Phospholes

The Dithieno[3,2-*b*:2′,3′-*d*]phosphole System: A Novel Building Block for Highly Luminescent π-Conjugated Materials[**]

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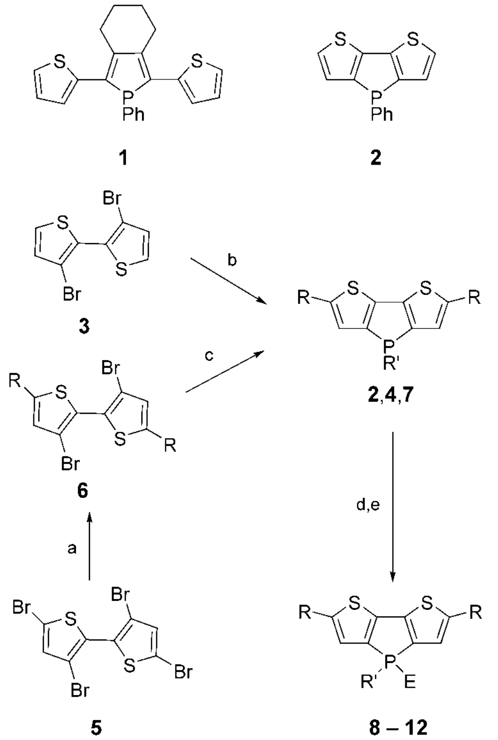
The incorporation of phosphorus centers into polymeric materials has recently attracted a great deal of attention.[1] The versatile reactivity and electronic properties of phosphorus offer considerable promise for the development of new functional materials with novel properties. Exploring the use of phosphole in this context should be of particular interest, as materials possessing the structurally related pyrrole and thiophene moieties are already well-established in the field of molecular electronics.[2] For example, thiophene-based materials show significant potential for application in electronic devices such as photovoltaic cells, organic and polymer light-emitting diodes (OLEDs, PLEDs), polymeric sensors, and TFT-based flat-panel displays.[3]

Careful consideration of the HOMO–LUMO gap, which strongly influences the optical and electronic properties of these materials, is essential for their utility.[4] The ability to fine-tune the electronic structure of the π-conjugated system is therefore highly desirable in order to achieve the required material properties. Recent work by Réau and co-workers incorporating the phosphole moiety into extended thiophene-containing π-conjugated systems (**1**, see Scheme 1), has demonstrated the advantageous electronic features of the phosphorus situated in this system.[1e,5] Due to the pyramidalization of the phosphorus center, orbital interaction with the conjugated π system is reduced. As a result, the lone pair at the phosphorus atom only functions as an n-dopant for the π system. Conveniently, the doping mode can be inverted easily from n- (electron donor) to p-type (electron acceptor) by simple chemical modifications such as oxidation or complexation at the phosphorus center.[1e,5] Although these intriguing features as well as theoretical calculations[6] strongly support the advantages of incorporating phosphole moieties into polymeric systems, only three examples of phosphole-containing macromolecules have been reported to date.[1e,7]

We now report on the synthesis and optoelectronic properties of novel dithieno[3,2-*b*:2′,3′-*d*]phospholes[8] and the preparation of a well-defined dithienophosphole-containing polymer built on a polystyrene backbone. The dithieno[3,2-*b*:2′,3′-*d*]phosphole **2** (Scheme 1) was chosen as a synthetic target since the annelation of aromatic rings has been found to be a powerful approach for tuning the band gap of conjugated materials.[4,9] This is further supported by a recent theoretical investigation in which thiophene-based, fused tricyclic polymers were found to have a much more favorable band gap than the related polythiophenes.[10] The incorporation of the phosphole moiety into a rigid, tricyclic dithieno system should therefore lead to a significantly higher degree of π conjugation than that reported for comparable systems.[11]



Scheme 1. Synthesis of dithienophosphole derivatives and precursors: a) 2 *n*BuLi, 2 tBuMe$_2$SiCl, THF, −78 °C (**6**: R = SitBuMe$_2$); b) 2 *n*BuLi, R′PCl$_2$, Et$_2$O, −78° → RT (**2**: R = H, R′ = Ph, **4**: R = H, R′ = 4-tBuC$_6$H$_4$); c) 2 *n*-BuLi, (4-vinylphenyl)PCl$_2$, TMEDA, Et$_2$O, −78° → RT (**7**: R = SitBuMe$_2$, R′ = 4-vinylphenyl); d) BH$_3$·SMe$_2$ (1 M in CH$_2$Cl$_2$), CH$_2$Cl$_2$, RT (E = BH$_3$; **8**: R = H, R′ = Ph, **9**: R = H, R′ = 4-tBuC$_6$H$_4$); e) H$_2$O$_2$ (30% in H$_2$O), pentane, RT (E = O; **10**: R = H, R′ = Ph, **11**: R = H, R′ = 4-tBuC$_6$H$_4$, **12**: R = SitBuMe$_2$, R′ = 4-vinylphenyl).

