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Synthesis, Electronic Properties, and Reactivity of Phospholes and 1,1′-Biphospholes Bearing 2- or 3-Thienyl *C*-Substituents

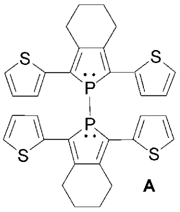
Omrane Fadhel,[a] Dénes Szieberth,[b] Valérie Deborde,[a] Christophe Lescop,[a] László Nyulászi,*[b] Muriel Hissler,*[a] and Régis Réau*[a]

Abstract: Two series of phospholes and 1,1′-biphospholes bearing either 2- or 3-thienyl substituents at the C atoms are prepared by using the Fagan–Nugent route. Their optical (UV/Vis absorption, fluorescence spectra) and electrochemical properties are systematically evaluated. Of particular interest, the first ever reported 3-thienyl-substituted phospholes exhibit higher LUMO levels than their 2-thienyl analogues, and show accordingly different physical properties. This study also reveals that the 1,1′-biphospholes exhibit σ–π conjugation. The phosphole and 1,1′-biphosphole derivatives bearing 3-thienyl substituents are characterized by X-ray diffraction study. The structure–property relationship established following the experimental data are fully supported by theoretical studies including time-dependent(TD)-DFT spectra. A photocyclization reaction performed on the thioxo- and oxophospholes having 3-thienyl substituents affords a novel ring-fused phosphole–thiophene derivative, which was characterized by an X-ray diffraction study. The structure and electronic properties of this novel dithienophosphole are discussed based on experimental and theoretical data.

Keywords: density functional calculations · phospholes · photocyclization · thiophenes · pi interactions

Introduction

Phospholes are the most widely investigated P-heterocycles due to their easy accessibility, substitution pattern variability, and versatile reactivity.[1] Beside intensive studies devoted to the elucidation of their electronic structure,[1,2] these heteroles have been extensively used as building blocks for the tailoring of ligands for homogeneous catalysis,[3] as precursors for other P-heterocycles,[1] and as subunits for the tailoring of π-conjugated systems.[4] In this last domain, phospholes are very appealing building blocks due to a set of unique properties.[1,2] First, it is possible to readily tune the electronic properties of phosphole-based π-conjugated systems by chemical modifications of the reactive P atoms.[1,4,5] Second, these heteroles exhibit a high electron affinity due to an effective σ*(PR)–π*(1,3-diene) orbital interaction.[5c,6] This hyperconjugation is especially effective in 1,1′-biphosphole derivatives **A** leading to a further reduction of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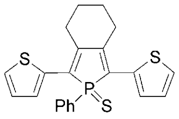
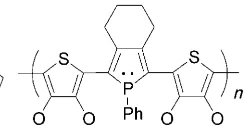
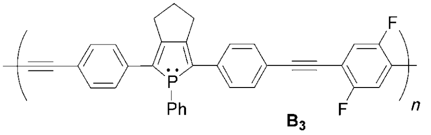

B$_1$


B$_2$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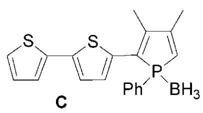
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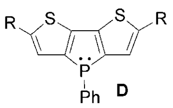
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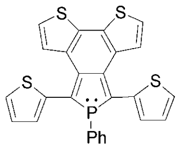
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[a] Dr. O. Fadhel, V. Deborde, Dr. C. Lescop, Prof. M. Hissler,
Prof. R. Réau
Sciences Chimiques de Rennes
UMR 6226 CNRS-Université de Rennes 1
Campus de beaulieu, 35042 Rennes Cedex (France)
Fax: (+33) 2-23-23-69-39
E-mail: muriel.hissler@univ-rennes1.fr
regis.reau@univ-rennes1.fr

[b] Dr. D. Szieberth, Prof. L. Nyulászi
Department of Inorganic and Analytical Chemistry
Budapest University of Technology and Economics
Gellért tér 4, 1111 Budapest (Hungary)
E-mail: nyulaszi@mail.bme.hu

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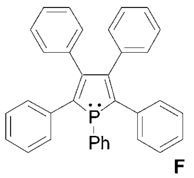
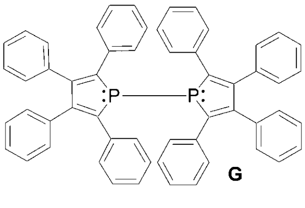
HOMO–LUMO gaps.[7] Lastly, the quite high thermal stability of phosphole-based conjugated oligomers such as $\mathbf{B_1}$ allows the use of these P-derivatives as materials in optoelectronic devices (organic light-emitting diodes (OLEDs)).[4a,8] There is therefore a growing interest in the design of π-conjugated materials containing phosphole subunits. For example, the synthesis of novel P-based π-conjugated systems is the subject of intensive research as illustrated by the work of Chujo and co-workers on polymers of type $\mathbf{B_3}$[4f,g] and of Mathey and co-workers on mixed phosphole–thiophene oligomers **C**.[4k] Quite recently, fused phosphole–thiophene systems have also been reported to exhibit very appealing functions. For example, Baumgartner and co-workers have developed highly fluorescent dithieno[*b*,*d*]phospholes **D**,[4h] and Matano and co-workers have reported bithiophene-fused benzo[*c*]phospholes **E**,[4d,e] which exhibit a high electron-transporting ability due to their low-lying LUMOs. It is noteworthy that mixed phosphole–thiophene derivatives are the most widely investigated phosphole-based π-conjugated systems,[4a–e,h–k] since i) this heterole's combination allows one to obtain derivatives with a low HOMO-–LUMO gap due to maximized orbital interactions, and ii) it is possible to exploit the rich chemistry of thiophene to readily obtain novel derivatives by Pd-catalyzed C−C coupling reactions or electropolymerization (see **B2**).

Considering the appealing functions of mixed phosphole–thiophene derivatives, there is a great interest in developing original structures to gain more insight into the structure–property relationship and to making further use of thiophene chemistry to prepare unprecedented conjugated P,S skeletons. The first phosphole and 1,1′-biphosphole to be prepared were obtained as fully phenyl-substituted compounds **F**[9a] and **G**,[9b,c] respectively and it is surprising to note that they are still the only fully aryl-substituted phosphole derivatives known to date. Considering the rarity of these structures and the intriguing electronic properties of mixed phosphole–thiophene derivatives, we decided to investigate phospholes and 1,1′-biphospholes bearing 2- or 3-thienyl substituents at their C atoms (see Scheme 1). 2-Thienyl building blocks are widely used for tailoring π-conjugated systems; in contrast 3-thienyl moieties have been scarcely employed for such a purpose. In fact, investigation of 3-thienyl building blocks is usually limited to the oligothiophene family due to the complicated derivatization of the ring at the β-position.[10] Interestingly, the conjugation energy of 3,3′-bithiophene was found to be slightly lower than for its 2,2′-isomer,[11] whereas the rotational barrier in the 3,3′-bithiophene was found to be the largest among the three possible bithiophenes.[12] These results clearly indicate that varying the nature of the thienyl building blocks (2- versus 3-) can be used for fine tuning the properties of π-conjugated systems.



F



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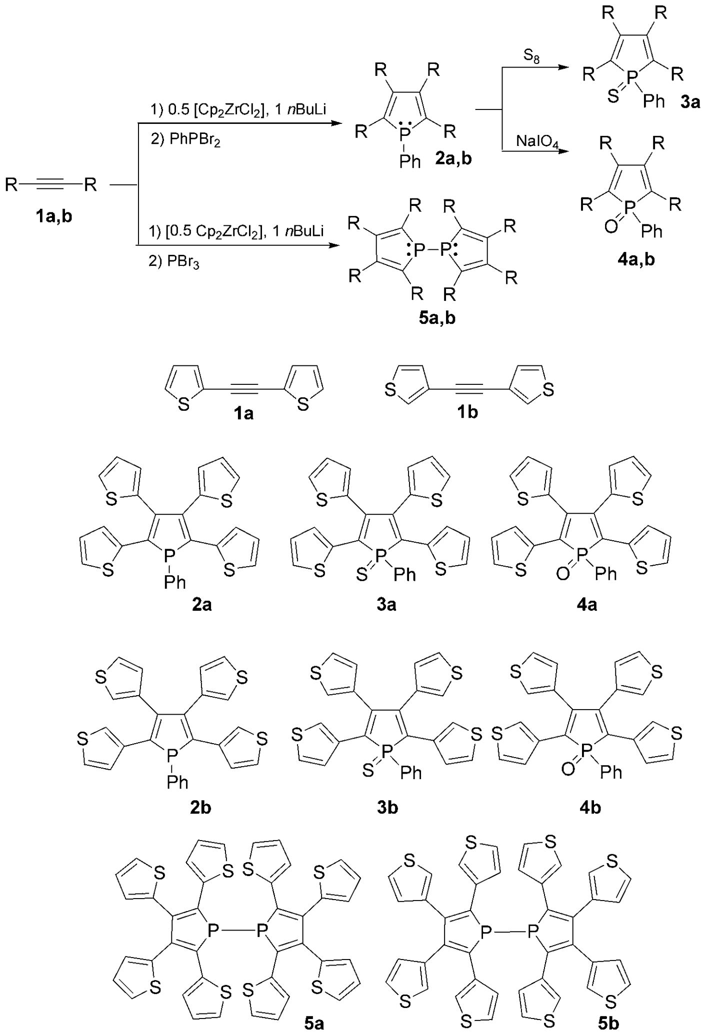
Herein, we describe the synthesis of these novel mixed phosphole- and 1,1′-biphosphole-thiophene π-conjugated systems (see Scheme 1) and the elucidation of their electronic properties by both experimental (UV/Vis spectroscopy, electrochemical behavior) and theoretical means. A comparative study of the influence of the substitution pattern of the thienyl substituent (2- versus 3-) on their electronic properties is also given. Furthermore, the preparation of a previously unknown di(bithiophene)-fused benzo[*b*,*d*]phosphole by a photocyclization process involving 3-thienyl substituents, an unprecedented reaction in phosphole chemistry, is reported. The electronic properties of this novel fused mixed phosphole–thiophene derivative are discussed on the basis of experimental and theoretical results.

