3D-conjugated systems based on oligothiophenes and phosphorus nodes†

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3D-conjugated systems based on oligothiophene segments grafted on a phosphorus or on a phosphine oxide node have been synthesized. Under Stille coupling conditions, bromide terminated thienyl phosphine derivatives undergo a breaking of the phosphorus–carbon bond attributed to a ligand exchange with the Pd catalyst. The electronic properties of the new compounds have been analyzed by UV-vis and fluorescence spectroscopy and cyclic voltammetry.

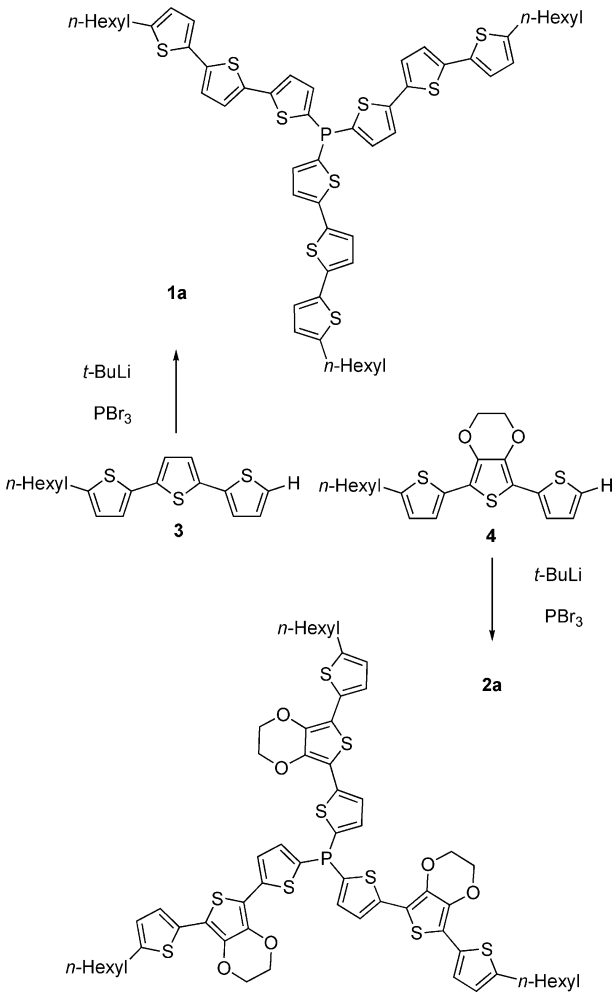
Introduction

Organic semiconductors (OSCs) are subject to a considerable current interest motivated by the perspective of achieving large area, low-cost, lightweight and flexible (opto)electronic devices.[1] Many organic semiconductors used as active materials in organic field effect transistors (OFETs) and photovoltaic cells derive from linearly π-conjugated systems such as oligoacenes[2] or thiophene-based oligomers or polymers.[3] However, due to their low dimensionality, these materials present anisotropic optical and charge-transport properties which can pose specific problems for device fabrication and operation.[4] In recent years, we and others have undertaken the development of new classes of OSCs possessing isotropic optical and charge-transport properties. Thus, it has been recently shown that 3D architectures consisting of a silicon,[5] twisted bithiophene[6] or triphenylamine[7] node functionalized with oligothiophene conjugated segments can lead to interesting active materials for organic solar cells, light emitting diodes (OLEDs) and field-effect transistors. Several examples of π-conjugated systems incorporating phosphorus[8] have been described and some of these compounds exhibit interesting properties as active materials in OLED. However, there are few examples of molecular architectures in which phosphorus is used as a node for connecting linear conjugated segments.[9] Métivier *et al.* have described a phosphorus oxide derivatized with three oligo(phenylacetylene) chains and analyzed its photophysical properties.[9] In our continuing interest in π-conjugated systems of high-dimensionality, we report here on the synthesis of compounds consisting of a phosphorus node derivatized with short-chain oligothiophene branches.

Results and discussion

Synthesis

Fixation of aromatic systems on phosphorus is generally achieved by addition of lithiated species or Grignard reagents on phosphorus tribromide or trichloride.[10] In the present case, phosphorus tribromide was reacted with the lithio-derivative of *n*-hexylterthiophene (**3**) and *n*-hexylthiophene-EDOT-thiophene[7] (**4**) to obtain the target compounds **1a** and **2a** in 35 and 25% yields respectively (Scheme 1).



