Polymeric Sensors

DOI: 10.1002/ange.200601844

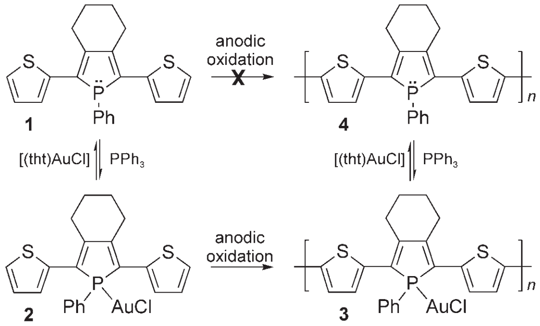
Phosphole-Modified Poly(thiophene)s: Unique Postfunctionalizable Conjugated Polymers That Sense Elemental Chalcogenides**

*Manuel Sebastian, Muriel Hissler, Claire Fave, Joëlle Rault-Berthelot, Christophe Odin, and Régis Réau**

Dedicated to Professor Ulrich Zenneck on the occasion of his 60th birthday

A fruitful strategy for diversifying the properties and expanding the functions of classical π-conjugated polymers such as poly(thiophene)s involves the incorporation of reactive heteroatoms into the conjugated chain.[1] This approach has been intensively investigated with Lewis acidic boron groups[2] which can, for example, bind anions or nucleophiles to afford sensor properties in the polymeric materials.[2e,f] In contrast, very few conjugated polymers incorporating Lewis basic σ^3,λ^3-phosphorus moieties are known[3] although the versatile reactivity of the P centers (nucleophilicity, coordination ability, etc.)[4] should allow a variety of postfunctionalizations. Herein, we describe the synthesis of the first poly(thiophene) modified by its P analogue, namely the σ^3,λ^3-phosphole ring. We show that the P centers are strongly electronically coupled with the conjugated π system and that they are recognition sites acting in a cooperative fashion, a property which is highly desirable for the design of efficient chemosensors.[5a–c] Moreover, the presence of the σ^3,λ^3-P moieties allows for the detection of elemental chalcogens, which are important oligoelements,[6] and thereby provides an unprecedented sensor property for organic conducting polymers.

σ^3,λ^3-Phospholes are a unique building block for the engineering of molecular π-conjugated systems[7] owing to the presence of reactive phosphorus centers which offer a direct access to novel derivatives with different electronic properties.[8] For example, the facile complexation of the bis(thienyl)-σ^3,λ^3-phosphole **1** with [(tht)AuCl] yields the σ^4 Au^I complex **2**[8c] (Scheme 1), which displays a red-shifted λ_{max} wave and lower oxidation potential than **1**. The challenge was thus to extend this unique *molecular* approach to *polymers* by synthesizing the σ^3,λ^3-phosphole-modified poly(thiophene) **4** (Scheme 1). Unfortunately, a direct access to **4** (**1**→**4**) is not viable because the σ^3-phosphole ring of **1** does not tolerate oxidative electropolymerization of thiophene units, probably as a result of reactions of the nucleophilic P atom either with radical cations or protons formed during the chain-growth process. In order to avoid these lone-pair interferences, we investigated a synthetic P-protection/electropolymerization/P-deprotection strategy since electropolymerization has been successfully applied for some thienyl-capped σ^4-phosphole monomers.[8a,b] Quite surprisingly, the reaction of **1** with BH_3, a common protecting group for σ^3-P atoms,[4] affords an unstable adduct. Therefore, the readily accessible, P-protected σ^4 Au^I complex **2** was submitted to anodic electropolymerization (**2**→**3**, Scheme 1) which was either performed by potentiostatic oxidation or by cyclic voltammetry (CV) on a Pt electrode. Upon repeated cycling between −0.5 V and 1.25 V in CH_2Cl_2, one observes the regular growth of a new reversible wave (0.5 V vs. ferrocene/ferrocenium (Fc/Fc$^+$)) and the increase of the main oxidation wave of **2** at 0.8 V versus Fc/Fc$^+$.[9] These data show the formation of an electroactive polymer film **3** (Scheme 1) since no shift to more positive potentials and no decrease of intensity were observed after 10 sweeps. The material which was dedoped at 0.0 V exhibits a reversible redox process at 0.5 V, and upon recurrent sweeps, the p-doping process of **3** appears to be stable and reversible between −0.5 and 0.85 V.[9]



Scheme 1. Synthesis of polymers **3** and **4**; tht = tetrahydrothiophene.