Results and Discussion

Synthesis and characterization of 2,3,4,5-(2-thienyl)- and 2,3,4,5-(3-thienyl)phosphole derivatives: The target σ^3-phospholes **2a**,**b** were prepared according to the Fagan–Nugent route.[13] The intramolecular oxidative coupling of 1,2-di(2-thienyl)ethyne (**1a**)[14a] and 1,2-di(3-thienyl)ethyne (**1b**)[14b,c] with 'zirconocenes' provided the in situ generated zirconacyclopentadienes, which were allowed to react with $PhPBr_2$ to afford phospholes **2a** and **2b**, respectively (Scheme 1). These mixed phosphole–thiophene compounds were isolated in medium yields (**2a**, 46 %; **2b**, 60 %) as air-stable solids after purification by flash column chromatography. They were characterized by high-resolution mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy. Their $^{31}P\{^1H\}$ NMR spectra display a singlet at classical chemical shifts for 1-phenylphosphole derivatives (**2a**, $\delta=+14.1$ ppm; **2b**, $\delta=+13.9$ ppm).[1] The ^1H and ^{13}C NMR spectra of these compounds are very simple with two sets of ^1H and ^{13}C NMR signals assignable to the thienyl substituents (2- or 3-) at the $C_{2,5}$ and $C_{3,4}$ atoms of the phosphole rings, respectively. Moreover the $^{13}C\{^1H\}$ NMR data of the phosphole moiety of **2a**,**b** are very similar, the PC_α signals being shielded by about 2 ppm in **2b** compared to **2a**.

Phosphole **2b** bearing 3-thienyl substituents was characterized by an X-ray diffraction study (Figure 1, Table 1). The angles and bond lengths of this compound are classical and compare well with those observed for other phosphole derivatives.[4,5] For example, the P atom has a strong pyramidal character ($\Sigma P_{ang}=302.8°$) and the endocyclic P−C bond lengths (1.801(2)–1.804(3) Å, Table 2) approach that of a P−C single bond (1.84 Å). The lengths of the C−C links between the heteroles are in the range expected for C_{sp^2}–C_{sp^2} single bonds (1.463(6)–1.485(3) Å, Table 2) and are slightly shorter for the thienyl rings at the 2- and 5-positions com-



Scheme 1. Synthesis of thienyl-capped phosphole and 1,1′-biphosphole derivatives.

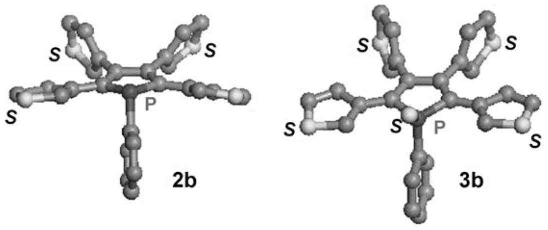


Figure 1. Molecular structures of phospholes **2b** and **3b** in the solid state. Hydrogen atoms are omitted for clarity.

pared to the 3- and 4-positions (Table 2). As already observed for linear oligomers bearing terminal thiophene rings[15] and other mixed phosphole–thiophene derivatives,[5b,c] the thienyl rings of **2b** exhibit a statistical disorder. Note that this statistical disorder prevents an accurate determination of certain bond lengths within the thienyl ring (vide supra). The sulfur atoms of the thienyl substituents in 2,5-positions have a *cis*-arrangement with respect to the central phosphorus atom in the prevailing conformation (ca. 70 %; Figure 1). The twist angles between the phosphole and the 3-thienyl rings at $C_{3,4}$-atoms are rather high (67.2° and 75.9°) presumably to avoid the steric encumbrance. In marked contrast, the angles between the 3-thienyl moieties at the $C_{2,5}$-atoms and the P ring are much smaller (18.7° and 19.1°; Figure 1) allowing an electronic interaction between these subunits to take place.

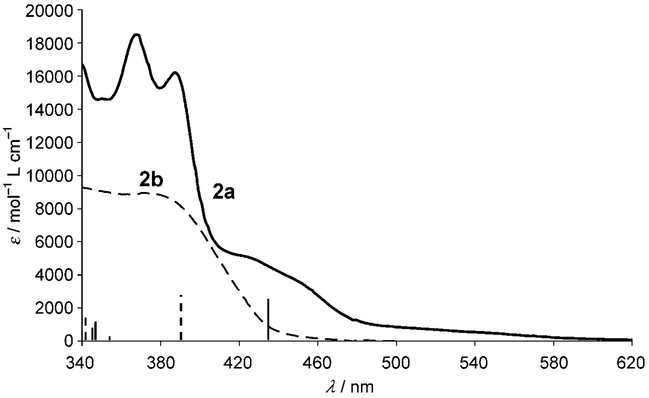


Figure 2. Absorption spectra of **2a,b** in CH_2Cl_2, and TD-DFT simulated spectra (vertical lines) of **2a** (continuous line) and **2b** (dashed line).

The presence of an extended π-conjugation in compounds **2a,b** was confirmed by the presence of absorption bands, assigned to π–π* transitions (vide supra), in the visible part of the absorption spectra (Figure 2). The absorption maximum of 2-thienyl-substituted **2a** (λ_{max} = 420 nm) compares with that observed for related 2,5-di(2-thienyl)-3,4-di(alkyl)phosphole derivatives.[5c] These data suggest that the π-conjugated pathway in **2a** mainly involves the phosphole ring and its 2,5-substituents. It is noteworthy that 3-thienyl-substituted **2b** (λ_{max} = 375 nm) exhibits an absorption maximum that is notably blue-shifted compared to that of **2a** (Figure 2). Therefore, as expected,[11] the electronic interaction of the phosphole π-system is more efficient with 2-thienyl than with 3-thienyl substituents. Cyclic voltammetry (CV) performed at 200 mV s^{-1} revealed that the redox processes observed for **2a,b** are irreversible, behavior that is typical for σ^3-phosphole-containing π-conjugated systems.[5] These two compounds exhibit similar oxidation potentials but derivative **2a** is more easily reduced than compound **2b** (Table 3). Note that phospholes **2a,b** are emissive derivatives ($\lambda_{em.}$ = **2a**, 515 nm; **3b**, 484 nm) but with low quantum yields (ca 0.2 %).

To get more insight into the electronic interactions between the phosphole ring and the 2- or 3-thienyl substituents, density functional calculations (B3LYP/6-31G*) have been performed on compounds **2a** and **2b**. It is worth noting that the computed structural data for **2b** are very similar to those obtained from the X-ray diffraction study (Table 2), with the exception of the C40–C42 bond length. This is probably due to the statistical disorder of the thienyl substituents (vide supra). Remarkably, these calculations revealed that compounds **2a,b** exhibit a similar gross struc-

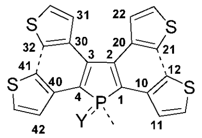
Table 1. Crystal data and structure refinement for **2b**, **3b**, **5b**, and **6b**.