To verify the synthetic accessibility of the dithienophosphole system as well as to explore its optoelectronic properties, we initiated our studies on model compounds and functionalized monomers. Dithienophospholes **2** and **4** are accessible by reaction of 3,3′-dibromo-2,2′-dithiophene (**3**) with *n*BuLi, then subsequent addition of the corresponding dichlorophosphine at low temperatures, followed by purification by filtration over neutral alumina (yields: **2**: 70%, **4**: 72%). Both compounds exhibit signals in the ^{31}P NMR spectrum (**2**: $\delta = -21.5$ ppm; **4**: $\delta = -22.5$ ppm) that are shifted significantly upfield from those of related phospholes, for example, those reported by Réau et al. (δ^{31}P = 11–45 ppm).[1e] The ^{1}H and ^{13}C NMR data, on the other hand, are not significantly different than data previously reported for related dithieno systems.[12] To our satisfaction, both **2** and **4** display strong,

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blue photoluminescence, and should thus have the desired optoelectronic properties (vide infra). We were able to obtain light-yellow crystals of **2** suitable for X-ray structure analysis[13] from a concentrated pentane/toluene (1:1) solution cooled to −30 °C. As expected, the rigid tricyclic dithienophosphole is planar and displays an *anti* configuration of the two thiophene moieties and the phosphole unit (see Figure 1). The high degree of π conjugation is apparent in the shortened single bonds {C2–C3 1.427(2), C4–C5 1.440(2), C6–C7 1.423(2) Å) as well as the elongated double bonds (C1–C2 1.365(2), C3–C4 1.384(2), C5–C6 1.382(2), C7–C8 1.364(2) Å) of the fused ring system. It is interesting to note that the bond shortening/elongation is significantly more pronounced in **2** than in the thienyl-substituted phosphole **1**,[5a] supporting the positive effects of the rigid ring system on the π conjugation. The endocyclic P–C bonds P1–C3 (1.8193(14) Å) and P1–C6 (1.8218(14) Å) are only slightly shorter than the exocyclic P1–C11 bond (1.8367(13) Å) due to minimal hyperconjugation of the phosphorus lone pair with the π system, which affords a reduced aromatic phosphole unit. This structural feature strongly supports the role of the phosphorus center as a dopant for the π-conjugated system, which is potentially interesting for the optoelectronic properties of the material.

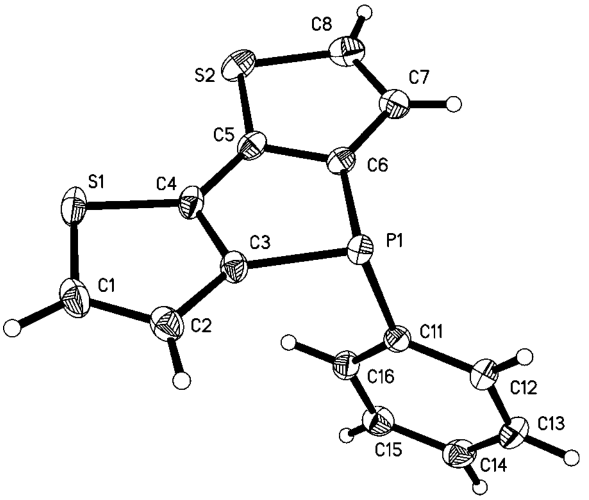


Figure 1. Molecular structure of **2** (50% probability level) in the solid state. Selected bond lengths [Å] and angles [°]: P1–C3 1.8193(14), P1–C6 1.8218(14), P1–C11 1.8367(13), C3–C4 1.3842(19), C5–C6 1.3817(18), C4–C5 1.4397(19); C6–C7 1.4228(18), C7–C8 1.364(2); C3-P1-C6 89.25(6), C3-P1-C11 103.82(6), C6-P1-C11 99.92(6).