Scheme 1

In order to synthesize building blocks that could be useful for the further synthesis of other symmetrical or unsymmetrical systems, phosphine derivatives **5a** and **6a** with terminal bromine

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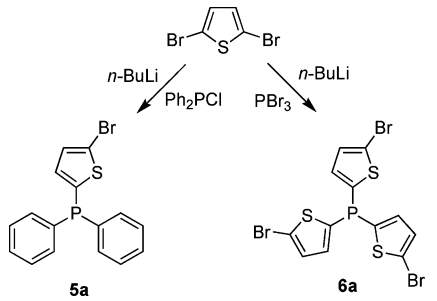
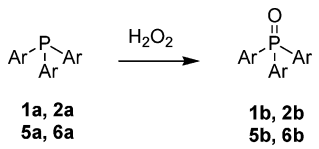
atom(s) have been prepared by treatment of 2,5-dibromothiophene by *n*-BuLi followed by addition of phosphorus tribromide or chorodiphenylphosphine (Scheme 2).



Scheme 2

All these compounds are stable in ambient conditions in the solid state, however they undergo a more or less rapid oxidation into the corresponding phosphorus oxides in solution. The oxidation process is rather slow for **1a** but extremely fast for **2a**. This difference can be related to the electron donating properties of the branches and attributed to orbital interactions between aromatics and phosphorus nodes.[11] Oxidation performed using hydrogen peroxide at room temperature in THF leads to quantitative conversion for all compounds. (Scheme 3).



Scheme 3

The X-ray structures of derivatives **6a** and **6b** are presented in Fig. 1. Both derivatives crystallize in the *P*1 $2_1/n$ space group. Compound **6a** presents a pyramidal geometry with thiophene–phosphorus–thiophene angles of 99°, 102° and 103° respectively. The oxidation of phosphine into phosphorus oxide in **6b** produces an increase of the thiophene–phosphorus–thiophene angles to 104°, 105° and 107°. This phenomenon is logical if one consider the decrease of the coulombic repulsions when passing from the lone pair to the bonded oxygen atom.

In order to synthesize systems with longer conjugated branches, compound **6a** bearing three terminal bromine atoms was used as reactant. Attempts to perform Suzuki or Kumada coupling with the appropriate thienyl derivatives failed. A Stille coupling with a stoichiometric amount of 2-tributylstannylthiophene in the presence of $Pd(PPh_3)_4$ as catalyst allowed to isolate the target compound **7a** in 40% yield together with 20% of undesired terthiophene **8**. The formation of terthiophene **8** implies a side-reaction with breaking of the C–P bond together with the expected cleavage of the C–Sn bond in the reagent. This assumption is confirmed by the use of an excess of stannic derivative which led to terthiophene (**8**) as the unique product (60% yield, Scheme 4).

Aryl–aryl exchange reactions in Pd complexes[12] involving C–P bond breaking have been already discussed in the literature and their influence on Suzuki[13] or Stille[14] coupling reactions is well documented. However, phosphorus compounds are generally used as ligands in the catalyst and not as reagent and the consequences

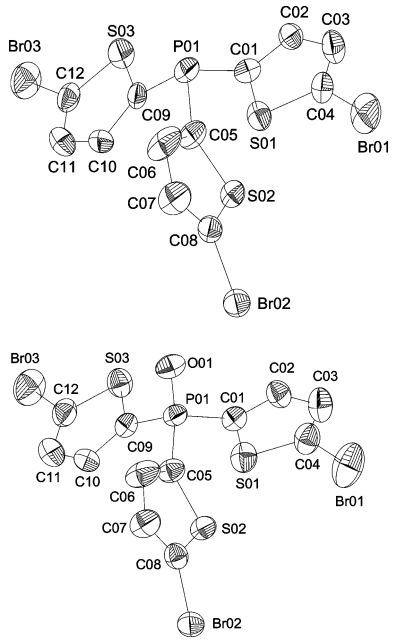
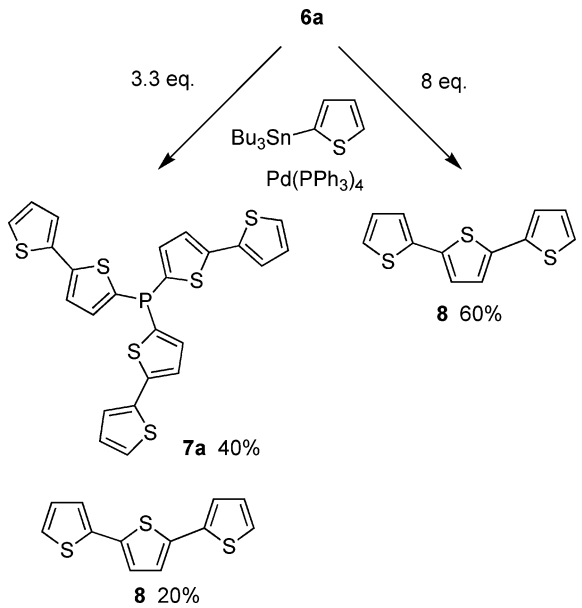


Fig. 1 ORTEP views of **6a** (top) and **6b** (bottom), ellipsoids drawn at 50% probability level.