	2b	**3b**	**6b**	**5b**
molecular formula	$C_{26}H_{17}PS_4$	$C_{26}H_{17}PS_5$	$C_{32}H_{19}PS_5$	$C_{40}H_{15.12}P_2S_8$
CCDC number	713600	713601	713602	713603
M_r	488.61	520.67	594.74	814.06
T [K]	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P21/c$	$P21/c$	$P\bar{1}$	$P21/c$
a [Å]	15.783(2)	11.843(5)	9.592(2)	13.446(2)
b [Å]	6.008(1)	17.398(5)	10.098(2)	13.836(1)
c [Å]	24.761(5)	12.615(5)	15.683(3)	21.006(3)
α [°]	90	90	71.535(1)	90
β [°]	94.972(6)	114.136(5)	79.969(2)	108.303(5)
γ [°]	90	90	69.163(2)	90
V [Å^3]	2339.0(7)	2372.0(15)	1343.4(5)	3710.0(8)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.387	1.458	1.470	1.457
wavelength $Mo_{K\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
crystal size [mm]	0.6 × 0.3 × 0.2	0.04 × 0.03 × 0.01	0.04 × 0.04 × 0.01	0.06 × 0.04 × 0.02
μ [mm^{-1}]	0.487	0.570	0.514	0.598
F(000)	1008	1072	612	1652
θ limit [°]	2.95–27.48	3.01 –27.48	2.94–27.54	1.60–24.54
index ranges hkl	$-20 \leq h \leq 20$, $-7 \leq k \leq 6$, $-32 \leq l \leq 32$	$-15 \leq h \leq 15$, $-22 \leq k \leq 22$, $-16 \leq l \leq 16$	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-20 \leq l \leq 20$	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-24 \leq l \leq 24$
reflections collected	9711	10639	11089	59870
independent reflections	5346	16116	6126	6207
reflections [$I > 2\sigma(I)$]	3203	5428	5174	4755
data/restraints/parameters	5346/0/279	5428/0/299	6126/0/343	6207/0/459
goodness-of-fit on F^2	1.044	1.053	0.916	1.119
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0523$ $wR2 = 0.1374$	$R1 = 0.0421$ $wR2 = 0.1145$	$R1 = 0.0337$ $wR2 = 0.0829$	$R1 = 0.0502$ $wR2 = 0.1557$
R indices (all data)	$R1 = 0.0966$ $wR2 = 0.1595$	$R1 = 0.0494$ $wR2 = 0.1212$	$R1 = 0.0437$ $wR2 = 0.0898$	$R1 = 0.0715$ $wR2 = 0.1879$
largest diff peak and hole [e Å^{-3}]	0.335 and −0.323	0.651 and −0.725	0.388 and −0.386	0.701 and −0.482

ture; the thienyl rings at the 2,5-positions are coplanar with the central phosphole moiety, whereas the thienyl rings at the 3,4-positions are almost perpendicular to the phosphole ring (Figure 3). Note that the calculated rotational barriers between the phosphole and the thiophene units at the 2,5-positions are smaller (**2a**, 1.1 kcal mol^{-1}; **2b**, and 0.9 kcal mol^{-1}) than that reported (3.7 kcal mol^{-1})[5c] for 2,5-bis(2-thienyl)phosphole having a fused saturated six-membered carbocycle at the 3,4-positions. The lowering of this rotational barrier, however, is not indicative of a diminished conjugative interaction between the phosphole and the thiophene substituents at $C_{2,5}$-atoms in **2a**,**b**. In the transition structure of this rotation process, the 2,5-thienyl substituents are perpendicular to the phosphole ring allowing the 3,4-thienyl substituents to be coplanar with the phosphole ring. This coplanarity allows a conjugative stabilization between the phosphole ring and the 3,4-thienyl groups, compensating somewhat for the loss of the conjugative stabilization with the thienyl moieties at the 2,5-positions. The frontier MOs of compounds **2a** and **2b** have been analyzed to rationalize their different spectroscopic and electrochemical behavior. The HOMO−1 and HOMO of these derivatives are the antibonding combination of the phosphole's HOMO−1 and HOMO with the HOMOs of the thiophene rings, respectively (Figure 3). There is no significant interaction in case of the HOMO−1 level of **2a** and **2b**, since the phosphole's HOMO−1 has a node at the connecting C atom. The HOMOs, however, are considerably destabilized with respect to the original phosphole orbitals. This destabilization is similar for **2a** and **2b**, owing to the small difference of the C_2 and C_3 coefficients in the thiophene's HOMO (Figure 3). The LUMO, which is a bonding combination of the phosphole's and thiophene's LUMOs, is stabilized in both cases (Figure 3). However since the thiophene's LUMO has a significantly larger coefficient at C_2 than at C_3, the LUMO of compound **2a** is more stabilized leading to a lower HOMO–LUMO separation by about 0.4 eV for **2a** compared to **2b**. This conclusion is also supported by the TD-DFT simulated spectra, which show an intense transition (LUMO←HOMO) at 438 nm and 393 nm for phospholes **2a** and **2b**, respectively (Figure 2). They are in good agreement with the experimental ones (**2a**, 420 nm; **2b**, 375 nm), reproducing the changes attributable to the nature of thienyl building blocks used as substituents. In summary, this theoretical study fits nicely with the experimental data (UV/Vis sprectroscopy, electrochemical behavior, Table 3), which shows that **2a** possesses a lower LUMO level and lower HOMO–LUMO separation than **2b**.

One key property of phosphole-based π-conjugated systems is that chemical modifications of the P atom result in a fine-tuning of their electronic property.[4] To check whether this property is retained within these novel mixed phosphole–thiophene series, derivatives **2a**,**b** were oxidized with elemental sulfur and sodium periodate (Scheme 1). The corresponding phosphole derivatives **3a**,**b** and **4a**,**b** were isolated in high yields (85–90%) as air-stable derivatives. The multinuclear NMR spectroscopic data of the isolated phospholes are typical[1] and support the proposed structures as do the high-resolution mass spectra and elemental analysis. In comparison with the σ^3-phospholes **2a**,**b**, the C_β of the corresponding σ^4-phosphole sulfides **3a**,**b** and oxides **4a**,**b** are slightly deshielded ($\Delta\delta$, **3a**/**2a**, 1.7 ppm; **3b**/**2b**, 1.2 ppm), whereas the C_α resonances are considerably more shielded ($\Delta\delta$, **3a**/**2a**, 9.3 ppm; **3b**/**2b**, 5.5 ppm). It is noteworthy that these effects are more pronounced for the series of compounds incorporating the 2-thienyl subtituents (i.e.

Table 2. Selected bond lengths [Å] and angles [°] and the corresponding calculated values (in brackets) for compounds **2b**, **3b**, **5b**, and **6b**.



	2b	**3b**	**5b**	**6b**
P1−C1	1.804(3) [1.820]	1.816(2) [1.832]	1.808(3)–11(3) [1.818–1.827]	1.7971(18) [1.824]
C1−C2	1.373(3) [1.376]	1.359(3) [1.365]	1.357(5)–1.367(5) [1.375–1.376]	1.405(2) [1.401]
C2−C3	1.471(3) [1.480]	1.491(3) [1.499]	1.455(5)–1.460(5) [1.474–1.476]	1.493(2) [1.493]
C3−C4	1.376(3) [1.374]	1.361(3) [1.365]	1.370(5)–1.369(5) [1.376–1.376]	1.404(2) [1.402]
C4−P1	1.801(2) [1.829]	1.818(2) [1.838]	1.804(3)–06(3) [1.817–1.825]	1.7905(17) [1.823]
C1−C10	1.463(3) [1.465]	1.458(3) [1.466]	1.474(5)–68(5) [1.465-1.467]	1.408(2) [1.410]
C10−C11	1.380(4) [1.382]	1.434(3) [1.443]	1.406(5)–00(5) [1.443–1.444][a]	1.459(2) [1.440]
C10−C12	1.413(3) [1.443]	1.386(3) [1.382]	1.377(6)–91(5) [1.381–1.384]	1.408(2) [1.414]
C2−C20	1.477(3) [1.484]	1.484(3) [1.480]	1.488(5)–87(5) [1.484–1.488]	1.433(2) [1.428]
C3−C30	1.485(3) [1.489]	1.483(3) [1.482]	1.490(5)–80(5) [1.489–1.483]	1.428(2) [1.428]
C4−C40	1.474(3) [1.467]	1.461(3) [1.443]	1.472(5)–78(5) [1.466–1.465]	1.410(2) [1.409]
C40−C41	1.396(3) [1.384]	1.385(3) [1.382]	1.399(5)–1.386(5) [1.383–1.382]	1.403(2) [1.414]
C40−C42	1.399(4) [1.442][a]	1.430(3) [1.443]	1.384(5)–1.405(5) [1.444-1.443][a]	1.444(2) [1.441]
C2-C1-C10	128.4(2) [128.5]	129.63(18) [129.0]	129.3(3)–126.9(3) [128.7–129.3]	122.68(15) [122.5]
C3-C4-C40	128.7(2) [129.4]	130.12(18) [129.5]	128.6(3)–129.3(3) [128.9–128.5]	122.98(15) [122.5]
C1-C2-C20	123.4(2) [123.4]	125.95(18) [123.5]	125.3(3)–124.2(3) [123.9–124.4]	118.01(15) [118.3]
C4-C3-C30	124.3(2) [124.1]	126.82(18) [123.9]	124.9(3)–124.5(3) [124.3–123.4]	118.09(15) [118.2]

[a] Discrepancy attributed to the statistical disorder of the thienyl substituents in the solid state.

2a and **3a**). These modifications of the NMR spectroscopic data suggest that the dienic moiety of the phosphole ring is perturbed by the chemical modifications involving the P atom.