Dedoped polymer **3** is an insoluble material, and its solid-state UV/Vis spectrum[9] is notably red-shifted compared to that of monomer **2** ($\Delta\lambda_{max} = 175$ nm, $\Delta\lambda_{onset} = 290$ nm). The elemental composition of film **3**, determined by energy-dispersive X-ray analysis (EDX),[9] is the same as the monomer **2** within experimental error. Solid-state, high-resolution ^{31}P NMR spectroscopy gives a clue to establishing the intimate structure of the insoluble polymer **3**. Its magic angle spinning (MAS) ^{31}P NMR spectrum (Figure 1) shows a main broad singlet at $\delta = 45$ ppm, which is a chemical shift characteristic of Au^I phosphole moieties (**2**: $\delta = 39$ ppm), and a minor signal at $\delta = 16$ ppm, which is probably the result of a small amount of P-decomplexed subunits (< 10%). Material

---

[*] Dr. M. Sebastian, Dr. M. Hissler, Dr. C. Fave, Dr. J. Rault-Berthelot, Prof. Dr. R. Réau
Sciences Chimiques de Rennes
CNRS UMR 6226 Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex (France)
Fax: (+33) 2-2323-6939
E-mail: regis.reau@univ-rennes1.fr
Dr. C. Odin
Groupe Matière Condensée et Matériaux
CNRS UMR 6626 Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex (France)

[**] We thank the Ministère de la Recherche, the Institut Universitaire de France, the CNRS, and the Deutsche Forschungsgemeinschaft.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

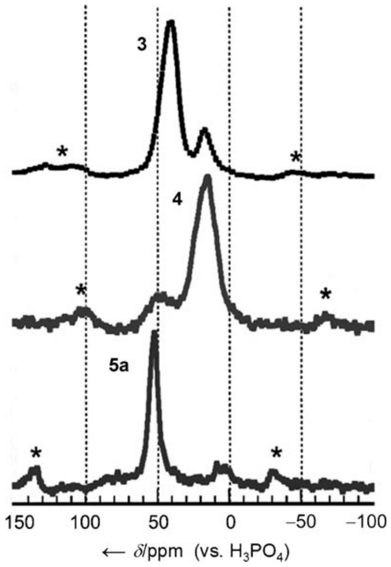


Figure 1. ^{31}P MAS NMR spectra (at 10 kHz spinning) of polymers **3**, **4**, and **5a** (an asterisk (*) indicates the rotation bands).

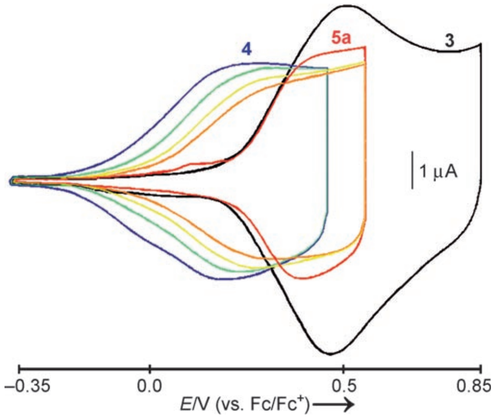


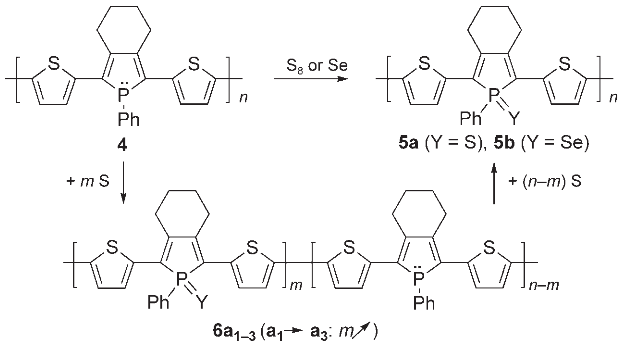
Figure 2. Cyclic voltammograms of polymers **3** (black), **4** (blue), **5a** (red), and **6a₁** (green, $t = 2^1/_2$ min), **6a₂** (yellow, $t = 5$ min), **6a₃** (orange, $t = 10$ min); t = contact time of **4** with a 0.3 M S_8 solution.

3 is one of the very rare poly(thiophene)s featuring metal centers intimately connected to the extended π-conjugated system.[10] It is noteworthy that **3** is not air- or moisture-sensitive; it can be stored for months in air without any modification of its physical properties.