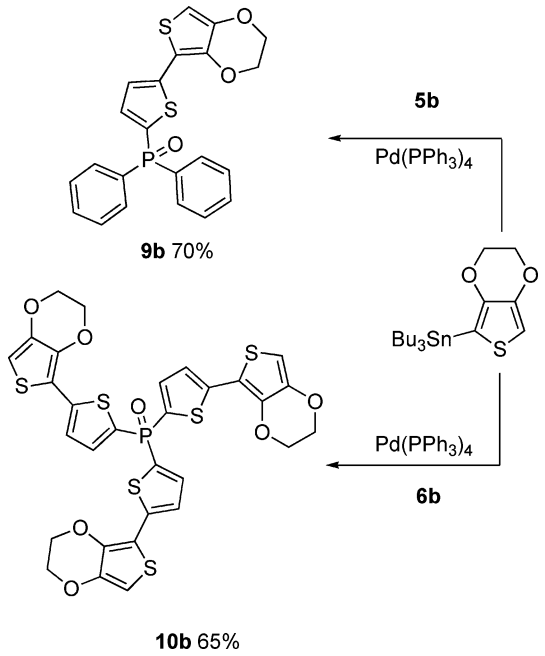


Scheme 4

of the observed exchanges are thus different. In the present case, the cleavage of the C–P bond probably involves a ligand exchange between the triphenylphosphine of the catalyst $Pd(PPh_3)_4$ and **6a**.

In order to test this hypothesis, phosphorus oxides **5b** and **6b** which are not subject to ligand exchange have been reacted with the stannyl derivative of 3,4-ethylenedioxythiophene (EDOT) in Stille conditions. In this case, the target compounds **9b** and **10b** were isolated in 70 and 65% yield respectively without any evidence of C–P bond cleavage (Scheme 5).

It is worth noting that after one week in refluxing toluene in the presence of the stannyl derivative of thiophene or EDOT and $Pd(PPh_3)_4$, compound **7a** or debrominated **5a** and **6a** were recovered unreacted and intact, thus demonstrating that the



Scheme 5

presence of a bromine atom at the terminal position of the thiophene is required for ligand exchange.

UV-vis absorption, fluorescence and cyclic voltammetry

Derivatives **1–4** undergo a non reversible oxidation process. Examination of the values of the anodic peak potential (E_{pa}) recorded by cyclic voltammetry (Table 1) shows that as expected, compounds **2** containing an EDOT unit are oxidized at lower potentials than compounds **1**. The non linear compounds **1–2** show slightly higher E_{pa} values than the corresponding individual branches **3** and **4**. The slight decrease of E_{pa} observed for the phosphorus oxide derivatives when compared with their phosphine analogues is rather intriguing. Whereas this phenomenon could be related to differences in diffusion coefficients,[15] further work is needed to clarify this point.

The UV-vis data show that the compounds **1b–2b** based on phosphine oxide nodes absorb practically at the same wavelength as the corresponding phosphine based system **1a–2a** (Table 1). Comparison of the fluorescence quantum efficiencies (ϕ_{em}) of compounds **1a** and **2a** to those of the corresponding terthienyls shows that the passage from the individual chains to the non linear molecules leads to a slight decrease of ϕ_{em}. Such an effect already observed for trianthrylphosphorus compounds[16] has been ascribed to the influence of the phosphorus lone pair and to through-space interactions between chromophores that contribute to fluorescence quenching. On the other hand, oxidation of phosphine into phosphine oxide produces a significant increase of ϕ_{em}, from 4 to 15%, between **2a** and **2b**.

In this case, the increase of the fluorescence may be due to the absence of the phosphorus lone pair together with a decrease of through-space interactions among the conjugated chains due to the increase of thiophene–phosphorus–thiophene angles in the oxyphosphorus derivatives as demonstrated by the X-ray structures of **6a** and **6b**.

Table 1 UV-Vis Absorption, fluorescence emission and oxidation potentials of the compounds

Compound	λ_{max}/nm[a]	λ_{em}/nm[a]	ϕ_{em}[b] (%)[c]	E_{pa}/V[c]
1a	392	445	6	1.16
1b	391	459	10	1.10
2a	404	462	4	0.96
2b	404	464	15	0.92
3	354	434	6	1.08
4	379	411	6	0.80

[a] In CH_2Cl_2. [b] *Versus* anthracene as standard. [c] Pt electrodes, 0.10 M *n*-Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1} ref. Ag/AgCl.

