π-Conjugated systems: Can phosphole offer more than pyrrole?*

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Abstract: An overview of the synthesis, physical properties, and use as material for organic light-emitting diodes (OLEDs) of linear organic π-conjugated systems incorporating phosphole and thiophene rings is presented.

Keywords: Conjugated systems; phospholes; electropolymerization; HOMO–LUMO gap; optoelectronics.

INTRODUCTION

The synthesis of new π-conjugated materials is currently the focus of numerous researches owing to their potential applications in optoelectronics (light-emitting diodes, thin film transistors…) [1]. A fruitful approach for the tailoring of π-conjugated systems involves the incorporation of heterocyclopentadienes (thiophene, pyrrole, silole…) into their backbones since these building blocks exhibit different electronic properties depending on the nature of the heteroatom [1,2]. Phospholes are appealing building blocks for such purpose since they display properties which are markedly different from those of the pyrrole rings [3]. In pyrrole, the N-atom adopts a planar geometry and its lone pair is in a pure *p*-orbital. In marked contrast, the P-atom of phosphole has a pyramidal shape and its lone pair has a high s-character [4]. As a consequence, pyrrole is a highly aromatic heterole with a nonreactive heteroatom, whereas phosphole possesses a weak aromatic character and a reactive P-atom. Furthermore, owing to the pyramidal shape of the P-center, the exocyclic P–R bond interacts with the endocyclic π-system, leading to σ-π hyperconjugation phenomenon [4].

We have exploited these unique properties of the phosphole ring for the tailoring of novel π-conjugated materials. Herewith, we give an account on our recent works devoted to the synthesis and study of the physical properties of co-oligomers alternating thiophene and phosphole rings with well-defined 2,5-linkages and of conductive polymers incorporating these two heterocycles.

RESULTS AND DISCUSSION

The well-defined thiophene–phosphole co-oligomers **1a–c** (Scheme 1) [5] can be prepared via intramolecular oxidative coupling of functionalized diynes with "zirconocene" followed by addition of dihalogenophenylphosphines [6]. These compounds are air-stable and can be purified by column chromatography. Note that the higher oligomers **1b,c** were isolated as a mixture of diastereoisomers [5c]. The X-ray diffraction study performed on compound **1a** revealed that the P-atom has a pyramidal geom-

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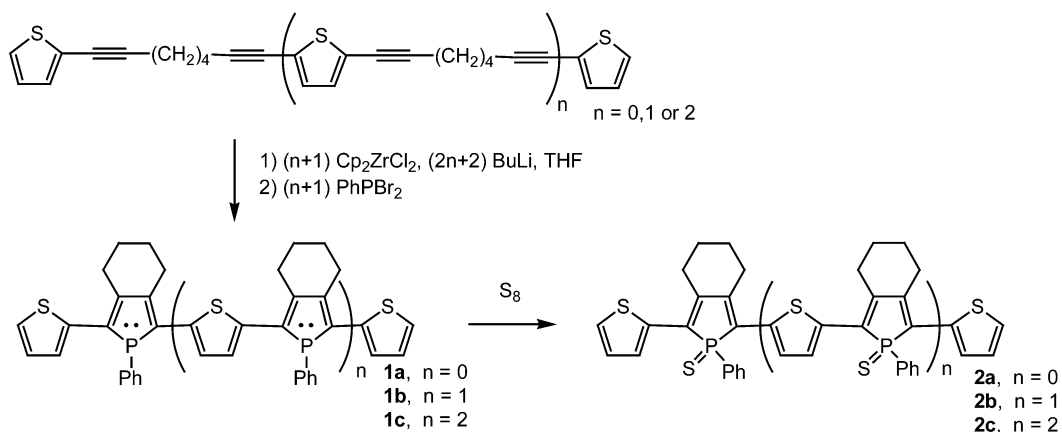
Scheme 1

etry and that the three heterocycles are almost coplanar. These solid-state data suggest (i) that the P-lone pair of the σ^3,λ^3-phosphole is not conjugated with the endocyclic dienic framework, and (ii) the presence of an extended delocalization pathway involving the dienic moiety of the phosphole ring and the two thienyl units. According to UV–vis data and theoretical calculations [5b], the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap of 2,5-di(2-thienyl)phosphole **1a** (λ_{max} = 412 nm) is smaller than that of 2,5-di(2-thienyl)pyrrole (λ_{max} = 355 nm) or *tert*-thiophene [7]. These observations establish that phospholes are excellent building blocks for the synthesis of π-conjugated systems with low HOMO–LUMO gap. This property is probably due to their low aromatic character, which favors the delocalization of the π-electrons [2a,4,8].

