Highly Fluorinated Dithieno[3,2-*b*:2′,3′-*d*]phospholes with Stabilized LUMO Levels

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A series of dithieno[3,2-*b*:2′,3′-*d*]phospholes with a perfluorophenyl substituent at the phosphorus center has been synthesized. Further cross-coupling reactions with additional fluorinated phenyl groups afforded extended conjugated materials with different substitution patterns. Investigation of the optoelectronic properties of the materials revealed smaller highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gaps for the extended materials that were also confirmed by theoretical density functional theory (DFT) calculations. These further indicated that the LUMO levels experience a more significant drop in energy than the respective HOMO levels. This fact can be attributed to the strongly electron-withdrawing nature of the fluoroaryls. In addition, the absolute energies of the frontier orbitals depend on the position of the fluoro substituents in the terminal aryl groups, with meta-positioned fluoro atoms having the strongest effect. Electrochemical investigations as well as theoretical calculations toward the electron affinity of the extended, highly fluorinated dithienophospholes revealed promising features that may prove useful for application as n-type semiconductors in corresponding organic field-effect transistors (OFETs).

Introduction

Organic electronics is an area of research that currently experiences a tremendous amount of attention, due to the (semi)conducting properties that a large variety of organic π-conjugated materials exhibit.[1−5] These features make them intriguing candidates for a large variety of applications, such as organic light-emitting diodes (OLEDs),[1] organic photovoltaics (OPVs),[2] organic field-effect transistors (OFETs),[3,4] or sensory materials.[5] Successfully operating devices have been reported for all the above applications, but only OLEDs are already being broadly used in commercial applications.[1] In the area of OFET materials/devices, the development of more efficient materials and device architectures continues to be an important task.[3] One of the latest trends involves the investigation of n-type (or n-channel) semiconducting materials, as this behavior can potentially provide improved device performances and also lead to different device types including complementary circuits.[4b] Remarkably, organic materials should intrinsically be able to exhibit ambipolar behavior (i.e., they should be both n-type as well as p-type semiconductors), but very often p-type behavior has been found to dominate.[4]

The incorporation of phosphorus centers into oligomeric or macromolecular materials in the context of organic electronics has also recently drawn a significant amount of attention.[6] Phosphole-containing materials are of particular interest, as this system exhibits a peculiar electronic structure resulting from some interaction between the endocyclic π-system of the butadiene moiety and the σ^*-orbital of the exocyclic P−C bond ($\sigma-\pi$ hyperconjugation).[6b] Furthermore, trivalent phosphorus species can react with oxidizing agents or Lewis acids, and they can also coordinate to transition metals. This offers a unique variety of synthetically facile possibilities that can be undertaken to efficiently modify the electronic properties of the product materials.[6] We were recently able to show that the incorporation of phosphorus centers into π-conjugated systems can furnish organic materials with a variety of beneficial features that include luminescence efficiency and tunability but, more importantly, potentially give access to ambipolar characteristics.[7] Particularly, heteropentacenes based on the dithieno[3,2-*b*:2′,3′-*d*]phosphole system, that has been developed by us, represent promising candidates for n-channel semiconductors that are also easily accessible and tunable via chemical modifications at the

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(1) *Organic Light Emitting Devices*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006.

(2) (a) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58. (b) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.

(3) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

(4) (a) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (b) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296. (c) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070. (d) Ong, B. S.; Wu, Y.; Li, Y.; Liu, P.; Pan, H. *Chem.—Eur. J.* **2008**, *14*, 4766. (e) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (f) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(5) (a) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(6) (a) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681 (correction: *Chem. Rev.* **2007**, *107*, 303). (b) Hobbs, M. G.; Baumgartner, T. *Eur. J. Inorg. Chem.* **2007**, 3611.

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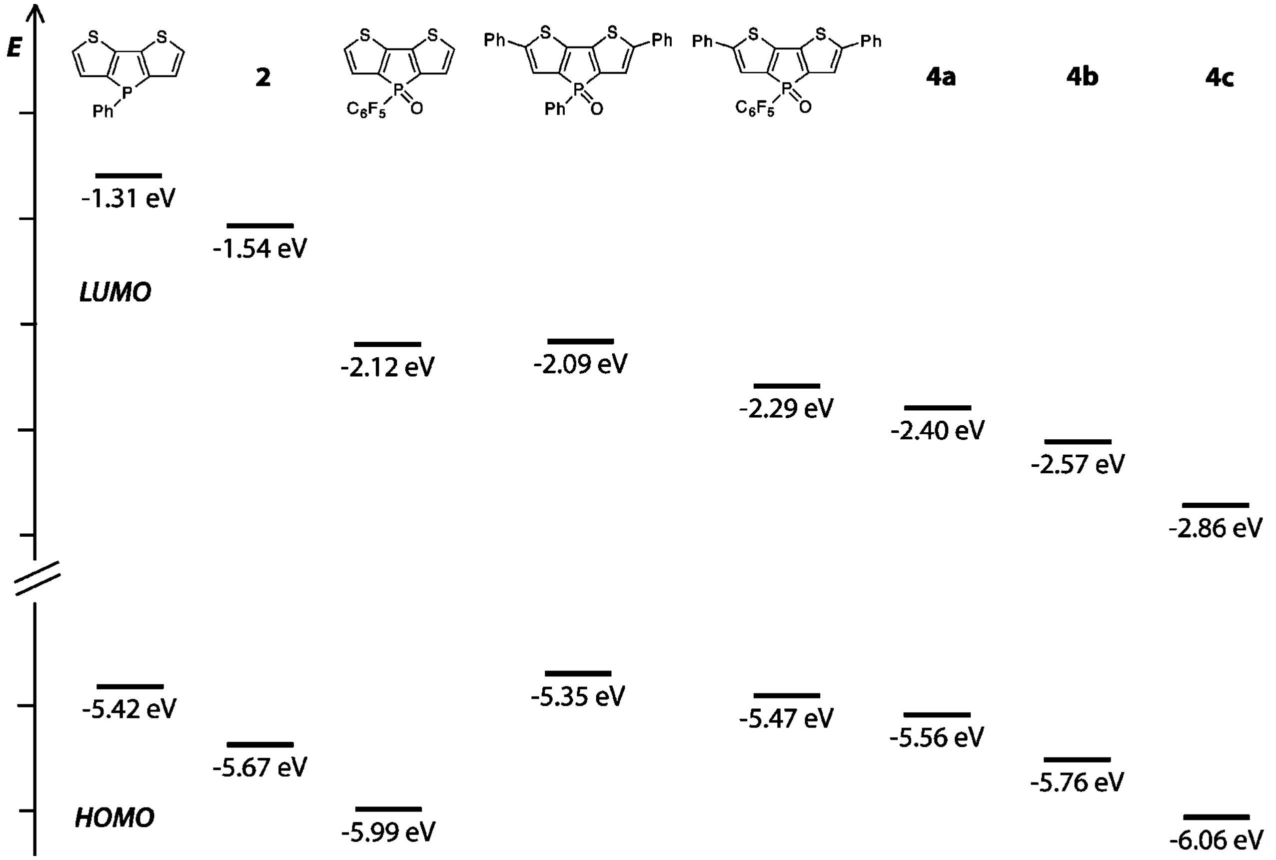