Conclusions

Star-shaped conjugated systems based on oligothiophenes grafted on a phosphorus node have been synthesized by condensation of lithiated species on halogenophosphorus nodes and by Stille coupling reactions. In the latter case, the analysis of the reaction conditions allowed us to identify an undesired reaction involving a ligand exchange with the catalyst. However, this parasitic reaction can be prevented when the phosphine node is oxidized into the corresponding oxide.

The electrochemical, UV-vis, fluorescence data together with X-ray diffraction results provide a coherent picture suggesting that in addition to electronic effects, the oxidation of the phosphorus node indirectly affects the electronic properties of the conjugated system through small geometrical changes.

Experimental

General

Solvents were purified and dried using standard protocols. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded by a Bruker Biflex-III, equipped with a N_2 laser (337 nm). For the matrix, dithranol in CH_2Cl_2 was used. High resolution mass spectra were recorded under FAB mode on a Jeol JMS 700 spectrometer. UV-visible optical data were recorded with a Perkin-Elmer Lambda 19 spectrophotometer. X-Ray diffraction experiments were carried out in the θ–2θ reflection mode with a Bruker D500 diffractometer equipped with a speed detector Vantec. Cyclic voltammetry was performed with an EG & G PAR 273A potentiostat with a standard three-electrode cell using platinum electrodes and a Ag/AgCl reference electrode.

Synthetic procedure

Tris(5″-hexyl-5-terthienyl)phosphine 1a. To 3 g of 5-hexyl-2,2′:5′,2″-terthiophene (9 mmol) dissolved in 150 mL of THF cooled at −70 °C, 6 mL (9 mmol) of *tert*-butyllithium 1.5 mol L^{-1} are slowly dropped. The mixture is stirred for 1 h 30 min at 0 °C and cooled again at −60 °C after which 530 mg (2 mmol) of phosphorus bromide are added. The mixture is stirred for 15 h at room temperature. The formed precipitate is dissolved in methylene chloride and the organic layer is washed with an

aqueous saturated solution of ammonium chloride and then twice with water. The organic layer is then dried on magnesium sulfate and the solvent is evaporated. Chromatography on silica gel using petroleum ether (PE)–methylene chloride (1 : 1) as eluent gives 1.1 g of an orange solid. Yield: 35%; mp = 155 °C; $R_f = 0.9$ (PE : CH_2Cl_2 1 : 1); NMR ^{1}H ($CDCl_3$): 7.30 (dd, 1H, $^3J_{H\text{-}H} = 3.72$ Hz; $^3J_{H\text{-}P} = 6.60$ Hz, H^4), 7.12 (dd, 1H, $^3J_{H\text{-}H} = 3.65$ Hz; $^4J_{H\text{-}P} = 1.39$ Hz, H^3), 7.08 (d, 1H, $^3J = 3.79$ Hz, H$^{3''}$), 6.97 (m, 2H, H$^{3'}$ and H$^{4'}$), 6.70 (d, 1H, $^3J = 3.75$ Hz, H$^{4''}$), 2.80 (t, 2H, ^3J= 7.00 Hz, T-CH_2), 1.70 (qt, 2H, $^3J = 7.00$ Hz, T-CH_2-CH_2), 1.40 (m, 6H, CH_2-CH_2-CH_2-CH_3), 0.90 (t, 3H, $^3J = 6.00$ Hz, CH_3); NMR ^{13}C ($CDCl_3$): 145.6, 143.7, 137.3, 136.6, 136.4, 136.3, 136.1, 134.4, 134.0, 124.7, 124.6, 123.3, 31.3, 29.9, 28.4, 22.3, 13.8; NMR ^{31}P ($CDCl_3$): −43.41; MS (Malditof) calcd for $C_{54}H_{57}PS_9$: 1024; found: 1024 ($M^{+\bullet}$); Anal. for $C_{54}H_{57}PS_9$ Found (Calcd): C, 63.78 (63.24); H, 5.75 (5.60); S, 28.33 (28.14).

