DOI: 10.1002/chem.200700399

Selective Tuning of the Band Gap of π-Conjugated Dithieno[3,2-*b*:2′,3′-*d*]phospholes toward Different Emission Colors

Yvonne Dienes,[a] Stefan Durben,[a] Tamás Kárpáti,[b] Toni Neumann,[a] Ulli Englert,[a] László Nyulászi,*[b] and Thomas Baumgartner*[a]

Abstract: The systematic extension of the π-conjugated system of strongly blue-luminescent dithieno[3,2-*b*:2′,3′-*d*]phospholes has been investigated with the goal of obtaining different emission colors. Functionalization of the 2- and 6-position of the dithienophosphole scaffold with halogen substituents provided functional building blocks for subsequent cross-coupling experiments with various homo- and heteroaryls to selectively decrease the band gap of the materials. By this strategy materials with different emission colors ranging from green via yellow to orange could be obtained. This feature supports their suitability for organic light-emitting diodes with respect to an application in full-color flat-panel displays. The experimental results were nicely supported by theoretical DFT calculations providing a deeper understanding of the electronic structure in the extended materials, and also allowing for the design of future materials based on a dithienophosphole core. Furthermore, the phosphorus center in the extended molecular materials can efficiently be fine-tuned in subsequent simple chemical functionalizations. This allows for a tailoring of the optoelectronic properties of the extended dithienophospholes to suit the requirements of potential applications.

Keywords: cross-coupling • density functional calculations • luminescence • organic electronics

Introduction

The steadily growing demand for smaller, more energy-efficient electronic devices has resulted in the development of a plethora of organic π-conjugated materials over the past three decades.[1–3] Organic materials have great potential for application in electronic devices such as molecular or polymer-based light-emitting diodes (OLEDs/PLEDs) for display as well as lighting applications, solar cells, field-effect transistors (FET), electrochromic or smart windows, photoresists, nonlinear optical (NLO) devices, or polymeric sensors.[1–7] Their organic nature allows for the fabrication of flexible, lightweight materials that can be conveniently processed, particularly for low power, low cost applications.[4,6a] In this context, the incorporation of phosphorus centers into π-conjugated materials has recently started to draw an increasing amount of attention.[8] The versatile reactivity and electronic nature of phosphorus offer considerable opportunities for the development of new materials with novel properties.[8a] It is well established that the performance of organic materials is mainly determined by their chemical structure and their supramolecular organization in the solid state.[2–4] For a successful application in organic electronics it is therefore essential, to be able to fine-tune, or better: to tailor the electronic structure, that is, the band gap of the respective materials.[9] Intriguingly, trivalent phosphorus derivatives can react with oxidizing agents or Lewis acids, but they can also coordinate to transition metals.[10] This offers a unique variety of synthetically facile possibilities that can be undertaken to efficiently modifying the electronic properties of the product materials. These modifications are generally not possible with this simplicity in genuine organic systems. Réau and co-workers were among the first to implement the

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[a] Dipl.-Chem. Y. Dienes, Dipl.-Chem. S. Durben,+ T. Neumann,
Prof. Dr. U. Englert, Prof. Dr. T. Baumgartner+
Institute of Inorganic Chemistry, RWTH-Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: thomas.baumgartner@ucalgary.ca

[b] Dr. T. Kárpáti, Prof. Dr. L. Nyulászi
Department of Inorganic and Analytical Chemistry
Budapest University of Technology and Economics
1521 Budapest Gellért tér 4 (Hungary)
Fax: (+36) 1463-3363
E-mail: nyulaszi@chem.bmu.hu

[+] Current address:
Department of Chemistry, University of Calgary
2500 University Drive NW
Calgary, AB T2N 1N4 (Canada)
Fax: (+1) 403-289-9488

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phosphole moiety, which is related to the well-established thiophene and pyrrole, into extended π-conjugated materials (**A**, Figure 1);[8a,b,d,11] Their systematic studies have successfully demonstrated the advantageous electronic features of the incorporated phosphorus centers in a series of phosphole-based OLED devices.[12]

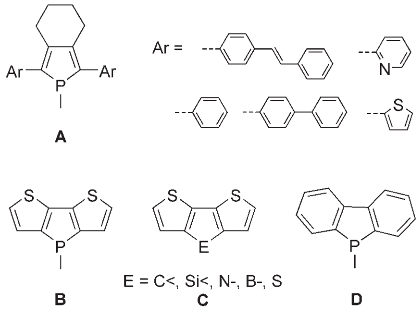


Figure 1. Phosphole- and dithieno-based materials.

With organic electronics being a focus of our research, we have recently established the dithieno[3,2-*b*:2′,3′-*d*]phosphole system **B**.[13] This building block, conjoining two thiophene subunits and a central phosphole moiety via anellation, also allows for the selective tuning of the electronic properties of the materials by functionalization of phosphorus atom.[13] Fused bithiophene compounds **C**, in general, are promising candidates for an application in organic electronics as they provide a high degree of π conjugation due to their rigidified, planar structure which intrinsically affords smaller HOMO–LUMO gaps.[9,14] Our extensive investigations to date have revealed this also being true for the dithienophosphole system **B** and we were able to confirm a doping function for the phosphorus center, rather than being an integral part of the π-conjugated system.[13] Dithienophospholes **B** can not be considered classic phospholes for that matter, but they relate to dibenzophospholes **D**.[8a,15] The materials obtained in the context of our studies, display highly advantageous, unprecedented photophysical properties with respect to emission wavelengths, intensity and tunability. Dithienophospholes are very strong emitters of blue light with photoluminescence efficiencies of up to 90% emphasizing their potential suitability for electronic devices. Their photophysical properties can efficiently be tuned by simple modifications (see Figure 2) at either the phosphorus center (E = lone pair) via oxidation (E = O, S) or complexation with main group ($E=BH_3$) or transition metals (E = [M]), or by variation of the substitution pattern (R^1 on the thienyl or R^2 on the central phosphorus atom).[13,16] Although very intriguing, as efficient materials for corresponding OLEDs are still rare, all modifications of the dithienophosphole system so far have afforded compounds with blue light-emitting features only ($\lambda_{em}=408$–470 nm).[13,16] With an application in, for example, full color OLED-based displays in mind, it would, however, be highly desirable to access further materials with different emission colors. This goal can be achieved by extending the degree of π conjugation within the materials, as this strategy generally affords smaller band gaps.[1–4,17]

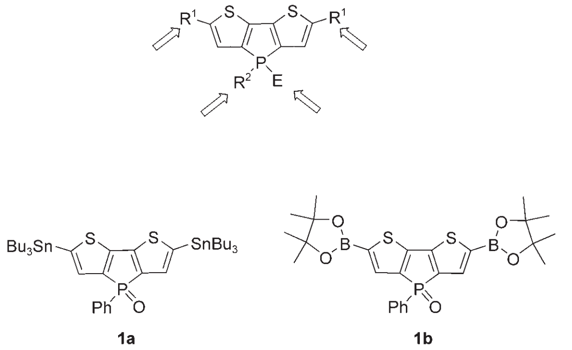
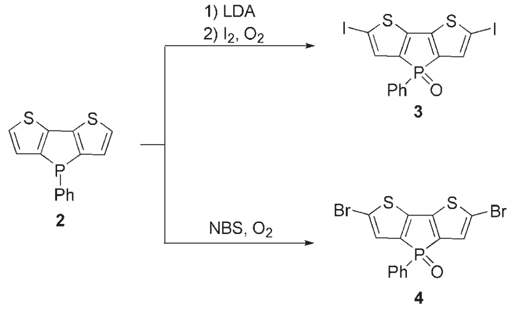


Figure 2. Possibilities for the functionalization of dithienophospholes.

In this present paper we now report our efforts in tailoring the band gap of the dithienophosphole moiety toward the generation of different emission colors through a variety of cross-coupling procedures to access extended, well-defined π-conjugated dithienophospholes. Their experimentally observed optoelectronic properties will be interpreted by theoretical DFT calculations and we will also discuss the potential of further fine-tuning the extended dithienophospholes generated.

Results and Discussion

Synthesis and characterization of halogen-functionalized dithieno[3,2-*b*:2′,3′-*d*]phospholes: As a related stannyl-functionalized dithienophosphole **1a** (Figure 2) was successfully cross-coupled in our previous studies to give a π-conjugated phenylene copolymer,[13b] our initial efforts toward extended dithienophospholes within this project involved the corresponding boryl-functionalized compound **1b**.[16c] However, all cross-coupling attempts so far have resulted only in the generation of the deborylated derivative. For that reason, we have shifted our focus towards a protocol with inverted functional groups, that is, halogenated dithienophospholes. In this context, we were able to successfully access the 2,6-diiodo as well as the 2,6-dibromo derivative **3** and **4**, respectively (Scheme 1). Double iodination of dithienophosphole **2**



Scheme 1. Synthesis of 2,6-di(halo)-functionalized dithienophospholes.

was achieved by dilithiation with LDA and subsequent treatment with molecular iodine at −78 °C followed by an in situ oxidation of the trivalent phosphorus center to afford **3** in low yields after recrystallization from acetone. Bromination of **2** with *N*-bromosuccinimide (NBS) and subsequent in situ oxidation, on the other hand, proceeded more efficiently at room temperature in an acetic acid/chloroform solution following a literature procedure for related thiophenes[18] to afford the 2,6-dibrominated derivative **4** in good yields.[19] The oxidation of the phosphorus center in **4** is supported by its ^{31}P NMR resonance at $\delta = 16.3$ ppm that relates to other known dithienophosphole oxides[13,16a,c] as well as the diiodo derivative **3** (δ^{31}P = 16.3 ppm). The same is true for the ^{1}H and ^{13}C NMR resonances for **3** and **4**.

For the purpose of successful cross-coupling procedures, we anticipated the oxidized phosphorus atom to be beneficial, as a poisoning of the catalyst employed would be prevented by "protection" of this center; in earlier studies we could confirm that dithienophospholes are excellent ligands for Group 10 metals such as palladium,[16b] commonly used in Suzuki–Miyaura and Stille cross-coupling protocols.[20] We were able to obtain single crystals suitable for X-ray structure analyses of both compounds **3** and **4** from concentrated acetone solutions. The molecular structures of **3** and **4** (Figure 3) in the solid state are very similar with almost identical cell parameters (space group *C*2/*c*). Slight differences in the structural data can be explained by the larger iodo substituents in **3** compared with the bromo functionalities in **4**. Their structural parameters do not differ considerably from those of other known dithienophospholes,[13] indicating a high degree of π conjugation within the systems. For comparison, selected bond lengths and angles can be found in Table 1.