To gain access to polymeric systems we functionalized the phosphorus center of the dithienophosphole with a vinylphenyl group. We also investigated silyl functionalization of the dithienophosphole ring to provide increased solubility for the targeted polymer. An additional benefit with respect to the optoelectronic properties was anticipated, as the silyl center provides an acceptor component expected to further extend the delocalized π system, thus optimizing the electronic structure of the dithienophosphole.[11]

The vinylphenyl-functionalized monomer **7** is accessible in a two-step reaction starting from 3,3′,5,5′-tetrabromo-2,2′-bithiophene (**5**). In the first step, the silyl functionalities were introduced by treating **5** with two equivalents of *n*BuLi and then adding *tert*-butyl(dimethyl)silyl chloride in THF at −78 °C to provide **6** in almost quantitative yield. The silyl-functionalized dithiophene **6** was then treated with another two equivalents of *n*BuLi in Et_2O at −78 °C, and dichloro(4-vinylphenyl)phosphane[14] was then added in the presence of an excess of TMEDA to afford the vinylphenyl-functionalized dithienophosphole **7** in good yields (ca. 80%) after filtration over neutral alumina. The dithienophosphole monomer **7** exhibits a resonance in the ^{31}P NMR spectrum of $\delta = -26.4$ ppm that is shifted slightly upfield from those observed for **2** and **4**. The ^{1}H and ^{13}C NMR data confirm the expected structure and are very similar to those recorded for **2** and **4**.

As previously noted, it should be possible to alter the electronic structure, thus inverting the doping mode of the phosphole, by either oxidation or complexation of the phosphorus atom. We therefore investigated the reaction of the dithienophospholes **2** and **4** with borane (applied as $BH_3{\cdot}SMe_2$) to afford the phosphole–borane adducts **8** and **9**, and hydrogen peroxide to give the phosphole oxides **10** and **11**, all in almost quantitative yields.[15] The NMR data for the borane adducts show downfield resonances in the ^{31}P NMR spectrum ($\delta(^{31}P) = 13.5$ (**8**), 14.6 ppm (**9**)) in correlation with the electron-withdrawing effect of the BH_3 group. This is even more pronounced in the case of the oxide functionality ($\delta(^{31}P) = 18.8$ ppm (**10**),[8] 19.1 (**11**)). The same effect was observed for the silyl-functionalized phosphole oxide **12** ($\delta(^{31}P) = 14.7$ ppm) that was synthesized in an analogous manner.[15] The ^{1}H and ^{13}C NMR data for all compounds show a similar trend, and fall within the range of values previously reported for related phospholes.[1e,5]

As indicated earlier, the dithienophosphole derivatives exhibit a strong blue photoluminescence. Fluorescence spectroscopy reveals the dependence of the optical properties on the electronic structure of the phosphorus center (Table 1). All compounds show a maximum excitation wavelength in the UV region, whereas the emission spectra show a maximum wavelength in the visible blue region. The dithienophosphole derivatives exhibit Stokes shifts of 70–80 nm similar to the related systems reported by Réau et al. (70–90 nm).[1e] It is interesting to note that the silyl-functionalized dithienophosphole monomer **7** shows a significant red shift of about

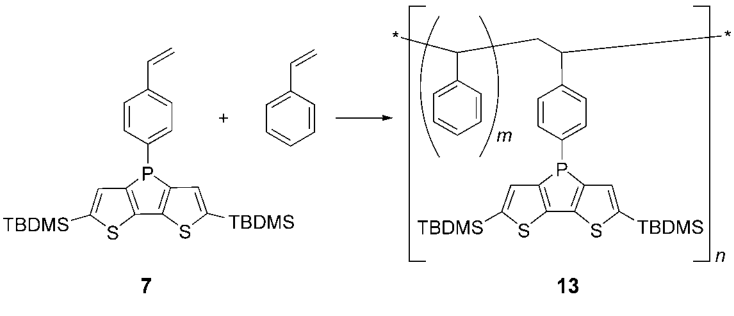
Table 1: Optical spectroscopy data for **2**, **4**, and **7**–**14**.

Cmpd.	λ_{ex} [nm][a]	λ_{em} [nm][b]	lgε	ϕ[c]
2 (**4**)	338 (336)	415 (408)	4.38 (4.50)	0.779 (0.881)
8 (**9**)	346 (346)	424 (423)	4.35 (4.47)	0.690 (0.753)
10 (**11**)	366 (363)	453 (450)	4.33 (4.45)	0.565 (0.590)
7	352	422	4.57	0.687
12	379	461	4.48	0.579
13[d]	352 (374)	424 (452)	4.87 (–)	0.743 (–)
14[d]	374 (352)	458 (456)	4.92 (–)	0.572 (–)

[a] λ_{max} for excitation in CH_2Cl_2. [b] λ_{max} for emission in CH_2Cl_2. [c] Relative to quinine sulfate (0.1 M H_2SO_4 solution); excitation at 365 nm. [d] Values for thin film in brackets.

