Organophosphorus π-conjugated materials: the rise of a new field

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Abstract

The synthesis and electronic properties of new linear organic π-conjugated systems incorporating phosphole rings are described. Well defined α,α′-(phosphole-thiophene) oligomers possess low HOMO–LUMO gaps and their optical and electrochemical properties can be tuned via chemical modifications of the P-atoms. The physical properties of these compounds make them valuable materials for OLED's. The coordination ability of phosphole-based dipoles has been exploited for the synthesis of efficient multipolar NLO-phores. Lastly, phospholes have been used for the synthesis of assemblies exhibiting through-bond interaction between two π-systems via P–P σ-skeletons.
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1. Introduction

Linear π-conjugated oligomers and polymers based on a planar backbone of sp^2-bonded carbon atoms have attracted huge interest in recent years owing to their potential applications for electronic devices (light-emitting diodes, thin film transistors, photovoltaïc cells, etc.) [1]. An intensive work has been undertaken with a view to preparing new linear conjugated frameworks of enhanced stability and performances [1]. With this aim, various heterocyclopentadienes (thiophene, pyrrole, silole, etc.) have been incorporated into the backbone of π-conjugated systems since their electronic properties are dependant on the nature of the heteroatom [1a–1c,1f,2]. Among these synthons, phospholes appear as appealing building blocks since they display electronic properties that are markedly different from those of the widely used highly aromatic thiophene and pyrrole rings [3]. The tricoordinated phosphorus atom of phospholes possesses a pyramidal geometry with a lone pair having a pronounced s-character. These geometric and electronic features prevent an efficient endocyclic conjugation of the electron-sextet. In fact, delocalisation within the phosphole ring arises from a hyperconjugation involving the exocyclic P–R σ-bond and the π-system of the dienic moiety [4]. As a consequence, the phosphole ring exhibits an unique set of properties (low aromatic character, reactive P-atom, σ–π hyperconjugation) that has motivated our approach toward the elaboration of new conjugated π-systems integrating this phosphorus heterocycle. Herein, we give an account of the results obtained in our group since 1998.

2. Co-oligomers containing phosphole rings

Beside oligophosphole **A** [5] and biphenylphosphole polymer **B** [6] (Fig. 1), almost no π-conjugated systems incorporating phosphole units were known before 1998 [7]. It is noteworthy, that in derivatives **A** and **B**, the π-conjugated system is disrupted due to either rotational
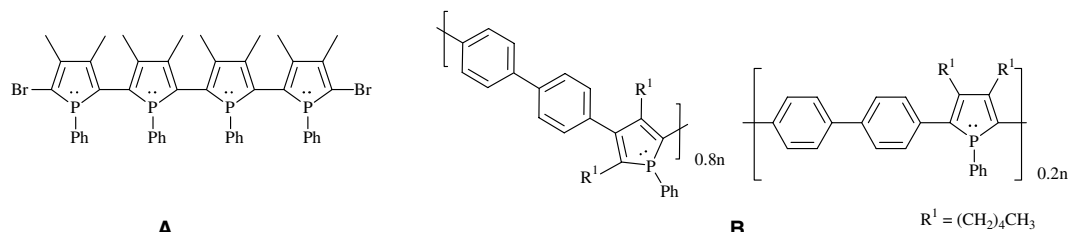

Fig. 1. Co-oligomers and co-polymers incorporating phosphole rings.

disorder (**A**: twist angles in the solid state, 25.1–49.7°), probably arising from repulsion of the phosphole substituents, or irregular structure (**B**: the 2,4-linked moieties are not conjugated). These results prompted us to prepare a family of co-oligomers alternating thiophene and phosphole rings with well defined 2,5-linkages (Scheme 1). These compounds are readily obtained via a general organometallic route known as the "Fagan–Nugent method" [8]. The intramolecular oxidative coupling of diynes **1**, possessing a $(CH_2)_4$ spacer in order to obtain the desired 2,5-substitution pattern, with 'zirconocene' provides the corresponding zirconacyclopentadienes **2** [8,9]. These extremely air and moisture sensitive organometallic intermediates react with dihalogenophosphines to give the corresponding phospholes **3** in medium to good yields (Scheme 1) [9]. Oligo(α,α'-thiophene- phosphole) derivatives (**3a–c**) with precise length and constitution up to seven rings have been obtained according to this synthetic procedure. The X-ray diffraction study performed on the model compound (**3a**) [9a] shows that the three heterocycles are almost coplanar, with the phosphorus atom being strongly pyramidalised. The lengths of the C–C linkages between the rings are in the range expected for Csp^2–Csp^2 bonds. These solid state data suggest a delocalisation of the π-system over the thienyl substituents and the endocyclic π-system of the phosphole ring. The value of λ_{max} recorded for (**3a**) (412 nm) [9a] and (**3b**) (490 nm) [9c] are considerably more red-shifted than those of related tert-thiophene (355 nm) [10] and quinquethiophenes (ca. 418 nm) [11], respectively. These results clearly