Figure 1. Calculated HOMO and LUMO levels (B3LYP/6-31G*) for nonfluorinated and highly fluorinated dithieno[3,2-*b*;2′,3′-*d*]phospholes.

phosphorus center.[8] Herein, we now report our efforts to further improve the electron-accepting properties of dithienophospholes via the introduction of a large number of fluorine atoms for lowering the LUMO energy level to facilitate electron injection. The synthesis, the modification, as well as the optoelectronic and redox properties including theoretical calculations of a series of highly fluorinated dithienophospholes are presented in detail.

Results and Discussion

Using (pentafluorophenyl)dichlorophosphane in our protocol toward dithieno[3,2-*b*:2′,3′-*d*]phospholes,[7] we were able to access the fluorinated species **2** from 3,3′-dibromo-2,2′-thiophene in excellent yield (isolated: 95%, Scheme 1). The high yield of this reaction is remarkable, since fluorinated arenes are also excellent electrophiles. It is well-known that reactions between carbanions with perfluoroarenes can be used to form C−C bonds in extended, thiophene-containing π-systems.[9] Due to the presence of lithiated thiophene intermediates, the latter could also have been a potential side reaction in this case. However, the electron donating character of the phosphorus atom seems to reduce the electrophilicity of the perfluoroaryl moiety significantly in this case, making it inert toward C−C coupling. The ^{31}P{^{1}H} NMR resonance at $\delta = -51.3$ with a triplet splitting $^{3}J(\text{P,F}) = 23.6$ Hz supports the generation of **2**. Its successful formation can also be monitored by the occurrence of intense photoluminescence (upon irradiation with UV light of 365 nm) during the reaction. Notably, the fluorescence emission at $\lambda_{em} = 471$ nm is strongly red-shifted from that of its nonfluorinated congener ($\lambda_{em} = 415$ nm),[7a] induced by the electron-withdrawing C_6F_5 group in **2** leading to both lowered highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (Figure 1). It is noteworthy that the high photoluminescence (PL) quantum yield of $\phi_{PL} = 0.48$ is typical for dithienophospholes.[7] We were also able to obtain single crystals of **2** from a concentrated acetonitrile solution at room temperature that were suitable for an X-ray diffraction study (Figure 2). The bond lengths and angles relate to those of the nonfluorinated congener.[7a] The same is true for the strongly pyramidal phosphorus center. The electron-withdrawing effect of the perfluoroaryl group can again explain slightly shortened bond lengths in **2**. Remarkably, this group also shows some intermolecular π-stacking interactions with the dithienophosphole scaffold of neighboring molecules in the solid state (distance = 3.5 Å). It should be mentioned in this context that fluoroaryl species, due to their polar character, often induce these specific organizational features that have been found to be beneficial for the device performance in general.[3,10]

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(7) (a) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197. (b) Baumgartner, T.; Bergmans, W.; Kárpáti, T.; Neumann, T.; Nieger, M.; Nyulászi, L. *Chem.—Eur. J.* **2005**, *11*, 4687. (c) Durben, S.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 5893. (d) Dienes, Y.; Durben, S.; Kárpáti, T.; Neumann, T.; Englert, U.; Nyulászi, L.; Baumgartner, T. *Chem.—Eur. J.* **2007**, *13*, 7487.

(8) Dienes, Y.; Eggenstein, M.; Kárpáti, T.; Sutherland, T. C.; Nyulászi, L.; Baumgartner, T. *Chem.—Eur. J.* **2008**, *14*, 9878.

(9) See, for example (a) Wang, Y.; Parkin, S. R.; Gierschner, J.; Watson, M. D. *Org. Lett.* **2008**, *10*, 3307. (b) Geramita, K.; McBee, J.; Shen, Y.; Radu, N.; Tilley, T. D. *Chem. Mater.* **2006**, *18*, 3261.

(10) (a) Koh, S. E.; Risko, C.; da Silva Filho, D. A.; Kwon, O.; Facchetti, A.; Brédas, J.-L.; Marks, T. J.; Ratner, M. A. *Adv. Funct. Mater.* **2008**, *18*, 332. (b) Tang, M. L.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 6064. (c) Subramanian, S.; Park, S. K.; Parkin, S. R.; Podzorov, V.; Jackson, T. N.; Anthony, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 2706.