Derivative **3b** was characterized by an X-ray diffraction study (Figure 1, Table 1). As observed for **2b**, a statistical disorder of the thienyl ring was observed for **3b**. The gross structure of this thiooxophosphole is very similar to that of its σ^3-precursor **2b**, with two rather small and large twist angles (Table 2) between the phosphole ring and the 3-thienyl substituents at the $C_{2,5}$- and $C_{3,4}$-positions, respectively. The oxidation of the phosphorus atom results in an increase in the C−C bond length alternation within the phosphole ring (**2b** versus **3b**, Table 2), indicating a decrease of the aromatic character on going from σ^3- to the σ^4-derivative. This is a classical behavior for phosphole-based π-conjugated systems.[6d] As classically observed for mixed thiophene–phosphole derivatives,[4a,5] i) the chemical modification of the P center has an impact on their optical and electrochemical properties, and ii) oxo and thiooxo derivatives exhibit similar properties. The oxidation of the P atom of **2a**,**b** induces a bathochromic shift of the λ_{max} (ca. 30 nm, Table 3, Figure 4) as well as an increase of the first oxidation and reduction potentials (**2a**→**3a**,**4a**; **2b**→**3b**,**4b**, Table 3). It is worth noting that the increase of the oxidation potential is more pronounced for the 3-thienyl than for the 2-thienyl series, whereas an opposite trend is observed for the reduction potentials. Nevertheless, the electrochemical HOMO–LUMO gap for the 2-thienyl series (Table 3) remains even smaller than for the 3-thienyl series.

Table 3. $^{31}P\{^1H\}$ NMR, optical, and electrochemical data for phosphole and 1,1′-biphosphole derivatives.

Derivatives	δ $^{31}P\{^1H\}$[a] [ppm]	Yield [%]	$\lambda_{max}/\lambda_{onset}$[b] [nm]	logε	E_{pa}[c] [V]	E_{pc}[c] [V]
2a	+14.1	46	420/488	3.71	+0.62	−2.22
2b	+13.9	60	375/435	3.95	+0.64	−2.53
3a	+52.4	85	454/538	3.75	+0.81	−1.70[d]
3b	+53.2	80	413/485	3.48	+0.97	−1.93[d]
4a	+41.1	90	456/530	3.83	+0.82	−1.72[d]
4b	+43.4	95	411/484	3.83	+0.98	−1.91[d]
5a	−0.8	55	375–452/570	4.31–3.94	+0.60	−1.65
5b	−5.9	50	343–423/500	4.31–3.78	+0.69	−1.90
6b	+41.6	10	391/520	3.56	+1.00[d]	−2.13[d]
7b	+33.6	26	389/525	3.63	+1.15	−2.15[d]

[a] In $CDCl_3$. [b] Measured in CH_2Cl_2. [c] All potentials were obtained during cyclic voltametric investigations in 0.2 M Bu_4NPF_6 in CH_2Cl_2. Platinum electrode diameter 1 mm, sweep rate : 200 mV s^{-1}. All reported potentials are referenced to the reversible formal potential of the ferrocene/ferrocenium couple. [d] Reversible processes, $E°_{ox}$ and $E°_{red}$ values provided.

The impact of the chemical modifications of the σ^3,λ^3-phosphorus atom have also been investigated by theoretical calculations. The calculated structural data of thiooxophosphole derivative **3b** are very similar to those recorded by an X-ray diffraction study (Table 2). The HOMO of **3b** is a π-orbital mainly localized on the carbon framework (see the Supporting Information, Figure S1), and its energy is stabilized in comparison with that of **2b**. It is surprising that the stabilization is less pronounced in the case of the LUMO, resulting in a slight increase of the calculated HOMO–LUMO gap. This is unusual, since the generally observed red shift of the phosphole derivatives upon oxidation was shown to be attributable mainly to the stabilization of the LUMO.[5c] Despite the increase of the calculated HOMO–LUMO gap of **3b**, the TD-DFT simulated spectrum (shown as vertical lines in Figure 4) has reproduced the experimental observations showing a red shift in the vertical absorption energy upon oxidation. These experimental and theoretical studies show that the fine-tuning of phosphole-based π-conjugated systems upon P modifications is effective whatever the nature (2-thienyl or 3-thienyl) of the substituent of the phosphole ring.

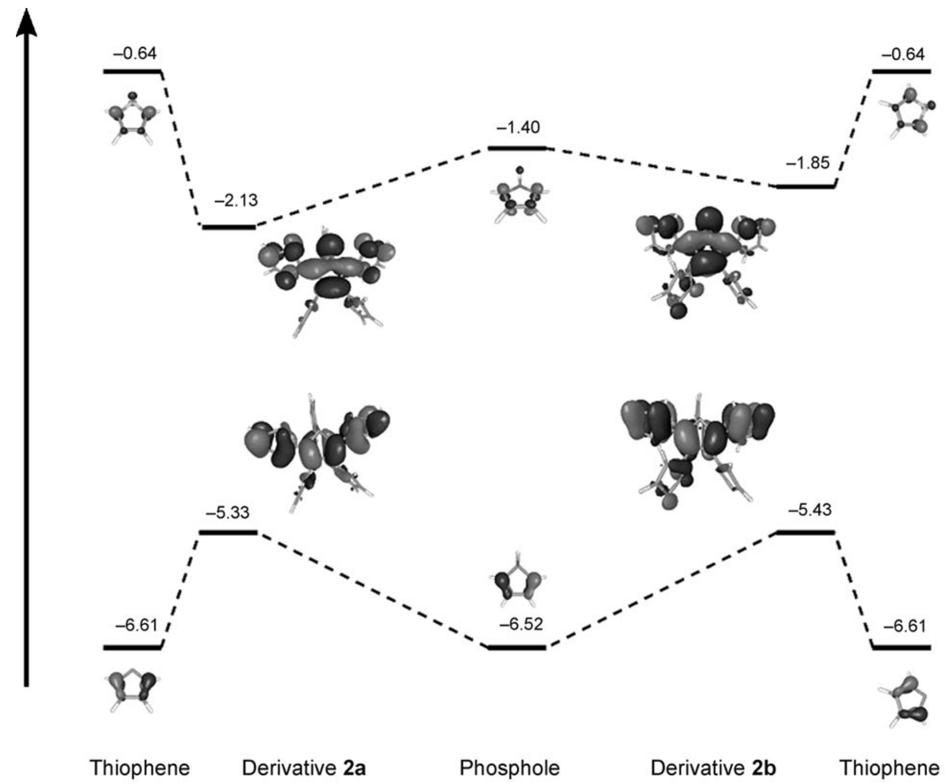


Figure 3. Frontier orbitals of thiophene, phosphole, and compounds **2a**,**b**.

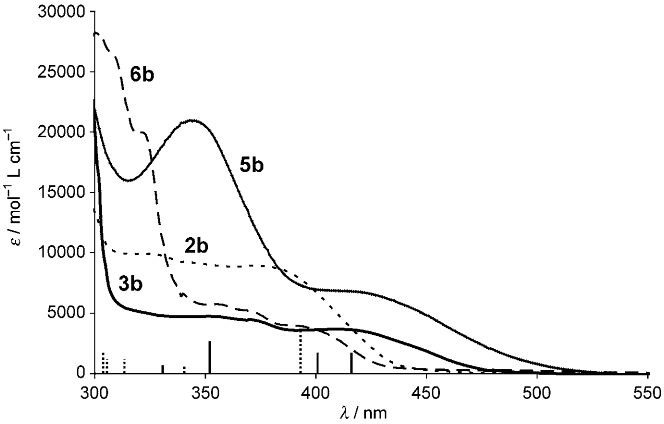


Figure 4. Electronic spectra of compounds **2b**, **3b**, **5b**, and **6b** in CH_2Cl_2, and TD-DFT simulated spectra (vertical lines) of **2b** (doted line) and **3b** (continuous line).

Synthesis and characterization of fully substituted (2-thienyl)- and (3-thienyl)-1,1′-biphosphole derivatives: 1,1′-Biphospholes bearing aromatic rings at the 2,2′- and 5,5′-positions are unique derivatives in which two π-systems composed of the phosphole butadienic moiety and its 2,5-substituents are in electronic interaction via a P−P bound (σ–π conjugation).[7] However, these types of derivative are still rare and only two of them have been structurally characterized to date.[7,9] The novel derivatives **5a**,**b** were readily obtained by an efficient synthetic route[7] involving the reaction of intermediate zirconacyclopentadienes with PBr_3 (Scheme 1). Their ^{1}H and ^{13}C NMR data are very similar to those of the corresponding phospholes **2a**,**b** and their $^{31}P\{^{1}H\}$ NMR spectra display a singlet at usual chemical shifts for 1,1′-biphospholes.[7] To complete the series of derivatives bearing 3-thienyl substituents (i.e. **2b** and **3b**, Scheme 1) and enable comparisons, 1,1′-biphosphole **5b** was subjected to an X-ray diffraction study (Figure 5, Table 1). As also observed for the two other 1,1′-biphospholes characterized by X-ray diffraction study,[7,9c] the two substituted phosphole moieties adopt a *gauche* conformation. The P−P (2.2141(13) Å) and P−C (1.804(3)–1.808(3)/ 1.806(3)–1.811(3) Å) distances are in the range expected for single bonds. The bond lengths and valence angles within the P ring are comparable to those observed for **2b** (Table 2, see note [a]) and the P atoms are strongly pyramidalized (ΣP_{ang}, 305.13°) (Figure 5), with rather acute C-P-P angles (101,42°(11)–108.33°(11)). The twist angles between the phosphole rings and their 2,2′- and 5,5′-thienyl subtituents range from 4.3° to 40.5°. The corresponding angles involving the 3,3′- and 4,4′-thienyl subtituents are much higher (>70°). This tendency was already observed with phosphole **2b** and its thiooxo derivative **3b** (Figure 1), and thus seems to have a general character.

