



Supporting Information

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

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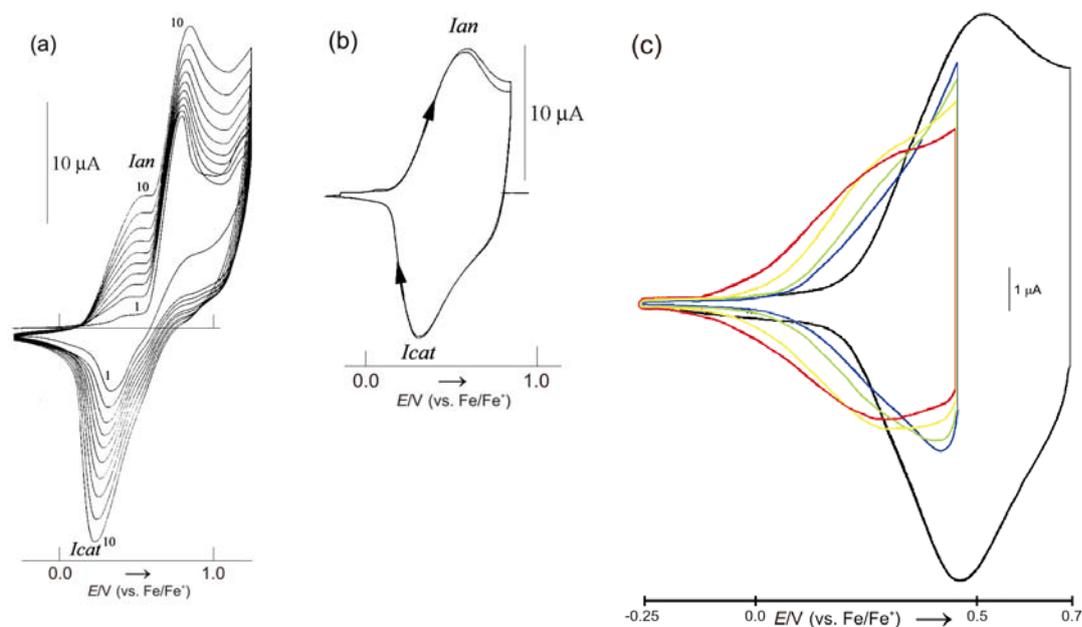
**MAS  $^{31}\text{P}$  NMR spectra** were recorded on a Bruker Avance 300WB (7.05 T; frequency of  $\sim 121.5$  MHz) at ambient temperature with a MAS spinning rate of 10.0 kHz. The zirconia rotors ( $\phi = 4$  mm) were carefully filled with the samples and small amounts of  $\text{Al}_2\text{O}_3$  were added to ensure rotation stability. The MAS spectra were acquired with single  $\pi/2$  pulses of typically 2  $\mu\text{s}$  length and recycle times of up to 500 s. Sufficient signal-to-noise ratios were achieved after up to 1024 accumulations. It was verified that  $^1\text{H}$  high power decoupling did not modify the residual line width.  $^{31}\text{P}$  NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85%  $\text{H}_3\text{PO}_4$ .

### **Cyclic voltammetry measurements and electropolymerisation experiments.**

Electrochemical measurements were performed in dichloromethane (Puran No. 02910E21) from SDS with less than 100 ppm of water. Tetra-N-butylammonium hexafluorophosphate from Fluka was used as received. Aluminum oxide from Woëlm (Super I) was heated at 300 °C under vacuum for 24 h and used at once under argon pressure. All the electrochemical investigations were carried out in a conventional three compartment cell: in all cases the anode, the cathode and the reference electrode were separated by a glass frit. The working electrode was a polished platinum disc, and the counter electrode was a glassy carbon rod. The reference electrode consisted of a silver wire in contact with 0.1 M  $\text{AgNO}_3$ . Ferrocene was added to the electrolytic solution at the end of a series of experiments. The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple served as an internal standard and all reported potentials are referenced to its reversible formal potential. All experiments were carried out under an argon atmosphere, and neutral alumina was added to the supporting electrolyte in the anodic compartment of the cell to remove excess moisture. The three-electrode cell was

connected to an EG&G PAR model173 potentiostat, monitored with a PAR model 179 signal generator and a digital coulometer PAR model 179. The cyclic voltammetry traces were recorded on an X-Y SEFRAM-Type TGM164 recorder.