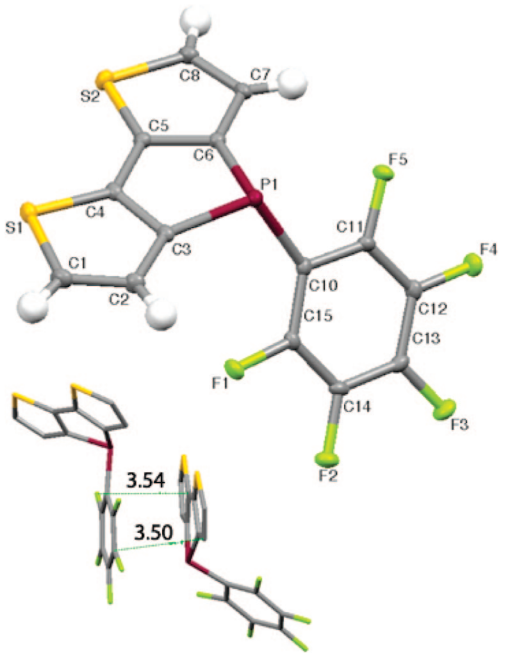
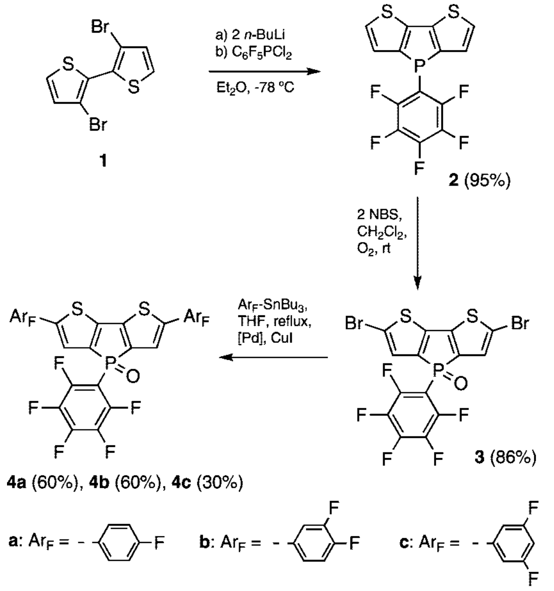


Figure 2. Molecular structure of **2** in the solid state (50% probability level, top) and π-stacking interactions ([Å], bottom). Selected bond lengths [Å]: P1−C3 1.815(2), P1−C6 1.818(2), P1−C10 1.833(2), C1−C2 1.359(2), C2−C3 1.421(2), C3−C4 1.383(2), C4−C5 1.440(2), C5−C6 1.380(2), C6−C7 1.417(2), C7−C8 1.366(2), C1−S1 1.7271(17), C4−S1 1.7182(16), C5−S2 1.7143(16), C8−S2 1.7229(17). Sum of angles around P1: 302.0°.

Scheme 1. Synthesis of Perfluorinated and Extended Dithieno[3,2-*b*:2′,3′-*d*]phospholes 2−4



However, due to the pyramidal nature of the phosphorus center in **2**, the π-stacking interactions in this case add another dimension, that may lead to interesting charge transport phenomena in the bulk phase.

To further narrow the band gap and particularly lower the LUMO levels of the materials, we have targeted perfluorinated dithienophospholes with expanded, electron-poor π-systems that are accessible via cross-coupling reactions, as shown by us earlier on nonperfluorinated dithienophospholes.[7d] In order to get a suitable synthon for cross-coupling procedures, dithienophosphole **2** was transformed into the 2,6-dibrominated phosphole oxide **3** using *N*-bromosuccinimide (NBS) under atmospheric conditions (Scheme 1, yield: 86%).[7d] Oxidation of the phosphorus center not only serves to further lower the LUMO of the compounds (see Figure 1), but also as a protecting group to prevent the Pd catalyst from being poisoned through coordination to this center.[7b,d] Successful transformation of **2** into **3** was confirmed by multinuclear NMR data, particularly with a relative lowfield shifted $^{31}P\{^1H\}$ NMR resonance at $\delta = 3.8$ that is typical for these systems. The red-shifted fluorescence emission at $\lambda_{em} = 504$ nm ($\phi_{PL} = 0.67$) further supported the formation of **3**.[7d]

Table 1. Photophysical Data of Compounds 2−4

compound	λ_{ex} [nm][a]	λ_{em} [nm][b]	ϕ_{PL}[c]
2	268, **383**	471	0.48
3	281, **408**	504	0.67
4a	280, 324, **439**	539	0.63
4a[d]	454, **533**	590	
4b	329, **435**	532	0.68
4b[d]	453, **514**	587	
4c	276, 332, **431**	526	0.69
4c[d]	**564**	634	

[a] λ_{max} for excitation in CH_2Cl_2 ($\pi-\pi^*$ transition in bold). [b] λ_{max} for emission in CH_2Cl_2. [c] Relative to quinine sulfate or fluorescein. [d] Solid state.

Compound **3** was then coupled with three stannylated aryls that exhibit fluorine atoms at different positions of the ring (4-fluoro-, 3,4-difluoro-, and 3,5-difluoro-phenyl). We were interested in whether the location of these substituents had an impact on the electronic properties (i.e., the electron affinity) of the materials, as indicated by theoretical calculations (vide infra). However, due to the electron-withdrawing nature of the substrates involved, the cross-coupling reactions were found to be quite sluggish. Successful coupling was, however, achieved using a Stille protocol under reflux conditions in tetrahydrofuran (THF) with $Pd(PPh_3)_4$ and CuI as catalysts (Scheme 1). The cross-coupled species could be isolated as red solids in decent yields (**4a**, 60%; **4b**, 60%; **4c**, 30%). $^{31}P\{^1H\}$ NMR resonances at $\delta = 4.4$ (**4a**), 4.0 (**4b**), and 3.8 (**4a**) support the successful formation of the extended systems, as do the red-shifted yellow/orange fluorescence emissions at $\lambda_{em} = 539$ nm (**4a**), 532 nm (**4b**), and 526 nm (**4c**). Furthermore, the inherent wavelength maxima for excitation $\lambda_{ex} = 439$ nm (**4a**), 435 nm (**4b**), and 431 nm (**4c**) are consistent with smaller band gaps of these materials, compared to **2** (cf. $\lambda_{ex} = 383$ nm).[7a] Notably, their PL quantum yields all range from $\phi_{PL} = 0.63$ to 0.68, and the fluorescence data of **4a−c** in the solid state are significantly red-shifted (see Table 1), indicating intermolecular interactions, likely via $\pi-\pi$-stacking. We were able to obtain suitable single crystals of **4b** from a concentrated toluene solution that confirmed this assumption. The X-ray diffraction study of **4b** (Figure 3) shows an almost fully coplanar extended π-system and several intermolecular π-stacking interactions, not only between the scaffolds of neighboring molecules but also between the C_6F_5 group and a cocrystallized, disordered toluene molecule (distance = 3.4 Å). Furthermore, some close contacts (3.1−3.6 Å) between the sulfur atoms and the C_6F_5 group of neighboring molecules can also be observed that might be beneficial for the carrier transport, which is generally governed by intermolecular overlap.[3,4] Surprisingly, the bond lengths of the central dithienophosphole core are almost identical to those of **2**, which can be attributed to the electronic effect of the C_6F_5 substituent in both cases. It should be mentioned that one of the 3,4-difluorophenyl groups shows some disorder, due to two possible placements for the 3-fluoro atom (Figure 3; F9, 85%; F9′, 15%). The coplanar arrangement of the molecules in the solid state is also