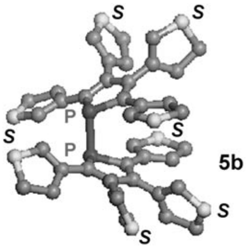


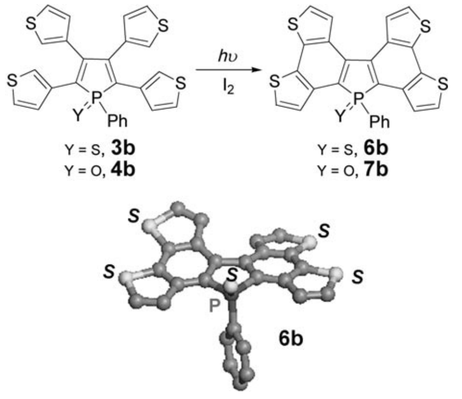
Figure 5. Molecular structure of **5b** in the solid state. Hydrogen atoms are omitted for clarity.

It was observed that while the absorption spectra of phosphole **2a**,**b** show only one absorption above 350 nm due to a π–π* transition (Figure 2), several bands are recorded for **5a**,**b** with one red-shifted broad shoulder (λ_{onset} = **5a**, 570 nm; **5b**, 500 nm) (Figure 4). It is noteworthy that 1,1′-biphospholes **5a**,**b** are more easily reduced than compounds **2a**,**b**, whereas the oxidation potentials of these two types of derivatives are essentially the same (Table 3). These experimental data clearly indicate that i) the HOMO–LUMO separation of 1,1′-biphospholes **5a**,**b** is smaller than that of the corresponding P-aryl phospholes **2a**,**b**, and ii) 1,1′-biphospholes **5a**,**b** possess a higher density of states than phospholes **2a**,**b**. Theoretical calculations on the present system confirmed both features, and the analysis of the orbitals has clearly shown the interaction of the σ_{PP} and σ^*_{PP} orbital with both di(thienyl)phosphole's π-systems. For example, the LUMO and the LUMO+1 of **5b** (shown as Figure S2 in the Supporting information) are the antibonding and the bonding combinations of the π-systems. This behavior is characteristic for through-bond coupling of two π-systems over an odd number of σ-bonds.[16] Since the through-bond interaction involves the occupied σ_{PP} and the unoccupied bonding combination of the LUMOs (π-type) of the di(thienyl)phosphole units (see the LUMO+1 orbital of **5b** in Figure S2 in the Supporting Information), some stabilization is expected as a result of this interaction. Indeed, the isodesmic reaction (1) revealed that assembly **5b** is stabilized by 3.6 kcal mol^{-1}, in spite of the apparently increased steric encumbrance (see Figure 3) in comparision with a simple diphosphine $Me_2P{-}PMe_2$.

$$\mathbf{5b}+2\,PhPMe_2 \rightarrow 2\,\mathbf{2b}+Me_2P{-}PMe_2 \qquad (1)$$

Note that theoretical calculations have also shown that σ,π-conjugation in 1,1′-biphospholes results in a narrowing of the HOMO–LUMO gap and an increased density of states compared to the corresponding 1-phenylphospholes. These data nicely corroborate and rationalize the experimental UV/Vis spectra (Figure 4).

Synthesis and characterization of fused phosphole–thiophene derivatives: An appealing property of mixed phosphole–thiophene derivatives is that the chemistry of the thiophene rings can be exploited towards the synthesis of original mixed π-conjugted P,S skeletons. This possibility was investigated by using 3-thienylphosphole derivatives with the aim to obtain novel fused phosphole–thiophene frameworks. Dithieno[*b*,*d*]phospholes and bithiophene-fused benzo[*c*]-phospholes have been receiving growing interest since they possess rigid and extented π-systems.[4] As recently noted by Matano et al., "*the number of ring-fused phosphole-based systems is quite limited and their potential in optoelectrochemical applications has not been fully addressed.*"[4d] The synthesis of phosphole derivatives **3b** and **4b** gave us the opportunity to investigate the synthesis of ring-fused phosphole-based systems with an unprecedented structure using a photocyclization reaction.[17] The aerobic irradiation at 320–400 nm in a Rayonet apparatus of a dilute toluene solution of **3b** and **4b** containing a catalytic amount of iodine afforded the air-stable derivatives **6b** and **7b**, respectively (Scheme 2). These compounds are the sole products of the reaction. However, as usually observed in this type of photocyclization process, they are obtained in low yields (ca. 15–20 %, reaction time of 12 h). Note that this reaction cannot be conducted with the σ^3-phosphole **2b** due to fast decomposition of this derivative under the reaction conditions. To the best of our knowledge, this is the first time that a photocyclization on phosphole-based derivatives is reported.



Scheme 2. Synthesis of fused phosphole-thiophene derivatives **6b** and **7b**. Molecular structure of **6b** in the solid state. Hydrogen atoms are omitted for clarity.

Fused derivatives **6b** and **7b** exhibit ^{31}P NMR chemical shifts that are slightly shifted to higher field compared to those of their precursors **3b** and **4b** (Table 3). The ^{1}H and ^{13}C NMR data of both fused phosphole–thiophene compounds are very similar and fully consistent with the proposed structures. The transformation of the compounds **3b** and **4b** into the corresponding fused derivatives **6b** and **7b** perturbs the phosphole ring as shown by the shielding of the ^{13}C NMR P-Cα signal (**3b/6b**, $\delta = 128.9$ ppm/125.9 ppm; **4b/7b**, $\delta = 129.1$ ppm/124.2 ppm). An X-ray diffraction study of **6b** (Table 1) revealed that the P atom adopts a distorted tetrahedral geometry and that the π-system has a helicoidal structure (helical curvature, ca. 38°; Scheme 2). This helicoidal structure is due to the *o*,*o*′-substitution pattern of the newly formed six-membered rings, which cause a steric repulsion of the two H atoms on the C31 and C22 atoms, respectively (Scheme 2). Note that theoretical calculations revealed that the inversion barrier of this helicoidal moiety is 8.5 kcal mol^{-1} only. These six-membered rings are almost planar (maximum deviation from the mean plane, 0.056 Å and 0.047 Å) and the C–C bond lengths vary from 1.403 Å to 1.428 Å. The C2–C20 and C3–C30 bonds are much longer than the other C–C distances (Table 2), probably due to the steric repulsion between the helix CH moieties (Scheme 2). However, the fact that these six-membered rings are planar and that the average C–C distance (1.41 ± 0.2 Å) is close to that of benzene clearly shows that they exhibit a high aromatic character. The aromaticity of the central five-membered ring, however, is somewhat less in the presence of the fused aromatic systems (NICS(0): **6b**, $\delta = +3.9$ ppm; **3b** $\delta = +0.4$ ppm). In the same vein, the NICS(0) data for different dithieno[3,2-*b*:2′,3′-*d*]phosphole oxides are between $\delta = +3.9$ and $+5.5$ ppm,[4h] while for 2,5-bis(2-thienyl)phosphole oxide a value of $\delta = -1.7$ ppm was reported.[18] Interestingly, similar changes can be seen when NICS(0) values of cyclopentadiene and fluorene ($\delta = -4.2$ ppm and $+0.5$ ppm) are compared at the HF/6-31G*//B3LYP/6-31G* level.[19] Although all the above-mentioned changes are small, they show a similar trend: the conjugation within the central five-membered ring system decreases upon formation of fused rings.[20] The competitive electronic delocalization within the fused "thiophene" and "benzene" moieties in **6b** is illustrated by the fact the C−C bond of the thiophene fragments is more localized in **6b** than in derivative **3b** (Scheme 2, Table 2). Likewise, the C=C bond length of the phosphole ring considerably increases on going from **3b** (1.360 ± 0.1 Å) to **6b** (1.404 ± 0.1 Å). It can be concluded from these solid-state data that **6b** has a considerable dibenzophosphole character. This conclusion is further supported by the optical and electrochemical behavior of compounds **6b** and **7b**. Compared to their respective precursors **3a**,**b**, fused derivatives exhibit blue-shifted absorption maxima, higher oxidation, and lower reduction values (**3b**/**6b**; **4b**/**7b**, Table 3, Scheme 1). These experimental data indicate a less efficient electron π-delocalization over the sp^2-C atoms of the fused carbon framework (i.e. an increased localization of the π-electron within the subunits), behavior that is typical for dibenzophosphole derivatives. Note that compounds **6b** and **7b** are emissive derivatives ($\lambda_{em.}$: **6b**, 475 nm; **7b**, 477 nm) but with low quantum yields (ca. 1 %).

