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Synthesis and Electronic Properties of Alternating α,α′-Thiophene-Phosphole Oligomers

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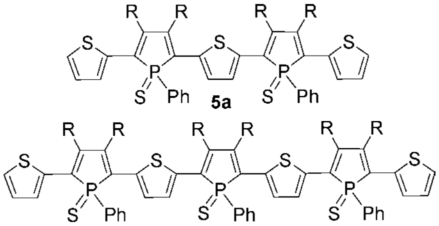
ABSTRACT



Alternating thiophene-phosphole oligomers up to seven rings in length have been synthesized. A regular decrease of the HOMO–LUMO gap is observed upon increasing the length of the π-conjugated system. The nature of the P-moieties dramatically influences the optical and electrochemical properties of these phosphole-based oligomers. Electro-oxidation of derivative 5a afforded an electroactive polymer exhibiting reversible p-doping.

The synthesis of thiophene-based oligomers has attracted considerable attention because of their use as precursors of conductive polymers and in technological applications, such as field-effect transistors or organic light-emitting diodes.[1] The possibility of diversifying their optical and electronic properties is a key issue for manifold applications of these materials.[2] This task has motivated a creative molecular engineering involving the tailoring of the thiophene substituents, the lengthening of the conjugated path, or the incorporation of heterocycles with different electronic properties in the main chain.[1,2] In this context, phosphole is a valuable building block due to its low aromatic character and the versatile reactivity of its P-center.[3] Indeed, 2,5-di-(2-thienyl)phosphole **A** (Figure 1) exhibits a lower HOMO−LUMO energy gap than *tert*-thiophene, and chemoselective reactions involving the phosphorus atom permit fine-tuning of its physical characteristics.[4] Exploiting this unique way of tailoring, access to the first organophosphorus-containing OLED material **B** (Y = S, Figure 1) has recently been achieved.[4d] The introduction of the phosphole ring does not perturb the classical chemistry of the thiophene rings, and conductive polymers **C** (Figure 1) are readily formed upon electro-oxidation of derivatives **B**.[4a,b] Materials **C** are attractive, they possess low band gaps, and their optical and

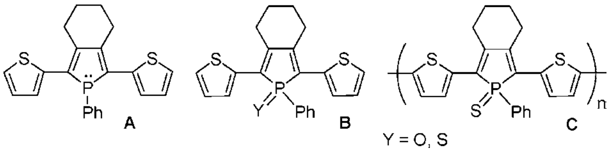


Figure 1. Known alternating thiophene-phosphole oligomers.

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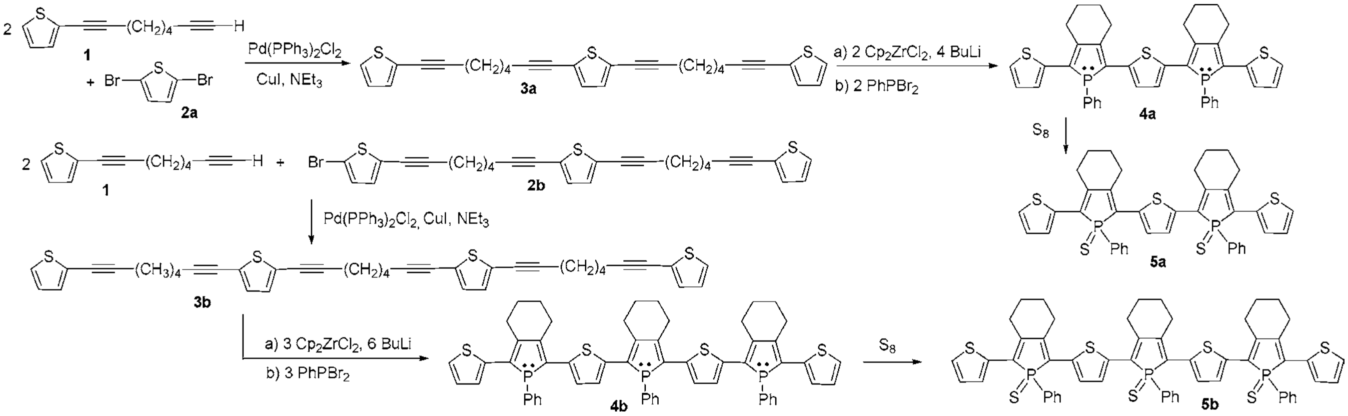
Scheme 1



electronic properties depend on the nature of the P-moieties. Considering the potential of small derivatives **A** and **B** and of the corresponding polymers **C**, the synthesis and characterization of well-defined thiophene-phosphole oligomers with increasing length is of primary interest to establish structure−property relationships for this new type of π-conjugated framework. To this end, we now report the synthesis and characterization of oligo(α,α'-thiophene-phosphole) derivatives with precise length and constitution up to seven rings.