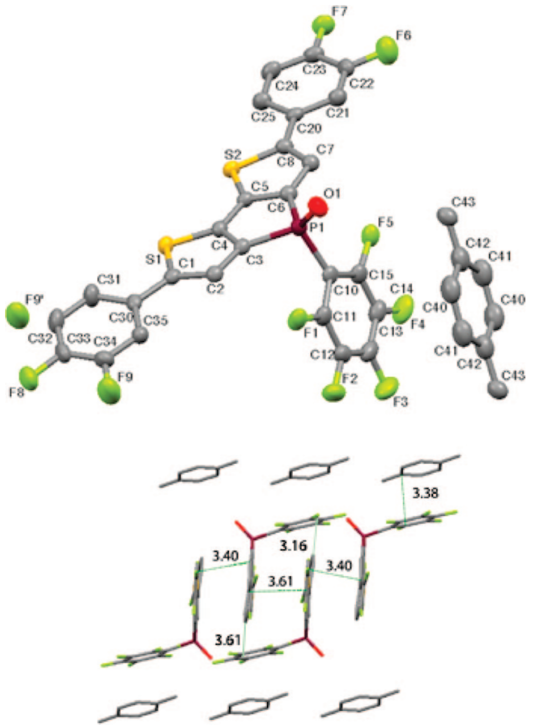
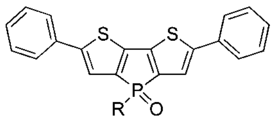


Figure 3. Molecular structure of **4b**·toluene in the solid state, 50% probability level (top, H-atoms omitted for clarity) and π-stacking interactions ([Å], bottom); toluene molecules are disordered; occupancy for F9 = 85% and F9′ = 15%. Selected bond lengths [Å]: P1−C3 1.815(3), P1−C6 1.809(3), P1−C10 1.835(3), P1−O1 1.473(2), C1−C2 1.377(4), C2−C3 1.411(4), C3−C4 1.384(4), C4−C5 1.444(4), C5−C6 1.374(4), C6−C7 1.416(4), C7−C8 1.382(4), C1−C30 1.475(4), C8−C20 1.468(4). Torsion angles [°]: C2−C1−C30−C35 11.3(5), C7−C8−C20−C21 2.8(5).

a good indication for the potential applicability in OFETs, as the larger molecular overlap has been found to provide better device performances, in contrast to an edge-to-face "herringbone" arrangement.[3] Remarkably, the three cross-coupled species show very good thermal stability with melting points at T_m = 239 °C for **4a**, 240 °C for **4b**, and 253 °C for **4c**, as determined by differential scanning calorimetry (DSC), and decomposition points beyond 350 °C (T_{dec} = 368 °C for **4a**, 382 °C for **4b**, and 387 °C for **4c**), as determined by thermogravimetric analysis (TGA).

Density functional theory (DFT) calculations reveal that the LUMO levels of the three extended compounds depend on the position of the fluoro-substituents (**4a**, $E = -2.40$ eV; **4b**, $E = -2.57$ eV; **4c**, $E = -2.86$ eV) and that they are all lower than those of the parent core species **2** and its P-oxidized relative (cf. **2**, $E = -1.54$ eV; **2=O**, $E = -2.12$ eV), supporting improved electron injection characteristics for the former. Theoretical calculations regarding the vertical electron affinities of the highly fluorinated dithienophospholes were performed on the B3LYP/6-311+G(2d,p) level of theory.[11] All optimized structures show C_s symmetry, with slightly twisted end groups (see the Supporting Information). The calculations furthermore reveal that the vertical electron affinities of the materials significantly depend on the number of fluorine atoms present in the systems but, more importantly, also on the position of the fluorine atoms at the terminal phenyl rings. Taking the nonfluorinated, phenyl-terminated species **5** (Figure 4) as a reference (E_{AV} = 1.20 eV), the vertical electron affinity is significantly larger, when the P-phenyl group is perfluorinated (**6**, E_{AV} = 1.48 eV). Further changes can be observed when the terminal phenyl groups are also fluorinated, increasing from species **4a** at E_{AV} = 1.58 eV over **4b** at E_{AV} = 1.76 eV to **4c** showing the largest vertical electron affinity at E_{AV} = 1.87 eV.



5: R = Ph; **6**: R = C_6F_5

Figure 4. Additional molecules used as basis/reference for theoretical calculations on vertical electron affinities.

Electrochemical investigations on the extended materials **4a−c** have revealed that the three compounds can indeed be reduced quasi-reversibly; however, their reduction potentials do not differ very much, with the 3,5-difluoro-species **4c** showing the highest potential at $E_{red} = -1.59$ V (cf. **4a**, −1.52 V; **4b**, −1.53 V; vs Ag/AgCl), in contrast to the theoretical calculations for the gas phase; oxidation of the materials, on the other hand, could not be observed in the accessible window ($E \leq 2.0$ V). However, the reductions were found to be rather slow, suggesting kinetically controlled processes in solution. It should also be mentioned in this context that the observed reduction potentials for **4a−c** are not significantly lower than those observed for related heteropentacenes based on the dithienophosphole system.[8] These observations could be attributed to rotational isomers present in solution that would show different electrochemical properties depending on the degree of conjugation/twisting within the π-conjugated scaffold. A low-energy rotational barrier about the "cross-coupled" C−C bonds is also supported by the rather larger Stokes shifts for **4a−c** that amount to 95, 97, and 100 nm, respectively, and is consistent with that of related nonfluorinated materials reported by us earlier.[7d] However, this rotational disorder should be minimized in the solid state of a potential OFET device due to intermolecular π-stacking interactions.