Conclusions

The study of these novel series of mixed phosphole–thiophene derivatives revealed that varying the nature of the thienyl substituents (2-thienyl versus 3-thienyl) is an efficient means to tune the electronic properties of these heteroatomic π-conjugated systems. Theoretical calculations, in accordance with experimental data, revealed that this fine-tuning is mainly due to a destabilization of the LUMO level on going from 2-thienyl- to 3-thienyl substituents. The family of 1,1′-diphospholes exhibiting σ,π-conjugation has been extended and the stabilization due to this hyperconjugation was evaluated by studying an isodesmic reaction. A novel type of fused thiophene–dibenzophosphole skeleton was synthesized by a photocyclization reaction. Although the yield of this reaction is quite modest, its high selectivity makes it a novel and valuable synthetic tool for preparing dibenzophosphole derivatives. The electronic properties of this unprecedented fused framework are intriguing since both experimental and theoretical data suggest that the central P ring exhibits slight antiaromatic character, reducing the extent of the delocalization of the π-system over the entire molecule. This work opens further possibilities to tune the electronic properties of conjugated π-systems by fully exploiting the chemistry of both P- and S-heteroles.

Experimental Section

Details of the X-ray crystallography studies: Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of **2b**, **3b**, or **5b** or by slow evaporation of a benzene solution of **6b** at room temperature. Single-crystal data collection was performed at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Reflections were indexed, Lorentz-polarization corrected, and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed by using the SCALEPACK program.[21] Structure determinations were performed by direct methods with the program SIR97,[22] which revealed all the non-hydrogen atoms. The SHELXL program[23] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.

In the case of the derivatives **2b** and **5b**, all the thienyl moieties were found disordered over two superposed orientations. This disorder was treated for each thienyl ring with a partition of these two orientations. For each of these orientations, the relative population was refined. In the case of the derivative **3b**, only one of the thienyl rings presented a similar disorder, which was treated according to the same procedure.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[24] Details of crystal data and structural refinements are given in Table 1. CCDC-713600 (**2b**), CCDC-713601 (**3b**), CCDC-713602 (**5b**), and CCDC-713603 (**6b**) 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

Computations: Density functional calculations were carried out at the B3LYP/6-31G* level[25] of theory by using the Gaussian 03 suite of programs.[26] This level of the theory has provided satisfactory results for the phosphole–thiophene oligomers before.[4c,h,5d,7] The geometries were fully optimized, and for the resulting structures, second derivatives were calculated, which revealed only positive eigenvalues of the Hessian matrix. The vertical excitation energies were calculated for the optimized structures by the time-dependent density functional (TD-DFT) method, using the B3LYP functional and the 6-31G* basis set. NICS(0) values[27] were calculated at the geometrical center of each ring. The MOLDEN program[28] was used for the visualization of the MOs.

Syntheses

General information: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Column chromatography was performed in air, unless stated in the text. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). [Cp_2ZrCl_2] was obtained from Alfa Aesar Chem. Co. *n*BuLi, CuI, and S_8 were obtained from Acros Chem. Co. 2-Bromothiophene, 3-bromothiophene, [$PdCl_2(PPh_3)_2$], 1,8-diazabicyclo[5.4.0]undec-7-ene, trimethylsilylacetylene, and elemental sulfur were obtained from Aldrich Chem. Co. All compounds were used as received without further purification. $PPhBr_2$,[29] 1,2-di(2-thienyl)ethyne (**1a**),[14a] and 1,2-di(3-thienyl)ethyne (**1b**)[14b,c] were prepared as described in the literature. Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016 A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063–0.200 mm) in 3.5–20 cm columns. Irradiation reactions were conducted by using a Heraeus TQ 150 mercury vapor lamp. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300 or DPX200. ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to $Si(CH_3)_4$ as an external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85 % H_3PO_4. Assignment of the proton atoms was based on a COSY experiment. Assignment of the carbon atoms was based on HMBC, HMQC, and DEPT-135 experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1.

Determination of optical data: UV/Vis spectra were recorded at room temperature on a UVIKON 942 spectrophotometer, and luminescence spectra were recorded in freshly distilled solvents at room temperature with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a xenon lamp. Quantum yields were calculated relative to fluorescein ($\Phi = 0.90$ in 0.1 N NaOH).[30]

Cyclic voltammetry measurements: The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with a three-electrode configuration: the working electrode was a platinum disk, the reference electrode a saturated calomel electrode, and the counter-electrode a platinum wire. All potentials were internally referenced to the ferrocene/ferrocenium couple. For the measurements, concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and degassed dichloromethane (*Lichrosolv*, Merck) and 0.2 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use.

1-Phenyl-2,3,4,5-tetra(2-thienyl)phosphole (2a): A solution of BuLi in hexanes (2.5 M, 0,38 mL; 0.95 mmol) was added dropwise at −78 °C to a solution of [$\mathrm{Cp_2ZrCl_2}$] (0.132 g, 0.45 mmol) and 1,2-di(2-thienyl)ethyne (**1a**; 0.172 g, 0.9 mmol) in THF (10 mL). After stirring overnight, the solution turned deep red and neat $\mathrm{PhPBr_2}$ (0.102 mL, 0.5 mmol) was added at −78 °C. The solution was stirred for an additional 5 h and filtered through basic alumina (THF, $R_\mathrm{f}=0.8$). All the volatile materials were removed under vacuum. 1-Phenyl-2,3,4,5-tetra(2-thienyl)phosphole (**2a**) was washed several times with pentane and isolated as an orange solid (0.10 g, yield 46 %).^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): δ = 6.82 (m, 2H; $\mathrm{H_{thienyl}}$), 6.96–7.10 (m, 8H; $\mathrm{H_{thienyl}}$), 7.30–7.40 (m, 5H; $\mathrm{H_{thienyl}}$, H_{meta}, and $\mathrm{H}_{para,\mathrm{phenyl}}$), 7.62 ppm (m, 2H; $\mathrm{H}_{ortho,\mathrm{phenyl}}$); ^{13}C{^{1}H} NMR (75.46 MHz, $\mathrm{CD_2Cl_2}$): $\delta=126.5$ (d, J(P,C) = 1.9 Hz, $\mathrm{CH_{thienyl}}$), 126.7 (s, $\mathrm{CH_{thienyl}}$), 126.9 (d, J(P,C) = 10.4 Hz, CH_{thienyl}), 127.0 (s, CH_{thienyl}), 127.3 (s, CH_{thienyl}), 129.0 (d, J(P,C) = 8.9 Hz, $CH_{meta,\mathrm{phenyl}}$), 129.2 (d, J(P,C) = 1.9 Hz, CH_{thienyl}), 130.4 (d, J(P,C) = 1.7 Hz, $CH_{para,\mathrm{phenyl}}$), 131.6 (d, J(P,C) = 10.9 Hz, $C_{ipso,\mathrm{phenyl}}$), 134.1 (d, J(P,C) = 20.7 Hz, $CH_{ortho,\mathrm{phenyl}}$), 137.0 (d, J(P,C) = 2.1 Hz, C_{thienyl}), 138.5 (d, J(P,C) = 20.8 Hz, C_α), 139.6 (d, J(P,C) = 8.6 Hz, C_{thienyl}), 141.3 ppm (d, J(P,C) = 3.9 Hz, C_β); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+14.1$ ppm (s); HR-MS (EI): m/z: 487.9960 $[M]^+$; $\mathrm{C_{26}H_{17}PS_4}$ calcd 487.99508; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}PS_4}$ (488.654): C 63.91, H 3.51, S 26.25; found: C 63.73, H 3.74, S 26.15.