establish that the replacement of a thiophene subunit by a phosphole ring induces an important decrease of the optical HOMO–LUMO gap. This observation is consistent with theoretical studies predicting that heterocyclopentadienes exhibiting low aromatic character are excellent building blocks for the synthesis of π-conjugated systems with low HOMO–LUMO gap [f,12].

In contrast to other heterocyclopentadienes (e.g., siloles and pyrroles), phospholes possess a reactive heteroatom. This feature allows direct access to a range of new π-conjugated systems (**4a–9a**) from the single P-containing chromophore (**3a**) (Scheme 2) [9b]. Significantly, these chemical modifications of the nucleophilic P-centre have a profound impact on the properties of the phosphole oligomers as a whole. For examples, alkylation or oxidation of the P-atom of (**3a**) induces a bathochromic shift of both the λ_{max} and the λ_{em} [(**3a**) vs (**4a**), (**5a**) and (**7a**), Table 1], as well as an augmentation of the first oxidation and reduction potentials. This illustrates nicely the contribution of phosphorus chemistry to tune the photophysical properties of π-conjugated systems. Note that electropolymerisation of monomers (**4a**), (**5a**) and (**7a**) afforded conductive materials exhibiting low HOMO–LUMO gap and reversible p- and n-doping at rather low potentials [9a]. Furthermore, as observed for the 2,5-di-(2-thienyl)phosphole monomers, the electrochemical and photophysical data of these materials depend on the nature of the phosphorus moiety.

Exploiting this unique way of tailoring π-conjugated systems has led to the optimisation of the properties of thiophene-phosphole co-oligomers, which have
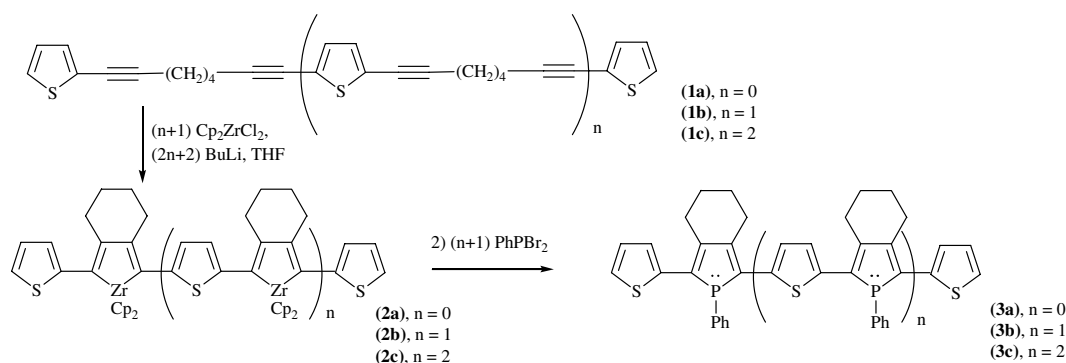
Scheme 1.
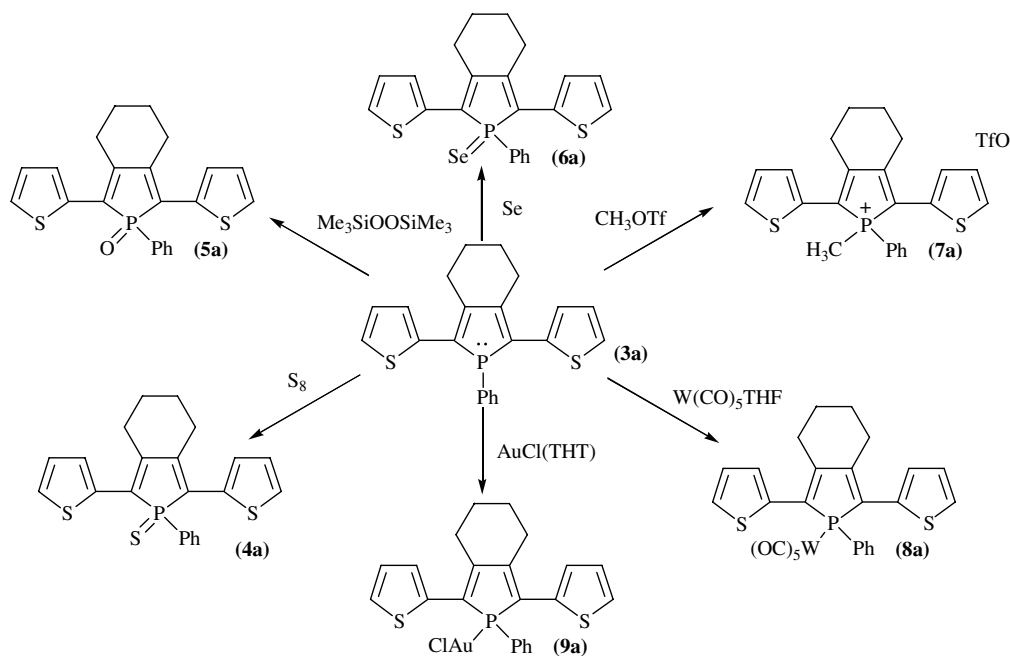
Scheme 2.