Conclusion

In conclusion, we have synthesized a perfluorophenyl-functionalized dithieno[3,2-*b*:2′,3′-*d*]phosphole precursor building block that was used to access extended materials exhibiting further fluoroaryl substituents. The presence of the fluorine atoms furnishes the dithienophosphole system with low-lying LUMO levels that are a necessary prerequisite for application as n-type semiconductor materials. The lowered band gaps are evident in significantly red-shifted photophysical properties that can be observed for the extended systems, compared to the perfluorinated core, but also the nonfluorinated parent system, for that matter. Theoretical calculations confirm that the introduction of the fluorine-containing functional groups lowers

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(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian Inc.: Wallingford, CT, 2007.

the energy levels of the frontier orbitals, with the effect on the LUMO being much more pronounced than that on the HOMO (relative to the nonfluorinated dithienophosphole core). Furthermore, the position of the fluoro substituents at the terminal aryl groups has a significant impact on the electronics of the system as a whole, as meta-positioned fluoro substituents lower the energy levels of the frontier orbitals most significantly. Electrochemical studies as well as theoretical calculations toward the electron affinity of the extended materials suggest that they are easily reduced, which makes them promising candidates for n-type organic semiconductors. Their suitability is currently under detailed investigation. Furthermore, we are also looking into the incorporation of perfluorinated groups in dithienophosphole heteropentacenes that are expected to exhibit a much more rigid molecular scaffold and thus potentially further improved n-type characteristics.

Experimental Section

General Procedures. Reactions were carried out in dry glassware and under inert atmosphere of purified argon or nitrogen using Schlenk techniques. Solvents were dried over appropriate drying agents and then distilled. *n*-BuLi (2.5 M in hexane), *N*-bromosuccinimide (NBS), 1-fluoro-4-bromobenzene, 3,4-difluoro-1-bromobenzene, 3,5-difluoro-1-bromobenzene, tetrakis(triphenylphosphane)palladium(0), and Na_2CO_3 were used as received. Tributyltin chloride was distilled prior to use. 3,3′-Dibromo-2,2′-dithiophene (**1**)[12] and pentafluorophenyl dichlorophosphane[13] were prepared by literature methods. ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{31}P{^{1}H} NMR, and ^{19}F{^{1}H}-NMR spectra were recorded on Bruker AC200, Bruker DMX-300, and Bruker DRX-400 spectrometers. Chemical shifts were referenced to external 85% H_3PO_4 (^{31}P), C_6F_6 (^{19}F), or TMS (^{13}C, ^{1}H). Elemental analyses were performed at the Institut für Organische Chemie, RWTH-Aachen University, and the Department of Chemistry at the University of Calgary. Optical spectroscopy experiments were recorded in a dichloromethane solution in a Jasco FP-6500/6600 spectrofluorometer and UV−vis-NIR Cary 5000 spectrophotometer. Thermal analysis was performed using TA-Q200 DSC and TA-Q50 TGA instruments. Electrochemical studies were performed using an Autolab PGSTAT302 instrument, with a Pt wire electrode (flamed in a torch) as working electrode, a Pt-mesh as counter electrode, as well as a Ag/AgCl/KCl-3M reference electrode, approximately 10 mM solution in THF, and supporting electrolyte was $[NBu_4]PF_6$.

Compound 2. *n*-BuLi (2.82 mL, 7.05 mmol) was added to a solution of **1** (1.14 g, 3.52 mmol) in diethyl ether (140 mL) at −78 °C. The reaction mixture was allowed to warm up to room temperature and stirred at this temperature for 10 min. After cooling the mixture to −78 °C again, $(C_6F_5)PCl_2$ (1.25 g, 3.53 mmol) was added. The reaction mixture was then allowed to warm up quickly to room temperature and stirred at this temperature for 1 h. All volatile materials where removed under vacuum. The residue was taken up in CH_2Cl_2 and filtered through neutral alumina. The product **2** was obtained as a light yellow powder after washing with diethyl ether and *n*-pentane. Needle shaped crystals of **2** suitable for X-ray structure analysis were obtained from a concentrated acetonitrile solution at room temperature (2.4 g, 95% yield). ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = -51.3$ (t, ^{3}J(P–F) = 23.6 Hz) ppm; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): $\delta = -129.6$ (dt, ^{3}J(F–F) = 24.4 Hz, ^{4}J(F–F) = 8 Hz; *o*-F), −151.28 (t, ^{3}J(F–F) = 22.1 Hz; *m*-F), −160.6 (dt, ^{3}J(F–F) = 20.5 Hz, ^{4}J(F–F) = 8.3 Hz; *p*-F) ppm; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (dd ^{3}J(H–H) = 4.9 Hz, ^{4}J(H–P) = 2.8 Hz, 2H; thiophene), 7.23 (dt ^{3}J(H–H) = 4.8 Hz; 2H; thiophene) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta =$ 147.2 (br, ^{1}J(C–F) = 253.24 Hz; *o*-Ph), 143.5 (d, ^{2}J(C–P) = 4.1 Hz; thiophene), 143.1 (br; *ipso*-Ph), 141.8 (d, ^{1}J(C–F) = 254.6 Hz; *p*-Ph), 137.5 (br, ^{1}J(C–F) = 254.9 Hz; *m*-Ph), 126.5 (d, ^{2}J(C–P) = 6.8 Hz; thiophene), 127.2 (dt, ^{4}J (C–F) = 2.5 Hz ^{1}J(C–P) = 20 Hz; *ipso*-thiophene) ppm. Elemental analysis calcd (%) for $C_{14}H_4F_5PS_2$ (362.38 g/mol): C, 46.41; H, 1.11. Found C, 46.45; H, 1.85.