Tris(3′,4′-ethylenedioxy-5″-hexyl-5-terthienyl)phosphine 2a. To 2 g of 3′,4′-ethylenedioxy-5-hexyl-2,2′: 5′,2″-terthiophene (5.1 mmol) dissolved in 80 mL of THF cooled to −70 °C, 3.4 mL (5.1 mmol) of *tert*-butyllithium 1.5 mol L^{-1} are slowly dropped. The mixture is stirred for 1 h 30 min at 0 °C and cooled again to −60 °C after which 310 mg (1.14 mmol) of phosphorus tribromide are added. The mixture is stirred for 15 h at room temperature. The formed precipitate is dissolved in methylene chloride and the organic layer is washed with an aqueous saturated solution of ammonium chloride and then twice with water. The organic layer is then dried on magnesium sulfate and the solvent is evaporated. Chromatography on silica gel using petroleum ether–methylene chloride (2 : 1 and then 1 : 1) as eluent gives 520 mg of a yellow solid. This compound is not stable in solution as it rapidly oxidizes. Yield: 25%; mp = 60 °C; $R_f = 0.7$ (PE : CH_2Cl_2 1 : 1); NMR ^{1}H ($CDCl_3$): 7.27 (dd, 1H, $^3J = 3.78$ Hz, $^3J_{H\text{-}P} = 6.40$ Hz, H^4), 7.17 (dd, 1H, $^3J = 3.64$ Hz, $^4J_{H\text{-}P}$= 1.46 Hz, H^3), 7.02 (d, 1H, $^3J = 3.60$ Hz, H$^{3''}$), 6.68 (d, 1H, $^3J = 3.59$ Hz, H$^{4''}$), 4.35 (m, 4H, O-CH_2-CH_2-O), 2.78 (t, 2H, $^3J = 7.61$ Hz, T-CH_2), 1.66 (quint, 2H, $^3J = 7.47$ Hz, T-CH_2-CH_2), 1.35 (m, 2H, T-CH_2-CH_2-CH_2), 1.29 (m, 4H, CH_2-CH_2-CH_3), 0.86 (m, 3H, CH_3); MS (Malditof) calcd for $C_{60}H_{63}O_6PS_9$: 1198; found: 1199 (M + H)$^+$.

Tris(5″-hexyl-5-terthienyl)phosphine oxide 1b. To 80 mg (0,078 mmol) of tris(5″-hexyl-2-terthienyl)phosphine dissolved in 30 mL of tetrahydrofuran, 1 mL of hydrogen peroxide (35% in water) is added. The mixture is stirred for 15 h after which 100 mL of methylene chloride are added. The organic phase is washed with water and then dried on magnesium sulfate. After evaporation of solvent, the residue is chromatographed on silica gel using dichloromethane–ethyl acetate (9 : 1) as eluent giving 77 mg of an orange solid. Yield: 95%; mp = 179 °C; $R_f = 0.75$ (CH_2Cl_2 : AcOEt 9 : 1); NMR ^{1}H ($CDCl_3$): 7.60 (dd, 1H, $^3J_{H\text{-}H} = 3.75$ Hz; $^3J_{H\text{-}P} = 6.50$ Hz, H^4), 7.20 (dd, 1H, $^3J_{H\text{-}H} = 3.75$ Hz, $^4J_{H\text{-}P} = 1.00$ Hz, H^3), 7.10 (d, 1H, $^3J = 3.75$ Hz, H$^{3'}$), 7.00 (2d, 2H, $^3J = 3.75$ Hz, H$^{3''}$ and H$^{4'}$), 6.70 (d, 1H, $^3J = 3.75$ Hz, H$^{4''}$), 2.70 (t, 2H, $^3J = 7.00$ Hz, T-CH_2), 1.70 (qt, 2H, $^3J = 7.00$ Hz, T-CH_2-CH_2-), 1.30 (m, 6H, CH_2-CH_2-CH_2-CH_3), 0.90 (t, 3H, $^3J = 6.00$ Hz, CH_3); NMR ^{13}C ($CDCl_3$): 146.5 ($J_{C\text{-}P} = 6.1$ Hz), 146.3, 138.8, 137.8 ($J_{C\text{-}P} = 9.9$ Hz), 133.9, 133.5, 132.3, 131.2, 126.1, 125.0, 124.3 ($J_{C\text{-}P} = 13.8$ Hz), 123.9, 123.7, 31.5, 30.2, 29.7, 28.7, 22.6, 14.1; NMR ^{31}P ($CDCl_3$): 4.55; MS (Malditof) calcd for $C_{54}H_{57}OPS_9$: 1040; found 1041 (M + H)$^+$.