subsequently been used as materials for OLEDs. Upon sublimation, phosphole (**3a**) decomposed while the more thermally stable thioxo-derivative (**4a**) formed homogeneous thin films on an indium–tin-oxide (ITO) semi-transparent anode, allowing a simple layer OLED to be prepared [13]. 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 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 (**4a**) was sandwiched between hole- and electron-transporting layers (α-NPD and Alq$_3$, respectively). Upon doping the "phosphole" layer with a red-emitting dopant (DCJTB), the EL efficiency is further enhanced up to 1.83% with a maximum brightness of ca. 37 000 cd m^{-2} [13]. The ligand behaviour of (**3a**) can be exploited in an innovative approach whereby metal complexes are investigated as materials for OLEDs. The Au(I) complex (**9a**) (Scheme 2) is thermally stable

enough to give homogeneous thin films upon sublimation in high vacuum. The corresponding single layer device exhibited an EL emission covering the 480–800 nm domain [13], a result which is encouraging for the development of white emitting OLEDs based on phosphole–Au complexes. Note that the low energy emissions are very probably due to aurophilic interactions in the solid state [14]. These results constitute the first application in optoelectronics of π-organophosphorus materials.

The ligand behaviour of phospholes has also been used for the synthesis of multipolar NLOphores. Phospholes (**10a**) and (**10b**) (Scheme 3), bearing an electron-deficient pyridine group and a classical electron-donor group at the 2- and 5-positions, respectively, have been prepared according to the Fagan–Nugent method [15]. They exhibit moderate NLO activities ($\beta_{1.9\ \mu m}$, ca. 30×10^{-30} e.s.u.) compared to classical chromophores such as Dispersed Red 1 (DR1) (β_0, 50×10^{-30} e.s.u.). These low values are consistent with the weak acceptor character of the pyridine group. The attractiveness of dipoles (**10a**) and (**10b**) in NLO lies into their P,N-chelate behaviour towards d^8 metal centres such as Pd(II) [16,17]. 2-(2-Pyridyl)phospholes (**10a,b**) reacted with [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ giving rise to the corresponding complexes (**11a,b**) (Scheme 3). In accordance with the *trans-influence* [18], heteroditopic P,N-dipoles (**11a,b**) undergo a stereoselective coordination imposing a close parallel alignment of the dipoles on the square-planar d^8 palladium template. Thus, the *trans-effect* can overcome the natural anti-parallel alignment tendency of dipolar chromophores at the molecular level. Complexes (**11a,b**) exhibit fairly high NLO activities with β values reaching $170–180 \times 10^{-30}$ e.s.u. These values are much