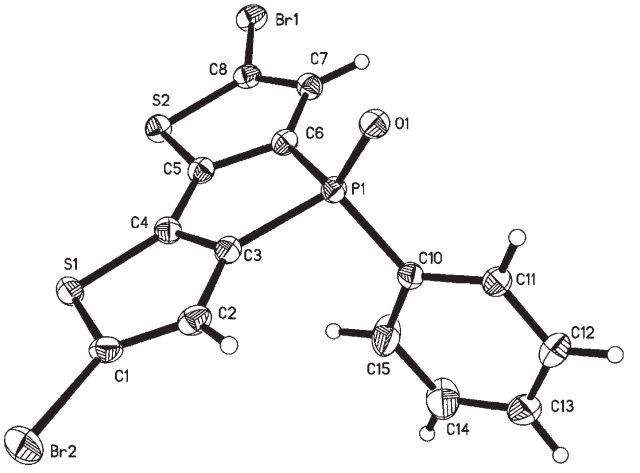
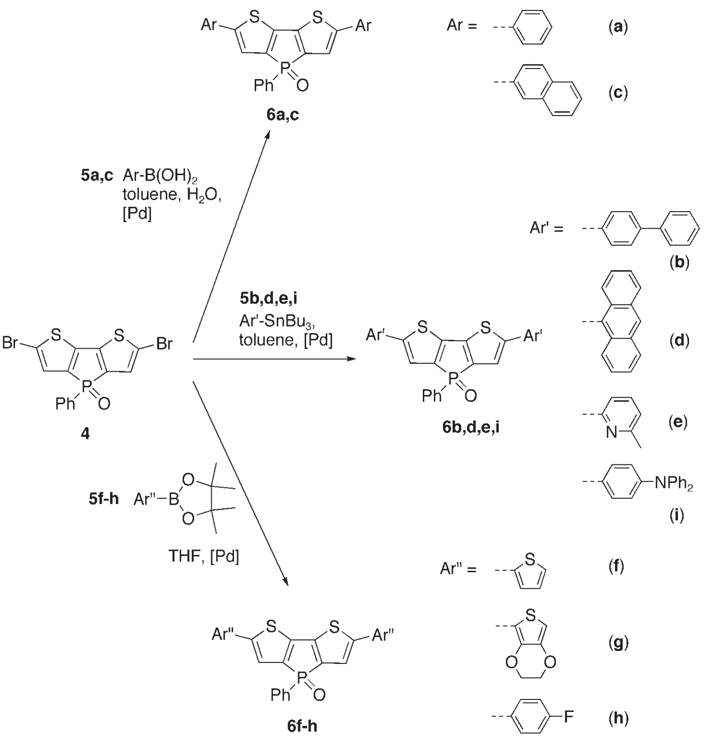


Figure 3. Molecular structure of **4** in the solid state (50 % probability level).

Table 1. Selected bonds lengths [Å] for compounds **3** and **4**.

	3	**4**
P–C$_{exo}$	1.787(6)	1.792(3)
P–C$_{endo}$	1.799(6), 1.823(6)	1.810(3), 1.806(3)
(C=C)$_P$	1.369(7), 1.374(8)	1.373(4), 1.376(4)
(C–C)$_P$	1.439(8)	1.446(4)
(C=C)$_S$	1.358(8), 1.349(9)	1.364(4), 1.371(4)
(C–C)$_S$	1.420(8), 1.410(8)	1.415(4), 1.420(4)
P–O	1.474(5)	1.486(2)
C–X	2.072(6), 2.056(6)	1.866(3), 1.856(3)



Scheme 2. Synthesis of extended dithienophospholes via cross-coupling reactions.

Cross-coupling of dithieno[3,2-*b*:2′,3′-*d*]phosphole monomers: With the dibrominated dithienophosphole oxide **4** at hand, in particular, several cross-coupling variations appropriate for different substrates[20] were accessible (Scheme 2). In a first series, we targeted homoarenes with increasing degree of π conjugation to extend the π-system of the dithienophosphole core (**6a–d**). The 2,6-bis(phenyl) derivative **6a** as well as the 2,6-bis(2′-naphthyl) derivative **6c** were obtained using the corresponding boronic acids **5a,c** through a Suzuki–Miyaura-based protocol in a biphasic (toluene/water) environment. Both compounds were obtained in decent yields as yellow/orange solids after work-up. A Stille coupling procedure involving the corresponding stannylated precursors **5b,d** in toluene solutions, gave access the orange 2,6-bis(4′-biphenyl) **6b** and 2,6-bis(9′-anthranyl) derivative **6d**, respectively. Unfortunately, the bis(9′-anthranyl) derivative **6d** turned out to be poorly soluble in most common solvents and could not be satisfactorily analyzed. The cross-coupled products **6a–c** on the other hand, were soluble and

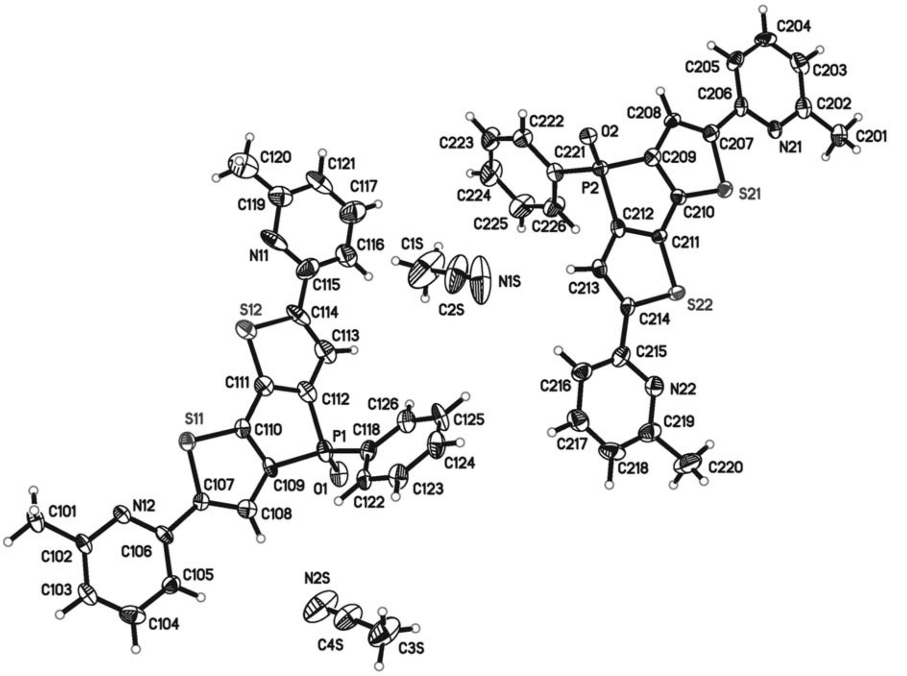


Figure 4. Molecular structure of **6e** in the solid state (50 % probability level). Selected bond lengths [Å]: P1–C118 1.790(6), P1–C109 1.799(6), P1–C112 1.798(7), C106–C107 1.461(8), C107–C108 1.371(8), C108–C109 1.396(8), C109–C110 1.372(8), C110–C111 1.466(8), C111–C112 1.376(8), C112–C113 1.378(8), C113–C114 1.348(9), C114–C115 1.443(10), P2–C221 1.816(5), P2–C209 1.798(6), P2–C212 1.819(6), C206–C207 1.451(8), C207–C208 1.370(8), C208–C209 1.435(8), C209–C210 1.390(8), C210–C211 1.454(8), C211–C212 1.373(8), C212–C213 1.397(8), C213–C214 1.370(8), C214–C215 1.471(8).

could thus be analyzed comprehensively. They show ^{31}P NMR resonances that are slightly downfield shifted from those of the halogenated monomers with $\delta^{31}\mathrm{P} = 17.4$ ppm (**6a**), 17.3 ppm (**6b**), 17.3 ppm (**6c**) whereas their ^{1}H and ^{13}C NMR spectra relate to corresponding dithienophospholes[13] with the addition of the expected resonances for the cross-coupled components.

To determine the effects of electron-poor as well as electron-rich substituents on the optoelectronic properties of the system, we also synthesized corresponding heteroarene-functionalized dithienophospholes. It is well established that such moieties help selectively adjust the LUMO or HOMO levels of organic materials, respectively.[2–4] Pyridine and thiophene moieties have already been established to improve the materials properties in related bridged bithiophenes and were thus considered suitable groups for our purpose.[21] The 2,6-bis(2′-6′-picolyl) derivative **6e** was accessible by a Stille protocol in toluene, according to the procedure used for **6b** and **6d**, whereas the thiophene-functionalized dithienophosphole **6f** was obtained by reaction of 2-pinacolboryl-thiophene **5f** in a Suzuki–Miyaura-type procedure using THF as solvent. The ^{31}P NMR resonances of $\delta = 17.0$ ppm for **6e** and $\delta = 16.9$ ppm for **6f** are only slightly different from the homoarene-functionalized compounds **6a–c** (cf.: $\delta^{31}\mathrm{P} = 17.3 \pm 1$ ppm).

We were able to obtain single crystals suitable for X-ray structure analyses for both compounds from concentrated solutions (**6e**: acetonitrile; **6f**: acetone) at room temperature. The molecular structure of **6e** in the solid state shows two independent molecules in the unit cell, accompanied by two acetonitrile solvent molecules (see Figure 4). Both dithienophosphole molecules exhibit essentially all-coplanar arrangements throughout the molecules, including the picolyl units (twist angles: 0.2–3.3°), and thus support the desired extension of the π-conjugated system. Surprisingly, the picolyl units exist in a *syn* arrangement with the thiophene subunits; oligothiophenes and -pyridines usually show an *anti*-configuration that is stabilized by intramolecular S···H/N···H interactions with the H atom attached to the thiophene/pyridine-C3.[3,22] However, the unusual *syn* arrangement is also found in the only other structurally characterized congener 2-(2′-(5′-acetyl)thienyl)pyridine.[23] B3LYP/6-31+G* computations also predict the stability of the *cis* form (by 3.4 kcal mol^{-1} with respect to the *trans*), thus this structural feature seems to be characteristic for the alternating thiophene–pyridine units also in the gas phase. The extended degree of π conjugation in both molecules of **6e** is also supported by elongated C–C double bonds as well as shortened C–C single bonds of the central framework (see Figure 4). Remarkably, the molecular packing of **6e** displays an intriguing feature for potential applications in organic electronics, as all molecules within the crystal show a significant degree of π stacking (mean distance ca. 3.5 Å) between the dithienophosphole moieties of different layers (Figure 6a). This feature could allow for a well-defined intermolecular communication of **6e** in the solid state that is essential for its performance in electronic devices.[2,4,6a]

We have carried out TD DFT calculations to establish the extent of communication between two molecules placed at the positions taken from the X-ray structure of **6e**. The lowest lying excitations of the various dimers differ from the excitation energy of the monomer by up to 10 nm, for some higher excited states the shift amounts 10 nm. The placement of the two molecules to ca. 3.0 Å (the other structural parameters being taken from the X-ray structure) results in a 40 nm splitting of the lowest excitation energies. This indicates that even with the experimentally observed separation of the individual molecules the extent of the interaction is not too large. But with minor structural changes the effect becomes significant, and therefore it is of importance in optoelectronic applications.

The molecular structure of 2,6-bis(2′-thienyl) **6f** also shows two independent molecules in the unit cell that both exhibit an almost all-coplanar arrangement throughout the terminal thiophene moieties (twist angles: 6.1–10.7°; see Figure 5). Due to their fairly symmetric shape and the enabled free rotation about the connecting single bond, the cross-coupled thienyl units are disordered, and both rotational isomers (*syn* and *anti*) can be found in the crystal. This feature is commonly observed with genuine oligothiophenes and usually does not have a strong impact on the π conjugation.[3,4] The bond lengths within the dithienophosphole moiety relate to those of picolyl **6e**, indicating the expected high degree of π conjugation in **6f**. In contrast to the solid-state arrangement of **6e**, the dithienophosphole scaffold in **6f** does not show any primary π-stacking interactions. However, intermolecular interactions can be observed between phenyl rings attached to the phosphorus centers with their counterparts of neighboring molecules (mean distance ca. 3.6 Å; Figure 6b).

