Synthesis, electronic properties and electropolymerisation of EDOT-capped σ^3-phospholes†

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EDOT-capped σ^3-phosphole self-rigidifies due to an unprecedented P–O interaction and can be electropolymerised affording functionalizable polymers.

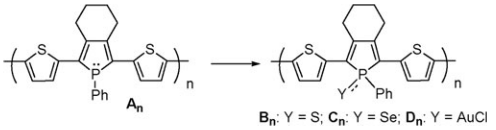


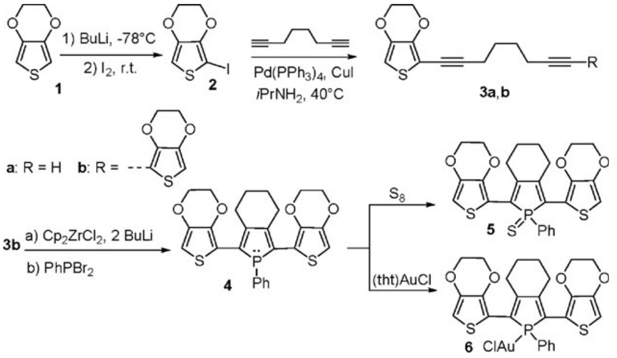
Fig. 1 Mixed phosphole–thiophene conjugated systems.

Hybrid phosphole-thiophene systems $\mathbf{A_n}$ (Fig. 1) have recently emerged as a novel class of π-conjugated material exhibiting appealing optoelectronic properties.[1] The most important attribute of these derivatives is the presence of reactive Lewis-basic σ^3,λ^3-P atoms, which permit a fine tuning of their electronic properties and also provide access to other new functionalised materials.[1] For example, phosphole-modified polythiophenes $\mathbf{A_n}$ are able to detect chalcogens, an unprecedented property for organic conducting polymers, due to the reactivity of their P centers towards S_8 and Se (Fig. 1).[2]

In this context, replacing the thienyl subunits of $\mathbf{A_1}$ by 3,4-ethylenedioxythiophene (EDOT) moieties, which have unique properties,[3a–e] represents an appealing method for the preparation of electronically different materials. Firstly, it was interesting to elucidate whether the O atom of EDOT could interact with the P atom of phosphole, inducing a self-rigidification (planarization). This type of non-covalent interaction is known to take place between O- and S-atoms in mixed EDOT-thiophene oligomers and is an invaluable tool for the design of π-conjugated materials.[3c–g] Secondly, due to the low oxidation potential and the high reactivity of EDOT radical cations,[3a,e] a direct electropolymerisation of **4** (Scheme 1) should be possible, even in the presence of oxidisable/nucleophilic σ^3,λ^3-P atoms. There is no previous precedent for this latter type of process, since σ^3-P atom of monomers such as $\mathbf{A_1}$ (Fig. 1) acts as a thiophene cation scavenger.[2,4] This synthetic approach, if indeed possible, would be of great interest since it would give a direct access to functionalizable phosphole–thiophene conjugated copolymers.

The synthesis of 2,5-bis{2-(3,4-ethylenedioxy)thienyl}-phosphole **4** was achieved in three steps from EDOT **1** (Scheme 1). Subsequent treatment of EDOT **1** with one equivalent of *n*-butyl lithium and iodine afforded derivative **2** in 90% yield. This compound decomposes within a few hours in the solid state at −5 °C. Therefore, it was rapidly engaged in a Sonogashira coupling with 1,7-octadiyne, affording products **3a** and **3b** (Scheme 1) that were isolated following purification on column chromatography in 46% and 37% yields, respectively. The mixed tricyclic derivative **4** was prepared according to a "zirconocene"-promoted coupling[1a] of **3b**, leading to an intermediate zirconacyclopentadiene, followed by subsequent addition of $PhPBr_2$ (Scheme 1).[1a] According to NMR analysis of the crude reaction mixture, phosphole **4** is formed quantitatively showing that the presence of the electron-donating and bulky EDOT substituents does not impede the Zr/P exchange. However, derivative **4** was obtained in 33% yield only following purification by flash column chromatography and crystallization. Bis-EDOT-phosphole **4** is soluble in common organic solvents (CH_2Cl_2, THF, $CHCl_3$). It is an air stable yellow solid that can be stored at room temperature under argon for months. Compound **4** exhibits a resonance in its $^{31}P\{^1H\}$ NMR spectrum at +16.5 ppm, a chemical shift typical for σ^3,λ^3-phosphole derivatives, and was further characterized by high resolution mass spectrometry and elemental analysis.