Tris(3′,4′-ethylenedioxy-5″-hexyl-5-terthienyl)phosphine oxide 2b. To 80 mg (0,067 mmol) of tris(3′,4′-ethylenedioxy-5″-hexyl-2-terthienyl)phosphine dissolved in 30 mL of tetrahydrofuran, 1 mL of hydrogen peroxide (35% in water) is added. The mixture is stirred for 15 h after which 100 mL of methylene chloride are added. The organic phase is washed with water and then dried on magnesium sulfate. After evaporation of solvent, the residue is chromatographed on silica gel using dichloromethane–ethyl acetate (9 : 1) as eluent allowing 60 mg of **2b** to be isolated as a brown solid. Yield: 74%; mp = 70 °C; $R_f = 0.35$ (CH_2Cl_2 : AcOEt 9 : 1); NMR ^{1}H ($CDCl_3$): 7.52 (dd, 1H, $^3J_{H\text{-}H} = 3.85$ Hz, $^3J_{H\text{-}P} = 8.22$ Hz, H^4), 7.23 (dd, 1H, $^3J_{H\text{-}H} = 3.84$ Hz, $^4J_{H\text{-}P} = 1.98$ Hz, H^3), 7.05 (d, 1H, $^3J = 3.59$ Hz, H$^{3''}$), 6.69 (d, 1H, $^3J = 3.61$ Hz, H$^{4''}$), 4.36 (m, 4H, O-CH_2-CH_2-O), 2.79 (t, 2H, $^3J = 7.56$ Hz, T-CH_2), 1.67 (quint, 2H, $^3J = 7.29$ Hz, T-CH_2-CH_2), 1.34 (m, 2H, CH_2-CH_2-CH_2-CH_3), 1.30 (m, 4H, CH_2-CH_2-CH_3), 0.88 (t, 3H, $^3J = 6.80$ Hz, CH_3); NMR ^{13}C ($CDCl_3$): 145.7, 143.7 ($J_{C\text{-}P} = 10.5$ Hz), 139.1, 137.1 ($J_{C\text{-}P} = 16.6$ Hz), 136.8, 131.3, 124.4, 123.4, 122.9, 122.8, 112.1, 107.6, 65.1, 64.9, 31.6, 31.5, 30.1, 28.8, 22.6, 14.1; NMR ^{31}P ($CDCl_3$): 5.92; MS (Malditof) calcd for $C_{60}H_{63}O_7PS_9$: 1214; found: 1215 (M + H)$^+$.

(5-Bromo-2-thienyl)(diphenyl)phosphine 5a. To 3 g of 2,5-dibromothiophene (12.4 mmol) dissolved in 50 mL of dry diethyl ether and cooled at −50 °C, 7.7 mL of *n*-butyllithium 1.6 mol L^{-1} (12.4 mmol) are added dropwise. The mixture is stirred for 1 h 30 min at 0 °C, cooled again at −50 °C and 2.7 g (11.2 mmol) of chlorodiphenylphosphine are added. After 15 h at room temperature and addition of methylene chloride (dissolution of the formed precipitate), the organic layer is washed with an aqueous saturated solution of ammonium chloride, with water and dried on magnesium sulfate. After evaporation, the residue is chromatographed on silica gel using petroleum ether as eluent to afford 3.2 g of a pale yellow solid. Yield: 75%; mp = 79 °C; R_f = 0.5 (PE); NMR ^{1}H ($CDCl_3$): 7.40 (m, 10H), 7.10 (dd, 1H, $^3J_{H\text{-}P} = 6.50$ Hz, $^3J_{H\text{-}H} = 3.75$ Hz, H^3), 7.05 (dd, 1H, $^3J_{H\text{-}H} = 3.75$ Hz, $^4J_{H\text{-}P} = 1.00$ Hz, H^4); NMR ^{31}P ($CDCl_3$): −18.7; MS (Malditof) calcd for $C_{16}H_{12}BrPS$: 345.9; found: 346.8 (M + H)$^+$.

Tris(2-bromo-5-thienyl)phosphine 6a. To 2 g of 2,5-dibromothiophene (8.27 mmol) dissolved in 20 mL of dry diethyl ether cooled at −50 °C, 5.2 mL (1 eq.) of *n*-butyllithium 1.6 mol L^{-1} are slowly dropped. The solution is then stirred for 1 h 30 min at 0 °C and cooled again at −60 °C after which 0.22 eq. of phosphorus bromide are added. The mixture is stirred for 15 h at room temperature. 20 mL of a saturated solution of ammonium chloride in water are then added at 0 °C after which the organic layer is washed twice with water. The organic layer is then dried on magnesium sulfate and the solvent is evaporated. Chromatography on silica gel using petroleum ether as eluent affords 610 mg of a white solid. Monocrystals were obtained by recrystallization in a methylene chloride, petroleum ether mixture (see ESI). Yield: 43%; mp = 93 °C; $R_f = 0.6$ (PE); NMR ^{1}H ($CDCl_3$): 7.10 (dd, 1H, $^3J_{H\text{-}H} = 3.50$ Hz, $^3J_{H\text{-}P} = 6.50$ Hz, H^4), 7.00 (dd, 1H, $^3J_{H\text{-}H} = 3.50$ Hz, $^4J_{H\text{-}P} = 1.00$ Hz, H^3); NMR ^{31}P ($CDCl_3$): −42; MS (Malditof) calcd for $C_{12}H_6Br_3PS_3$: 514; found: 516.