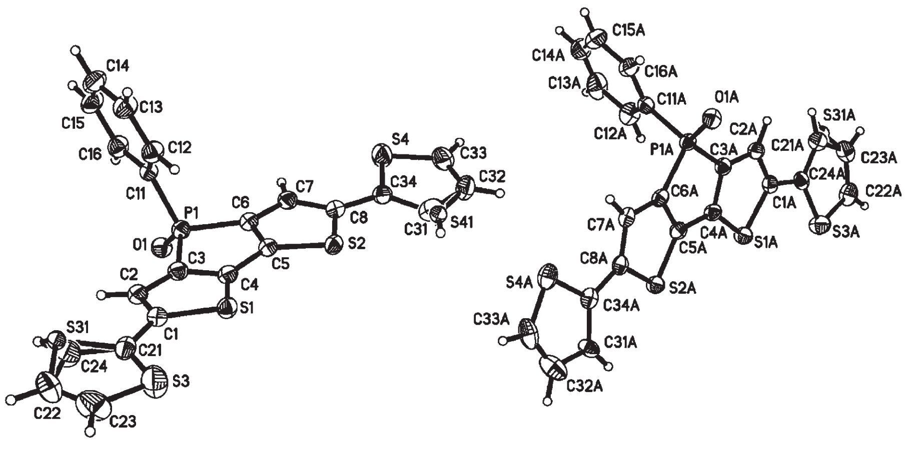


Figure 5. Molecular structure of **6f** in the solid state (50% probability level). Selected bond lengths [Å]: P1–C3 1.806(2), P1–C6 1.800(2), P1–C11 1.804(2), C21–C1 1.494(4), C1–C2 1.378(3), C2–C3 1.408(3), C3–C4 1.387(3), C4–C5 1.448(3), C5–C6 1.392(3), C6–C7 1.408(3), C7–C8 1.382(3), C8–C34 1.455(3); P1A–C3A 1.804(2), P1A–C6A 1.811(3), P1A–C11A 1.797(2), C24A–C1A 1.460(3), C1A–C2A 1.371(3), C2A–C3A 1.409(3), C3A–C4A 1.382(3), C4A–C5A 1.448(3), C5A–CA 1.382(3), C6A–C7A 1.406(3), C7A–C8A 1.374(3), C8A–C34A 1.468(3).

These results clearly emphasize the fact that small structural changes can indeed have strong effects on the supramolecular organization of organic materials in the solid state and thus potentially affect their performance in corresponding devices significantly. It appears to be essential to cover a broad range of substrates for tuning the packing properties of these materials towards a successful application. We have therefore also looked into potential substituents that were expected to serve two purposes: optimizing the molecular packing in the solid state as well as implementing additional electronic features to fine-tune the band gap of the resulting extended dithienophospholes. In this context, we tried to access 2,6-bis(3′,4′-ethylenedioxothienyl) (EDOT) **6g** by a similar route as employed for the genuine bis(2′-thienyl) derivative **6f** using the (pinacol)boryl-functionalized EDOT (Scheme 2). The resulting functionalized dithienophosphole was expected to exhibit a fairly narrow band gap due to the pronounced electron-donor properties of the EDOT-moiety.[3,4] This expectation was also supported by the computed excitation energies (see below). Unfortunately, immediately after work up, the cross-coupled compound formed some polymeric material that was insoluble in common solvents and could therefore not be analyzed to satisfaction. The increased reactivity of the EDOT-coupled product can be attributed to strongly activated H atoms at the 5′-position of the EDOT units.

We then turned our focus on a variety of differently functionalized phenyl moieties. The 4′-fluorophenyl derivative **6h** was accessible by a Suzuki–Miyaura procedure similar to the thienyl derivative using the (pinacol)boryl-functionalized 4-fluorobenzene in toluene (Scheme 2). Its ^{31}P resonance of $\delta =$ 17.4 ppm relates very well to the one for the native bis(phenyl) compound **6a** (cf.: δ^{31}P = 17.4 ppm). We were able to obtain single crystals of **6h** from various solvents that were, however, too small for a satisfactory X-ray structure analysis. To also cover donor-function-

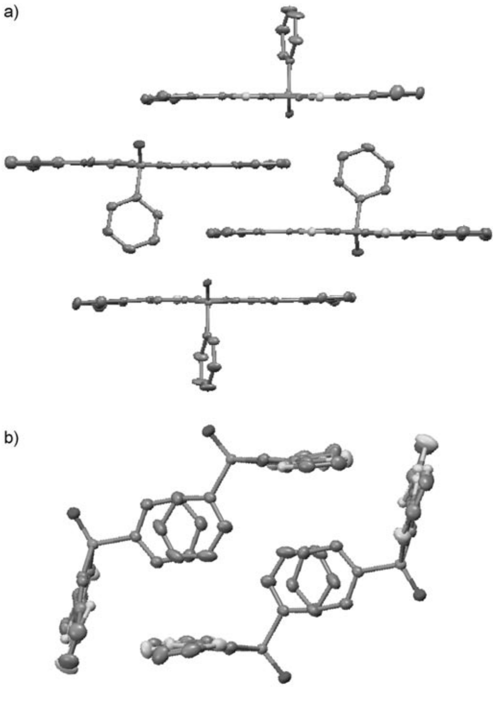


Figure 6. Molecular packing of a) **6e** and b) **6f** in the solid state.

alized phenyl substituents, we synthesized 2,6-bis(4′-diphenylanilino) **6i** via Stille-type protocol using the stannyl-functionalized triphenyl amine precursor **5i** in toluene (Scheme 2). The NPh_2 group was expected to further expand the degree of π conjugation throughout the nitrogen centers, as triphenyl amines are generally planar.[24] With respect to a potential application in organic devices, arylamino groups also introduce desirable hole-transport properties to the materials.[25] Surprisingly, the ^{31}P NMR resonance of $\delta = 17.5$ ppm for **6i** is comparable those of the homoaryl-functionalized dithienophospholes **6a–c**. This observation, in combination with the fact that the ^{31}P NMR resonances of all cross-coupled compounds **6a–i** are very similar ($\Delta\delta^{31}$P ≈ 1 ppm), indicates that the phosphorus center is indeed not very sensitive toward the extension of the π-conjugated system with varying substituents.

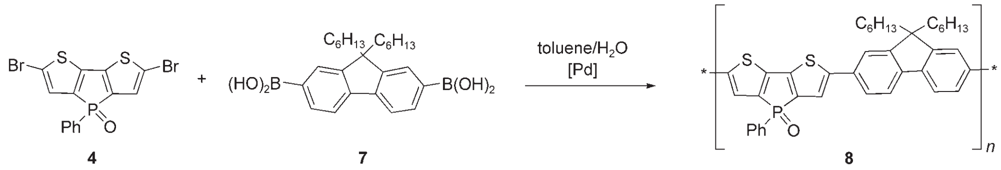
Optoelectronic properties: As mentioned in the introduction, all chemical modifications of the dithienophosphole scaffold reported so far, have resulted in materials with blue light-emitting features ($\lambda_{em} = 408$–470 nm).[13,16] Introduction of the halide substituents in **3** and **4** affords materials that showed emission in the blue-green region of the optical spectrum (**3**: $\lambda_{abs}(\pi\text{–}\pi^*) = 416$ nm, $\lambda_{em} = 471$ nm; **4**: $\lambda_{abs}(\pi\text{–}\pi^*) = 394$ nm, $\lambda_{em} = 473$ nm), which can be attributed to the electron-withdrawing character of these groups leading to a decrease of the LUMO energy levels.[13] A more significant red-shift of the optoelectronic features, could, however, be detected during the cross-coupling experiments, when irradiated with a UV lamp at 365 nm, as the fluorescence emission of the reaction mixtures noticeably started to change from blue-green to yellow/orange after a few hours. This feature supported the successful extension of the π-conjugated system and the feasibility of the general approach. Table 2 summarizes the optoelectronic data of the halogenated monomers **3** and **4** as well as the cross-coupled materials **6a–i**. As can be seen from the data, the increasing degree of π conjugation within the homoaryl series phenyl → biphenyl → naphthyl → anthranyl (**6a–d**) results in red-shifted absorption/emission properties affording green-yellow emitting materials (**6a**: $\lambda_{em} = 520$ nm; **6b**: $\lambda_{em} = 529$ nm; **6c**: $\lambda_{em} = 535$ nm; **6c**: $\lambda_{em} = 540$ nm), however, with significantly reduced photoluminescence quantum yield efficiencies of $\phi_{PL} = 0.36$–0.38, compared with the halogenated derivative ($\phi_{PL} = 0.56$ for **3**; 0.57 for **4**) and other known dithienophospholes ($\phi_{PL} = 0.51$–0.89).[13,16] This observation could be attributed to the additional degrees of freedom resulting from rotation about the ′cross-coupled′ single bonds in **6a–c**; for example, in case of **6e** the B3LYP/6-31+G* transition structure for the rotation about the "cross-coupled" single bond was 7.3 kcal mol^{-1} only. In fact, twisted end groups have been found to act as traps for the electron transport in related dithienosilole systems before.[21a] Nevertheless the drop of the quantum efficiency is surprising, as related extended dithienopyrroles show a drastic increase in their quantum efficiencies (0.1 → 50%!) compared with the native systems.[21d]

Table 2. Experimental and theoretical optical spectroscopy data for **3**,**4**, and **6a–i**.

Compound	λ_{abs} [nm][a]	λ_{em} [nm][b]	Intensity[e]	ϕ_{PL}
3 (4)	**416 (397)**	471 (473)		0.56[c] (0.57)[c]
6a	285, 299, 339, 382, **460**	520		0.36[d]
calcd	296, 305, 310, 317, **432**		0.72	
6b	295, 347, **452**	529		0.63[d]
calcd	–		–	
6c	279, 303, 353, 386, **486**	535		0.38[d]
calcd	–		–	
6d	285, 396, 453, **495**	540		0.38[d]
calcd	388, 389, 391, **397**, 407, 408		0.50	
6e	287, 331, 400(s), **454**	511		0.60[c]
calcd	308, 312, 329, **445**		0.90	
6f	290, 338, **485**	545		0.43[d]
calcd	314, 320, 325, 353, **467**		0.79	
6g	338, **456**, 488	456		0.37[d]
calcd	333, 335, 339, 369, **487**		0.87	
6h	292, 332, 393(s), **445**	519		0.68[c]
calcd	299, 307, 309, 320, **433**		0.72	
6i	278, 329, 380, 415, **527**	566		0.48[d]
calcd	–		–	

[a] λ_{max} for excitation in CH_2Cl_2 (π–π* transition in bold). [b] λ_{max} for emission in CH_2Cl_2. [c] Fluorescence quantum yield, relative to quinine sulfate (0.1 M H_2SO_4 solution) ±10%; excitation at 365 nm. [d] Fluorescence quantum yield, relative to rhodamine 101 (0.1 mm EtOH solution) ±10%; excitation at the respective excitation maximum (460–527 nm). [e] The calculated values in bold correspond to the intense transitions, for which the oscillator strength is given in the column "Intensity". The computed oscillator strength for the other transitions is smaller by at least one order of magnitude.

The functionalization with heteroaryls (2′-6′-picolyl: **6e**; 2′-thienyl: **6f**) revealed that the electron-rich thienyl moiety has a much stronger effect on the optoelectronic properties than the electron-poor picolyl group. The electron-accepting nature of the phosphorus center that, in combination with the donating ability of the thienyl groups in **6f**, should generate a smaller band gap than the presence of two acceptor groups in **6e** could explain this observation. The picolyl-functionalized derivative **6e** showed features ($\lambda_{abs}(\pi\text{–}\pi^*) = 454$ nm; $\lambda_{em} = 511$ nm) that were even slightly blue shifted from the bis(phenyl) derivative **6a**, however, with a significantly greater quantum yield efficiency ($\phi_{PL} = 0.60$), probably due to the intramolecular fixation of the picolyl end groups (see above). The bis(2′-thienyl) derivative **6f**, on the other hand, exhibited a rather large red shift ($\lambda_{abs}(\pi\text{–}\pi^*) = 485$ nm; $\lambda_{em} = 545$ nm) showing a yellow/orange emission with a decent quantum yield efficiency of $\phi_{PL} = 0.43$. The Kohn–Sham orbital energies obtained from the computations are consistent with these observations. The HOMO level of the thienyl derivative **6f** is by 0.11 eV higher than that of **6e** and the LUMO is at lower energy by 0.07 eV, resulting in a decrease of the band gap. We have shown before[13b] that both the HOMO and the LUMO of the dithienophosphole have a significant contribution at the position of the substitution, allowing for an interaction with the aryl group, the extent of which depends on the nature of the substituent MOs, as well as on their energies. In fact, the



4 **7** **8**

Scheme 3. Synthesis of a π-conjugated dithienophosphole polymer via Suzuki–Miyaura protocol.