An X-ray diffraction study revealed that the three heterocycles of **4** are not coplanar in the solid state (Fig. 2). One



Scheme 1 Synthesis of EDOT-capped phosphole derivatives.

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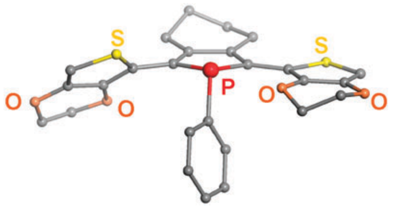

Fig. 2 Molecular structure of **4** in the solid state. Hydrogen atoms have been omitted for clarity.

EDOT substituent lies in the plane of the phosphole ring (dihedral angle, 3.5°) whereas the second one exhibits a twist angle of 46.2°. Note that the intramolecular distance between the P and O atoms of the coplanar phosphole and the EDOT rings (2.87 Å) is markedly smaller than the sum of the van der Waals radii (3.42 Å). To get more insight into the nature of this unprecedented P–O interaction, density functional calculations (B3LYP/6-31G*) have been performed.[5] Full geometry optimization results in a structure that is similar to that obtained in the solid state with a small intramolecular P–O distance (3.03 Å). The presence of a weakly stabilizing interaction between these P and O atoms is supported by the Bader analysis[6] of the B3LYP/6-31G* electron density, revealing a bond critical point (ρ = 0.01) and also by the Wiberg index (0.08).[7] A B3LYP/6-31G* scan of the rotation about one C–C bond of **4** (Fig. 3) reveals that the most stable form of **4** is that obtained by constraint-less optimization, with the fully planar structure being a local maximum. In marked contrast, for the model parent compound $\mathbf{A_1}'$, the planar structure is a minimum (Fig. 3). Together, these data suggest that the P–O interactions favour a planar structure for **4**, but that they are not strong enough to overcome the steric repulsion of the ether ring of the EDOT moieties and the phosphole substituents (Ph and C_4-bridge). The fact that **4** can not reach a planar structure probably explains that its λ_{max} is blue shifted ($\Delta\lambda_{max}$ = 42 nm) relative to that of its less sterically crowded thienyl-capped analogue $\mathbf{A_1}$ (Fig. 1), which is known to be planar (see also Fig. 3 for a comparison between **4** and the parent derivative $\mathbf{A_1}'$).[1]

Tuning the electronic properties of EDOT-capped tricyclic co-oligomers by changing the nature of the central unit, initially investigated by Reynolds and coworkers,[9] is a widely used and fruitful approach. The most appealing property of the phosphole ring as a component of conjugated systems is the versatile reactivity of the P-atom offering straightforward access to a family of derivatives without the need for multi-step synthesis.[1a–e] It was thus of interest to check whether this possibility was maintained in the presence of the electron-rich and potentially reactive EDOT moieties. Indeed, phosphole **4** reacted with elemental sulfur and ClAu(tetrahydrothiophene) to afford thioxophosphole **5** and complex **6**, respectively (Scheme 1). These compounds were purified by column chromatography and isolated in good yields (**5**, 76%; **6**, 82%) as air stable orange powders. Their multinuclear NMR data are typical and support the proposed structures.[1h] These compounds have also been characterized by high resolution mass spectrometry and elemental analysis. Notably, the chemical modifications of the P-centre have a profound impact on the properties of the phosphole-based conjugated systems. A significant bathochromic shift of the absorption ($\Delta\lambda_{max}$ > 60 nm) and emission ($\Delta\lambda_{max}$ > 40 nm) maxima was observed along with an increase of the oxidation potentials with respect to bis-EDOT-phosphole **4** (Table 1). These results nicely illustrate the ease with which the electronic properties of mixed EDOT-phosphole co-oligomers can be tuned by taking advantage of the versatile reactivity of the P-building block.