An appealing property of π-conjugated systems **1a,c** is the presence of reactive σ^3,λ^3-P atoms. Simple chemical modifications of these reactive P-centers allow a fine-tuning of their optical and electrochemical properties [5]. For example, oxidation of the P-atom with elemental sulfur led to oligo(α,α'-thiophene–phosphole) **2a–c** presenting stabilized LUMO and HOMO levels and smaller HOMO–LUMO gaps than their precursors **1a–c** (Scheme 1) [5b,c]. Of particular importance, the thermal stability of phosphole-based oligomers is considerably increased upon oxidation of the P-atoms with sulfur. These results illustrate nicely the contribution of phosphorus chemistry to tune the properties of π-conjugated systems.

Exploitation of this unique way of tailoring the properties of π-conjugated systems led to optimized thiophene–phosphole co-oligomers, which have been used as materials for organic light-emitting diodes (OLEDs). Upon sublimation, phosphole **1a** decomposed while the more thermally stable thioxoderivative **2a** formed homogeneous thin films on an indium-tin-oxide (ITO) semi-transparent anode, allowing a simple-layer OLED to be prepared [9]. This device exhibits yellow emission for a relatively low turn-on voltage of 2 V. The comparatively low maximum brightness (3613 cd m^{-2}) and the electroluminescence (EL) quantum yield (0.16 %) can be increased by nearly one order of magnitude using a more advanced device, in which the organic layer consisting of **2a** was sandwiched between hole- and electron-transporting layers (α-NPD and Alq$_3$, respectively). Upon doping the "phosphole" layer with the red-emitting dopant (DCJTB), the EL quantum yield is further enhanced up to 1.83 % with a maximum brightness of ca. 37 000 cd m^{-2} [9]. These results constitute the first application in optoelectronics of π-conjugated organophosphorus materials.

The evolution of the optical and electrochemical properties with increasing the chain length is one of the central parameters in the understanding of characteristics of novel π-conjugated systems [1,2]. A regular red shift of λ_{max} and λ_{onset} ("optical band gap" [1c]) is observed upon increasing the length of oligomers **2a–c** suggesting that no saturation of the delocalization is observed up to seven units (Table 1) [5c]. The electrochemical behavior of oligomers **2a–c** depends also on the number of repeat-

ing subunits. Oligomer **2a** presents irreversible redox processes, in contrast, oligomer **2b** exhibits four reversible redox states (Table 1) [5b,c]. Thus, the stability of the reduced and oxidized forms increases with the number of thiophene–thiooxophosphole subunits. Moreover, the chain extension leads to a decrease of the oxidation potentials and an increase of the reduction potentials. These data are in line with the conclusion of the optical study, which showed a lowering of the HOMO–LUMO gap upon increasing the length of the α,α'(thiophene–thiooxophosphole) oligomers.

**Table 1**. Optical and electrochemical data for oligomers **2a–c**.

Compounds	$\lambda_{max}/\lambda_{onset}$[a] (nm)	Log ε	E_{pa} (V)[b]	E_{pc} (V)[b]
2a	432/496	3.98	+0.68, +0.90	−1.95
2b	508/590	4.26	+0.45, +0.65[c]	−1.82, −2.05[c]
2c	550/665	4.42	–	–

[a]Measured in THF.
[b]All potentials were obtained during cyclic voltametric investigations in 0.2 M Bu_4NPF_6 in CH_2Cl_2, platinum electrode diameter 1 mm, sweep rate 100 mV^{-1}. All potentials are referenced to the reversible formal potential of ferrocene/ferrocenium couple.
[c]Reversible processes, E° ox and E° red values provided.