Compound 3. NBS (2.4 g, 13.2 mmol) was added to a solution of **2** (1.6 g, 4.4 mmol) in acetic acid (20 mL) and $CHCl_3$ (30 mL) at room temperature. The solution was stirred for 5 h. After neutralizing the reaction mixture with NaOH, the product was extracted with $CHCl_3$. The organic layer was washed successively with aqueous NaOH and H_2O and then dried with $MgSO_4$. After evaporation of the solvent, the crude product **3** was obtained as a light yellow powder (2.1 g, 86% yield). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = -3.52$ (s) ppm; ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): $\delta = -129.4$ (d, ^{3}J(F–F) = 19.9 Hz *o*-F), −144.3 (mt, (^{3}J(F–F) = 20.6 Hz; *m*-F), −157.9 (m, *p*-F) ppm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.72$ (dt, ^{3}J(H–P) = 2.5 Hz, ^{6}J(H–F) = 2.5 Hz, 2H; thiophene) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): $\delta = 147.6$ (d br, ^{1}J(C–F) = 258.8 Hz; Ph), 146.3 (s; thiophene), 145.9 (s; thiophene), 144.4 (d br, ^{1}J(C–F) = 255.4 Hz; Ph), 137.9 (d br, ^{1}J(C–F) = 261.9 Hz; Ph), 135.2 (d, ^{1}J(C–P) = 122.9 Hz; *ipso*-thiophene), 129.7 (dt, ^{5}J(C–F) = 5.1 Hz, ^{2}J (C–P) = 15.0 Hz; thiophene), 115.4 (d, ^{3}J(C–P) = 20.5 Hz; thiophene-Br) ppm. Elemental analysis calcd (%) for $C_{14}H_2Br_2OF_5PS_2$ (536.07 g/mol): C, 31.37; H, 0.38. Found: C, 31.62; H, 0.97.

4-Tributyltin-fluorobenzene.[14] To a solution of 1-fluoro-4-bromobenzene (1.59 g, 9.1 mmol) in THF (20 mL), *n*-BuLi (3.64 mL, 9.1 mmol) was added dropwise at −78 °C. After stirring for 55 min at the same temperature, $ClSnBu_3$ (2.96 g, 9.1 mmol) was added at −78 °C, and the reaction mixture was further stirred at room temperature overnight. Subsequently, all volatiles were removed under vacuum, Et_2O was added to the white remaining solid, and the mixture was filtered through neutral alumina. After the solvent was removed under vacuum, a colorless oil was obtained (yield: 2.45 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (t, $J = 7.4$ Hz, 2H), 7.04 (t, $J = 8.8$ Hz, 2H), 1.54 (m, 6H, alkyl-CH_2), 1.33 (m, 6H, alkyl-CH_2), 1.05 (m, 6H, alkyl-CH_2), 0.89 (m, 9H, alkyl-CH_2) ppm; ^{13}C{^{1}H, APT} NMR (100 MHz, $CDCl_3$): $\delta =$ 163.3 (d, ^{2}J (C−F) = 245.0 Hz), 137.8 (d, ^{3}J (C−F) = 6.5 Hz), 136.6 (d, ^{4}J (C−F) = 4.3 Hz), 115.1 (t, ^{2}J (C−F) = 18.8 Hz), 29.1, 27.4, 13.7, 9.7 ppm.

1,2-Difluoro-4-tributyltinbenzene. To a solution of 3,4-difluoro-1-bromobenzene (1.99 g, 10.3 mmol) in Et_2O (30 mL), *n*-BuLi (4.12 mL, 10.3 mmol) was added dropwise at −78 °C. After stirring for 40 min at the same temperature, $ClSnBu_3$ (3.35 g, 10.3 mmol) was added at −78 °C, and the reaction mixture was further stirred at room temperature overnight. Subsequently, the mixture was filtered through neutral alumina, and the solvent was removed under vacuum, affording a colorless oil (yield: 2.78 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.20$ (m, 1H), 7.08 (m, 1H), 6.92 ppm (dt, ^{4}J (H−F) = 8.7 Hz, ^{3}J (H−F) = 9.3 Hz, 1H), 1.53 (m, 6H, alkyl-CH_2), 1.30 (m, 8H, alkyl-CH_2), 1.09 (m, 4H, alkyl-CH_2), 0.88 (td, $J = 1.8$ Hz, ^{3}J (H−H) = 7.2 Hz, 9H); ^{13}C{^{1}H, APT} NMR (100 MHz, $CDCl_3$): $\delta = 150.5$ (dd, ^{2}J (C−F) = 3.4, ^{1}J (C−F) = 250.8 Hz), 150.7 (dd, ^{2}J (C−F) = 13.3, ^{1}J (C−F) = 245.1 Hz, 3,5-difluorophenyl), 138.5 (d, ^{3}J (C−F) = 5.3 Hz, 3,5-difluorophenyl), 132.3 (t, ^{3}J (C−F) = 4.8 Hz, 3,5-difluorophenyl), 124.3 (d, ^{2}J (C−F) = 13.2 Hz, 3,5-difluorophenyl), 117.0 (d, ^{2}J (C−F) = 15.3 Hz, 3,5-difluorophenyl), 29.0, 27.4, 13.6, 9.8 ppm.

1,3-Difluoro-5-tributyltinbenzene. To a solution of 3,5-difluoro-1-bromobenzene (2.50 g, 12.95 mmol) in Et_2O (30 mL), *n*-BuLi

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(12) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034.

(13) Diemert, K.; Kottwitz, B.; Kuchen, W. *Phosphorus Sulfur* **1986**, *26*, 307.

(14) Adam, M. J.; Ruth, T. J.; Jivan, S.; Pate, B. D. *J. Fluorine Chem.* **1984**, *25*, 329.

