The thermal stability of the phosphonium salts **3**–**5** was evaluated by thermogravimetric analysis (TGA) and all showed decomposition temperatures between 225–235 °C, which indicate good thermal stability.

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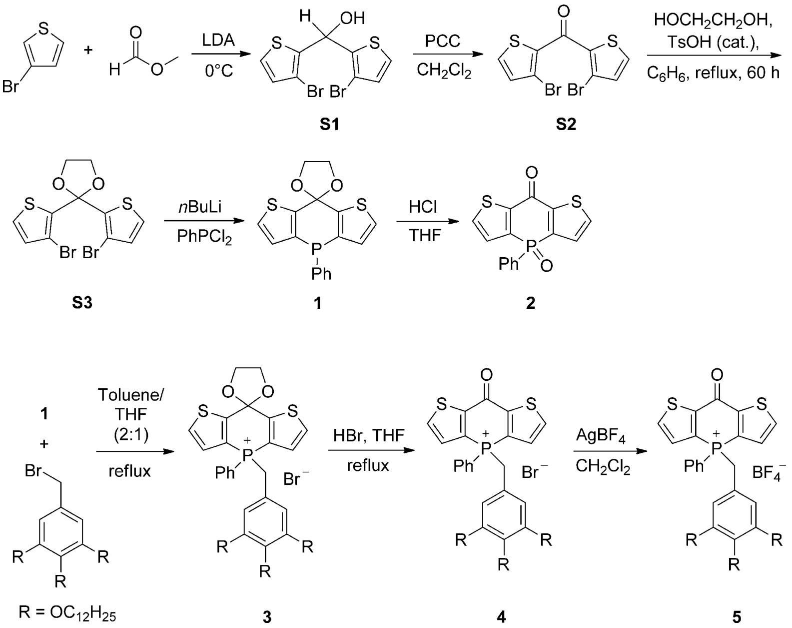

**Scheme 2.** Synthesis and functionalization of dithieno[2,3-*b*;3′,2′-*e*]-4-keto-1,4-dihydrophosphinines. LDA = lithium diisopropylamide, PCC = pyridinium chlorochromate.

Importantly, the molecular structure of phosphonium salt **4** could be successfully determined by single-crystal X-ray crystallography (Figure 1). As a result of its high flexibility, literature reports on the structure of species containing the 3,4,5-tris(dodecyl-1-oxy)benzyl group are few and far between.[10] Selected bond lengths and angles are summarized in Table S1 in the Supporting Information. The conjugated tricyclic core is highly planar and the phosphorus center adopts a typical pyramidal geometry. The solid-state packing clearly reveals a lamellar bilayer architecture, where the lipophilic layers created by three long alkyl chains surround the ionic layers. This solid packing not only supports our previously proposed structures of the phosphole-lipid liquid crystals,[9] but also predicts that **4** should form a similar smectic liquid-crystal phase. In the ionic layer, inter- and intramolecular hydrogen-bonding interactions between the two benzylic hydrogen atoms and two bromide anions are observed, which result in a stable diamond motif (Figure 1 b) with two C–H···Br distances of 3.95 and 3.68 Å. The bromide ion acts a bridge that connects two individual molecules to stabilize the layer. Moreover, two adjacent conjugated phosphinine cores also exhibit partial π–π interactions with a distance of 3.46 Å (Figure 1 c).

The optical and electrochemical features were investigated by UV/Vis spectroscopy and cyclic voltammetry, respectively, and the data are summarized in Table 1. Keto-protected compounds **1** and **3** only exhibit a high-energy absorption band at 262–270 nm, while conversion into their corresponding keto-containing counterparts **2** and **4** is accompanied by a large red-shift in the absorption, thus indicating the off-on switching of the electronic communication through the π orbital of the carbonyl group (Figure 2 a). Compared to the phosphonium model compound with a benzyl group (**4M**; R = H), **4** exhibits a low-energy tail to 500 nm, which is assigned to an intramolecular charge transfer from the electron-donating trialkoxyphenyl ring to the electron-accepting phosphinine backbone (Figure 2 b). In addition, a small blue shift in the absorption was observed when the solvent was changed from $CH_2Cl_2$ to methanol (see Figure S1 in the Supporting Information), which suggests the suppression of the hydrogen-bonding interactions. A slight blue shift is also observed in **5** with the weakly coordinating $BF_4^-$ ion (see Figure S2 in the Supporting Information). In contrast to the established dithienophosphole and the recently reported DTDKP, however, the new phosphinines are not fluorescent.