The final step towards target polymer **4** (Scheme 1) required the deprotection of the P atoms of **3** by release of the Au^{I} fragments. At the molecular level, the addition of an excess of triphenylphosphine to a CH_2Cl_2 solution of complex **2** instantly affords the free phosphole **1** and [(PPh$_3$)AuCl]. Hence, a Pt electrode coated with polymer **3** was immersed in a CH_2Cl_2 solution of PPh$_3$ (0.1 M) for one minute and then washed with pure CH_2Cl_2. This treatment resulted in a mass loss of polymer **3** (monitored by microgravimetric quartz-crystal microbalance analysis[9]) corresponding to the release of more than 90 % of the {AuCl} protecting groups. EDX analysis[9] of the novel material **4** indicated a low gold content ($Au/P < 0.1$), and its ^{31}P MAS NMR spectrum (Figure 1) consists of a major resonance at $\delta = 15$ ppm, which is characteristic of σ^3,λ^3-phosphole fragments (**1**: $\delta = 13$ ppm), along with a small peak centered at $\delta = 45$ ppm (non-deprotected P centers). These results show that the metalated conjugated polymer **3** exhibits the same coordination behavior as the molecular complex **2** and that more than 90 % of the P moieties of the insoluble material **3** are accessible for chemical reactions. Furthermore, they illustrate the analytical power of ^{31}P MAS NMR spectroscopy in characterizing chemical modifications of phosphole-containing poly(thiophene)s. Indeed, molecular P chemistry (ligand exchange, NMR spectroscopic analysis, etc.) can be simply extended to P-containing conductive materials. The easily synthesized σ^3,λ^3-phosphole-modified poly(thiophene) **4** is not air- or moisture-sensitive and can therefore be handled without special care. On going from **3** to **4** (Scheme 1), a significant negative shift of the oxidation current offset ($\Delta E_{pa} = 260$ mV, Figure 2) and a blue shift of the UV/Vis band[9] associated with π–π* transitions ($\Delta\lambda_{onset} = 41$ nm) were recorded. These modifications of the electrochemical and optical properties, which parallel those observed at the molecular level (that is, **1** has a lower oxidation potential and higher optical HOMO–LUMO gap than **2**),[8c] clearly indicate a close electronic coupling of the P moieties with the π-conjugated system of the polymer backbones. It is likely that, as observed for molecular phosphole-based systems, the intimate coupling of the P moieties with the π-conjugated pathway involves hyperconjugation effects.[8f]

The postfunctionalization of **4** through P modifications was then investigated since conjugated polymers that can covalently attach molecules and translate this chemical information into an observable optical/electrochemical response are very attractive sensor materials.[5] Hence, we tried to duplicate the reactivity pattern of molecular σ^3,λ^3-phosphole **1** with the solid polymeric material **4**. At first, deposited **4** was treated with [(tht)AuCl] to re-form polymer **3** (Scheme 1), a chemical modification which was easily monitored by CV (Figure 2). Hence, owing to the presence of the reactive phosphole moieties, polymer **4** fulfils the prerequisite of sensor materials. This result prompted us to investigate the reactivity of polymer **4** towards elemental sulfur and selenium since chalcogens are well-known to oxidize σ^3,λ^3-P centers at the molecular level.[4] The detection of these chalcogens is of special interest because they are essential oligoelements and also because their sensing is particularly challenging as a result of their chemical and binding inertia under mild reaction conditions.

Polymer **4**, deposited on a Pt electrode, was submerged in a toluene solution of S_8 (0.3 M) for 20 minutes and was then rinsed with pure toluene. The formation of σ^4-thiophosphole polymer **5a** (Scheme 2) is supported by its SEM–EDX analysis,[9] which revealed an S/P ratio of about 3:1, and its ^{31}P MAS NMR spectrum (Figure 1), which shows a signal at $\delta = 52$ ppm, is consistent with the proposed structure.[8b] These results prove that almost all of the σ^3,λ^3-P centers of **4** have been transformed into sulfurized σ^4,λ^5-P centers. The responses accompanying the transformation **4**→**5a** are: 1) a large positive shift of the oxidation current offset ($\Delta E_{pa} =$



Scheme 2. Chemical modification of polymer **4** with S_8 or Se yielding **5a**,**b** and **6a**$_{1-3}$.