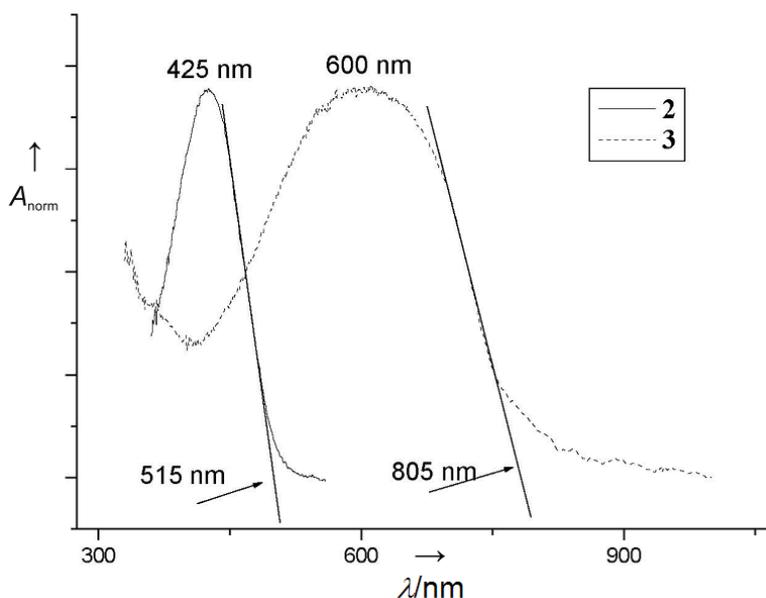
**Figure S1.** Cyclic voltammograms in  $\text{Bu}_4\text{NPF}_6$  (0.2 M) and  $\text{Al}_2\text{O}_3$ . (a) **2** ( $5 \cdot 10^{-3}$  M), 10 sweeps between  $-0.3$  and  $1.25$  V, working electrode: platinum disk ( $d = 1$  mm). (b) Working platinum disk ( $d = 1$  mm) coated by **3** prepared in (a),  $\text{CH}_2\text{Cl}_2$  solution free of the monomer **2**, two scans between  $-0.3$  and  $0.8$  V. Scan rate =  $0.1 \text{ V} \cdot \text{s}^{-1}$ . (c) Observation of the gradual decomplexation (**3**  $\rightarrow$  **4**) of **3** with  $\text{PPh}_3$ ; contact time of deposit **3** (black) and a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{PPh}_3$  ( $10^{-6}$  M): 2 (blue), 3 (green) and 5 min (yellow) and in a final step (red): 3 min in a  $10^{-3}$  M  $\text{PPh}_3$ -solution in  $\text{CH}_2\text{Cl}_2$ . **3** was prepared by oxidation of a  $\text{CH}_2\text{Cl}_2$  solution of **2** ( $5 \cdot 10^{-3}$  M) at  $1.45$  V, amount of charge:  $3.0 \cdot 10^{-4}$  C.



### Spectroscopy of Thin Films.

The UV/vis spectra were recorded using a Guided Wave model 150 spectrophotometer with optical fibres in solution for monomer **2** and in solid state for polymer **3**.