(5-Bromo-2-thienyl)(diphenyl)phosphine oxide 5b. To 0.5 g (1.44 mmol) of (5-bromo-2-thienyl)(diphenyl)phosphine dissolved

in 50 mL of tetrahydrofuran, 2 mL of hydrogen peroxide (35% in water) are added. The mixture is stirred for 20 h after which 100 mL of methylene chloride are added. The organic phase is washed five times with 100 mL of water and then dried on magnesium sulfate. After evaporation of solvent, the residue is chromatographed on silica gel using dichloromethane and then dichloromethane–ethyl acetate (9 : 1) as eluent giving 420 mg of **5b** as a white solid. Yield: 80%; mp = 117 °C; NMR ^{1}H ($CDCl_3$): 7.72 (m, 4H, phenyl), 7.57 (m, 2H, phenyl), 7.48 (m, 4H, phenyl), 7.21 (dd, 1H, $^3J_{H\text{-}P} = 8.00$ Hz, $^3J_{H\text{-}H} = 3.76$ Hz), 7.13 (dd, 1H, $^3J_{H\text{-}H} = 3.82$ Hz, $^4J_{H\text{-}P} = 1.96$ Hz); NMR ^{31}P ($CDCl_3$): 20.94; MS (Malditof) calcd for $C_{16}H_{12}BrOPS$: 361.9; found: 363.0 $(M + H)^+$.

Tris(2-bromo-5-thienyl)phosphine oxide 6b. To 0.5 g (0.97 mmol) of tris(2-bromo-5-thienyl)phosphine dissolved in 50 mL of tetrahydrofuran, 5 mL of hydrogen peroxide (35% in water) are added. The mixture is stirred for 4 h after which 100 mL of methylene chloride are added. The organic phase is washed five times with 100 mL of water and then dried on magnesium sulfate. After evaporation of solvent, the residue is chromatographed on silica gel using dichloromethane and then dichloromethane–ethyl acetate (95 : 5) as eluent allowing the isolation of 440 mg of **6b** as white crystals (see ESI). Yield: 87%; mp = 155 °C; NMR ^{1}H ($CDCl_3$): 7.35 (dd, 1H, $^3J_{H\text{-}H} = 8.90$ Hz, $^3J_{H\text{-}P} = 3.80$ Hz), 7.17 (dd, 1H, $^3J_{H\text{-}P} = 3.80$ Hz, $^4J_{H\text{-}H} = 2.30$ Hz); NMR ^{31}P ($CDCl_3$): 1.94.

Tris(5-bithienyl)phosphine 7a. To 100 mg (0.19 mmol) of tris-5-(2-bromothienyl)phosphine dissolved in 20 mL of toluene, 240 mg (0.63 mmol) of 2-tributylstannylthiophene and 30 mg of $Pd(PPh_3)_4$ are added under inert atmosphere. The mixture is refluxed for 12 h after which the organic layer is washed with brine and dried on magnesium sulfate. The residue is chromatographed on silica gel using petroleum ether–methylene chloride (4 : 1) as eluent affording 40 mg of **7a** isolated as a white solid. Yield: 40%; mp = 150 °C; $R_f = 0.4$ (PE : CH_2Cl_2 4 : 1); NMR ^{1}H ($CDCl_3$): 7.30 (dd, 1H, $^3J = 3.75$ Hz, $^3J_{H\text{-}P} = 6.50$ Hz, H^4), 7.22 (dd, 1H, $^3J = 5.00$ Hz, $^4J_{H\text{-}P} = 1.00$ Hz, H$^{5'}$), 7.20 (d, 1H, $^3J = 3.75$ Hz, H^3), 7.15 (dd, 1H, $^3J = 3.75$ Hz, $^4J = 1.00$ Hz, H$^{3'}$), 7.00 (dd, 1H, $^3J = 5.00$ Hz, $^3J = 3.75$ Hz, H$^{4'}$); MS (Malditof) calcd for $C_{24}H_{15}PS_6$: 525.9; found: 525.6 $(M)^+$.

(3′,4′-Ethylenedioxy-2′,5-bithiophene)(diphenyl)phosphine oxide 9b. 0.21 g (0.58 mmol) of (5-bromo-2-thienyl)(diphenyl)-phosphine oxide, 0.75 g (1.74 mmol) of 3,4-ethylenedioxy-2-tributylstannylthiophene and a catalytic amount of $Pd(PPh_3)_4$ are dissolved in 50 mL of degassed toluene. The mixture is refluxed under nitrogen atmosphere for 20 h. After cooling, the organic phase is washed with brine and dried on magnesium sulfate. The solvent is evaporated and the residue is chromatographed on silica gel using dichloromethane and then dichloromethane–ethyl acetate (9 : 1) as eluent allowing the isolation of 170 mg of **9b** as a yellow oil. Yield: 70%; NMR ^{1}H ($CDCl_3$): 7.74 (m, 4H), 7.57 (m, 2H), 7.53 (m, 4H), 7.45 (dd, 1H, $^3J_{H\text{-}P} = 7.60$ Hz, $^3J_{H\text{-}H} = 3.76$ Hz), 7.23 (dd, 1H, $^3J_{H\text{-}H} = 3.81$ Hz, $^4J_{H\text{-}P} = 1.98$ Hz), 6.26 (s, 1H), 4.27 (m, 2H, CH_2), 7.00 (m, 2H, CH_2); NMR ^{31}P ($CDCl_3$): 22.01 (s).