230 mV, Figure 2) and 2) a bathochromic shift of the UV/Vis band ($\Delta\lambda_{\text{onset}} = 38$ nm).[9] Hence, this quantitative chemical transformation of the P centers ($P \rightarrow P{=}S$) induces significant modifications of the conjugated polymer properties. Note that **4** can display a real-time response to elemental sulfur (1 minute) upon addition of a small amount of NEt_3 (acting as an S_8 activator) to the toluene solution. In the same way, material **4** also reacts with a suspension of selenium (gray or red) in CH_2Cl_2 to yield **5b** (Scheme 2). This reaction is rather slow because of the poor solubility of selenium, and is accompanied by a significant anodic shift (about 110 mV after 5 hours). Indeed, phosphole-modified polythiophene **4** is the first conjugated polymer which can detect elemental chalcogens. The ability of σ^3-P centers to react with elemental sulphur and selenium is trivial in molecular phosphorus chemistry. However, transposed to the field of conjugated polymers, this reaction is the key to affording unprecedented sensing properties since these chemical postmodifications result in easily measurable macroscopic responses.

Intriguingly, when a Pt electrode that is modified with the polymer **4** is submerged in a solution of S_8 (0.3 M) for just 2.5 minutes, a 60-mV positive offset shifting of the oxidation wave of the resulting material **6a**$_1$ is observed (CV in green, Figure 2). It is important to recall that the complete transformation **4**→**5a** (Scheme 2) requires 20 minutes. Further similar sequential exposures of **6a**$_1$ to the S_8 solution resulted in a gradual shift of the oxidation peak (**6a**$_1$→**6a**$_2$→**6a**$_3$, Figure 2) until a signal similar to that of **5a** was recorded. Having fully characterized the final adduct **5a**, it is obvious that increasing the contact time involves a progressive sulfurization of the σ^3,λ^3-P centers of **4** ($m(\mathbf{6a_1}) < m(\mathbf{6a_2}) < m(\mathbf{6a_3})$, Scheme 2).[11] Despite the fact that **6a**$_{1-3}$ feature both σ^3- and σ^4-P centers, cyclovoltammetric measurements show just one collective response (Figure 2). Hence, the modification of a collective system response (shift in E_{pa}) upon gradual binding of the σ^3,λ^3-P sites of polymer **4** shows that these recognition sites act in a cooperative fashion. This behavior, which is also observed upon treating **4** with [(tht)AuCl],[9] is an essential prerequisite for the design of sensors that show signal amplification.[5a,b]

In conclusion, these results show that molecular P chemistry (coordination chemistry, P derivatization, NMR analysis, etc.) can be extended to conjugated polymers, and they illustrate the specific properties that directly result from the incorporation of σ^3,λ^3-phosphole moieties into the conjugated backbone. Owing to its intimate coupling with the π system, the P moiety has the capacity to influence the overall properties of the conductive material in a cooperative way. Moreover, its versatile reactivity allows for the detection of elemental chalcogens, thus representing a novel development in the field of molecular recognition by conjugated polymers. The optimization of this P-based material, in terms of selectivity, reversibility, and sensitivity, to obtain an applicable chemosensor is under active investigation.

Received: May 10, 2006
Published online: August 14, 2006

Keywords: chalcogens · cyclic voltammetry · electropolymerization · phosphorus heterocycles · sensors

---

[1] a) K. Müllen, G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, **1998**; b) D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley, New York, **1999**.

[2] a) Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin, J.-F. Halet, *J. Solid State Chem.* **2000**, *154*, 5 – 12; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574 – 4585; c) R. J.-P. Corriu, T. Deforth, W. E. Douglas, G. Guerrero, W. S. Siebert, *Chem. Commun.* **1998**, 963 – 964; d) N. Matsumi, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **1998**, *120*, 10776 – 10777; e) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2001**, *123*, 11372 – 11375; f) A. Sundararaman, M. Victor, R. Varughese, F. Jäkle, *J. Am. Chem. Soc.* **2005**, *127*, 13748 – 13749.

[3] a) S. S. H. Mao, T. D. Tilley, *Macromolecules* **1997**, *30*, 5566 – 5569; b) B. L. Lucht, N. O. St. Onge, *Chem. Commun.* **2000**, 2097 – 2098; c) Y. Morisaki, Y. Aiki, Y. Chujo, *Macromolecules* **2003**, *36*, 2594 – 2597; d) Z. Jin, B. L. Lucht, *J. Am. Chem. Soc.* **2005**, *127*, 5586 – 5595.