10–15 nm for the maximum excitation and emission wavelengths ($\lambda_{ex} = 352$, $\lambda_{em} = 422$ nm) compared to the model compounds **2** ($\lambda_{ex} = 338$, $\lambda_{em} = 415$ nm) and **4** ($\lambda_{ex} = 336$, $\lambda_{em} = 408$ nm), supporting the electron-accepting character of the silyl center. The same trend is observed when the doping mode of the phosphorus center is inverted to p-type in the borane adducts **8** and **9** and the phosphole oxides **10**–**12**. In correlation with the low-field shift of the ^{31}P NMR resonances, the maximum wavelengths for excitation and emission experience a red shift of about 10 nm for the borane adducts and an even stronger red shift of about 30 nm (excitation) and 40 nm (emission) for the phosphole oxides. In the case of the silyl-functionalized phosphole oxide **12**, a cumulative effect of both electron-accepting centers (Si and P) is observed (see Table 1). It should be mentioned that the observed photoluminescence is very intense, particularly for the borane adducts and the phosphole oxides. More importantly, the quantum yields for all compounds range between 55 and almost 90%, which is unprecedented for phospholes[1e] and dithieno systems.[12a,16] Therefore, the optoelectronic data strongly emphasize the potential of the dithienophosphole system for applications in optoelectronic devices such as blue-light-emitters and sensory materials.

The favorable properties of macromolecules in terms of processability (e.g. as thin films) would be an added benefit for future materials applications. We therefore investigated the possibility of generating a polymer that would display the extraordinary blue photoluminescence of the model compounds by incorporating the dithienophosphole system as side-chain functionalities. Radical polymerization of functionalized styrene seemed to be the method of choice since it is usually not affected by the presence of phosphine centers.[14b] To reduce the steric bulk in the polymeric material caused by the dithienophosphole ring system, which could potentially terminate the polymerization process at an early stage, we targeted the copolymer **13** by using styrene as solvent for the reactions (**7**/styrene ca. 1:30, Scheme 2). The resulting "dilution" of the dithienophosphole centers in the polymeric material was expected to also enhance the optoelectronic properties, due to the great distance between the emitting centers, reducing the potential for quenching processes that could occur at higher densities.[17] The polymerization was performed in a sealed ampule under vacuum at 110 °C for 16 h using a catalytic amount of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)[18] as the initiator (Scheme 2). The material obtained after precipitation into degassed pentane was a white amorphous solid. Analysis by gel permeation chromatography (GPC) revealed a high molecular weight of $M_n = 147\,650$ g mol^{-1} with a relatively narrow polydispersity (PDI) of 2.46. Analysis of the smart polystyrene **13** by differential scanning calorimetry (DSC) showed a glass transition temperature of $T_g = 114.2$ °C (cf. native polystyrene: < 100 °C[19]) and a thermal decomposition temperature of 428.2 °C. The ^{31}P NMR spectrum for **13** shows a broad signal at $\delta(^{31}P) = -25.0$ ppm (cf.: $\delta = -26.4$ ppm for **7**), confirming the existence of dithienophosphole units within the polymeric material. ^{1}H and ^{13}C NMR data revealed a ratio of ca. 1:30 for dithienophosphole/styrene as was expected from the reaction conditions.



Scheme 2. Synthesis of the dithienophosphole-containing polymer **13**: cat. TEMPO, 110 °C, 16 h. TBDMS = *tert*-butyl(dimethyl)silyl.

The smart polymer **13** exhibits a very strong blue photoluminescence upon irradiation with UV light. The maximum of the excitation and emission wavelengths of **13** ($\lambda_{ex} = 352$ nm; $\lambda_{em} = 424$ nm; dissolved in CH_2Cl_2) nicely match the values observed for the vinylphenyl-functionalized monomer **7** (Figure 2), supporting the expected side-chain functionalization. The dithienophosphole-containing polymer **13** can be oxidized conveniently with hydrogen peroxide (in analogy to the model compounds) to afford the phosphole oxide containing polymer **14**. It should be mentioned that the same oxidation process is observed within a day when a solution of **13** is exposed to air, whereas the solid material does not show any significant signs of oxidation—even after several weeks.

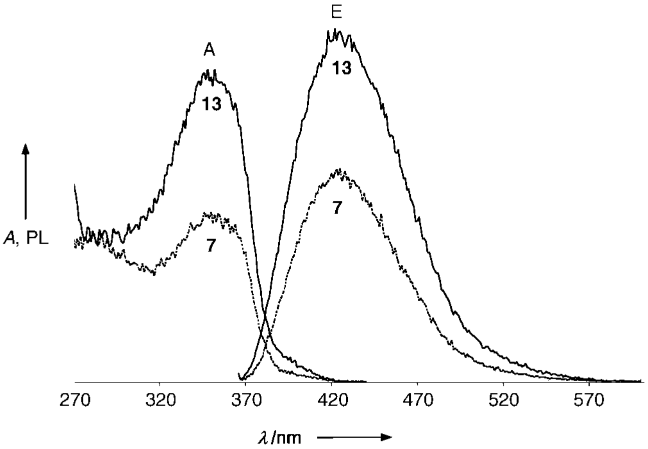


Figure 2. Excitation (A) and emission (E) spectra of **7** and **13** in CH_2Cl_2.