1-Phenyl-2,3,4,5-tetra(3-thienyl)phosphole (2b): A solution of BuLi in hexanes (1.6 M, 0,656 mL; 1.05 mmol) was added dropwise at −78 °C to a solution of [$\mathrm{Cp_2ZrCl_2}$] (0.146 g, 0.5 mmol) and 1,2-di(3-thienyl)ethyne (**1b**; 0.190 g, 1 mmol) in THF (10 mL). After stirring overnight, the solution turned deep red and neat $\mathrm{PhPBr_2}$ (0.103 mL, 0.5 mmol) was added at −78 °C. The solution was stirred for an additional 5 h and filtered through basic alumina (THF, $R_\mathrm{f}=0.8$). All the volatile materials were removed under vacuum. 1-Phenyl-2,3,4,5-tetra(3-thienyl)phosphole (**2b**) was washed several times with pentane and isolated as an orange solid (0.145 g, yield 60 %). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): $\delta=6.69$ (d, 2H; ^3J(H,H) = 4.6 Hz, $\mathrm{H_{thienyl}}$), 6.83 (d, 2H; ^3J(H,H) = 4.6 Hz, $\mathrm{H_{thienyl}}$), 7.00 (m, 4H; $\mathrm{H_{thienyl}}$), 7.09 (m, 2H; $\mathrm{H_{thienyl}}$), 7.26 (m, 2H; $\mathrm{H_{thienyl}}$), 7.36 (m, 3H; H_{meta} and $\mathrm{H}_{para,\mathrm{phenyl}}$), 7.57 ppm (m, 2H; $\mathrm{H}_{ortho,\mathrm{phenyl}}$); ^{13}C{^{1}H} NMR (75.46 MHz, $\mathrm{CD_2Cl_2}$): $\delta=121.6$ (d, J(P,C) = 9.9 Hz, $\mathrm{CH_{thienyl}}$), 123.4 (d, J(P,C) = 2.3 Hz, $\mathrm{CH_{thienyl}}$), 124.0 (s, $\mathrm{CH_{thienyl}}$), 124.2 (s, $\mathrm{CH_{thienyl}}$), 127.0 (d, J(P,C) = 7.2 Hz, $\mathrm{CH_{thienyl}}$), 128.1 (d, J(P,C) = 8.6 Hz, $\mathrm{CH}_{meta,\mathrm{phenyl}}$), 128.2 (d, J(P,C) = 1.7 Hz, $\mathrm{CH_{thienyl}}$), 129.2 (d, J(P,C) = 1.5 Hz, $\mathrm{CH}_{para,\mathrm{phenyl}}$), 130.9 (d, J(P,C) = 11.6 Hz, $\mathrm{C}_{ipso,\mathrm{phenyl}}$), 133.2, (d, J(P,C) = 19.7 Hz, $\mathrm{CH}_{ortho,\mathrm{phenyl}}$), 136.3 (d, J(P,C) = 18.8 Hz, C_α), 137.3 (d, J(P,C) = 2.7 Hz, $\mathrm{C_{thienyl}}$), 139.5 (s, $\mathrm{C_{thienyl}}$), 141.8 ppm (d, J(P,C) = 10.0 Hz, C_β); ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 121.5 MHz): $\delta=+13.9$ ppm (s); HR-MS (EI): m/z: 487.9966 $[M]^+$; $\mathrm{C_{26}H_{17}PS_4}$ calcd 487.99508; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}PS_4}$ (488.654): C 63.91, H 3.51, S 26.25; found: C 63.61, H 3.86, S 26.31.

1-Phenyl-2,3,4,5-tetra(2-thienyl)thiooxophosphole (3a): An excess of elemental sulfur was added at room temperature to a solution of 1-phenyl-2,3,4,5-tetra(2-thienyl)phosphole **2a** (0.150 g, 0.31 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The reaction mixture was stirred for two days, filtered, and the solvent was removed in vacuo. After purification on silica gel (heptane/$\mathrm{CH_2Cl_2}$, 20:80, v/v), **3a** was obtained an air-stable orange solid (yield: 0.136 g, 0.26 mmol, 85 %). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): $\delta=6.88$ (dd, 2H; ^3J(H,H) = 3.8 Hz, ^3J(H,H) = 5.2 Hz, $\mathrm{H_{thienyl}}$), 7.09 (m, 4H; $\mathrm{H_{thienyl}}$), 7.22 (d, 2H; ^3J(H,H) = 5.2 Hz, $\mathrm{H_{thienyl}}$), 7.41 (d, 2H; ^3J(H,H) = 3.8 Hz, $\mathrm{H_{thienyl}}$), 7.51 (dd, 2H; ^3J(H,H) = 4.9 Hz, ^4J(H,H) = 1.2 Hz, $\mathrm{H_{thienyl}}$), 7.58 (m, 3H; $\mathrm{H}_{meta,\mathrm{phenyl}}$, $\mathrm{H}_{para,\mathrm{phenyl}}$), 8.11 ppm (ddd, 2H; ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.9 Hz, J(P,H) = 14.2 Hz, $\mathrm{H}_{ortho,\mathrm{phenyl}}$); ^{13}C{^{1}H} NMR (75.46 MHz, $\mathrm{CD_2Cl_2}$): $\delta=126.7$ (s, $\mathrm{CH_{thienyl}}$), 127.5 (s, $\mathrm{CH_{thienyl}}$), 128.6 (s, $\mathrm{CH_{thienyl}}$), 128.8 (s, $\mathrm{CH_{thienyl}}$), 128.7 (d, J(P,C) = 96.3 Hz, $\mathrm{C}_{ipso,\mathrm{phenyl}}$), 129.2 (d, J(P,C) = 90.2 Hz, C_α), 129.3 (d, J(P,C) = 12.7 Hz, $\mathrm{CH}_{meta,\mathrm{phenyl}}$), 129.6 (d, J(P,H) = 5.2 Hz, $\mathrm{CH_{thienyl}}$), 129.8 (s, $\mathrm{CH_{thienyl}}$), 130.5 (d, J(P,C) = 11.7 Hz, $\mathrm{CH}_{ortho,\mathrm{phenyl}}$), 132.6 (d, J(P,C) = 3.1 Hz, $\mathrm{CH}_{para,\mathrm{phenyl}}$), 134.4 (d, J(P,C) = 15.8 Hz, $\mathrm{C_{thienyl}}$), 134.6 (d, J(P,C) = 17.5 Hz, $\mathrm{C_{thienyl}}$), 140.2 ppm (d, J(P,C) = 23.3 Hz, C_β); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+52.4$ ppm (s); HR-MS (EI) : m/z: 519.9682 $[M]^+$; $\mathrm{C_{26}H_{17}PS_5}$ calcd: 519.96715; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}PS_5}$ (520.718): C 59.97, H 3.29, S 30.79; found: C 60.01, H 3.38, S 30.95.

1-Phenyl-2,3,4,5-tetra(3-thienyl)thiooxophosphole (3b): An excess of elemental sulfur was added at room temperature to a solution of 1-phenyl-2,3,4,5-tetra(3-thienyl)phosphole (**2b**; 0.350 g, 0.77 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). This mixture was stirred overnight at room temperature, and then all the volatile materials were removed under vacuo. The precipitate was washed with pentane (4×10 mL) and 1-phenyl-2,3,4,5-tetra(3-thienyl)thiooxophosphole (**3b**) was obtained as an air-stable orange solid (0.320 g, 80 % yield). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): $\delta=6.67$ (d, 2H; ^3J(H,H) = 5.1 Hz, $\mathrm{H_{thienyl}}$), 6.81 (dd, 2H; ^3J(H,H) = 4.9 Hz, ^4J(H,H) = 1.1 Hz, $\mathrm{H_{thienyl}}$), 7.04 (dd, 2H; J(P,H) = 2.9 Hz, ^4J(H,H) = 1.1 Hz, $\mathrm{H_{thienyl}}$), 7.11 (m, 2H; $\mathrm{H_{thienyl}}$), 7.32 (dd, 2H; ^3J(H,H) = 4.9 Hz, J(P,H) = 2.9 Hz, $\mathrm{H_{thienyl}}$), 7.42 (m, 2H; $\mathrm{H_{thienyl}}$), 7.54 (m, 2H; $\mathrm{H}_{meta,\mathrm{phenyl}}$), 7.57 (m, 1H; $\mathrm{H}_{para,\mathrm{phenyl}}$), 8.07 ppm (ddd, 2H; ^4J(H,H) = 1.5 Hz, ^3J(H,H) = 8.3 Hz, J(P,H) = 13.8 Hz, $\mathrm{H}_{ortho,\mathrm{phenyl}}$); ^{13}C{^{1}H} NMR (75.46 MHz, $\mathrm{CDCl_3}$): $\delta=124.1$ (s, $\mathrm{CH_{thienyl}}$), 124.8 (s, $\mathrm{CH_{thienyl}}$), 124.9 (s, $\mathrm{CH_{thienyl}}$), 125.0 (s, $\mathrm{CH_{thienyl}}$), 126.6 (d, J(P,H) = 6.3 Hz, $\mathrm{CH_{thienyl}}$), 127.5 (s, $\mathrm{CH_{thienyl}}$), 127.6 (d, J(P,C) = 74.3 Hz, $\mathrm{C}_{ipso,\mathrm{phenyl}}$), 128.4 (d, J(P,C) = 12.5 Hz, $\mathrm{CH}_{meta,\mathrm{phenyl}}$), 129.8 (d, J(P,C) = 11.5 Hz, $\mathrm{CH}_{ortho,\mathrm{phenyl}}$), 130.8 (d, J(P,C) = 79.1 Hz, C_α), 131.5 (d, J(P,C) = 2.9 Hz, $\mathrm{CH}_{para,\mathrm{phenyl}}$), 131.8 (d, J(P,C) = 12.6 Hz, $\mathrm{C_{thienyl}}$), 134.9 (d, J(P,C) = 16.3 Hz, $\mathrm{C_{thienyl}}$), 143.0 ppm (d, J(P,C) = 23.7 Hz, C_β); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+53.2$ ppm (s); HR-MS (EI) : m/z: 519.9672 $[M]^+$; $\mathrm{C_{26}H_{17}PS_5}$ calcd: 519.96715; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}PS_5}$ (520.718): C 59.97, H 3.29, S 30.79; found: C 59.71, H 3.13, S 30.85.