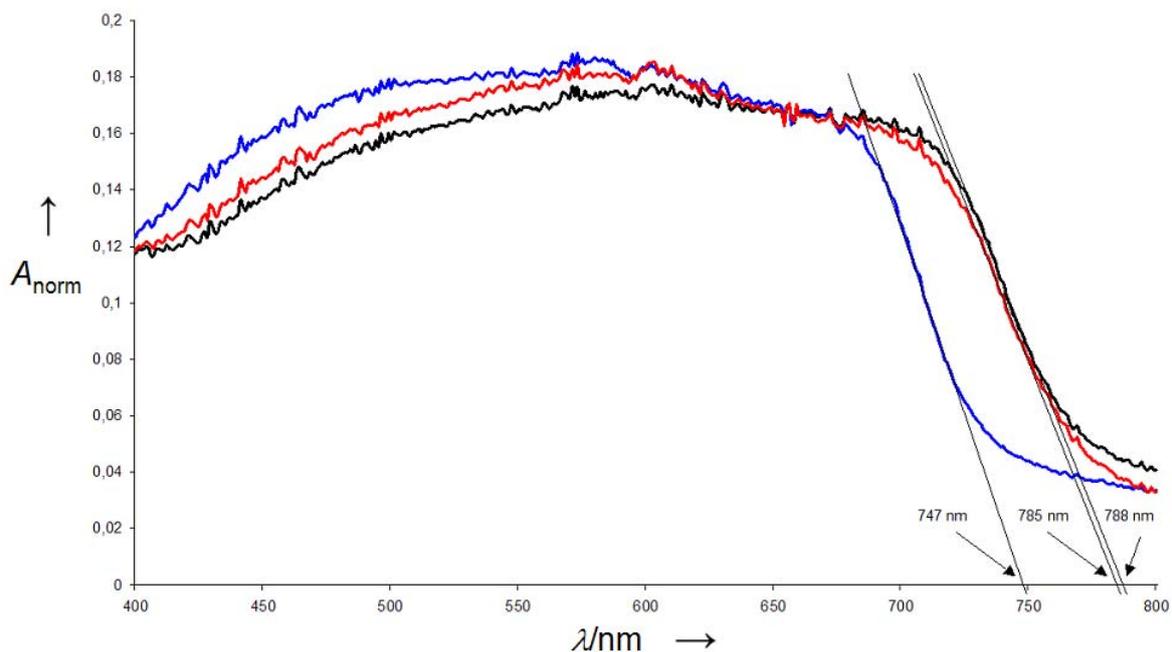
**Figure S2.** Electronic absorption spectra of **2** in CH<sub>2</sub>Cl<sub>2</sub> and of neutral **3** deposited on a platinum concave disk by a potentiostatic oxidation of **2** at 1.35 V followed by a reduction of the polymer at -0.3 V. Potentials refer to ferrocene/ferrocenium. Absorbance: arbitrary units.



**3** was deposited at 1.35 V on disks of “mirror-polished” platinum and then dedoped at -0.3 V. UV/vis spectrum of **3** is considerably red-shifted compared to that of the monomer **2** (Figure S2). It exhibits a large band with an unresolved maximum at about 600 nm and a value of  $\lambda_{\text{onset}}$  of about 805 nm indicating a narrow bandgap polymer.

**3** was also deposited at 1.35 V on transparent ITO glass electrodes and dedoped at -0.3 V. Subsequently, deposit **3** was treated with a 0.1 M PPh<sub>3</sub>-solution in CH<sub>2</sub>Cl<sub>2</sub> for 1 min and was rinsed with pure CH<sub>2</sub>Cl<sub>2</sub> yielding polymer **4**. Afterwards, **4** was immersed into a  $6 \cdot 10^{-3}$  M S<sub>8</sub>-solution in CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub> (5:1) for 5 min to afford polymer **5a** which was again rinsed with pure CH<sub>2</sub>Cl<sub>2</sub>. UV/vis spectra of **3**, **4**, and **5a** recorded on a spectrophotometer Shimadzu are presented in Figure S3.

**Figure S3.** Electronic absorption spectra of neutral **3** (black), **4** (blue), and **5a** (red). Normalized absorbance: arbitrary units.



### Microgravimetric Quartz-Crystal-Microbalance Analysis

In order to study the yield of the decomplexation reaction (**3** → **4**), electrodepositions of **3** were performed using Platinum quartz as working electrode. Three deposits of different mass were prepared varying the duration of the electrodeposition. The masses of the deposits (765 to 2819 ng) were calculated from the frequency variation of the quartz before and after deposition using the Sauerbrey equation.<sup>1</sup>

After on, the deposits were immersed 5 min in a  $10^{-3}$  M solution of  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$ . The new masses of the three deposits were measured after rinsing the deposits in  $\text{CH}_2\text{Cl}_2$  several times. Experimental mass losses (mass of deposit minus new mass of deposit) are given in table S1. Theoretical mass loss (table S1) was calculated taking into account an initial polymer unit mass of 610 g for **3** and a final polymer unit mass of 378 g for **4**, as a result of the loss of AuCl groups. Finally, the yield of this decomplexation reaction (**3** → **4**) was calculated as the ratio of the experimental mass loss to the theoretical mass loss multiplied by 100. As shown in the last line of table S1, the yield of the polymer modification is between 79 and 97%.