Considering the good stability of oligomers **2a–c** and the lowering of the gap upon increasing their lengths, it was tempting to investigate the synthesis of polymers based on phosphole and thiophene building blocks. Such polymers can be readily obtained via electro-oxidation of the terminal thiophene moieties of the corresponding monomers **2a** and **2b** (Scheme 2) [5b,c]. The electropolymerization was accomplished by repeating cycling. The oxidation current increased with the number of cycles, and an oxidation wave appeared at less positive potential than that recorded for the monomer oxidation, indicating the formation of an electroactive film on the surface of the working electrode [5b,c]. As usually observed for electro-generated polythiophenes, the electro-deposed materials **3a** and **3b** are insoluble in common organic solvents. They exhibit both *n*- and *p*- doping processes, and it is worth noting that the electrochemical properties of **3a** and **3b** vary with the length of the monomers [*p*-doping: **3a**, 0.30/0.65 V; **3b**, 0.22/0.62 V] [5b,c]. Thin film absorption spectrum of **3a** exhibits one broad absorption band in the visible at about 529 nm with a λ_{onset} at 750 nm. The λ_{onset} is red-shifted in comparison with those observed for the corresponding monomer **2a** (Δ λ_{onset} = 254 nm) and oligomer **2b** (Δ λ_{onset} = 150 nm), suggesting that **3a** consists of rather long oligomers featuring 2,5-dithienylphosphole as repeating unit [5c].

2a, n = 0
2b, n = 1

3a, n = 0
3b, n = 1
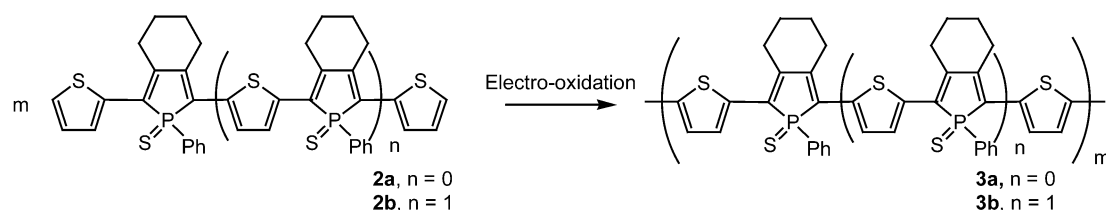
Scheme 2

The linear oligomers described above possess extended delocalization pathway involving the dienic moiety of the phosphole ring and the thienyl units. The fact that the exocyclic P–R bond of the phosphole ring interacts with the endocyclic π-system prompted us to investigate the possible interaction of two of these π-systems through a P–P bridge. This σ-π conjugation ("through bond interaction") [10] should be favored by the fact that the P–P bond possesses a low σ-σ * gap.

Compound **5** (Scheme 3) [11], assembling two di(2-thienyl)phosphole chromophores via a P–P bond, was prepared according to the classical route to 1,1'-biphospholes [12]. This synthetic pathway implies a coupling of the corresponding phospholyl anion **4** upon oxidation with iodine (Scheme 3). An X-ray diffraction study performed on **5** revealed a P–P single bond [2.224(1) Å] and showed that the P atoms are strongly pyramidalized [Σ bond angles, 293.7°] [11]. It is noteworthy that the bond lengths and valence angles of the organophosphorus frame of **5** compare with those of the 2,5-dithienylphosphole **1a** [11].
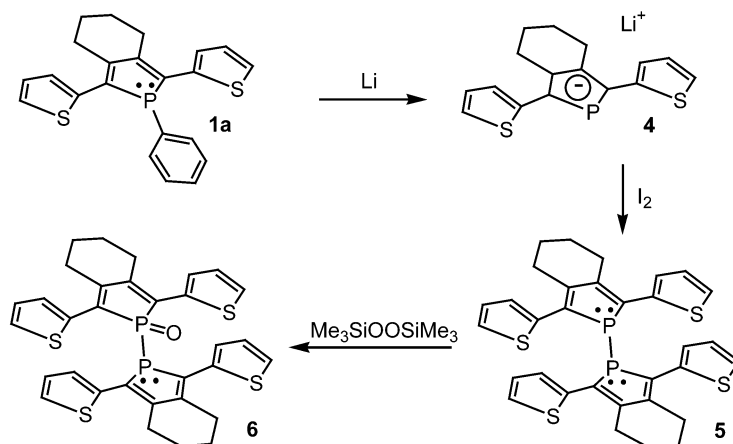