Co-oligomer Th-Phos-Th **A** was prepared by a "zirconocene"-promoted coupling of a thiophene-capped octa-1,7-diyne (leading to an intermediate zirconacyclopentadiene) followed by subsequent addition of PhPBr$_2$, the Fagan−Nugent method.[4a,5] Encouraged by the work of Don Tilley et al. on oligo(phenylene-thiophene-1-oxide),[6] we investigated this synthetic strategy to prepare the target oligomers Th(-Phos-Th)$_{2,3}$ **4a** and **4b** (Scheme 1). The key bisdiyne **3a** and trisdiyne **3b** were obtained in medium yields (ca. 50%) via Sonogashira coupling of 2 equiv of derivative **1**[4b] with 2,5-dibromothiophene **2a** and 2-bromothiophene-capped octa-1,7-diyne **2b**, respectively (Scheme 1).

Derivative **3a** was then engaged in the Fagan−Nugent procedure (Scheme 1). After filtration of the solution over basic alumina to remove Zr-containing species, the Th-(Phos-Th)$_2$ oligomer **4a** was isolated as an air stable violet solid in 55% yield after flash column chromatography. Derivative **4a** has been characterized by high-resolution mass spectroscopy and elemental analysis. Its ^{31}P{^{1}H} NMR spectrum consists of two singlets of comparable intensity at +12.7 and +12.5 ppm. These data indicate that **4a** exists as a mixture of diastereoisomers due to the presence of stereogenic P-centers. Upon addition of elemental sulfur to **4a**, the new oligomer Th-[Phos(S)-Th]$_2$ **5a** (Scheme 1) was obtained as a mixture of diastereisomers in 78% yield after purification on silica gel. These compounds exhibit expected ^{31}P{^{1}H} NMR chemical shifts (Table 1), and their structure was supported by high-resolution mass spectrometry and elemental analysis.

Having demonstrated the feasibility of preparing oligomer **4a** via the Fagan−Nugent method, synthesis of the longer derivative Th-(Phos-Th)$_3$ **4b** was then investigated starting from tris(diyne) **3b** (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture after filtration on basic alumina consisted of two sets of several singlets centered at +11.5 and +12.5 ppm. The chemical shifts are in the expected range for λ^3,σ^3-phospholes (Table 1), and the presence of several lines could be due to the presence of diastereoisomers. However, high-resolution mass spectrometry showed that, besides target derivative **4b**, the mixture contains two other compounds bearing one or two butadiene units in place of phosphole moieties. This result revealed a partial Cp$_2$Zr/PPh metathesis. Addition of CuI or variation of the reaction conditions did not significantly improve the fate of the reaction. The three oligomers are not separable by column chromatography, preventing the σ^3,λ^3-derivative **4b** from being obtained in a pure form. However, after oxidation of the P-atoms with elemental sulfur, column chromatography on silica gel allowed to be isolated pure the thiooxo-derivative Th-[Phos(S)-Th]$_3$ **5b** in 32% yield (Scheme 1). Four lines are observed in the ^{31}P{^{1}H} NMR spectrum at chemical shifts close to those recorded for **5a** (Table 1); high-resolution mass spectroscopy and elemental analysis support the proposed structure. The dramatic decrease of the yield associated with the increase of the oligomer length precludes the use of the Fagan−Nugent method for the preparation of longer derivatives. However, we have now in hand a family

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Table 1. $^{31}P\{^1H\}$ NMR, Optical and Electrochemical Data for α,α′-(Thiophene-phosphole) Oligomers

compd	δ $^{31}P\{^1H\}^a$ (ppm)	yield (%)	$\lambda_{max}/\lambda_{onset}{}^b$ (nm)	log ϵ	$\lambda_{em}{}^b/\Phi^c$ (nm)	$E_{pa}{}^d$ (V)	$E_{pc}{}^d$ (V)
Th-Phos-Th **A**[5]	+12.7	75	412/468	3.93	501/0.05	+0.40, +1.00	←2.50
[Th-Phos]$_2$-Th **4a**	+12.7, +12.5	55	490/595	4.35	590/0.003	+0.15, +0.40	−2.28, −2.50
Th-Phos(S)-Th **B**[5]	+52.6	93	432/496	3.98	548/0.046	+0.68, +0.90	−1.95
[Th-Phos(S)]$_2$-Th **5a**	+52.1, +52.2	78	508/590	4.26	615/0.002	+0.45, +0.65^e	−1.82, −2.05^e
[Th-Phos(S)]$_3$-Th **5b**	+51.3, +51.4 +51.8, +52.0	32	550/665	4.42			

[a] In $CDCl_3$. [b] Measured in THF. [c] Fluorescence quantum yields determined using fluorescein as standard, ± 15%. [d] 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 s^{-1}. All reported potentials are referenced to the reversible formal potential of the ferrocene/ferrocenium couple. [e] Reversible processes, $E°_{ox}$ and $E°_{red}$ values provided.

of well-defined alternating α,α′-(thiophene-phosphole) oligomers, allowing structure−property relationships in this series to be established.