Table 1
Photophysical data for compound **3a**–**9a** and **3b** in THF solutions at room temperature[a]

	λ_{max} (nm), ε (mol^{-1} l cm^{-1})	λ_{em} (nm)
3a	412 (8500)	501
3b	490 (22 300)	590
4a	432 (9500)	548
5a	434 (9300)	556
6a	423 (12 300)	547
7a	442 (8300)	593
8a	408 (10 900)	506
9a	428 (15 100)	544

[a] Absorption and emission maxima, ±3 nm.
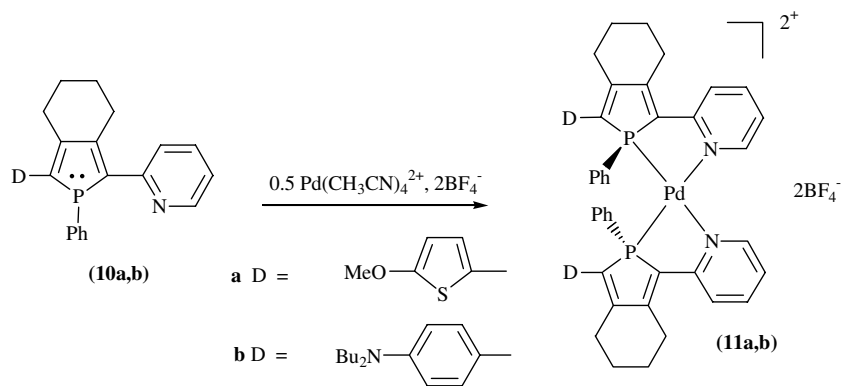
Scheme 3.

higher than the sum of the contributions of two sub-chromophores (**10a,b**). The enhancement of the NLO activity upon coordination was tentatively attributed to ligand-to-metal-to-ligand charge transfers that contribute coherently to the second harmonic generation [15]. Thus, coordination chemistry offers a simple synthetic methodology for controlling the in-plane parallel arrangement of P,N-dipoles in a molecular assembly.

One of the properties of the phosphole ring is the hyperconjugation of the exocyclic P–R bond with the endocyclic π-system. We have exploited this unique property to prepare novel assemblies exhibiting σ–π conjugation. Although the interaction of two π-chromophores through a σ-skeleton was theoretically rationalized in the early 70s [19a], this type of through-bond conjugation is still rare [19]. We anticipated that P–P bridges could be potentially good candidates to mediate through-bond conjugation since they possess a low σ–σ* gap. Compound (**12**) (Scheme 4) [20], assembling two di(2-thienyl)phosphole chromophores via a P–P bond, was prepared according to the classical route to 1,1′-biphospholes, implying a coupling of the corresponding phospholyl anion upon oxidation with iodine [21]. An X-ray diffraction study performed on (**12**) re-