HOMO energy of thiophene is higher than the highest energy π orbital of pyridine, while the opposite is true for the LUMO energies.[26] Accordingly, the combination of the dithienophosphole FMOs with these orbitals in the extended π system should behave similarly, resulting in a decreased HOMO–LUMO gap for **6f**, as it has indeed been observed.

The 4′-fluorophenyl-functionalized dithienophosphole **6h**, showed similar emission features to the native phenyl derivative **6a** (**6h**: $\lambda_{abs}(\pi-\pi^*)=445$ nm; $\lambda_{em}=519$ nm; cf. **6a**: $\lambda_{abs}(\pi-\pi^*)=460$ nm; $\lambda_{em}=520$ nm), however, with a larger Stokes shift of 74 nm compared with 60 nm for **6a**. The computed (Kohn–Sham) HOMO–LUMO gap is of similar value (3.23 eV) for both **6a** and **6h**, the gap remains unchanged since both orbitals of **6h** are stabilized in case by 0.1 eV. This selective modification of the absorption properties by functionalization of the 2,6-substituents has previously been established for related dithienophospholes.[13b] Remarkably, the quantum yield efficiency of $\phi_{PL}=0.68$ for **6h** is almost twice as high as that for **6a**. This observation, and the fact that the excitation spectrum of **6h** also shows fewer features than that for **6a**, supports the significant effect of the fluoro substituents on the optoelectronic properties of **6h**, even in case of molecules with similar HOMO–LUMO gap. Since the increase of the quantum yield is likely to be related to the flexibility of the system (allowing fast relaxation via activating low frequency vibrations) we have computed the rotational barriers of the phenyl group for **6a** (3 kcal mol^{-1}) and for the 4′-F-phenyl group for **6h** (2.8 kcal mol^{-1}). The difference between the two barriers is minor, it seems that other factors should be responsible for the observed difference in the quantum yield.

The diphenylanilino derivative **6i**, on the other hand, showed the strongest red shift of the extended molecular materials present herein, with a bright orange emission ($\lambda_{em}=566$ nm). The excitation spectrum is dominated by the π–π* transition ($\lambda_{abs}=527$ nm) that is very narrow, indicating a fairly rigid π-conjugated system.[27] The quantum yield efficiency of $\phi_{PL}=0.48$ is relatively high for the series **6a–i** and also supports the rigid, extended structure in **6i**.

Synthesis and optoelectronic properties of a π-conjugated dithienophosphole-fluorene copolymer: To verify whether a more significant extension of the degree of π conjugation would afford a material with red emission features, we targeted the dithienophosphole–fluorene copolymer **8**. The polymer was accessible via Suzuki–Miyaura protocol, in analogy to the synthesis of **6a** and **6c**, in a biphasic medium (toluene/water) using **5** and an appropriately diborylated fluorene (**7**) with solubilizing hexyl groups (Scheme 3). Upon progression of the reaction under reflux for 20 h, the fluorescence of the solution slowly shifted from green to orange. Unfortunately, the compound started to precipitate out of the reaction mixture due the reduced solubility of the product and the reaction could thus not proceed any further. However, the strong red shift ($\Delta\lambda > 100$ nm) in the optoelectronic features of the compound (**8**: $\lambda_{abs}=507$ nm; $\lambda_{em}=546$ nm, $\phi_{PL}=0.48$) clearly indicated the successful cross-coupling step (cf. **4**: $\lambda_{abs}=366$ nm; $\lambda_{em}=453$ nm). Note that the red shift observed for the polymer **8** is not as strong as that for the diphenylanilino derivative **6i** (cf.: $\lambda_{abs}(\pi-\pi^*)=527$ nm; $\lambda_{em}=566$ nm) indicating the presence of short polymer chains only. Due to the extremely low solubility of the polymer, no comprehensive NMR analysis could be performed. A GPC analysis, on the other hand, afforded a molecular weight of $M_w=3200$ g mol^{-1} (PDI=1.37) for the THF-soluble fraction of the product, which was only a minor portion of the bulk sample. The results, however, indicate that corresponding polymers are accessible, but further studies are needed to drastically increase the solubility of the macromolecular materials. It appears essential to keep the polymer in solution for as long as possible to achieve a chain length that eventually supports red light-emitting features for the material.

A potential option to achieve this goal, comes with the substituent at the phosphorus center that can conveniently be modified in the synthesis of the dithienophosphole precursors.[13] Suitable substituents for this purpose could either be alkyls such as 2-ethylhexyl or functionalized phenyl groups. Studies toward the synthesis of suitable dithienophosphole monomers and corresponding polymers are currently underway.[28]

Theoretical calculation of the structural parameters: The computed structural properties of the investigated molecules are similar to those obtained from the X-ray structures. The substitution of the dithieno[3,2-*b*:2′,3′-*d*]phospholes does not have a large effect on the structure. All the molecules are planar, with the exception of **6d**, where the anthranyl substituent occupies a perpendicular position to the central dithieno[3,2-*b*:2′,3′-*d*]phosphole unit due to steric reasons. Accordingly, this compound exhibits the highest HOMO–LUMO gap, and also the largest excitation energy. The aromaticity measures (Bird index or NICS(0) values, given as Supporting Information) do not provide too much information, since they differ only slightly between the different cross-coupled compounds. Furthermore, they do not represent the conjugation in the entire system, but only a fragment cycle. The distribution of the CC bond lengths, however, correlates with the band gap as it is shown in Figure 7.

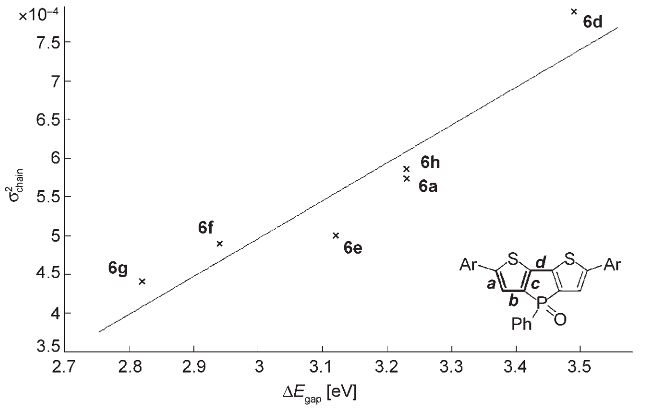


Figure 7. Standard deviation of the computed carbon–carbon bond lengths in the central dithienophosphole unit against the Kohn–Sham band gap.

The compound with the smallest HOMO–LUMO gap (**6g**) exhibits the most even distribution of the CC bond lengths.

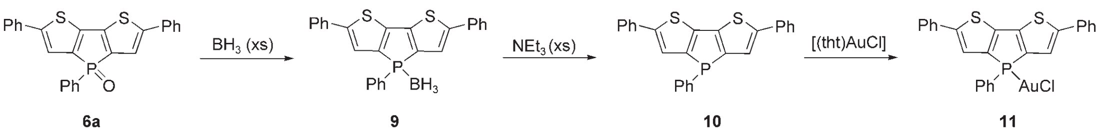
Fine-tuning of cross-coupled, extended dithieno[3,2-*b*:2′,3′-*d*]-phospholes: To prevent potential poisoning of the catalyst employed during the cross-coupling procedure, we decided to use the oxidized dibromodithienophosphole **4**; this strategy successfully gave access to the desired extended π-conjugated products **6a**–**i** (see above). However, the resulting products seem to have lost their potential to be fine-tuned via modification of the phosphorus center. This feature, on the other hand, is the major advantage of phosphorus-based molecular materials over their genuine organic counterparts. For that reason we performed studies toward the regeneration of the trivalent phosphorus center to then again be able to tailor the properties of the extended materials via systematic modification of this center. To our satisfaction, the trivalent phosphorus center can conveniently be recovered in a two-step, one-pot reaction (Scheme 4). Treatment of the 2,6-bis(phenyl)-functionalized dithieno-phosphole oxide **6a** with a slight excess of borane (applied as dimethyl sulfide adduct) gave access to the borane adduct **9**, which was then converted into the phosphole **10** by addition of an excess of triethylamine. The successful conversion of the phosphorus center was easily monitored by ^{31}P NMR spectroscopy resulting in only one, characteristically shifted,[13] resonance signal, respectively (**6a**: $\delta = 17.4$ ppm; **9**: $\delta = 14.9$ ppm; **10**: $\delta = -22.2$ ppm). The same is true for the optoelectronic properties of the compounds **6a**, **9** and **10**, showing characteristic blue-shifted values for their π–π* absorptions (**6a**: $\lambda_{abs} = 460$ nm, **9**: $\lambda_{abs} = 440$ nm, **10**: $\lambda_{abs} = 431$ nm), and their fluorescence emissions (**6a**: $\lambda_{em} = 520$ nm, **9**: $\lambda_{em} = 485$ nm, **10**: $\lambda_{em} = 470$ nm, see also Table 3).[13] With the phosphorus center in **10** recovered, we were then able to access the corresponding gold-complex **11** in almost quantitative yield (δ^{31}P = 14.9 ppm). Gold complexes of dithienophospholes were found to exhibit strong fluorescence intensities with characteristic absorption and emission properties.[16b] The same is true for gold-complex **11**, at least to some extent, as the absorption spectrum shows less high-energy transitions between 280 and 380 nm, and the π–π* transition dominates the spectrum. Furthermore, the emission wavelength of $\lambda_{em} = 497$ nm nicely fits within the series of the compounds described herein closing the gap between $\lambda_{em} = 485$ nm for **9** and $\lambda_{em} = 511$ nm for **6e**. It should also be mentioned that the quantum yield efficiency of **11** ($\phi_{PL} = 0.64$) is in the range usually observed for dithienophospholes emphasizing the value of the functionalization with a gold moiety.

Table 3. Optical spectroscopy data for **6a**, **8**–**11**.

Compound	λ_{abs} [nm][a]	λ_{em} [nm][b]	ϕ_{PL}
8	275, 356, 457, **515**	546	0.48[d]
6a	285, 299, 339, 382, **460**	520	0.36[d]
9	285, 323, 376, **440**	485	0.58[c]
10	291, 322, 363, **431**	470	0.49[c]
11	284, 328, **432**	497	0.64[c]

[a] λ_{max} for excitation in CH_2Cl_2 (π–π* transition in bold). [b] λ_{max} for emission in CH_2Cl_2. [c] Fluorescence quantum yield, relative to quinine sulfate (0.1 m H_2SO_4 solution) ±10%; excitation at 365 nm. [d] Fluorescence quantum yield, relative to rhodamine 101 (0.1 mm EtOH solution) ±10%; excitation at 460 or 515 nm, respectively.