All α,α′-(thiophene-phosphole) oligomers (Scheme 1) are air stable and soluble in common organic solvents such as CH_2Cl_2 or THF. This good solubility, which is crucial for purification and isolation as well as for physical characterization, is probably due to the presence of the aryl P-substituent and of the fused carbocycle. The UV/vis and fluorescence spectra of all derivatives were recorded in THF, a non-hydrogen-bond donor.[4b] Each molecule exhibits an intense band attributed to the $\pi-\pi^*$ transitions of the conjugated system (Table 1). Two features are noteworthy. First, the λ_{max} of Th-(Phos-Th)$_2$ **4a** (490 nm) is considerably higher than those recorded for quinquethiophenes (ca. 418 nm).[7] Thus, as observed for the model molecule **A**, replacing 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 a low aromatic character are excellent building blocks for the synthesis of π-conjugated systems with low HOMO−LUMO gap.[8] Second, chemical modification of the P-centers of α,α′-(thiophene-phosphole) oligomers has an impact on their optical and electrochemical properties. Sulfuration of the P-atoms of **4a** induces a bathochromic shift of both the λ_{max} and the λ_{em} as well as an augmentation of the first oxidation and reduction potentials (**4a**/**5a**, Table 1). Similar trends have been observed with the smaller oligomers **A**/**B**;[4b] hence, they appear now to be general: oligo(α,α′-thiophene-phosphole) incorporating σ^4-P rings have stabilized LUMO and HOMO levels and smaller HOMO−LUMO gaps relative to those based on σ^3-P rings. These results illustrate nicely the contribution of P-chemistry to tune the photophysical properties of π-conjugated systems.

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.[2] The absorption maxima (λ_{max}), as well as the longest wavelength absorption (λ_{onset}), of Th-(Phos-Th)$_2$ **4a** are considerably red-shifted compared to the shorter derivative Th-Phos-Th **A** (Table 1). The same trend is observed for the Th-[Phos(S)-Th]$_{1-3}$ series: both the λ_{max} and the λ_{onset} regularly shift to lower energy as the extent of the π-conjugated path increases (Figure 2). It is likely that the saturation of the effective conjugation has not been reached with oligomer **5b** containing seven rings. This result, along with the good stability and solubility of Th-(Phos-Th)$_{2,3}$, should encourage the search for new pathways to longer oligomers with alternating thiophene and phosphole subunits. Except for [Th-Phos(S)]$_3$-Th **5b**, all compounds

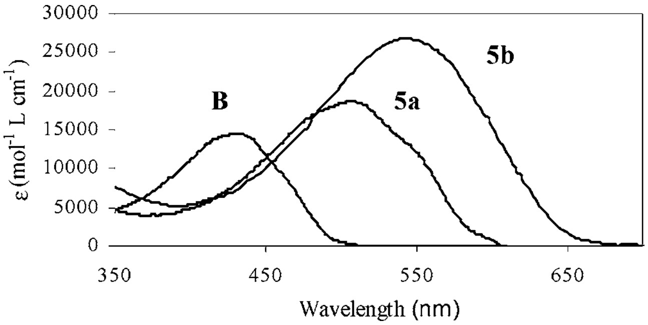

Figure 2. Electronic spectra of oligo(α,α′-thiophene-phosphole) derivatives **B**, **5a**, and **5b** in THF.

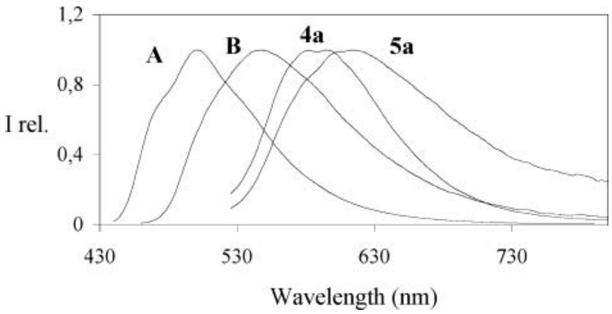

Figure 3. Emission spectra of oligo(α,α′-thiophene-phosphole) derivatives **A**, **B**, **4a**, and **5a** in THF.