**Table 1:** Optical and electrochemical data for **1**–**4**.

| Compd | $\lambda_{abs}$[a] [nm] ($\varepsilon$ [$dm^3\,mol^{-1}\,cm^{-1}$]) | $E_{red}$[b] [V] |
|---|---|---|
| **1** | 262 (17250) | NA |
| **2** | 272 (12090), 314 (7320), 345 (8520) | −1.53 |
| **3** | 270 (23200) | NA |
| **4** | 272 (17820), 345 (8690) | −1.12, −1.75 |

[a] In $CH_2Cl_2$ solution at 298 K. [b] Half-potentials versus Fc/Fc$^+$, 0.1 M $nBu_4NPF_6$ as the supporting electrolyte, in $CH_2Cl_2$. NA: not available.

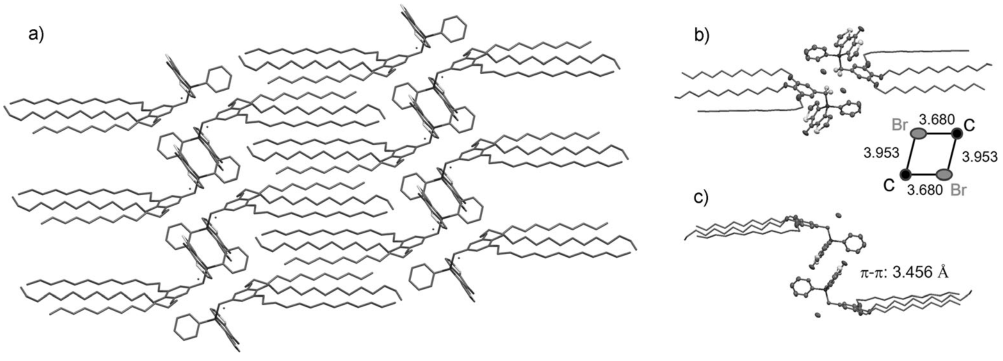

**Figure 1.** a) Layer structure of **4** in the solid state, b) inter- and intramolecular hydrogen-bonding interactions, and c) π–π interactions (for the crystal data, molecular structure, bond lengths, and angles, see the Supporting Information).

As expected, the introduction of the carbonyl group endows this new class of phosphinines with excellent electron-accepting properties. As shown

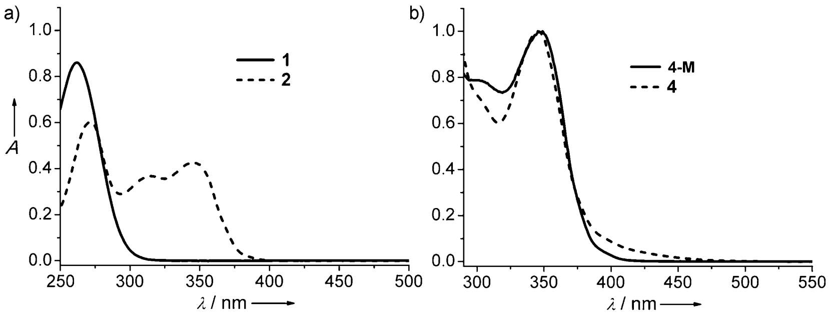

***Figure 2.*** a) UV/Vis spectra of **1** and **2** in $CH_2Cl_2$ at a concentration of $5\times10^{-5}$ M. b) Normalized UV/Vis spectra of **4** and a phosphonium model (**4M**; R = H) in $CH_2Cl_2$.

in Figure 3, **2** exhibits one reversible reduction at $E_{1/2} = -1.53$ V. Interestingly, the phosphonium salt **4** shows two reversible reduction processes at $E_{1/2} = -1.12$ V and $-1.75$ V; its cationic nature can likely help stabilize the negative charge formed during the process. By using ferrocene as an internal reference, the LUMO energies ($E_{\mathrm{LUMO}}$) of **2** and **4** were