We were also able to obtain single crystals of **11** from a concentrated acetone solution at room temperature that were suitable for an X-ray diffraction study. The most distinct feature of the molecular structure of **11** in the solid state is an apparent Au–Au interaction (distance: 2.975 Å)[29] resulting from the formation of dimers linked via the Au centers (Figure 8). Note that the center of this Au–Au bond is also a crystallographic inversion center. The fixation of the two molecules in close proximity leads to an almost coplanar arrangement of the dithienophosphole frameworks indicating some π interactions (distance: 3.7–4.3 Å). The terminal phenyl groups, however, are significantly twisted out of the plane of the dithienophosphole core



Scheme 4. Regeneration of the trivalent P-center in extended dithienophospholes and subsequent functionalization with AuCl.

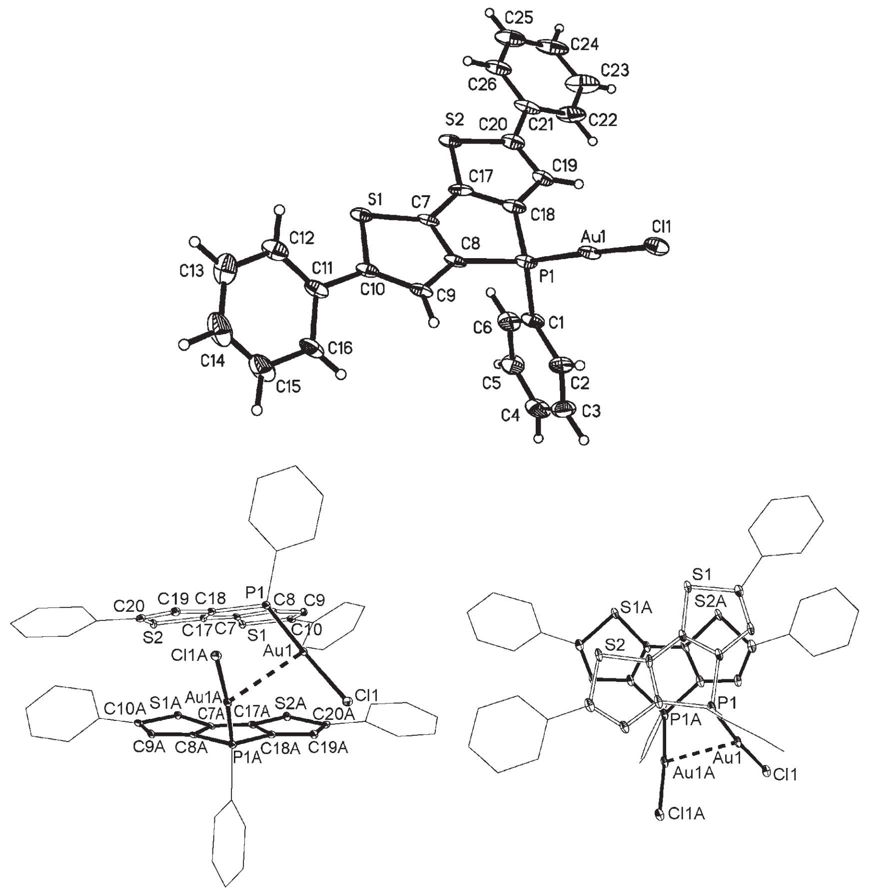


Figure 8. Molecular structure (top) and dimeric organization (bottom) of **11** in the solid state (40% probability level). One acetone solvent molecule is omitted for clarity. Selected bond lengths [Å]: Au1−P1 2.228(2), Au1−Cl1 2.303(2), Au1−Au1A 2.9757(8), P1−C1 1.808(7), P1−C18 1.808(8), P1−C8 1.812(8), C7−C8 1.389(11), C7−C17 1.420(10), C8−C9 1.405(10), C9−C10 1.368(12), C10−C11 1.476(11), C17−C18 1.415(12), C18−C19 1.418(10), C19−C20 1.382(12), C20−C21 1.477; torsion angles: C20-S2-Ph: 31.5, C10-S1-Ph: 14.4°.

(torsion angles = 14.4, 31.5°), which can be attributed to packing effects resulting from the close proximity of the two dithienophosphole moieties. The P-Au distance of 2.228(2) Å compares to that of a related dithienophosphole Au complex (2.2249(12) Å).[16b] The same is true for the bond lengths and angles of the dithienophosphole framework that relate to other structurally characterized dithienophospholes reported in the literature as well as herein. The presence of the Au–Au interaction in the solid state motivated us to also investigate the photophysical properties of **11** in the solid state.[30] However, in contrast to the studies performed on a related thienyl-substituted phosphole Au-complex by Réau et al.,[12a] complex **11** does not show the corresponding transitions at lower energies. The absence of d^{10}-Au–Au transitions in the solid state, on the other hand, was also found with gold complexes of bis(phosphino)dithiophenes, reported by Wolf and co-workers.[31] The gold complex **11** shows a maximum wavelength for absorption at $\lambda_{abs} = 486$ nm and a single emission maximum at $\lambda_{em} = 522$ nm, red-shifted from its values in solution, likely due to intermolecular interaction in the solid state.

Conclusion

In summary we have presented the 2,6-functionalization of dithieno[3,2-*b*:2′,3′-*d*]phospholes with halides that opened up the access to extended, well-defined π-conjugated molecular materials via several cross-coupling strategies. Depending on the degree on π conjugation within cross-coupled moieties as well as their electron-donor/acceptor character, the materials **6a–i** show red-shifted optoelectronic properties with different emission colors ranging form green via yellow to orange. Although some of the modifications led to materials with noticeably decreased photoluminescence quantum yields compared with their “non-extended” congeners, the exceptionally pronounced emission intensities of the dithienophosphole core, still provided materials with intriguing properties for an application in organic electronic devices. Our investigations have revealed that small changes in the functional groups can have significant impact on the structural (packing) but also the optoelectronic properties of the extended materials, emphasizing the importance of systematic studies focusing upon structure/property relationships. As the presence of proper intermolecular interactions are key to the success of organic electronics, a broad variety of related materials need to be investigated to optimize their potential use. DFT calculations on the extended π-conjugated dithienophospholes have again been proven to very valuable, helping to understand the effects of the different functional groups and predicting their structural as well as their optoelectronic properties. The studies also revealed that the electronic structure of the materials could selectively be designed by either targeting the HOMO- or the LUMO levels of the respective materials via proper choice of the cross-coupled aryl group or the functionalization of the phosphorus center. In the context of our investigations, we were able to “regenerate” the trivalent phosphorus center in the extended π-conjugated dithienophospholes to allow further fine-tuning of the materials properties. The latter represents the most valuable tool for organophosphorus-based materials, setting them apart from their genuine organic counterparts. The trivalent phosphorus center in the materials can conveniently be manipulated in many different ways via very simple chemical reactions that have a significant effect on their optoelectronic properties. In order to access red-emitting materials we targeted a copolymer based on dithienophosphole and fluorene building-blocks, but its reduced solubility prevented the formation of long chains with the desired emission properties. The isolation of the poorly soluble, orange-emitting polymer **8**, on the other hand, provided the proof-of-principle, indicating that our strategy can be successful, when suitable solubilizing groups can be found. We are currently performing detailed studies that address this issue. However, as the diphenylanilino derivative **6i** shows the strongest red shift of all the extended materials presented in the context of this work, it appears possible, to also access red-emitting molecular materials with a well-defined π-conjugated system. We are therefore currently also looking into suitable aryl groups with very pronounced donor or acceptor properties, respectively, as well as asymmetrically substituted dithienophospholes, to eventually cover the full optical spectrum.

Experimental Section

Crystallographic data: CCDC-639257 (**3**), -639256 (**4**), -639259 (**6e**), -639260 (**6f**), -639258 (**11**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; see also Table 4.

Calculations: Theoretical calculations have been carried out at the B3LYP/6-31G* level[32] by using the GAUSSIAN 03 suite of programs.[33] This level of the theory has provided satisfactory results for the phosphole–thiophene oligomers before.[13b] The geometries were fully optimized and at the resulting structures second derivatives were calculated.

Table 4. Crystal data and structure refinement for **3**, **4**, **6e**, **6f** and **11**.[a]

	3	**4**	**6e**	**6f**	**11**
formula	$C_{14}H_7I_2OPS_2$	$C_{14}H_7Br_2OPS_2$	$C_{26}H_{19}N_2OPS_2\cdot CH_3CN$	$C_{22}H_{13}OPS_4$	$C_{27.5}H_{20}OPS_2AuCl$
M_r	540.09	446.11	511.58	452.53	685.94
T [K]	120(2)	295(2)	133(2)	130(2)	140(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	$C2/c$ (no.15)	$C2/c$ (no.15)	$P\bar{1}$ (no.2)	$P\bar{1}$ (no.2)	$Pccn$(no.56)
a [Å]	21.604(13)	21.116(3)	11.724(2)	11.3290(11)	19.185(5)
b [Å]	10.378(6)	10.293(2)	13.901(3)	11.5898(11)	13.654(3)
c [Å]	17.111(10)	16.289(10)	18.049(4)	16.3997(15)	18.905(5)
α [°]	90	90	81.94(3)	79.759(2)	90
β [°]	121.291(12)	121.809(3)	71.10(3)	75.610(2)	90
γ [°]	90	90	65.33(3)	73.166(2)	90
V [Å^3]	3279(3)	3015.9(8)	2528.9(9)	1983.3(3)	4952.2(2)
Z	8	8	4	4	8
ρ_{calcd} [Mg m^{-3}]	2.168	1.965	1.344	1.516	1.937
μ [mm^{-1}]	4.179	5.749	0.301	0.571	6.305
F(000)	1976	1728	1064	928	2800
crystal size [mm^3]	0.24 × 0.19 × 0.06	0.47 × 0.22 × 0.21	0.18 × 0.12 × 0.05	0.45 × 0.38 × 0.10	0.10 × 0.12 × 0.20
θ range [°]	2.21–28.61	2.26–28.31	1.19–27.06	2.13–29.05	2.83–23.94
index ranges	$-28 \leq h \leq 27$	$-28 \leq h \leq 27$	$-14 \leq h \leq 14$	$-15 \leq h \leq 15$	$-25 \leq h \leq 25$
	$-13 \leq k \leq 13$	$-13 \leq k \leq 13$	$-17 \leq k \leq 17$	$-15 \leq k \leq 15$	$-18 \leq k \leq 13$
	$-23 \leq l \leq 21$	$-21 \leq l \leq 21$	$-21 \leq l \leq 22$	$-22 \leq l \leq 22$	$-25 \leq l \leq 17$
reflections collected	12111	19916	19863	27983	32110
independent reflections	4134	3732	10836	10466	6174
R(int)	0.1236	0.0319	0.0785	0.0323	0.0953
completeness to θ [°] (%)	28.61 (98.7)	28.31 (99.2)	27.06 (97.8)	29.05 (98.7)	28.33 (99.9)
absorption correction	empirical	empirical	empirical	empirical	empirical
max./min. transmission	0.7876/0.4337	0.3782/0.1731	0.9479/0.9851	0.9720/0.9042	0.5715/0.3655
data/restraints/ parameters	4134/0/181	3732/0/181	10836/192/637	10466/18/508	6174/0/291
GOF on F^2	1.023	0.953	1.196	1.079	1.011
final R indices [$I > 2\,s(I)$]					
R_1	0.0590	0.0320	0.0801	0.0493	0.0508
wR_2	0.1209	0.1077	0.1642	0.1305	0.1123
R indices (all data)					
R_1	0.0882	0.0381	0.1936	0.0648	0.0940
wR_2	0.1385	0.1163	0.2430	0.1393	0.1289
largest diff. peak/hole [e Å^3]	1.735/−2.256	1.287/−0.665	0.743/−0.615	1.544/−0.463	1.294/−2.341

[a] The refinement method was full-matrix least-squares on F^2 for all five compounds.