vealed a P–P single bond [2.224(1) Å] [22] and showed that the P atoms are strongly pyramidalised [(Σ)bond angles, 293.7°]. The bond lengths and valence angles of the organophosphorus frame of (**12**) compare with those of the 2,5-dithienylphosphole (**3a**) [20]. The absorption spectrum of 1,1′-biphosphole (**12**) differs notably from that of the corresponding phosphole (**3a**). While the spectrum of (**3a**) shows only one absorption due to a π–π* transition (412 nm), several bands are recorded for (**12**) with one red shifted broad shoulder (λ_{onset} = 560 nm) (Fig. 2) [20]. The TD-DFT simulated absorptions of (**12**) (vertical lines, Fig. 2), in its more stable gauche-conformation, and that of (**3a**) fit nicely to the experimental ones (Fig. 2). The calculated spectrum of (**12**) contains two intense transitions at 378 nm (LUMO + 1 ← HOMO − 1) and 398 nm (LUMO + 1 ← HOMO) (experimental values: 361 and 391 nm), and two further low intensity transitions at 479 nm (LUMO ← HOMO − 1) and 512 nm (LUMO ← HOMO) corresponding to the broad shoulder (440–560 nm). These data fit nicely with theoretical studies predicting a splitting of the HOMO and LUMO upon interaction of π-systems through a σ-Bridge (hyperconjugation) [19a]. P–P bridges are thus excellent σ-scaffold to mediate
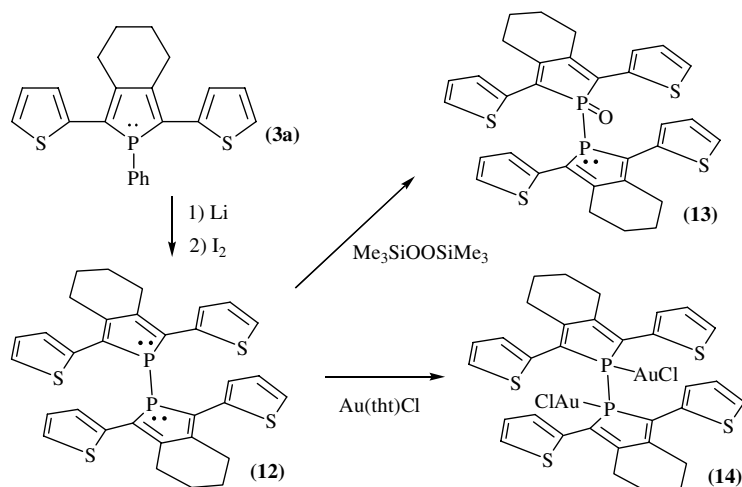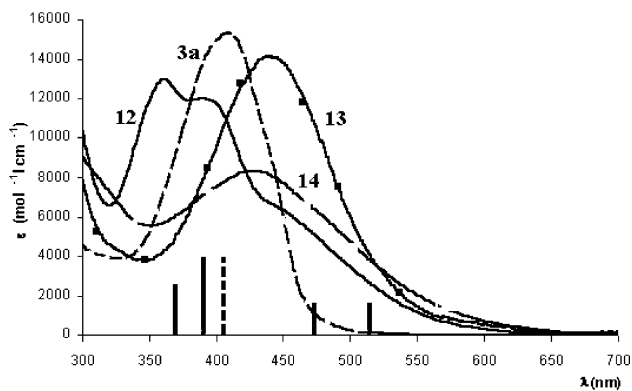

Scheme 4.

Fig. 2. Absorption spectra of **3a** (- - -), **12** (—), **13** (-•-), **14** (– –) in CH$_2$Cl$_2$ (up) and TD-DFT simulated spectra (vertical lines) of **3a** (dashed) and **12** (plain).

through bond delocalisation. Furthermore, the two P-atoms are still reactive allowing chemical modifications of the bridge. For example, oxidation of one P-center or complexation of the two P-atoms with Au(I) metal ions have been performed. These chemical modifications result in a further bathochromic shift of the band onset compared to 1,1′-biphosphole (**12**) (Fig. 2) [20]. This narrowing of the optical HOMO–LUMO gap strongly suggests that the modified σ-P–P bridges still participate in the interaction of the two π-systems by the hyperconjugative effect. These results nicely illustrate the possible tuning of the optical properties of assembly (**12**) via chemical modifications of the P–P σ-skeleton.

3. Conclusion

This work clearly evidenced the specific appealing properties offered by the phosphole ring compared to their widely used sulfur or nitrogen analogues. First, due to their low aromatic character, phospholes are suitable building blocks for the tailoring of low band gap materials. Additionally, an attractive way to modulate the physical properties of these P-containing π-conjugated systems is offered by the possibility of operating chemical modifications of the λ^3-P centres. Lastly, the fact that phospholes exhibit σ-π hyperconjugation has been exploited to construct assemblies presenting through bond electronic interaction between π-conjugated chromophores. Of particular interest, the possibility of using organophosphorus π-conjugated systems for applications in the field of non linear optics and organic light emitting diodes has been demonstrated. We have realised a systematic approach to fully exploit the unique properties and versatile reactivity of the phosphole ring to construct π-conjugated systems. Considering the richness and diversity of phosphorus chemistry, it seems likely that in the near future novel and more elaborated materials incorporating P-moieties will be described, as exemplified by recent contributions of others groups [23].

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