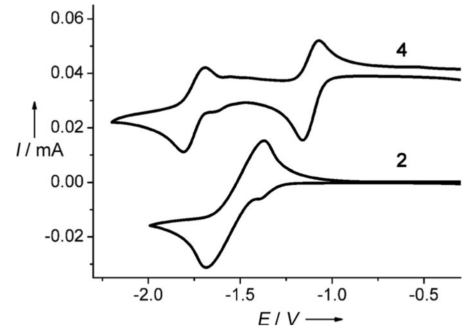

***Figure 3.*** Cyclic voltammograms of **2** (2 mM) and **4** (2 mM) in $CH_2Cl_2$ solution with 0.1 M $nBu_4NPF_6$ as a supporting electrolyte. Scan rate: 100 mV $s^{-1}$. Ferrocene was added as an internal standard and referenced to 0 V.

determined to be $E = -3.27$ and $-3.68$ eV, respectively [$E_{\mathrm{LUMO}} = -(E_{\mathrm{red1}} + 4.8)$ eV].[11] The diffusion coefficient of **4** is calculated to be $3.0\times10^{-7}$ $cm^2 s^{-1}$, according to the Randles–Sevcik equation.[12] In addition, two similar reduction processes were also observed in the thin film of **4** (see Figure S4 in the Supporting Information) which reflect the retention of its electron-acceptor features in the self-assembled structures. Both **2** and **4** show better electron-accepting properties than DTDKP ($E_{\mathrm{LUMO}} = -3.14$ eV), thus suggesting their potential application as n-type materials for optoelectronics. In this context, Matano and co-workers recently demonstrated that fused phospholes with a reduction potential in the range of $-1.82$ to $-1.40$ V (versus the ferrocene/ferrocenium ($Fc/Fc^+$) couple), indeed display promising electron mobilities up to $2.4\times10^{-3}$ $cm^2 V^{-1} s^{-1}$.[13]

To better understand the optical and electronic characteristics, DFT calculations (B3LYP/6-31G(d) level of theory)[14] were performed on **2** and **4′** (dodecyl replaced by Me). Table 2 shows the corresponding frontier orbital energies. Compared to the calculated LUMO energies of a related dithienophosphole oxide ($E_{\mathrm{LUMO}} = -1.86$ eV)[15] and DTDKP ($E_{\mathrm{LUMO}} = -2.66$ eV),[3] **2** shows an even lower LUMO energy level at $E_{\mathrm{LUMO}} = -2.99$ eV, thus supporting its improved electron-accepting capability, which is in good agreement with the electrochemical studies. The frontier orbitals (LUMO+1, LUMO, HOMO, and HOMO-1) are depicted in Figure S5 in the Supporting Information. Interestingly, the LUMO and LUMO+1 orbitals mainly represent the π and π* orbitals of the phosphinine core in **2** and **4′**, and not the HOMO and LUMO orbitals, which is typically observed in dithienophosphole and DTDKP systems. The HOMO level of **2** consists of the π system of the exocyclic phenyl ring, a lone pair of electrons on the oxygen atom, as well as some minor contribution from the phosphinine core. By contrast, the HOMO of **4′** shows no contribution from the phosphinine core, but from the π orbital from the trialkoxyphenyl ring, thereby supporting the possibility of a charge-transfer process from this group to the electron-deficient phosphinine core, which is consistent with the low-energy tail in the UV/Vis spectrum (Figure 2b).

***Table 2:*** Frontier orbital energies [eV] for **2** and **4′**.

| Compd[a] | LUMO+1 | LUMO | HOMO | HOMO-1 |
|---|---|---|---|---|
| **2** | −1.34 | −2.99 | −6.98 | −7.01 |
| **4′**[b] | −4.43 | −5.77 | −8.29 | −8.40 |

[a] Calculated at the Gaussian 03; B3LYP/6-31G(d) level of theory.[14] [b] The cationic portion was calculated using PCM solvation ($CH_2Cl_2$).

The self-assembly of **4** was studied by differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD). The DSC experiments revealed several thermal phase transitions (Figure 4). Heating **4** from −50 °C resulted in two endothermic transitions at 30 °C and 35 °C, which are assigned