Scheme 3

Theoretical studies have shown that the interaction of two π-systems through a σ-bridge (hyperconjugation) results in a splitting of the HOMO and LUMO of these π-systems. This induces a narrowing of the HOMO–LUMO gap and an increased density of states [10], two features which can be observed by UV–vis spectroscopy. Hence, it is of interest to compare the UV–vis spectrum of **1a**, having only one π-system, and **5** having two π-systems connected by the P–P bridge. The absorption spectrum of **1a** shows only one absorption due to a π-π* transition (412 nm) (Fig. 1). In contrast, several bands have been recorded for **5** with one red-shifted broad shoulder (λ_{onset} = 560 nm) (Fig. 1) [11]. These UV–vis data fit with an interaction of the two π-systems through the σ-(P–P) bridge in **5**. This conclusion has been confirmed by a theoretical study, showing a splitting in energy of the LUMO and HOMO levels [11]. Furthermore, the LUMO of **5** is the anti-bonding combination and the LUMO+1 is the bonding combination, a behavior which is characteristic for through bond coupling of two π-systems over an odd number of σ-bond [10a].

We have already demonstrated that chemical modifications of the σ^3,λ^3-P atom of thienyl-capped chromophores **1a–c** (Scheme 1) offer an unique way to diversify their properties and are key issues for optoelectronic applications of phosphole-based materials. The same behavior was also found for derivative **5**, which possesses two σ^3,λ^3-P atoms. The band onset of the UV–vis spectrum of derivative **6** (Scheme 3), which is readily obtained using a stoichiometric amount of bis(trimethylsilyl)peroxide, is bathochromic-shifted compared to that of 1,1'-biphosphole **5** (Scheme 3). This narrowing of the optical HOMO–LUMO gap strongly suggests that the modified σ-P–P bridge still interacts with the two π-systems by the hyperconjugative effect.

Interestingly, electro-active polymers can be readily obtained by electropolymerization of thienyl-capped derivative **5** [11]. The regular growth of the two initial anodic peaks (no shift to more positive potentials and no decrease in intensity) along the recurrent sweeps, indicate the conductivity of the deposit. The electrode modified by poly(**5**) exhibits a stable and reversible *p*-doping process. The UV–vis spectra of poly(**5**) shows a large band with an unresolved maximum at about 594 nm and a high value
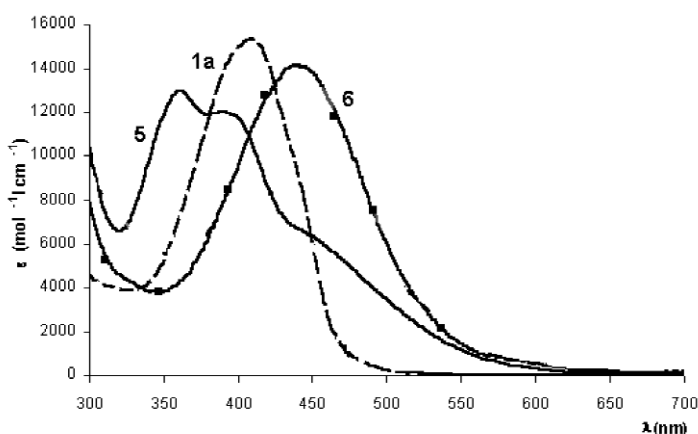
Fig. 1 Absorption spectra of **1a** (– – –), **5** (——), **6** (-■-) in CH_2Cl_2.s.

of λ_{onset} (730 nm), indicating a narrow optical HOMO–LUMO gap compared to monomer **5**. This result shows that not only molecular species, but also low-gap electroactive materials based on 1,1'-biphosphole units can be readily obtained from **5**.

CONCLUSION

It has been clearly established that organophosphorus derivatives offer specific advantages in comparison with their widely used sulfur or nitrogen analogs. First, phospholes appear to be excellent building blocks for the tailoring of low band-gap materials due to their *low aromatic character*. Second, the possibility of *chemically modifying* their λ^3-P centers gives a unique way to tune the physical properties of these P-containing π-conjugated systems. Third, the presence of *hyperconjugation* has been exploited for the preparation of assemblies exhibiting σ-π conjugation. These results nicely illustrate the specific contribution of phosphole compared to its *N*-analog, the pyrrole ring.

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