For the minima only positive eigenvalues of the Hessian matrix were obtained, while the rotational transition structures were characterized by a single imaginary frequency of the rotational motion. The vertical excitation energies were calculated at the optimized structures by the time dependent density functional (TD) method, using the B3LYP functional and the 6-31G* basis set. The Bird index was calculated according to the original procedure of Bird,[34] however, when using the Gordy equation[35] to obtain bond orders from the calculated bond lengths we used the "a" and "b" constants developed from the B3LYP/6-31G* optimized single and double bonded molecules (e.g. for the CC bond we used ethane and ethylene having bond orders 1 and 2, respectively). Nucleus Independent Chemical Shifts[36] were calculated at the ring center (NICS(0)), since the out of plane substituents at the phosphorus could possibly affect the shielding values.

General procedures: Reactions were carried out in dry glassware and under inert atmosphere of purified argon using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled. *n*BuLi (2.5 M in hexane), H_2O_2 (30 % in H_2O), $BH_3{\cdot}SMe_2$ (1 M in CH_2Cl_2), iodine, NBS, thiophene, 4-bromobiphenyl, 1-fluoro-4-iodobenzene, phenylboronic acid, naphthalene-2-boronic acid, CsF, and $[Pd(PPh_3)_4]$ were used as received. 2-Isopropoxy-4,4′,5,5′-tetramethyldioxoborolane, Bu_3SnCl, and Et_3N were freshly distilled prior to use. Dithieno[3,2-*b*:2′,3′-*d*]phosphole **2**,[13a] and [(tht)AuCl][37] were prepared by literature methods. ^{1}H, ^{13}C, ^{31}P, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker DRX 400, Varian Mercury 200 or Unity 500 MHz-spectrometer. Chemical shifts were referenced to external 85 % H_3PO_4 (^{31}P), $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F) or TMS (^{13}C, ^{1}H). SIMS Mass spectra were collected on a Finnigan MAT95 instrument using a nitrobenzyl alcohol martix and Cs ions. Elemental analyses were performed by the Microanalytical Laboratory of the Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, Mainz and the Institut für Organische Chemie, RWTH-Aachen University. Crystal data and details of the data collection are provided in Table 4. Diffraction data for **3**, **4**, **6e**, **6f**, and **11** were collected on a Bruker SMART D8 goniometer with APEX CCD detector, using $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å (graphite monochromator). The structures were 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.

Synthesis of 3: LDA (3.6 mmol in 2.0 mL THF) was added to a solution of dithieno[3,2-*b*:2′,3′-*d*]phosphole **2** (0.5 g, 1.8 mmol) in THF (40 mL) at −78 °C and the yellow/brown suspension was stirred for 10 min at that temperature before elemental iodine (1.1 g, 4.3 mmol) was added. The resulting dark brown solution was then warmed to room temperature and stirred for another 20 min. After removal of the solvent under vacuum the residue was taken up in dichloromethane and filtered over neutral alumina. The filtrate was evaporated to dryness, taken up in acetone and exposed to air overnight. Brown single crystals of **3**, suitable for X-ray structure analysis, were obtained from the concentrated acetone solution at room temperature (0.1 g, 10 %). ^{31}P{^{1}H} NMR (202.2 MHz, $CDCl_3$): $\delta = 16.3$ ppm; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.70$ (br dd, $^{3}J(H,P) = 13.7$, 13.7 Hz, 2 H; o-Ph), 7.56 (br t $^{3}J(H,H) = 7.3$ Hz, 1 H; p-Ph), 7.40 (br dt, $^{3}J(H,H) = 7.6$, 3.4 Hz, 2 H; *m*-Ph), 7.28 ppm (d, $^{2}J(H,H) = 2.1$ Hz, 2 H; thiophene-H); ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$): $\delta = 149.8$ (d, $J(C,P) = 22.5$ Hz; Ar), 139.5 Hz (d, $^{1}J(C,P) = 108.4$ Hz; *ipso*-Ar), 134.9 (d, $^{2}J(C,P) = 12.9$ Hz; *o*-Ar), 132.9 (d, $^{4}J(C,P) = 3.3$ Hz; *p*-Ph), 130.8 (d, $^{3}J(C,P) = 10.7$ Hz; *m*-Ar), 128.5 (d, $^{1}J(C,P) = 110.6$ Hz; *ipso*-Ph), 129.0 (d, $J(C,P) = 18.2$ Hz, *o*-Ph), 76.4 ppm (d, $^{3}J(C,P) = 16.1$ Hz; Ar-I); elemental analysis calcd (%) for $C_{14}H_7I_2OPS_2$ (540.12 g mol^{-1}): C 31.13, H 1.31, S 11.87; found: C 31.28, H 1.32 S 11.88.

Synthesis of 4: NBS (7.1 g, 40 mmol) was added to a solution of dithieno[3,2-*b*:2′,3′-*d*]phosphole **2** (2.7 g, 10 mmol) in acetic acid (75 mL) and $CHCl_3$ (150 mL) at room temperature. The solution was stirred for 5 h. After neutralizing the reaction mixture with aqueous NaOH the product was extracted with $CHCl_3$. The organic layer was washed with aqueous NaOH and H_2O, respectively, and dried with $MgSO_4$. After evaporation of the solvent the crude product **4** was obtained as a yellow powder (3.3 g, 76 %). Recrystallization from acetone provided yellow crystals of **4** suitable for X-ray structure analysis. ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = 16.3$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.72$ (dd, $^{3}J(H,P) = 13.8$, 7.2 Hz, 2 H; *o*-Ph), 7.48 (t, $^{3}J(H,H) = 7.4$ Hz, 1 H; *p*-Ph), 7.48 (td, $^{3}J(H,H) = 7.5$, $^{4}J(H,P) = 3.2$ Hz, 2 H; *m*-Ph), 7.14 ppm (d, $^{3}J(H,P) = 2.2$ Hz, 2 H; thiophene-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 145.2$ (d, $J(C,P) = 22.5$ Hz; Ar), 137.6 Hz (d, $^{1}J(C,P) = 110.9$ Hz; *ipso*-Ar), 132.9 (d, $^{4}J(C,P) = 2.6$ Hz; *p*-Ph), 130.8 (d, $^{2}J(C,P) = 11.3$ Hz; *o*-Ar), 128.3 (d, $^{1}J(C,P) = 110$ Hz; *ipso*-Ph), 129.2 (d, $^{2}J(C,P) = 13.0$ Hz, *o*-Ph), 128.4 ppm (d, $^{3}J(C,P) = 13.8$ Hz; *m*-Ph), 115.3 ppm (d, $^{3}J(C,P) = 18.2$ Hz; Ar-Br); elemental analysis calcd (%) for $C_{14}H_7Br_2OPS_2$ (446.12): C 37.69, H 1.58, S 14.38; found: C 37.54, H 1.52, S 14.34.

Synthesis of (4-biphenyl)tributyltin (5b): *n*BuLi (3.43 mL, 8.5 mmol) was added drop wise to a solution of 4-bromobiphenyl (2.0 g, 8.5 mmol) in THF (20 mL) at −78 °C. After adding Bu_3SnCl (2.76 g, 8.5 mmol) the mixture was stirred 1 h at room temperature. All volatiles were subsequently removed from the yellow solution by evaporation. The residue was taken up in diethyl ether and filtered over neutral alumina. The product **5b** was obtained as colorless oil (3.2 g, 85 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.32$–6.85 (m; 9 H; biphenyl), 1.45–1.19 (m; 6 H; alkyl-CH_2), 1.16–0.91 (m; 12 H; alkyl-CH_2), 0.65–0.55 ppm (m; 9 H; alkyl-CH_3).

Synthesis of 2-tributyltin-6-methylpyridine (5e): *n*BuLi (6.4 mL, 16 mmol) was added drop wise to a solution of 2-bromo-6-methylpyridine (2.5 g, 14.5 mmol) in THF (35 mL) at −78 °C and stirred for 90 min. After adding Bu_3SnCl (4.73 g, 14.5 mmol) the mixture was allowed to warm up to room temperature. H_2O (15 mL) was added and the product was extracted with diethyl ether (3×20 mL). All volatile substances where removed by evaporation. The residue was taken up in a mixture of pentane and acetone and filtered over neutral alumina. Evaporation of the solvent afforded the product **5e** as colorless oil (4.9 g, 90 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.35$ (t, $^{3}J(H,H) = 7.3$ Hz, 1 H; 4-pic), 7.18 (d, $^{3}J(H,H) = 7.3$ Hz, 1 H; 5-pic), 6.95 (d, $^{3}J(H,H) = 7.8$ Hz, 1 H; 3-pic), 2.58 (s, 3 H; pic-CH_3), 1.66–1.52 (m, 6 H; alkyl-CH_2), 1.41–1.32 (m, 6 H; alkyl-CH_2), 1.22–1.09 (m, 6 H), 1.07–0.87 ppm (m, 9 H; alkyl-CH_3).

Synthesis of 2-pinacolborylthiophene (5f): *n*BuLi (4.0 mL, 10 mmol) was added drop wise to a solution of thiophene (8.41 g, 10 mmol) in THF (20 mL) at −78 °C. The solution was stirred for 30 min at room temperature. After cooling to −78 °C, 2-isopropoxy-4,4′,5,5′-tetramethyldioxoborolane (1.86 g, 10 mmol) was added and the reaction mixture was stirred for 20 min at room temperature. The solvent was removed under vacuum and the residue was taken up in $CHCl_3$. Under vigorous stirring, aqueous 5 N HCl was added (20 mL). The organic layer was collected and dried over $MgSO_4$. After evaporation of the solvent the product **5f** was recrystallized from pentane (2.0 g, 95 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.64$ (d, $^{3}J(H,H) = 3.2$ Hz, 1 H; 3-thiophene), 7.62 (d, $^{3}J(H,H) = 4.6$ Hz, 1 H; 5-thiophene), 7.24 (dd, $^{3}J(H,H) = 4.8$, 3.6 Hz, 1 H; 4-thiophene), 1.33 ppm (s, 12 H; CH_3).

Synthesis of 1-fluoro-4-pinacolborylbenzene (5h): *n*BuLi (4.8 mL, 12 mmol) was added drop wise to a solution of 1-fluoro-4-bromobenzene (1.75 g, 10 mmol) in a solvent mixture of toluene (16 mL) and THF (4 mL) at −78 °C. The solution was stirred for 30 min at −20 °C, then 2-isopropoxy-4,4′,5,5′-tetramethyldioxoborolane (2.23 g, 12 mmol) was added at that temperature and the reaction mixture was stirred for another 20 min at room temperature. The solvent was removed under vacuum and the residue taken up in CH_2Cl_2. Under vigorous stirring, aqueous 5 N HCl was added (20 mL). The organic layer was collected and dried with $MgSO_4$. After evaporation of the solvent, the product **5h** was obtained as colorless oil (2.0 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.85$ (dd, $^{3}J(H,H) = 8.5$ Hz, 2 H; 3-Ar), 7.15 (m, 2 H; 2-Ar), 1.35 ppm (s, 12 H; CH_3); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -108.3$ ppm (tt, $^{3}J(H,F) = 9.1$, $^{4}J(H,F) = 6.1$ Hz).