We were also interested in the optoelectronic properties of a thin film of **13** with regards to applications as a PLED material. A thin film was obtained from a concentrated solution of **13** in CH_2Cl_2 by slow evaporation of the solvent. Relative to the properties of the CH_2Cl_2 solution, the very intense blue photoluminescence of the thin film of **13** is red-shifted approximately 20 nm for excitation and roughly 30 nm for emission ($\lambda_{ex} = 374$ nm; $\lambda_{em} = 452$ nm). Surprisingly, the emission wavelength for a thin film of the oxidized polymer (**14**, $\lambda_{em} = 456$ nm) almost matches that observed for the nonoxidized material **13**, whereas the value for the excitation wavelength is blue-shifted to 352 nm in **14** (cf. 374 nm for **13**; Figure 3). With respect to resistance to light, **13** was found to exhibit fairly good stability; this is intrinsically important for the lifetime of optoelectronic devices. Irradiation of a solution of **13** in CH_2Cl_2 at 352 nm for 2 h results in a stable emission (intensity detected at 424 nm) within a loss of at most 3 %, suggesting a potential use in optoelectronic devices. The same is true for a thin film of the oxidized polymer (**14**) with a margin of 5 %.

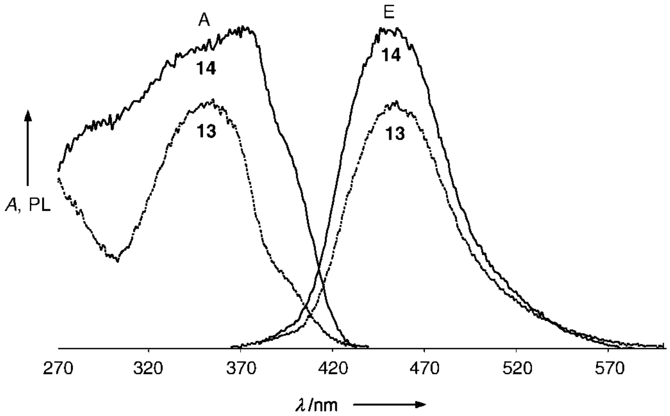


Figure 3. Excitation (A) and emission (E) spectra of **13** and **14** as thin films.

In conclusion, we have synthesized novel dithieno[3,2-*b*:2′,3′-*d*]phosphole derivatives in a convenient one- or two-step synthesis, demonstrating that a broad variety of functionalized systems are accessible by this method. The optoelectronic properties of the dithienophospholes are extraordinary with respect to wavelength, intensity, and tuneability, allowing for the possibility of fine-tuning the electronic structure by simple chemical modifications. Additionally, we have shown that it is possible to incorporate the dithienophosphole moiety into polymeric systems, opening up potential applications in optoelectronic devices such as blue-light-emitting PLEDs and polymeric sensors. We are currently probing the range of dithienophosphole-based sensory materials by tuning the optoelectronic properties with different functionalities and modifications of the phosphorus center. Furthermore, the incorporation of polymers **13** and **14** into optoelectronic devices is currently under investigation.

Experimental Section

Dithienophospholes: To a solution of **3** (1.62 g, 5 mmol) in Et_2O (100 mL) was added *n*BuLi (4 mL, 10 mmol) dropwise at −78 °C. Subsequently, $RPCl_2$ (R = Ph: 0.90 g, 5 mmol; R = 4-*t*Bu-C_6H_4, 1.18 g, 5 mmol) dissolved in Et_2O (10 mL), was added slowly to the reaction mixture, and the resulting suspension was allowed to warm quickly to room temperature. The solvent was then removed under vacuum, the residue taken up in pentane (ca. 60 mL) and filtered over neutral alumina to remove LiCl and a small amount of brown impurities. The filtrate was evaporated to dryness, and **2** and **4** were obtained as light-yellow solids (**2**: 1.1 g, 70 % yield; **4**: 1.2 g, 72 % yield).