Tris(3′,4′-ethylenedioxy-2′,5-bithiophene)phosphine oxide 10b. 0.15 g (0,28 mmol) of tris(2-bromo-5-thienyl)phosphine oxide, 0.81 g (1.82 mmol.) of 3,4-ethylenedioxy-2-tributylstannylthiophene and a catalytic amount of $Pd(PPh_3)_4$ are dissolved in 40 mL of degassed toluene. The mixture is refluxed under nitrogen atmosphere for 24 h. After cooling the organic phase is washed with brine and dried on magnesium sulfate. The solvent is evaporated and the residue is chromatographed on silica gel using dichloromethane and then dichloromethane–ethyl acetate (85 : 15) as eluent allowing the isolation of 130 mg of **10b** as a yellow solid. Yield: 65%; mp (decomp.) ≈ 93 °C; NMR ^{1}H ($CDCl_3$): 7.51 (dd, 1H, $^3J_{H\text{-}P} = 8.30$ Hz, $^3J_{H\text{-}H} = 3.80$ Hz), 7.17 (dd, 1H, $^3J_{H\text{-}H} = 3.80$ Hz, $^4J_{H\text{-}P} = 2.20$ Hz), 6.29 (s, 1H), 4.32 (m, 2H, CH_2), 4.22 (m, 2H, CH_2); NMR ^{13}C ($CDCl_3$): 144.0, 141.9, 138.9, 137.0, 132.2, 130.9, 111.1, 98.7, 65.1, 64.5; NMR ^{31}P ($CDCl_3$): 5.86; MS (Malditof) calcd for $C_{30}H_{21}O_7PS_6$: 715.9; found: 715.7 $(M)^+$.

Crystallographic data

Data collection was performed at 293 K on a STOE-IPDS diffractometer for **6b** and on a BRUKER KappaCCD diffractometer for **6a**, both equipped with a graphite monochromator utilizing MoKα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SIR92) and refined on F^2 by full matrix least-squares techniques using the SHELX-97 package. All non-H atoms were refined anisotropically and the H atoms were included in the calculation without refinement. Absorption was corrected by the Gaussian technique for **6b** and by Sadabs program for **6a**.

Crystal data for 6a. Colorless prism (0.56 × 0.18 × 0.14 mm^3), $C_{12}H_6Br_3P_1S_3$, $M_r = 517.05$, monoclinic, space group $P2_1/n$, $a = 9.563(1)$ Å, $b = 9.483(1)$ Å, $c = 18.527(3)$ Å, $\beta = 101.93(1)°$, $V = 1643.9(4)$ Å^3, $Z = 4$, $\rho_{calc} = 2.089$ g cm^{-3}, μ (MoKα) = 7.823 mm^{-1}, $F(000) = 984$, $\theta_{min} = 2.42°$, $\theta_{max} = 25.02°$, 27411 reflections collected, 2887 unique ($R_{int} = 0.058$), restraints/parameters = 0/172, $R_1 = 0.0404$ and w$R_2 = 0.0860$ using 2162 reflections with $I > 2\sigma(I)$, $R_1 = 0.0680$ and w$R_2 = 0.0960$ using all data, GOF = 1.061.

Crystal data for 6b. Colorless prism (0.48 × 0.27 × 0.13 mm^3), $C_{12}H_6Br_3O_1P_1S_3$, $M_r = 533.05$, monoclinic, space group $P2_1/n$, $a = 9.8214(9)$ Å, $b = 9.4798(8)$ Å, $c = 18.488(2)$ Å, $\beta = 102.87(1)°$, $V = 1678.1(3)$ Å^3, $Z = 4$, $\rho_{calc} = 2.110$ g cm^{-3}, μ (MoKα) = 7.671 mm^{-1}, $F(000) = 1016$, $\theta_{min} = 2.17°$, $\theta_{max} = 25.89°$, 13628 reflections collected, 3243 unique ($R_{int} = 0.080$), restraints/parameters = 0/181, $R_1 = 0.0538$ and w$R_2 = 0.1421$ using 2192 reflections with $I > 2\sigma(I)$, $R_1 = 0.0803$ and w$R_2 = 0.1546$ using all data, GOF = 1.002.

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