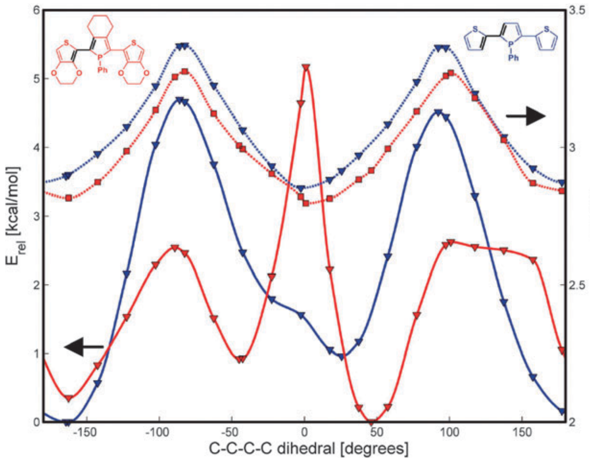

Fig. 3 B3LYP/6-31G* rotational potential energy (full lines) and TD-DFT calculated excitation energy (dotted lines) for bis-EDOT-phosphole **4** (red) and for parent thienyl capped phosphole $\mathbf{A_1}'$ (blue) (the valence angles of the bonds in bold are fixed).[8]

The next crucial question was to investigate whether the presence of EDOT-substituents would render electropolymerization of phosphole **4** feasible in spite of the presence of the reactive σ^3-P centre. As expected, the onset ($E_{p_{onset}}$ = 0.10 V) and peak (E_p^{ox} = 0.22 V) potentials *vs.* Fc/Fc$^+$ (CH_2Cl_2, Bu_4NPF_6 0.2 M) of **4** are more negative than those of thienyl-capped $\mathbf{A_1}$ ($E_{p_{onset}}$ = 0.33 V; E_p^{ox} = 0.80 V). Note that the E_p of bis-EDOT-phosphole **4** is quite low compared to bis-EDOT-silole (0.29 V) or bis-EDOT-thiophene (0.33 V) and is in the range of that for ter-EDOT (0.20 V).[9a,b] The electropolymerization experiments were conducted using CH_2Cl_2

Table 1 $^{31}P\{^1H\}$ NMR, optical and electrochemical data for α,α′-(EDOT-phosphole) oligomers

Compounds	$\delta^{31}P\{^1H\}^a$/ppm	Yield (%)	$\lambda_{max}{}^b$/nm	log ε	$\lambda_{em}{}^b\Phi^c$/nm per %	E_{onset}/V^d	E_{pa}/V^d
EDOT-Phos-EDOT **4**	+16.4	33	363	3.83	514/0.5	0.10	0.22
EDOT-Phos(S)-EDOT **5**	+55.2	76	424	3.74	553/0.1	0.38	0.49
EDOT-Phos(AuCl)-EDOT **6**	+43.7	82	433	4.20	563/0.7	0.35	0.47

[a] In $CDCl_3$. [b] Measured in CH_2Cl_2. [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: 200 mV s^{-1}. All reported potentials are referenced to the reversible formal potential of the ferrocene/ferrocenium couple.