2: ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, $CDCl_3$): $\delta = -21.5$ ppm; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 7.31$ (br, 2 H; *o*-Ph), 7.26–7.23 (m., 5 H; Ar-H), 7.14 ppm (d, ^{3}J(H,H) = 5.0 Hz, 2 H; Ar-H); ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, $CDCl_3$): $\delta = 146.6$ (d, *J*(C,P) = 8.0 Hz; Ar), 141.7 (d, *J*(C,P) = 2.3 Hz; Ar), 133.5 (d, *J*(C,P) = 15.3 Hz; Ar), 132.2 (d, ^{2}J(C,P) = 20.5 Hz; *o*-Ar), 129.1 (s; *p*-Ph), 128.5 (d, ^{3}J(C,P) = 7.6 Hz; *m*-Ar), 126.4 (d, ^{2}J(C,P) = 19.6 Hz; *o*-Ar), 126.0 ppm (d, ^{3}J(C,P) = 6.2 Hz; *m*-Ar); MS (70 eV): *m*/*z* (%): 272 (100) [M^+], 239 (90) [M−S]$^+$, 195 (40) [M−Ph]$^+$; elemental analysis calcd (%) for $C_{14}H_9PS_2$: C 61.75, H 3.33, S 23.55; found: C 61.77, H 3.45, S 23.38.

4: ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, $CDCl_3$): $\delta = -22.5$ ppm; ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): $\delta = 7.28$–7.23 (m., 6 H; Ar-H), 7.13 (d, ^{2}J(H,H) = 4.9 Hz, 2 H; Ar-H), 1.24 ppm (s, 9 H; *t*Bu); ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, $CDCl_3$): $\delta = 152.4$ (s; *p*-Ar), 147.0 (d, *J*(C,P) = 8.7 Hz; Ar), 141.6 (d, *J*(C,P) = 2.1 Hz; Ar), 132.1 (d, *J*(C,P) = 20.5 Hz; *o*-Ar), 129.7 (d, ^{1}J(C,P) = 11.4 Hz; Ar), 126.5 (d, ^{2}J(C,P) = 16.9 Hz; *o*-Ar), 125.9 (d, ^{3}J(C,P) = 5.7 Hz; *m*-Ar), 125.7 (d, ^{3}J(C,P) = 8.5 Hz; *m*-Ar), 34.5 (s; *C*Me$_3$), 31.0 ppm (s; C(*C*H$_3$)$_3$). MS (70 eV): *m*/*z* (%) 328 (100) [M^+], 271 (50) [*M*-*t*Bu]$^+$, 195 (90) [$M-C_{10}H_{13}$]$^+$, 57 (25) [*t*Bu]$^+$; elemental analysis calcd (%) for $C_{18}H_{17}PS_2$: C 65.83, H 5.22, S 19.53; found: C 65.42, H 5.39, S 19.46.

7: To a solution of 3,3′-dibromo-5,5′-bis(*tert*-butyldimethylsilyl)-2,2′-bithiophene (1.11 g, 2 mmol) and TMEDA (1.51 mL, 10 mmol) in Et_2O (50 mL) was added *n*BuLi (1.6 mL, 4 mmol) dropwise at −78 °C. Subsequently, (4-vinylphenyl)PCl_2 (0.41 g, 2 mmol), dissolved in Et_2O (10 mL), was added slowly to the reaction mixture, and the resulting mixture was allowed to warm quickly to room temperature. The solvent was then removed under vacuum, and the residue taken up in pentane (ca. 60 mL) and filtered to remove LiCl. The filtrate was concentrated and left for crystallization at −30 °C. **7** was obtained as white amorphous powder in 80 % yield (0.84 g).

^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, $CDCl_3$): $\delta = -26.4$ ppm; ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$): $\delta = 7.32$ (br, 2 H; Ar-H), 7.31 (s, 2 H; Ar-H), 7.26 (s, 2 H; Ar-H), 6.65 (dd, ^{3}J(H,H) = 17.7 Hz, ^{3}J(H,H) = 11.3 Hz, 1 H; C*H*=CH$_2$), 5.73 (d, ^{3}J(H,H) = 17.7 Hz, 1 H; CH=C*H*H), 5.73 (d, ^{3}J(H,H) = 11.3 Hz, 1 H; CH=CH*H*), 0.93 (s, 18 H; Si*t*Bu), 0.31 (s, 6 H; SiMe$_2$), 0.30 ppm (s, 6 H; SiMe$_2$); ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, $CDCl_3$): $\delta = 148.7$ (d, ^{1}J(C,P) = 10.3 Hz; *ipso*-Ar), 147.0 (s; Ar), 139.8 (d, ^{2}J(C,P) = 6.2 Hz; Ar), 139.5 (d, ^{1}J(C,P) = 19.6 Hz; Ar), 138.4 (s; *p*-Ar), 136.3 (s; *C*H=CH$_2$), 134.3 (d, ^{2}J(C,P) = 16.6 Hz; *o*-Ar), 132.8 (d, ^{2}J(C,P) = 21.7 Hz; *o*-Ar), 126.4 (d, ^{3}J(C,P) = 8.3 Hz; *m*-Ar), 114.7 (s; CH=*C*H$_2$), 26.4 (s; SiC(*C*H$_3$)$_3$), 17.0 (s; Si*C*(CH$_3$)$_3$), −4.9 ppm (s; SiMe$_2$); elemental analysis calcd (%) for $C_{26}H_{37}PS_2Si_2$: C 63.83, H 7.46, S 12.17; found: C 63.66, H 7.68, S 12.14.