Synthesis of *N,N*-diphenyl-4-tributyltinaniline (5i): *n*BuLi (4.0 mL, 10 mmol) was added drop wise to a solution of 4-bromo-*N,N*-triphenylamine (1.75 g, 10 mmol) in THF (50 mL) at −78 °C and stirred 30 min at this temperature. Bu_3SnCl (3.42 g, 10.5 mmol) was added and the reaction mixture was stirred 3 h at room temperature. After removing all volatile materials in vacuum the residue was taken up in pentane and filtered through neutral alumina. After evaporation of the solvent **5i** was obtained as colorless oil (3.7 g, 67 %). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$

7.35 (m, 5H; Ar), 7.06 (m, 9H; Ar), 1.44 (m, 14H; alkyl-$\mathrm{CH_2}$), 1.03 (m, 4H; alkyl-$\mathrm{CH_2}$), 0.89 ppm (t, ^{3}J(H,H) = 7.1 Hz, 9H; alkyl-$\mathrm{CH_3}$).

Cross-coupling reactions

Synthesis of 6a: Phenylboronic acid **5a** (0.51 g, 4.15 mmol) and **4** (0.93 g, 2.07 mmol) were dissolved in toluene (40 mL). After adding an aqueous 2 M $\mathrm{Na_2CO_3}$ solution (23 mL) and $[\mathrm{Pd(PPh_3)_4}]$ (0.35 g, 0.3 mmol) the reaction mixture was refluxed for 24 h at 120 °C. The precipitated product and the organic layer were subsequently separated. After removing all volatile materials, the product was washed with pentane, heptane and diethyl ether to provide **6a** as a yellow powder (800 mg, 90 %). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta = 17.4$ ppm; ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): $\delta =$ 7.82 (dd, ^{3}J(H,P) = 13.5, 7.0 Hz, 2H; *o*-Ph), 7.55 (m, 5H), 7.46 (td, ^{3}J(H,H) = 7.5, ^{4}J(H,H) = 3.2 Hz, 2H; *m*-Ph), 7.39 (td, ^{3}J(H,H) = 7.0 Hz, 4H), 7.36 (d, ^{2}J(H,P) = 2.5 Hz, 2H; thiophene), 7.32 ppm (m, 2H); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 148.5$ (d, J(C,P) = 13.8 Hz; Ar), 144.4 (d, ^{3}J(C,P) = 23.4 Hz; Ar), 139.2 (d, ^{1}J(C,P) = 111.8 Hz; *ipso*-Ar), 133.3 (s; phenyl), 132.6 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 130.9 (d, ^{2}J(C,P) = 11.3 Hz; *o*-Ar), 130.0 (s; phenyl), 129.2 (s; phenyl), 129.0 (d, ^{3}J(C,P) = 13 Hz; *o*-Ph), 128.4 (s; phenyl), 126.7 (s; phenyl), 125.7 (s; phenyl), 121.5 ppm (d, ^{2}J(C,P) = 14.7 Hz; *m*-Ph); elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}OPS_2}$ (440.52): C 70.89, H 3.89; found: C 70.46, H 4.35.

Synthesis of 6b: Compounds **4** (956 mg, 2.14 mmol) and **5b** (1.9 g, 4.28 mmol) were dissolved in toluene (30 mL). A catalytic amount of $[\mathrm{Pd(PPh_3)_4}]$ (120 mg, 0.1 mmol) was added and the reaction mixture was refluxed for 20 h at 120 C. After evaporating all volatile materials the product **6b** was taken up in acetone, filtered over neutral alumina and washed with pentane, heptane and diethyl ether. The product was obtained as an orange powder (650 mg, 52 %). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta = 17.3$ ppm; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 7.83$ (7.77), 17.4 (dd, ^{3}J(H,P) = 13.8, 7.2 Hz, 2H; *o*-Ph), 7.85 (7.78) (td, ^{3}J(H,H) = 13.5, ^{4}J(H,H) = 1.2 Hz, 2H; *m*-Ph),7.62 (m, 9H),7.46 (m, 6H), 7.38 (m 4H), 7.14 (7.12) (d, ^{2}J(H,P) = 2.5 Hz, 2H; thiophene); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 145.2$ (d, J(C,P) = 22.5 Hz; Ar), 141.1 (d, ^{3}J(C,P) = 18.1 Hz; Ar), 138.0 (d, ^{1}J(C,P) = 110.1 Hz; *ipso*-Ar), 133.1 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 131.5 (d, ^{1}J(C,P) = 105.7; *ipso*-Ar), 130.8 (d, ^{2}J(C,P) = 11.3 Hz; *o*-Ar), 129.2 (s; biphenyl), 129.2 (d, ^{3}J(C,P) = 13 Hz; *o*-Ph), 129.1 (s; biphenyl), 128.9 (s; biphenyl), 128.4 (s; biphenyl), 128.3 (s; biphenyl), 127.8 (s; biphenyl), 127.5 (s; biphenyl), 126.9 (s; biphenyl), 121.5 ppm (d, ^{2}J(C,P) = 13.9 Hz; *m*-Ph).

Synthesis of 6c: Naphtalene-2-boronic acid **5c** (0.26 g, 1.5 mmol) and **4** (0.33 g, 0.74 mmol) were dissolved in toluene (10 mL). Aqueous 2 M $\mathrm{Na_2CO_3}$ solution (8.3 mL) and $[\mathrm{Pd(PPh_3)_4}]$ (0.09 g, 0.075 mmol) were added and the reaction mixture refluxed for 20 h at 120 °C upon which the orange product precipitated from solution. After separating the product from the aqueous layer it was washed with diethyl ether, pentane and acetone. Small red crystals of **6c** could be obtained from acetone and acetonitrile (380 mg, 90 %). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta =$ 17.3 ppm; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 7.90$ (d, ^{4}J(H,H) = 1.2 Hz, 2H; 1-naph.), 7.86 (dd, ^{3}J(H,H) = 7.0, ^{3}J(H,P) = 7.0 Hz, 2H; *o*-Ph), 7.80 (m, 6H), 7.63 (dd, ^{3}J(H,H) = 8.5, ^{4}J(H,H) = 1.7, 2H; 8-naph.), 7.55 (td, ^{3}J(H,H) = 7.5, ^{4}J(H,H) = 1.5 Hz, 1H; *p*-Ph), 7.49 (dd, ^{3}J(H,H) = 6.7, ^{4}J(H,H) = 1.5 Hz, 2H; naph.), 7.49 (dd, ^{3}J(H,H) = 6.7, ^{4}J(H,H) = 1.5 Hz, 2H; naph.), 7.47 (d, ^{3}J(H,H) = 1.7 Hz, 4H; thiophene and 3-naph.), 7.44 ppm (dd, ^{3}J(H,H) = 6.7, ^{4}J(H,H) = 1.2 Hz, 2H; naph.); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 148.6$ (d, J(C,P) = 14.7 Hz; Ar), 144.5 (d, ^{3}J(C,P) = 23.4 Hz; Ar), 139.1 (d, ^{1}J(C,P) = 111.8 Hz; *ipso*-Ar), 132.4 (s; naph.), 133.0 (s; naph.), 132.6 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 130.9 (d, ^{2}J(C,P) = 12.1 Hz; *o*-Ar), 130.7 (s; naph.); 129.5 (d, ^{3}J(C,P) = 13.2 Hz; *o*-Ph), 129.5 (d, ^{1}J(C,P) = 105.0 Hz; *ipso*-Ph), 128.9 (s; naph.); 128.0 (s; naph.), 127.7 (s; naph.), 126.8 (s; naph.), 126.4 (s; naph.), 124.2 (s; naph.), 123.6 (s; naph.), 121.7 ppm (d, ^{4}J(C,P) = 13.0 Hz; *m*-Ph); elemental analysis calcd (%) for $\mathrm{C_{34}H_{21}OPS_2{\cdot}0.5}$ acetone (568.64): C 74.85, H 4.25, S 11.26; found: C 74.88, H 4.40, S 11.11.

Synthesis of 6e: Compounds **5e** (0.31 g, 0.74 mmol) and **4** (0.17 g, 0.37 mmol) were dissolved in toluene (20 mL). $[\mathrm{Pd(PPh_3)_4}]$ (0.02 g, 0.015 mmol) was added and the mixture was refluxed for 20 h at 120 °C. After removing the solvent in vacuum, a brownish oil was obtained that was dissolved in acetone and filtered over neutral alumina to yield **6e** as yellow powder (162 mg, 93 %). Recystallization of the product from acetonitrile afforded single crystals of **6e** suitable for X-ray structure analysis. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta = 17.0$ ppm; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.72$ (dd, ^{3}J(H,P) = 13.1, 7.2 Hz, 2H; *o*-Ph), 7.47 (m, 5H), 7.37 (td, ^{3}J(H,H) = 7.6, ^{4}J(H,H) = 3.2 Hz, 2H; *m*-Ph), 7.30 (d, ^{3}J(H,H) = 7.9 Hz, 2H; pic), 6.95 (d, ^{3}J(H,P) = 7.6 Hz, 2H; thiophene-H), 2.49 ppm (s, 6H; $\mathrm{CH_3}$-pic); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 158.6$ (s; 2-pic), 150.8 (s; 6-pic), 150.1 (d, J(C,P) = 13.2 Hz; Ar), 139.5 (d, ^{1}J(C,P) = 112.5 Hz; *ipso*-Ar), 136.9 (s; 4-pic), 132.5 (d, ^{4}J(C,P) = 2.9 Hz; *p*-Ph), 130.9 (d, ^{3}J(C,P) = 12.0 Hz; *o*-Ar), 129.0 (d, ^{2}J(C,P) = 13.2 Hz; *o*-Ph), 122.3 (d, ^{3}J(C,P) = 14.4; *m*-Ph), 122.2 (s; 3-pic), 115.6 (s; 5-pic), 24.4 ppm (s; $\mathrm{CH_3}$-Pic); elemental analysis calcd (%) for $\mathrm{C_{26}H_{19}N_2OPS_2}$ (470.55): C 66.36, H 4.07, N 5.95, S 13.63; found: C 66.12, H 4.18, N 6.14, S 13.47.

Synthesis of 6f: Compounds **4** (1.95 mmol, 0.87 g) and **5f** (3.9 mmol, 0.82 g) were dissolved in THF (30 mL). After adding CsF (12 mmol, 1.8 g) and a catalytic amount of $[\mathrm{Pd(PPh_3)_4}]$ (0.12 mmol, 0.14 g), the reaction mixture was refluxed at 80 °C for 12 h. The product was extracted with $\mathrm{CHCl_3}$ taken up in acetone and filtered through neutral alumina. After washing with hot heptane, the product **5f** was recrystallized from acetonitrile (600 mg, 68 %). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta =$ 16.9 ppm; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 7.73$ (dd, ^{3}J(H,P) = 13.6, 7.28 Hz, 2H; *o*-Ph), 7.48 (td, ^{3}J(H,H) = 7.5, ^{3}J(H,H) = 1.7, 1H; *p*-Ph), 7.38 (td, ^{3}J(H,H) = 7.5, ^{4}J(H,P) = 3.0 Hz, 2H; *m*-Ph), 7.17 (dd, ^{3}J(H,H) = 5.20, ^{4}J(H,H) = 1.00 Hz, 2H; 2-thiophene), 7.09 (dd, ^{3}J(H,H) = 3.5, ^{3}J(H,P) = 1.00 Hz, 4H; 4,4′-thiophene), 6.94 ppm (dd, ^{3}J(H,H) = 5.0, ^{4}J(H,H) = 1.00 Hz, 2H; 3-thiophene); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 143.5$ (d, ^{3}J(C,P) = 22.5 Hz; Ar), 141.3 (d, ^{2}J(C,P) = 15.6 Hz; Ar), 139.1 (d, ^{1}J(C,P) = 111.8 Hz; *ipso*-Ar), 135.9 (s; 2-thiophene), 132.6 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 130.9 (d, ^{3}J(C,P) = 11.2 Hz; *o*-Ar), 129.1 (d, ^{1}J(C,P) = 13 Hz; *o*-Ph), 129.4 (d, ^{1}J(C,P) = 108 Hz; *ipso*-Ph), 128.1 (s; 4-thiophene), 125.5 (s; 5-thiophene), 124.5 (s; 3-thiophene), 121.9 ppm (d, ^{3}J(C,P) = 14.7 Hz; *m*-Ph); elemental analysis calcd (%) for $\mathrm{C_{22}H_{13}OPS_4}$ (452.58): C 58.38, H 2.90; found: C 58.22, H 2.96.