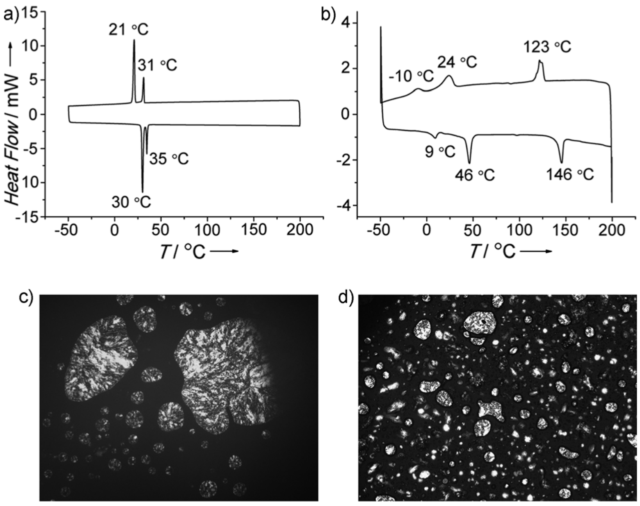

***Figure 4.*** DSC traces of **4** (a) and **5** (b) with heating and cooling rates at 5 °C $min^{-1}$ (negative values for the heat flow indicate an endothermic process); and polarized optical micrographs of **4** (c) at 180 °C and **5** (d) at 100 °C.

to a crystal to soft crystal, and soft crystal to liquid crystal transition, respectively. As the temperature increased to 215 °C, compound **4** started to exhibit phase transitions to an isotropic liquid, where a dark homeotropic area was observed. As anticipated from the lamellar layer structure in the single crystal of **4**, smectic liquid-crystal properties are observed within a very broad temperature range (30–200 °C), which was further confirmed by PXRD analysis (see Figure S7 in the Supporting Information). At 200 °C, **4** gives an intense sharp, low-angle peak at $2\theta = 3.16°$, which corresponds to a $d$ spacing of 27.9 Å for a smectic phase indexed to the (100) plane, and is consistent with the calculated reflection from the single-crystal X-ray data. In addition, a broad peak at $2\theta = 20°$ indicates the liquidlike state of the long alkyl chains. At 30 °C, the PXRD pattern of **4** exhibits a more crystalline structure, with several new reflection peaks in both the low and high angle regions observed. The thickness of the layers tends to decrease at low temperature, thus indicating closer packing.

The formation of a liquid-crystal phase of **4** is also confirmed by polarized optical microscopy (POM). However, the optical texture of **4** observed by POM is not recovered after several scans, probably because of its very close melting ($T_m$) and the decomposition ($T_d$) points ($T_m = 215$ °C, $T_d = 227$ °C). To improve the stability, we assumed that weakening the intermolecular hydrogen bonding or π–π interactions would be helpful in decreasing the melting point of the material while maintaining the high decomposition temperature. To approach the first goal of decreasing the strength of the hydrogen bonding, we designed **5** by exchanging the counterion from $Br^-$ to the weakly coordinating $BF_4^-$ ion, which is a very important tunable parameter for ionic liquid crystals.[9a] The bulky keto-protected precursor **3** provides a good model to approach the second goal by weakening the π-π interaction. Indeed, as summarized in Table 3, **3** and **5** show much lower melting than decomposition temperatures (**3**: $T_m = 185$ °C, $T_d = 225$ °C; **4**: $T_m = 146$ °C, $T_d = 235$ °C). However, **3** and **5** show distinctly different liquid-crystal performances. While a liquid-crystalline mesophase is observed for **5** that is similar to that of **4**, its DSC diagram and the optical texture observed by POM (Figure 4) are indeed repeatable over several cycles. By contrast, **3** does not show any liquid-crystal behavior, clearly supporting the necessity of π–π interactions for the formation of mesophases.

***Table 3:*** Decomposition ($T_d$) and melting ($T_m$) temperatures of **3**–**5**.

| | 3 | 4 | 5 |
|---|---|---|---|
| $T_d$ [°C] | 225 | 227 | 235 |
| $T_m$ [°C] | 185 | 215 | 146 |

In summary, a novel electron-accepting organophosphorus building block, dithieno[2,3-*b*;3′,2′-*e*]-4-keto-1,4-dihydrophosphinine, has been designed and synthesized, and the new core could be successfully combined with self-assembly features to create liquid crystals. The supramolecular organization of the liquid-crystal phase could unequivocally be confirmed by single-crystal X-ray crystallography. Moreover, the stability and behavior of the self-assembled liquid crystal could be controlled by adjusting weak intermolecular forces, such as hydrogen bonding and π–π interactions. Future studies will involve the extension of this novel electron-accepting building block with various electron-donating moieties for donor–acceptor conjugated oligomers and polymers for sustainable energy applications and will be reported in due course.

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**Keywords:** electron acceptors · liquid crystals · phosphorus heterocycles · self-assembly

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