Polymerization: To a solution of **7** (0.26 g, 0.5 mmol) dissolved in styrene (2 mL, 17.5 mmol) in an ampule was added a catalytic amount of TEMPO. The ampule was then evacuated, sealed, and kept overnight at 110 °C. The resulting yellowish solid obtained after the reaction mixture had cooled to room temperature was then dissolved in ca. 10 mL of dichloromethane and precipitated into degassed pentane. After the solvent had been decanted off and the residue dried under vacuum, polymer **13** was obtained as a white solid (1.76 g, ca. 85 %). GPC: $M_n = 147650\ \mathrm{g\,mol^{-1}}$, PDI = 2.46; DSC: $T_g = 114.2$ °C, $T_{decomp} = 428.2$ °C; ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, CD_2Cl_2): $\delta = -25.0$ ppm; ^{1}H NMR (500 MHz, 25 °C, CD_2Cl_2): $\delta = 7.09$ (m br, ca. 132 H; Ar-H), 6.53 (m br, ca. 88 H; Ar-H); 1.84 (m br, ca. 48 H; C*H*CHH); 1.48 (m br, ca. 96 H; CHC*HH*), 0.98 (br, 18 H; Si*t*Bu), 0.35 ppm (br, 12 H; SiMe$_2$); ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, CD_2Cl_2): $\delta = 149.3$ (br; Ar), 145.0 (br; Ar), 140.2 (br; Ar), 134.9 (br; Ar), 132.2 (br; Ar), 128.4 (br; Ar), 128.0 (br; Ar), 126.0 (br; Ar), 45.0 (m br; *C*HCH$_2$), 40.8 (m br; CH*C*H$_2$), 26.6 (br; SiC(*C*H$_3$)$_3$), 17.2 (br; Si*C*(CH$_3$)$_3$), −4.7 ppm (br; SiMe$_2$).