(5.18 mL, 12.95 mmol) was added dropwise at −78 °C. After stirring for 40 min at the same temperature, $ClSnBu_3$ (4.21 g, 12.95 mmol) was added at −78 °C, and the reaction mixture was further stirred at room temperature overnight. Subsequently, the mixture was filtered through neutral alumina, and the solvent was removed under vacuum to afford a colorless oil (yield: 3.39 g, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.97 (ddd, ^5J (H−F) = 2 Hz, ^4J (H−H) = 2.4, ^3J (H−F) = 4 Hz, 2H), 6.71 (tt, ^4J (H−H) = 2.4, ^3J (H−F) = 9.2, 1H), 1.61−1.53 (m, 6H), 1.41−1.31 (m, 6H), 1.13−1.09 (m, 6H), 0.99−0.87 (m, 6H), 0.94−0.90 (t, 9H) ppm; $^{13}C\{^1H$, APT$\}$ NMR (100 MHz, $CDCl_3$): δ = 163.3 (dt, ^1J (C−F) = 255 Hz,^3J (C−F) = 5.3 Hz, 3,5-difluorophenyl), 137.8 (d, ^2J (C−F) = 6.5 Hz, 3,5-difluorophenyl), 136.6 (d, ^3J (C−F) = 4.3 Hz, 3,5-difluorophenyl), 115.1 (d, ^2J (C−F) = 18.8 Hz, 3,5-difluorophenyl), 29.1, 27.4, 13.7, 9.7 ppm.

Compound 4a. Compound **3** (0.71 g, 1.33 mmol) and 4-tributyltin-fluorobenzene (1.08 g, 2.80 mmol) were dissolved in THF (35 mL). $Pd(PPh_3)_4$ (0.33 g, 0.28 mmol) and CuI (0.053 g, 0.28 mmol) were added, and the mixture was refluxed for 20 h at 120 °C. After removing the solvent under vacuum, a red oil was obtained. The mixture was dissolved in $CHCl_3$ and filtered over neutral alumina. The filtrate was evaporated to dryness and washed with pentane, affording a red solid. Compound **4a** was further purified by column chromatography (yield: 0.45 g, 60%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 4.35 ppm; $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2): δ = −113.3 (m, *p*-F-phenyl), −130.1 (d br, J = 20.9, *o*-F_5C_6), −146.5 (t br, J = 20.6, *p*-Ph), −159.6 (m, *m*-Ph) ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, ^3J (H−H) = 8.8 Hz, ^4J (H−F) = 5.2 Hz, 4H, *m*-F-phenyl), 7.52 (dd, ^3J (H−P) = 2.8 Hz, ^6J (H−F) = 5.6 Hz, 2H, thiophene), 7.13 (t, ^3J (H−F) = 8.8, ^3J (H−H) = 8.8 Hz, 4H, *o*-F-phenyl) ppm; $^{13}C\{^1H$, APT$\}$ NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, ^1J (C−F) = 248.1 Hz, *ipso*-F-phenyl), 147.6 (d br, ^1J (C−F) = 249.0 Hz, Ph), 147.1 (d, ^2J (C−P) = 16.1 Hz, thiophene), 145.0 (d, ^2J (C−P) = 28.1 Hz, thiophene), 141.1 (d br, ^1J (C−F) = 265.4 Hz, Ph), 137.8 (d br, ^1J (C−F) = 254.2 Hz, Ph), 136.5 (d, ^2J (C−P) = 28.1 Hz, *ipso*-thiophene), 129.2 (d, ^4J (C−F) = 3.3 Hz, *p*-F-phenyl), 127.6 (d, ^4J (C−F) = 8.2 Hz, *p*-F_5C_6), 122.8 (dt, ^5J (C−F) = 4.9 Hz,^2J (C−P) = 14.9 Hz, thiophene), 116.3 (d, ^2J (C−F) = 21.9 Hz, *m*-F_5C_6) ppm. Elemental analysis calcd (%) for $C_{26}H_{10}F_7OPS_2$ (566.45): C, 55.13; H, 1.78. Found: C, 54.69; H, 2.02.

Compound 4b. Compound **3** (0.65 g, 1.21 mmol) and 1,2-difluoro-4-tributyltinbenzene (1.05 g, 2.60 mmol) were dissolved in THF (40 mL). $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol) and CuI (0.057 g, 0.30 mmol) were added, and the mixture was refluxed for 20 h. After removing the solvent under vacuum, a red oil was obtained. The mixture was then dissolved in $CHCl_3$ and filtered over neutral alumina. The filtrate was evaporated to dryness and washed with pentane, affording a red solid. Compound **4b** was further purified by preparative TLC (yield: 0.43 g, 60%). Recrystallization from toluene at room temperature afforded **4b** as red single crystals suitable for X-ray structure analysis. $^{31}P\{^1H\}$ NMR (400 MHz, CD_2Cl_2): δ = 3.98 ppm; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ = −130.2 (dm, ^3J (F−F) = 20.6, 2F, *o*-F_5C_6), −137.1 (ddd, J = 7.8 Hz, J = 10.9 Hz, ^3J (F−F) = 20.0 Hz, 2F, 3,4-difluorophenyl), −137.8 (m, 2F, 3,4-difluorophenyl), −146.2 (ttd, ^3J (F−F) = 20.6, ^4J (F−F) = 5.6, ^5J (F−P) = 2.8, 1F, *p*-F_5C_6), −159.3 (tm, ^3J (F−F) = 27.1, 2F, *m*-F_5C_6) ppm; ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.56 (dd, ^3J (H−P) = 2.4 Hz, ^6J (H−F) = 8.8 Hz, 2H), 7.48−7.43 (m, 2H), 7.45 (ddd, ^4J (H−H) = 2.1 Hz, ^3J (H−H) = 7.5 Hz, ^3J (H−F) = 9.6 Hz, 2H), 7.40−7.43 (m, 2H) 7.26 (dt, ^4J (H−F) = 8.1 Hz, ^3J (H−F) = 9.9 Hz, 2H) ppm; $^{13}C\{^1H$, APT$\}$ NMR (100 MHz, $CDCl_3$): δ = 151.8 (dt, ^2J (C−F) = 12.2 Hz, ^1J (C−F) = 248.3 Hz, 3,4-difluorophenyl), 147.6 (d br, ^2J (C−F) = 251.4 Hz, *o*- F_5C_6), 146.0 (d, ^3J (C−P) = 16.1 Hz, thiophene), 145.3 (d, ^2J (C−F) = 27.7 Hz, thiophene), 144.3 (d br, ^1J (C−F) = 258.4 Hz, *p*-F_5C_6), 137.9 (d br, J (C−F) = 260.8 Hz, *m*-F_5C_6), 136.9 (d, ^1J (C−P) = 122.9 Hz, *ipso*-thiophene), 130.0 (d, J (C−F) = 4.7 Hz, 3,4-difluorophenyl), 123.6 (dt, ^2J (C−F) = 4.9 Hz,^2J (C−P) = 15.0 Hz, thiophene), 122.1 (dd, J (C−F) = 3.6 Hz, J (C−P) = 6.1 Hz, thiophene), 118.3 (dd, ^2J (C−F) = 3.6 Hz, ^5J (C−P) = 6.1 Hz, thiophene), 116.3 (d, ^2J (C−F) = 17.7 Hz, 3,4-difluorophenyl), 115.0 (d, J (C−F) = 18.7 Hz, 3,4-difluorophenyl) ppm. Elemental analysis calcd (%) for $C_{26}H_{10}F_7OPS_2$ (602.43): C, 51.84; H, 1.34. Found: C, 51.51; H, 1.27.