<sup>1</sup> Sauerbrey equation:  $\Delta f \text{ (Hz)} = -1.155 \cdot 10^{-5} \cdot \Delta m \cdot f_0^2$ ;  $\Delta m$  in g and  $f_0$  in Hz.

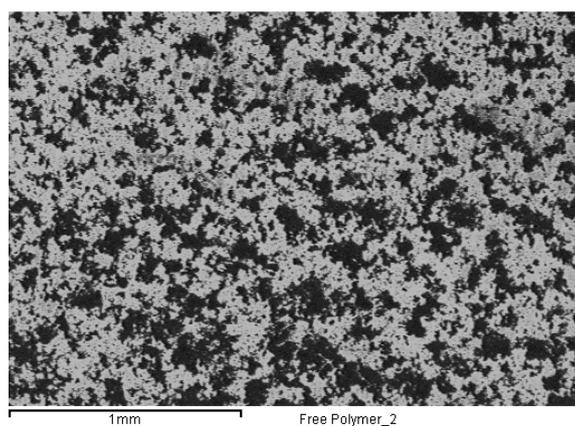
**Table S1.** Mass of three deposits of **3** and after decomplexation.

	Deposit 1	Deposit 2	Deposit 3
Mass of deposit	765 ng	2185 ng	2819 ng
Experimental mass loss	245 ng	805 ng	848 ng
Theoretical mass loss	291 ng	830 ng	1072 ng
Yield of decomplexation ( <b>3</b> → <b>4</b> )	<b>85 %</b>	<b>97 %</b>	<b>79 %</b>

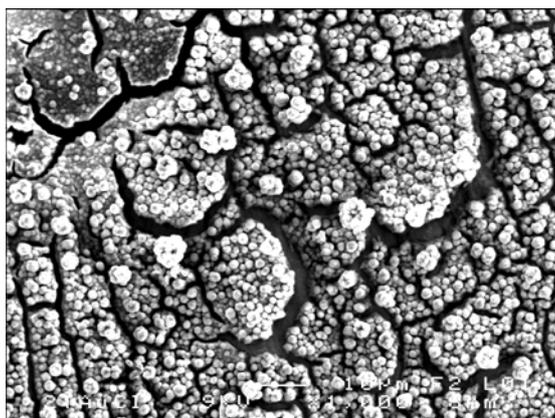
### SEM-EDX analysis

The measurements were performed on a scanning electron microscope (JSM 6400) with an embedded energy dispersive X-ray analyzer (Oxford Link Isis) or a field emission scanning electron microscope (JSM 6301F).

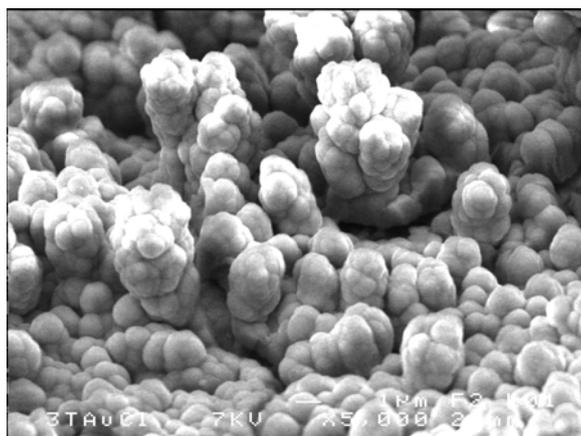
**Figure S4.** The SEM image of the surface of polymer **4** using x60 magnification and an acceleration voltage of 20 kV.