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[13] Crystal data for **2**: ($C_{14}H_9PS_2$): $M_r = 272.30$, $T = 153(2)$ K, monoclinic, space group $P2(1)/c$, $a = 12.740(3)$, $b = 8.2365(16)$, $c = 11.729(2)$ Å, $\alpha = 90$, $\beta = 92.62(3)$, $\gamma = 90°$, $V = 1229.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.471$ Mg m^{-3}, $\mu = 0.534$ mm^{-1}, $\lambda = 0.71073$ Å, $2\theta_{max} = 56.62°$, 12358 measured reflections, 3046 [$R(int) = 0.0227$] independent reflections, GOF on $F^2 = 1.080$, $R_1 = 0.0317$, w$R_2 = 0.0857$ ($I > 2\sigma(I)$), $R_1 = 0.0332$, w$R_2 = 0.0868$ (for all data), largest difference peak and hole 0.429 and −0.248 e Å^{-3}. The intensity data were collected on a Bruker SMART D8 goniometer with an APEX CCD detector. The structure was solved by direct methods (SHELXTL) and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model. CCDC-244042 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] Selected physical data: **9**: ^{31}P{^{1}H} NMR (80.9 MHz, 25 °C, CDCl$_3$): $\delta = 14.6$ ppm; ^{1}H NMR (500 MHz, 25 °C, CDCl$_3$): $\delta =$ 7.54 (dd, ^3J(H,P) = 11.6 Hz, ^3J(H,H) = 8.4 Hz, 2 H; *o*-Ph), 7.40 (dd, ^3J(H,H) = 8.4 Hz, ^3J(H,P) = 2.1 Hz, 2 H; *m*-Ph), 7.34 (dd, ^3J(H,H) = 4.9 Hz, ^3J(H,P) = 3.1 Hz, 2 H; Ar-H), 7.16 (dd, ^3J(H,H) = 4.9 Hz, ^4J(H,P) = 1.2 Hz, 2 H; Ar-H), 1.29 (s, 9 H; *t*Bu); ^{13}C{^{1}H} NMR (125.6 MHz, 25 °C, CDCl$_3$): $\delta = 150.5$ (d, ^2J(C,P) = 2.9 Hz; Ar-Ar), 144.9 (d, ^4J(C,P) = 10.5 Hz; *p*-Ph), 139.3 (d, ^1J(C,P) = 63.3 Hz; *ipso*-Ar), 131.8 (d, J(C,P) = 10.5 Hz; Ar-H), 128.1 (d, J(C,P) = 12.5 Hz; Ar-H), 126.1 (d, J(C,P) = 16.3 Hz; Ar-H), 126.1 (d, J(C,P) = 11.5 Hz; Ar-H), 122.3 (d, ^1J(C,P) = 54.7 Hz; *ipso*-Ph), 35.0 (s; *C*Me$_3$), 31.0 ppm (s; CH$_3$); ^{11}B NMR (160.3 MHz, 25 °C, CDCl$_3$): $\delta = -39.2$ ppm. **11**: ^{31}P{^{1}H} NMR (126.0 MHz, 25 °C, CDCl$_3$): $\delta = 19.1$ ppm; ^{1}H NMR (400 MHz, 25 °C, CDCl$_3$): $\delta = 7.62$ (dd br, ^3J(H,P) = 13.2 Hz, ^3J(H,H) = 8.5 Hz, 2 H; *o*-Ph), 7.40 (dd br, ^3J(H,H) = 8.5 Hz, ^4J(H,P) = 3.0 Hz, 2 H; *m*-Ph), 7.26 (dd, ^3J(H,H) = 5.0 Hz, ^3J(H,P) = 3.4 Hz, 2 H; Ar-H), 7.12 (dd, ^2J(H,H) = 5.0 Hz, ^4J(H,P) = 2.5 Hz, 2 H; Ar-H), 1.26 ppm (s, 9 H; *t*Bu); ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, CDCl$_3$): $\delta = 155.9$ (s; *p*-Ar), 145.4 (d, ^2J(C,P) = 24.0 Hz; Ar), 139.0 (d, ^1J(C,P) = 111.9 Hz; Ar), 130.6 (d, ^2J(C,P) = 11.8 Hz; *o*-Ar), 128.0 (d, ^2J(C,P) = 14.7 Hz; *o*-Ar), 126.0 (d, ^1J(C,P) = 111.1 Hz; Ar), 125.9 (d, ^3J(C,P) = 13.2 Hz; *m*-Ar), 125.8 (d, ^3J(C,P) = 12.8 Hz; *m*-Ar), 34.9 (s; *C*Me$_3$), 30.8 ppm (s; C(*C*H$_3$)$_3$). **12**: ^{31}P{^{1}H} NMR (162.0 MHz, 25 °C, CDCl$_3$): $\delta =$ 14.7 ppm; ^{1}H NMR (500 MHz, 25 °C, CDCl$_3$): $\delta = 7.70$ (dd, ^3J(H,P) = 12.8 Hz, ^3J(H,H) = 8.2 Hz, 2 H; Ar-H), 7.46 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,P) = 2.8 Hz, 2 H; Ar-H), 7.19 (d, ^3J(H,P) = 2.4 Hz, 2 H; Ar-H), 6.71 (dd, ^3J(H,H) = 17.4 Hz, ^3J(H,H) = 10.7 Hz, 1 H; C*H*=CH$_2$), 5.83 (d, ^3J(H,H) = 17.4 Hz, 1 H; CH=C*H*H), 5.35 (d, ^3J(H,H) = 10.7 Hz, 1 H; CH=CH*H*), 0.91 (s, 18 H; Si*t*Bu), 0.28 (s, 6 H; SiMe$_2$), 0.27 ppm (s, 6 H; SiMe$_2$); ^{13}C{^{1}H} NMR (125.7 MHz, 25 °C, CDCl$_3$): $\delta = 150.8$ (d, ^1J(C,P) = 23.9 Hz; *ipso*-Ar), 142.8 (d, J(C,P) = 14.3 Hz; Ar), 141.4 (d, J(C,P) = 18.2 Hz; Ar), 140.4 (s; *p*-Ar), 135.9 (s; *C*H=CH$_2$), 133.3 (d, ^2J(C,P) = 15.3 Hz; *o*-Ar), 131.3 (d, ^2J(C,P) = 12.4 Hz; *o*-Ar), 129.0 (d, ^1J(C,P) = 110.2 Hz; *ipso*-Ar), 126.6 (d, ^3J(C,P) = 12.4 Hz; *m*-Ar), 116.5 (s; CH=*C*H$_2$), 26.2 (s; SiC(*C*H$_3$)$_3$), 16.8 (s; Si*C*(CH$_3$)$_3$), −5.0 (s; SiMe), −5.1 ppm (s; SiMe).

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