Synthesis of 6h: Compounds **5h** (590 mg, 2.67 mmol) and **4** (596 mg, 1.3 mmol) were dissolved in THF (40 mL). $[\mathrm{Pd(PPh_3)_4}]$ (90 mg, 0.081 mmol) and CsF (1.23 g, 8.1 mmol) were added and the reaction mixture was refluxed 20 h at 80 °C. The product was extracted with $\mathrm{CHCl_3}$, the organic layer washed with water and dried with $\mathrm{MgSO_4}$. After evaporation of the solvent the residue was taken up in $\mathrm{CHCl_3}$ again and filtered through neutral alumina. The product was obtained as an orange solid (562 mg, 91 %). Recrystallization from acetonitrile afforded **6h** as small red needle-shaped crystals. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta = 17.4$ ppm; ^{19}F NMR (470 MHz, $\mathrm{CDCl_3}$): −112.6 ppm (m); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 7.74$ (dd, ^{3}J(H,P) = 13.5, ^{3}J(H,H) = 7.0 Hz, 2H; *o*-Ph), 7.47 (m, 5H), 7.39 (td, ^{3}J(H,H) = 7.7, ^{4}J(H,P) = 3.2 Hz, 2H; *m*-Ph), 7.21 ppm (d, ^{2}J(H,P) = 2.5 Hz, 2H; thiophene), 7.02 ppm (t, ^{3}J(H,H) = 8.5 Hz, 4H; F-phenyl); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta =$ 162.8 (d, ^{1}J(C,F) = 248 Hz; *ipso*-F-phenyl), 147.3 (d, J(C,P) = 14.7 Hz; Ar), 144.3 (d, ^{3}J(C,P) = 22.5 Hz; Ar), 139.7 (d, ^{1}J(C,P) = 111.8 Hz; *ipso*-Ar), 132.6 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 130.9 (d, ^{2}J(C,P) = 11.2 Hz; *o*-Ar), 129.6 (d; ^{4}J(C,F) = 2.6 Hz; *p*-F-phenyl), 129.1 (d, ^{3}J(C,P) = 13.0 Hz; *o*-Ph), 127.5 (d; ^{3}J(C,F) = 8.7 Hz; *m*-F-phenyl), 121.5 (d, ^{4}J(C,P) = 14.7 Hz; *m*-Ph); 116.2 ppm (d, ^{2}J(C,F) = 22.5 Hz; *o*-F-phenyl); elemental analysis calcd (%) for $\mathrm{C_{26}H_{15}BF_2OPS_2}$ (476,5): C 65.54, H 3.17; found: C 65.17, H 3.38.

Synthesis of 6i: Compounds **5i** (1.92 g, 3.6 mmol) and **4** (822 mg, 1.8 mmol) were dissolved in toluene (40 mL). $[\mathrm{Pd(PPh_3)_4}]$ (0.21 g, 0.18 mmol) was added and the mixture was refluxed for 20 h at 120 °C. After removing the solvent in vacuum, a red oil was obtained that was dissolved in acetone and filtered over neutral alumina. The filtrate was evaporated to dryness and washed with pentane and diethyl ether to afford **6i** as red solid (1.23 g, 88 %). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (80 MHz, $\mathrm{CDCl_3}$): $\delta =$ 17.6 ppm; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 7.80$ (m, 2H; *o*-Ph), 7.54 (m, 1H; *p*-Ph), 7.45 (m, 2H; *m*-Ph), 7.39 (4H, *m*-Ar), 7.27 (m, 6H), 7.24 (d, 2H; thiophene), 7.08 ppm (m, 15H); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 148.4$ (d, J(C,P) = 14.7 Hz; Ar), 148.0 (s; N-Ph), 147.2 (s; N-Ph), 143.6 (d, J(C,P) = 24.3 Hz), 138.7 (d, ^{1}J(C,P) = 111.8 Hz; *ipso*-Ar), 132.5 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 130.9 (d, ^{2}J(C,P) = 11.9 Hz; *o*-Ar), 129.4 s, 128.9

(d, ^2J(C,P) = 13.0 Hz; *o*-Ph), 127.0 (s; N-Ph), 126.4 (s; N-Ph), 124.8 (s; N-Ph), 123.3 (d, J(C,P) = 38.2 Hz; Ar), 120.4 ppm (d, ^3J(C,P) = 14.7; *m*-Ph); MS (FAB): + VE 774.2 (100) [M$^+$]; elemental analysis calcd (%) for $C_{50}H_{35}N_2OPS_2$ (774.93): C 77.50, H 4.55 N 3.61; found: C 75.26, H 4.68 N 3.27.

Synthesis of the polymer 8: To a solution of phosphole **4** (0.55 g, 1.23 mmol) and fluorene(bisboronic) acid **7** (0.52 g, 1.23 mmol) in toluene (20 mL) was added an aqueous solution of Na_2CO_3 (730 mg, 6.9 mmol, in 5 mL H_2O). The emulsion was stirred vigorously, [Pd(PPh$_3$)$_4$] (71 mg, 0.06 mmol, 5 mol%) was added and the mixture was then refluxed for 20 h. During that time, the fluorescence of the solution changed from green to orange and a bright orange solid precipitated from the reaction mixture. The orange precipitate was filtered off, washed twice with water, hot heptane and acetone, respectively, and evaporated to dryness under vacuum to afford **8** as orange powder (594 mg; 78%). The reduced solubility of the polymer precluded its comprehensive analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.63$ (br m, 13H; Ar), 1.94 (br s, 4H; 1-alkyl), 0.85 ppm (br m, 22H; CH$_3$-/CH$_2$-hexyl). GPC analysis (THF solution): $M_W = 3200\ \mathrm{g\,mol^{-1}}$; $M_n = 2400\ \mathrm{g\,mol^{-1}}$; $PDI = 1.37$.

Synthesis of 9: To a solution of **6a** (100 mg, 0.22 mmol) in CH_2Cl_2 (20 mL) an excess of $BH_3{\cdot}SMe_2$ (2 mmol) was added at room temperature and the reaction mixture was stirred for 1 h. Subsequently all volatile materials were removed under vacuum providing **9** as a yellow solid (89 mg, 95%). ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = 14.9$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.71$ (m, 2H; *o*-Ph), 7.69 (dd, ^3J(H,H) = 7.0 Hz, 4H), 7.59 (m, 4H), 7.49 (m, 1H, *p*-Ph), 7.41 (m, 8H), 7.32 (tt, ^3J(H,H) = Hz, 2H), 1.1 ppm (br s, 3H; BH$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta =$ 148.3 (d, ^2J(C,P) = 11.3 Hz; thiophene), 143.8 (s; phenyl), 141.1 (d, ^2J(C,P) = 12.1 Hz; thiophene), 139.7 (s; phenyl), 139.5 (d, ^1J(C,P) = 62.4 Hz; *ipso*-thiophene), 133.5 (s; phenyl), 132.1 (d, ^1J(C,P) = 10.4 Hz; *ipso*-Ph), 129.2 (s; phenyl), 129.1 (d, ^4J(C,P) = 3.5 Hz; *p*-Ph), 128.3 (s; phenyl), 125.7 (s; phenyl), 121.7 ppm (d, ^3J(C,P) = 15.6 Hz; *m*-Ph); ^{11}B{^{1}H} NMR (128.4 MHz, $CDCl_3$): $\delta = -39.5$ ppm.

Synthesis of 10: NEt$_3$ (506 mg, 5 mmol) was added to a solution of compound **9** (0.2 mmol) in CH_2Cl_2 at room temperature and stirred for 2 h. After removing all volatile materials in vacuum the residue was taken up in diethyl ether and filtered over neutral alumina. The filtrate was evaporated to dryness and washed with pentane (72 mg, 85%). ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = -22.2$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$ (m, 4H; *o*-Ar), 7.45 (m, 2H; *o*-Ph), 7.29 (s, 2H; thiophene), 7.28 (td, 4H; *p*-Ar), 7.17 ppm (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 146.6$ (d, ^1J(C,P) = 8.6 Hz; *ipso*-thiophene), 145.0 (d, ^3J(C,P) = 6.0 Hz; Ar), 140.1 (d, J(C,P) = 2.6 Hz; Ar), 133.3 (s; phenyl), 132.4 (d, ^1J(C,P) = 14.7 Hz; *ipso*-Ph), 131.6 (d, ^2J(C,P) = 20.8 Hz; *o*-Ar), 131.1 (d, 11.27 Hz; *o*-Ph), 128.5 (s; phenyl), 127.9 (s; phenyl), 127.7 (d, ^3J(C,P) = 7.8 Hz; *m*-Ph), 126.5 (s; phenyl), 124.5 (s; phenyl), 121.5 ppm (d, ^2J(C,P) = 19.9 Hz; *m*-Ph); elemental analysis calcd (%) for $C_{26}H_{17}PS_2$ (424.52): C 73.56, H 4.04; found: C 73.80, H 4.43.

Synthesis of 11: [Au(tht)Cl] (53 mg, 0.16 mmol) was added to a solution of **10** (70 mg, 0.16 mmol) in CH_2Cl_2. After stirring 2 h at room temperature the solvent was removed in vacuum. The light yellow solid was filtered with pentane through neutral alumina. Small yellow needles could be obtained from a concentrated ether solution (99 mg, 95%). Crystals of **11**, suitable for X-ray analysis were obtained at room temperature from a concentrated acetone solution. ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = 6.5$ ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.65$ (m, 2H; *o*-Ph), 7.54 (td ^3J(H,H) = 7.0, ^4J(H,H) = 1.5 Hz, 4H; *p*-Ar), 7.40 (m, 9H), 7.35 ppm (tt, ^3J(H,H) = 7.2, ^4J(H,H) = 1.25 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 147.5$ (d, ^2J(C,P) = 13.2 Hz; thiophene), 142.9 (d, ^2J(C,P) = 13.8 Hz; thiophene), 137.0 (d, ^1J(C,P) = 67.6 Hz; *ipso*-thiophene), 132.5 (d, ^1J(C,P) = 15.6 Hz; *ipso*-Ph), 132.1 (s; phenyl), 131.7 (d, ^4J(C,P) = 3.5 Hz; *p*-Ph), 128.5 (d, ^2J(C,P) = 13.0 Hz; *o*-Ph), 128.4 (s; phenyl), 128.2 (s; phenyl), 127.5 (s; phenyl), 124.7 (s; phenyl), 120.5 ppm (d, ^3J(C,P) = 17.3 Hz; *m*-Ph); elemental analysis calcd (%) for $C_{26}H_{17}AuClPS_2{\cdot}1/2\,CH_2Cl_2$ (699.41): C 45.07, H 2.55; found C 45.22, H 2.74.

Acknowledgements

The authors would like to thank Professor Jun Okuda for his generous support of this work. Financial support of the Fonds der Chemischen Industrie, BMBF, Deutsche Forschungsgemeinschaft (DFG) and from OTKA (Grant No. T 049258) is gratefully acknowledged. We thank Dr. K. Beckerle for the GPC analyses; T.B. thanks the University of Calgary for start-up funding.

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Received: March 9, 2007