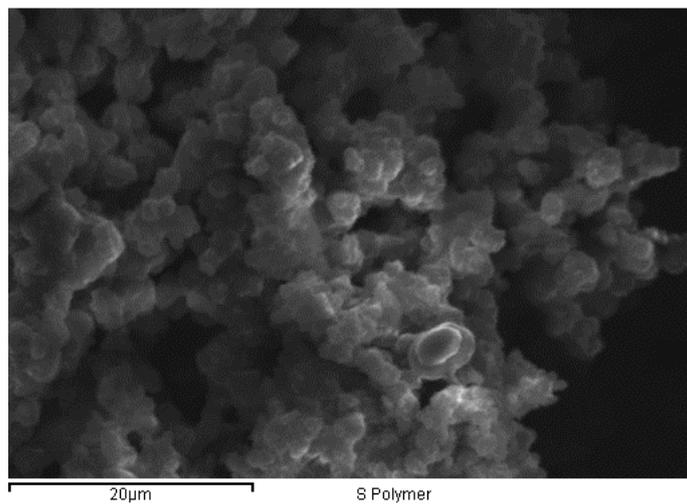
*Figure S5.* The SEM image of the surface of polymer **3** using x1000 magnification and an acceleration voltage of 9 kV.



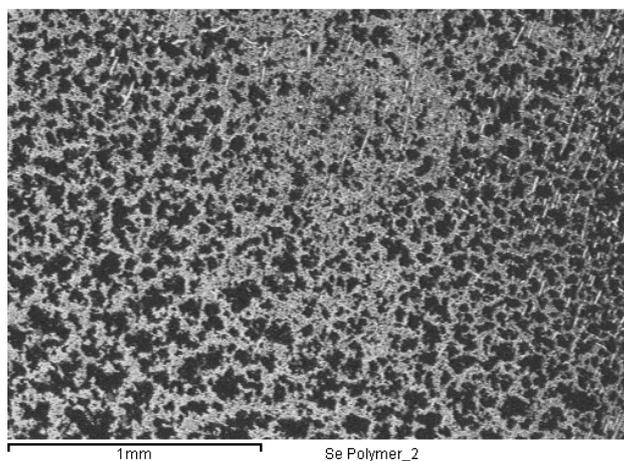
**Figure S6.** The SEM image of the surface of polymer **3** using x5000 magnification and an acceleration voltage of 7 kV.



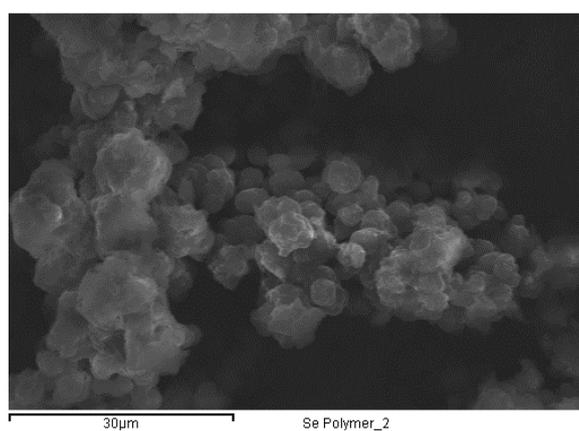
**Figure S7.** The SEM image of the surface of polymer **5a** using x3000 magnification and an acceleration voltage of 20 kV.



**Figure S8.** The SEM image of the surface of polymer **5b** using x60 magnification and an acceleration voltage of 20 kV.



**Figure S9.** The SEM image of the surface of polymer **5b** using x1800 magnification and an acceleration voltage of 20 kV.



**Table S2.** Elemental composition (atomic %) of polymers **3**, **4**, **5a-b** determined by energy dispersive X-ray analysis.<sup>a</sup>

	P (atomic %)	S (atomic %)	Au (atomic %)	Se (atomic %)
Polymer <b>4</b>	38.0	56.0	6.0	-
Polymer <b>3</b>	20.6	56	23.4	-
Polymer <b>5a</b>	23.8	73.2	3.0	-
Polymer <b>5b</b>	29.0	52.4	4.6	14.0

<sup>a</sup> Averages of 6 points chosen randomly on the surface.