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fluoresce (Table 1). The emission wavelengths depend on the length of the oligomers; a red-shift is observed upon increasing the conjugation path in the σ^3-P and σ^4-P series (Table 1, Figure 3, **A**/**4a** and **B**/**5a**). Note that the quantum yields decrease by nearly 1 order of magnitude for the higher homologues.

The electrochemical behavior of α,α′-(thiophene-phosphole) oligomers was studied by cyclic voltammetry (CV) on a Pt electrode in CH_2Cl_2 with $(Bu)_4NPF_6$ (0.2 M) as the supporting electrolyte. These studies were focused on compounds **4a** and **5a** only. In contrast to small oligomers **A**/**B**, four accessible redox states were observed for longer derivatives **4a** and **5a** (Table 1). Furthermore, the redox processes recorded for **5a** are reversible on the CV time scale, an unprecedented feature for α,α′-(thiophene-phosphole) oligomers. Thus, the stability of the reduced and oxidized forms increases with the number of thiophene-phosphole subunits in the σ^4-P series. Chain extension leads to a decrease of the oxidation potentials and an increase of the reduction potentials (Table 1). These data are in line with the conclusion of the optical study, which showed a lowering of the HOMO−LUMO gap upon lengthening the α,α′-(thiophene-phosphole) oligomers.

Up to now, derivatives **A**/**B** are the sole organophosphorus monomers giving materials via electropolymerization.[4a,b,9] This process, involving coupling of the oxidized forms of the terminal thienyl rings, was thus investigated with the novel oligomers **4a** and **5a**. Electropolymerization was accomplished by repeating cycling between −0.1 V and +1.0 V. The oxidation currents increased with the number of cycles, indicating formation of electroactive films on the surface of the Pt working electrode (Figure 4). The films are insoluble in all common solvents (CH_2Cl_2, THF, DMF, acetone, acetonitrile, MeOH). The modified electrodes were rinsed with CH_2Cl_2 and studied by CV's in monomer-free CH_2Cl_2 solutions containing 0.2 M Bu_4NPF_6 at a scan rate of 100 mV/s. The polymers exhibited n- and p-doping processes, with only the latter presenting good reversibilities (>90%) (Figure 4). The p-doping range depends on the nature of the P-moieties [poly(**4a**): 0.30/0.90 V; poly(**5a**), 0.22/0.62].

In summary, we have demonstrated that modifying oligothiophene by incorporating phosphole rings is an attractive strategy for attaining low HOMO−LUMO gaps. Chemical modifications of the P-atom of the phosphole ring allows the optical and electrochemical properties to be tuned, while the presence of terminal thiophene rings allows the preparation of polymers by electro-oxidation. Each heterocyclopentadiene, with its own specific properties, contributes to making this new type of mixed oligomers highly versatile.

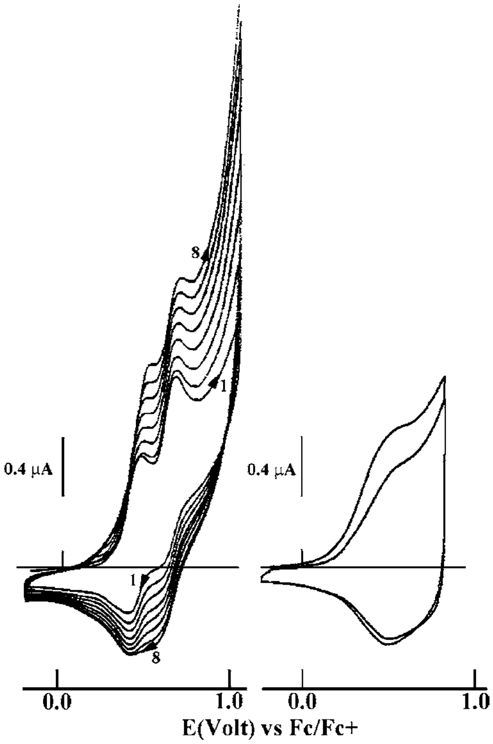

Figure 4. Cyclic voltammogram in CH_2Cl_2. Left: **5a** ($c < 2 \times 10^{-3}$ M), eight recurrent cycles. Right: Poly(**5a**), working electrode: platinum disk modified during oxidation of **5a**.

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Supporting Information Available: Experimental procedures and NMR and mass spectrometry data for diynes and thiophene-phosphole oligomers. CV's of **5a** in CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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