[4] a) F. Mathey, *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*, Elsevier Science, Oxford, **2001**; b) F. Mathey, J. F. Nixon, K. B. Dillon, *Phosphorus: The Carbon Copy*, Wiley-VCH, Weinheim, **1997**.

[5] a) T. M. Swager, *Acc. Chem. Res.* **1998**, *31*, 201 – 207; b) D. T. McQuade, A. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537 – 2574; c) A. Rose, Z. Zhu, C. F. Madigan, T. M. Swager, V. Bulovic, *Nature* **2005**, *434*, 876 – 879; d) M. Leclerc, *Adv. Mater.* **1999**, *11*, 1491 – 1498.

[6] a) *The Biological Chemistry of the Elements*; (Eds.: J. J. R. Fraústo da Silva, R. J. P. Williams, Oxford University Press, Oxford, **2001**; b) M. P. Rayman, *Lancet* **2000**, *356*, 233 – 241; c) J. Chen, M. J. Berry, *J. Neurochem.* **2003**, *86*, 1 – 12.

[7] a) O. M. Bevierre, F. Mercier, L. Richard, F. Mathey, *Angew. Chem.* **1990**, *102*, 672 – 675; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 655 – 657; b) E. Deschamps, L. Richard, F. Mathey, *Heteroat. Chem.* **1991**, *2*, 377 – 383; c) O. M. Bevierre, F. Mercier, F. Mathey, S. Jutand, C. Amatore, *New J. Chem.* **1991**, *15*, 545; d) T. Baumgartner, T. Neumann, B. Wirges, *Angew. Chem.* **2004**, *116*, 6323 – 6328; *Angew. Chem. Int. Ed.* **2004**, *43*, 6197 – 6201; e) T. Baumgartner, W. Bergmans, T. Kárpáti, T. Neumann, M. Nieger, L. Nyulászi, *Chem. Eur. J.* **2005**, *11*, 4687 – 4699; f) T. Baumgartner, W. Wilk, *Org. Lett.* **2006**, *8*, 503 – 506.

[8] a) C. Hay, C. Fischmeister, M. Hissler, L. Toupet, R. Réau, *Angew. Chem.* **2000**, *112*, 1882 – 1885; *Angew. Chem. Int. Ed.* **2000**, *39*, 1812 – 1815; b) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, *Chem. Eur. J.* **2001**, *7*, 4222 – 4236; c) C. Fave, T.-Y. Cho, M. Hissler, C.-W. Chen, T.-Y. Luh, C.-C. Wu, R. Réau, *J. Am. Chem. Soc.* **2003**,

125, 9254 – 9255; d) C. Fave, M. Hissler, T. Kárpáti, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulászi, R. Réau, *J. Am. Chem. Soc.* **2004**, *126*, 6058 – 6063; e) H.-C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C.-C. Wu, R. Réau, *J. Am. Chem. Soc.* **2006**, *128*, 983 – 995; f) L. Nyulászi, O. Hollóczki, C. Lescop, M. Hissler, R. Réau, *Org. Biomol. Chem.* **2006**, *4*, 996 – 998; g) J. Casado, R. Réau, J.-T. Lopez-Navarrete, *Chem. Eur. J.* **2005**, *11*, 3759 – 3767.

[9] See the Supporting Information.

[10] a) O. Clot, M. O. Wolf, B. Patrick, *J. Am. Chem. Soc.* **2000**, *122*, 10456 – 10457; b) D. Weinberger, T. Higgins, C. Mirkin, L. Liable-Sands, A. L. Rheingold, *Angew. Chem.* **1999**, *111*, 2748 – 2750; *Angew. Chem. Int. Ed.* **1999**, *38*, 2565 – 2568; c) O. Clot, M. O. Wolf, B. Patrick, *J. Am. Chem. Soc.* **2001**, *123*, 9963 – 9973; for reviews, see: d) M. O. Wolf, *Adv. Mater.* **2001**, *13*, 545 – 553; e) B. J. Holliday, T. M. Swager, *Chem. Commun.* **2005**, 23 – 36.

[11] The exact degree of sulfurization in $\mathbf{6a_{1-3}}$ cannot be determined because: 1) of the impossibility to obtain sufficient sample quantities for ^{31}P MAS NMR spectroscopy at each step (ca. 50 mg), 2) the mass alterations were not significant for microgravimetric quartz-crystal microbalance analysis, and 3) the random distribution of the sulfurized σ^4,λ^5-P moieties in $\mathbf{6a_{1-3}}$ prevents a reliable determination by SEM–EDX analysis.