Table 2. Crystallographic Data for 2 and 4b

compound	**2**	**4b**
formula	$C_{14}H_4F_5PS_2$	$C_{29.5}H_{11.5}F_9OPS_2$
M_r	362.26	647.98
T/K	110(2)	173(2)
crystal system	orthorhombic	triclinic
space group	*Pcab*	*P*-1
a/Å	11.0038(11)	8.872(3)
b/Å	14.7512(16)	10.929(4)
c/Å	15.7784(16)	13.668(5)
α/°	90	76.85(2)
β/°	90	81.90(2)
γ/°	90	88.95(2)
V/Å^3	2561.1(5)	1277.5(8)
Z, D_c/Mg cm^{-3}	8, 1.879	2, 1.684
F(000)	1440	649
μ (Mo Kα)/mm^{-1}	0.592	0.363
θ range for data collection	2.58−30.87	3.31−27.50
reflections collected/ unique (R_{int})	19 045/3471 (0.0675)	10 865/5818 (0.0490)
data/restraints/ parameters	3471/0/199	5818/0/392
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0358$, $wR2 = 0.0939$	$R1 = 0.0521$, $wR2 = 0.1123$
R indices (all data)	$R1 = 0.0423$, $wR2 = 0.0965$	$R1 = 0.0998$, $wR2 = 0.1368$
GOF on F^2	1.014	0.988
largest diff. peak and hole/e Å^3	0.528 and −0.321	0.279 and −0.421

Compound 4c. Compound **3** (0.73 g, 1.35 mmol) and 1,3-difluoro-5-tributyltinbenzene (1.13 mg, 2.80 mmol) were dissolved in THF (40 mL). $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol) and CuI (0.057 g, 0.30 mmol) were added, and the mixture was refluxed for 20 h. After removing the solvent under vacuum, a red oil was obtained. The mixture was dissolved in $CHCl_3$ and filtered over neutral alumina. The filtrate was evaporated to dryness again, and washed with pentane, affording a red solid. Compound **4c** was purified by preparative TLC (0.24 g, 30%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ = 3.84 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −109.2 (t, ^3J (F−H) = 8.178, 4F, 3,5-difluorophenyl), −130.1 (dm, ^3J (F−F) = 20.9, 2F, *o*-F_5C_6), −145.9 (tm, ^3J (F−F) = 20.3, 1F, *p*-F_5C_6), −159.3 (m, 2F, *m*-F_5C_6) ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, ^6J (H−F) = 2.4 Hz, ^3J (H−P) = 5.6 Hz, 2H, thiophene), 7.11 (dd, ^4J (H−F) = 8.0 Hz, ^3J (H−H) = 2.0 Hz, 4H, 3,5-difluorophenyl), 6.82 (tt, ^3J (H−F) = 8.8 Hz, ^4J (H−H) = 2.4 Hz, 2H, 3,5-difluorophenyl) ppm; $^{13}C\{^1H$, APT$\}$ NMR (100 MHz, $CDCl_3$): δ = 164.7 (dd, ^1J (C−F) = 252.4 Hz,^3J (C−F) = 13.1 Hz, 3,5-difluorophenyl), 147.6 (d br, ^2J (C−F) = 252.4 Hz, *o*-F_5C_6), 146.0 (d br, ^3J (C−P) = 16.0 Hz, thiophene), 145.6 (d, ^2J (C−F) = 27.7 Hz, thiophene), 142.1 (d br, ^1J (C−F) = 200.4 Hz, *p*-F_5C_6), 137.9 (d br, J (C−F) = 247.3 Hz, *m*-F_5C_6), 137.2 (d, ^1J (C−P) = 123 Hz, *ipso*-thiophene), 135.7 (d, J (C−F) = 10.1 Hz, 3,5-difluorophenyl), 124.3 (dt, ^5J (C−F) = 5.1 Hz,^2J (C−P) = 14.9 Hz, thiophene), 108.8 (dd, ^3J (C−F) = 7.9 Hz, ^2J (C−F) = 19.2 Hz, 3,5-difluorophenyl), 104.0 (t, ^2J (C−F) = 25.3 Hz, 3,5-difluorophenyl) ppm. Elemental analysis calcd (%) for $C_{26}H_{10}F_7OPS_2$ (602.43): C, 51.84; H, 1.34. Found: C, 51.95; H, 1.74.

X-ray Structure Determination. For compound **2**, data were collected on a Bruker SMART D8 goniometer with an APEX CCD detector at 110 K, and for compound **4b** on a Nonius KappaCCD diffractometer at 173 K, using Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The SADABS[15] method of correcting absorption was applied for **2**, whereas the multiscan[16] method was applied for **4b**. The structures were solved by direct methods (SHELXTL)[17] and refined on F^2 by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined using a riding model. Crystal data and details of data collection and structure refinements are given in Table 2. Crystallographic data for the structures of **2** and **4b** have been deposited in the Cambridge Crystallographic Data Centre, deposition numbers CCDC 698475, 698476.

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Supporting Information Available: Crystallographic data in cif format, detailed theoretical calculation data, and differential pulse voltammograms of **4a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, 1996.

[16] Hooft, R. *COLLECT*; Nonius BV: Delft, The Netherlands, 1998.

[17] Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker AXS Inc.: Madison, WI, 1998.