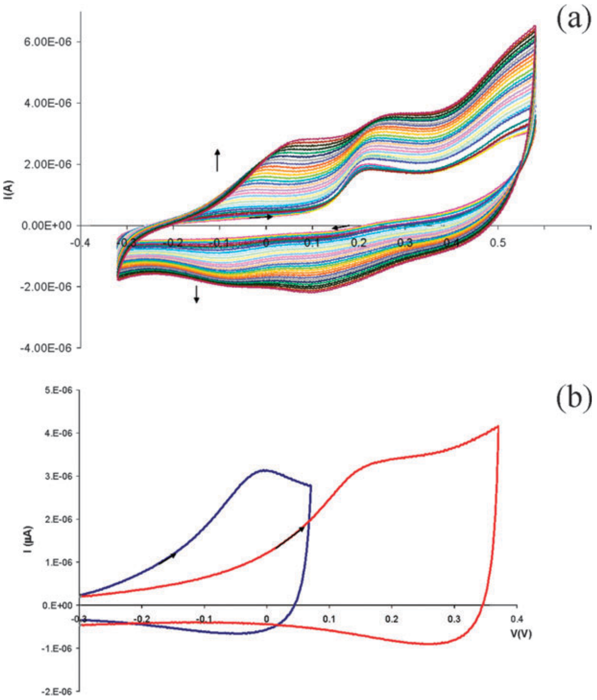

Fig. 4 Cyclic voltammograms in dry CH_2Cl_2 containing Bu_4NPF_6 (0.2 M): (a) **4** (10^{-3} M), 10 sweeps between −0.3 and 0.6 V, working electrode: platinum disc (d = 1 mm); (b) Working electrode: platinum disc (d = 1 mm) coated by poly(bis-EDOT-phosphole) (blue line), after reaction with Au(tht)Cl (red line). All potentials referred to ferrocene/ferrocenium.

solutions of **4** (1 mM) with Bu_4NPF_6 (0.2 M) as supporting electrolyte. Upon repeated cycling between −0.32 V and 0.58 V, a new redox process regularly develops at lower potential, indicating the deposition of an electroactive film on the surface of the working Pt electrode (Fig. 4a). The film formed is insoluble in all common solvents (CH_2Cl_2, THF, DMF, acetone, acetonitrile, MeOH). The electrochemical CV of this material, recorded in monomer-free electrolytic medium, shows an anodic wave that it is stable upon cycling at 0.1 V (Fig. 4b). The shape of the new anodic wave and the regular growth of the initial anodic peak (no shift to more positive potentials and no decrease in intensity) along the recurrent sweeps (Fig. 4) indicate conducting properties of the deposit. Therefore, it is indeed possible to perform the electropolymerisation of σ^3-phosphole-containing monomer **4** due to the low oxidation potential of EDOT and the high reactivity of the corresponding radical cation. This unprecedented result opens the very appealing perspective toward the synthesis of functionalizable conductive materials. To illustrate this key point, poly(bis-EDOT-phosphole) deposited on a Pt electrode was plunged into a toluene solution of (tht)AuCl (0.3 M) for 20 min and was then rinsed with pure toluene. This treatment resulted in a shift to higher potential (*ca.* 170 mV) of the oxidation potential of the polymeric material (Fig. 4b). This trend, which parallels that observed during the transformation of $\mathbf{A_n}$ into $\mathbf{D_n}$ (Fig. 1), clearly proves that poly(bis-EDOT-phosphole) contains reactive σ^3-P centres. Bis-EDOT-phosphole **4** is thus the first monomer offering straightforward access to conjugated polymers incorporating functionalizable σ^3-P centres *via* electropolymerisation.

In summary, the study of EDOT-capped phosphole **4** has revealed novel and important results that open new perspectives for the molecular engineering of P-based conjugated systems. Favourable σ^3-P–O interactions able to induce a self-rigidification have been clearly demonstrated. Moreover, the presence of the terminal EDOT ring permits the direct preparation of polymers incorporating reactive σ^3,λ^3-P atoms, a synthetically challenging type of macromolecule.[10] Each heterocyclopentadiene, with its own specific properties, contributes to making this new type of mixed EDOT-phosphole oligomers and polymers highly versatile.

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