1-Phenyl-2,3,4,5-tetra(2-thienyl)oxophosphole (4a): An excess of sodium periodate in aqueous solution (10 mL) was added to a solution of 1-phenyl-2,3,4,5-tetra(2-thienyl) phosphole **2a** (0.100 g, 0.2 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). This mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with $\mathrm{CH_2Cl_2}$ (4×10 mL) and then dried under $\mathrm{MgSO_4}$. Then all the volatiles materials were removed under vacuo. The precipitate was washed with pentane (2×10 mL), and 1-phenyl-2,3,4,5-tetra(2-thienyl)oxophosphole (**4a**) was obtained as an air-stable brownish solid (0.93 g, 90 % yield). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_3}$): $\delta=6.91$ (dd, 2H; ^3J(H,H) = 5.1 Hz, ^3J(H,H) = 3.9 Hz, $\mathrm{H_{thienyl}}$), 7.03 (dd, 2H; ^3J(H,H) = 3.9 Hz, ^4J(H,H) = 1.2 Hz, $\mathrm{H_{thienyl}}$), 7.09 (dd, 2H; ^3J(H,H) = 5.1 Hz, ^3J(H,H) = 3.6 Hz, $\mathrm{H_{thienyl}}$), 7.20 (d, 2H; ^3J(H,H) = 5.1 Hz, $\mathrm{H_{thienyl}}$), 7.44 (d, 2H; ^3J(H,H) = 3.6 Hz, $\mathrm{H_{thienyl}}$), 7.50 (dd, 2H; ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.2 Hz, $\mathrm{H_{thienyl}}$), 7.58 (m, 3H; $\mathrm{H}_{meta,\mathrm{phenyl}}$ and $\mathrm{H}_{para,\mathrm{phenyl}}$), 8.00 ppm (ddd, 2H; ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.4 Hz, J(P,H) = 12.6 Hz, $\mathrm{H}_{ortho,\mathrm{phenyl}}$); ^{13}C{^{1}H} NMR (75.46 MHz, $\mathrm{CD_2Cl_2}$): $\delta=126.9$ (s, $\mathrm{CH_{thienyl}}$), 127.5 (s, $\mathrm{CH_{thienyl}}$), 128.6 (s, $\mathrm{CH_{thienyl}}$), 128.8 (s, $\mathrm{CH_{thienyl}}$), 128.7 (d, J(P,C) = 96.4 Hz, $\mathrm{C}_{ipso,\mathrm{phenyl}}$), 128.9 (d, J(P,C) = 92.8 Hz, C_α), 129.4 (d, J(P,C) = 12.4 Hz, $\mathrm{CH}_{meta,\mathrm{phenyl}}$), 129.6 (s, $\mathrm{CH_{thienyl}}$), 129.7 (d, J(P,H) = 4.5 Hz, $\mathrm{CH_{thienyl}}$), 130.5 (d, J(P,C) = 10.7 Hz, $\mathrm{CH}_{ortho,\mathrm{phenyl}}$), 132.7 (d, J(P,C) = 2.8 Hz, $\mathrm{CH}_{para,\mathrm{phenyl}}$), 134.2 (d, J(P,C) = 18.3 Hz, $\mathrm{C_{thienyl}}$), 135.0 (d, J(P,C) = 15.0 Hz, $\mathrm{C_{thienyl}}$), 140.1 ppm (d, J(P,C) = 26.7 Hz, C_β); ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 121.5 MHz): $\delta=+41.1$ ppm (s); HR-MS (EI) : m/z: 505.0007 $[M+\mathrm{H}]^+$; $\mathrm{C_{26}H_{17}POS_4+H^+}$ calcd: 504.99782; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}POS_4}$ (504.653): C 61.88, H 3.40, S 25.42; found: C 61.78, H 3.53, S 25.47.

1-Phenyl-2,3,4,5-tetra(3-thienyl)oxophosphole (4b): An excess of sodium periodate in aqueous solution (10 mL) was added to a solution of 1-phenyl-2,3,4,5-tetra(3-thienyl)phosphole (**2b**; 0.510 g, 1.10 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). This mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with $\mathrm{CH_2Cl_2}$ (4×10 mL) and then dried under $\mathrm{MgSO_4}$. Then all the volatiles materials were removed under vacuo. The precipitate was washed with pentane (2×10 mL), and 1-phenyl-2,3,4,5-tetra(3-thienyl)oxophosphole (**4b**) was obtained as an air-stable brownish solid (0.49 g, 95 % yield). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$):

$\delta=6.66$ (d, 2H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $\mathrm{H_{thienyl}}$), 6.74 (dd, 2H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $^{4}J(\mathrm{H,H})=1.1$ Hz, $\mathrm{H_{thienyl}}$), 6.95 (dd, 2H; $J(\mathrm{P,H})=2.9$ Hz, $^{4}J(\mathrm{H,H})=1.1$ Hz, $\mathrm{H_{thienyl}}$), 7.06 (ddd, 2H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $^{4}J(\mathrm{H,H})=1.0$ Hz, $J(\mathrm{P,H})=2.9$ Hz, $\mathrm{H_{thienyl}}$), 7.26 (dd, 2H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $J(\mathrm{P,H})=2.9$ Hz, $\mathrm{H_{thienyl}}$), 7.38 (m, 2H; $\mathrm{H_{thienyl}}$), 7.50 (m, 3H; $\mathrm{H}_{\mathit{meta},\mathrm{phenyl}}$ *and* $\mathrm{H}_{\mathit{para}'\mathrm{phenyl}}$), 7.95 ppm (ddd, 2H; $^{3}J(\mathrm{H,H})=8.1$ Hz, $^{4}J(\mathrm{H,H})=1.4$ Hz, $J(\mathrm{P,H})=12.3$ Hz, $\mathrm{H}_{\mathit{ortho},\mathrm{phenyl}}$);$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.46 MHz, $\mathrm{CDCl_3}$): $\delta=125.1$ (s, $\mathrm{CH_{thienyl}}$), 125.2 (s, $\mathrm{CH_{thienyl}}$), 125.7 (d, $J(\mathrm{P,H})=5.9$ Hz, $\mathrm{CH_{thienyl}}$), 125.9 (s, $\mathrm{CH_{thienyl}}$), 126.9 (d, $J(\mathrm{P,H})=6.6$ Hz, $\mathrm{CH_{thienyl}}$), 127.6 (d, $J(\mathrm{P,C})=95.0$ Hz, $\mathrm{C}_{\mathit{ipso},\mathrm{phenyl}}$), 128.1 (s, $\mathrm{CH_{thienyl}}$), 129.1 (d, $J(\mathrm{P,C})=12.0$ Hz, $\mathrm{CH}_{\mathit{meta},\mathrm{phenyl}}$), 129.1 (d, $J(\mathrm{P,C})=94.0$ Hz, $\mathrm{C_\alpha}$), 130.6 (d, $J(\mathrm{P,C})=10.4$ Hz, $\mathrm{CH}_{\mathit{ortho},\mathrm{phenyl}}$), 132.3 (d, $J(\mathrm{P,C})=2.9$ Hz, $\mathrm{CH}_{\mathit{para},\mathrm{phenyl}}$), 132.8 (d, $J(\mathrm{P,C})=11.4$ Hz, $\mathrm{C_{thienyl}}$), 135.4 (d, $J(\mathrm{P,C})=17.7$ Hz, $\mathrm{C_{thienyl}}$), 143.4 ppm (d, $J(\mathrm{P,C})=27.2$ Hz, $\mathrm{C_\beta}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+43.4$ ppm (s); HR-MS (EI) : *m*/*z*: 503.9820 $[M]^+$; $\mathrm{C_{26}H_{17}POS_4}$ calcd: 503.98999; elemental analysis calcd (%) for $\mathrm{C_{26}H_{17}POS_4}$ (504.653): C 61.88, H 3.40, S 25.41; found: C 61.78, H 3.63, S 25.67.

1,1′-[2,3,4,5-Tetra(2-thienyl)]bisphosphole (5a): A solution of BuLi in hexanes (2.5 M, 0.86 mL; 2.1 mmol) was added dropwise at −78 °C to a solution of $[\mathrm{Cp_2ZrCl_2}]$ (0.301 g, 1.0 mmol) and 1,2-di(2-thienyl)ethyne (**1a**; 0.391 g, 2 mmol) in THF (30 mL). After stirring overnight, the solution turned deep red and neat $\mathrm{PBr_3}$ (0.19 mL, 1 mmol) was added at −78 °C. The solution was stirred for four days at room temperature and turned light red. The solution was then filtered through basic alumina (THF, $R_\mathrm{f}=0.8$) and all volatile materials were removed under vacuum. The precipitate was washed several times with *n*-heptane/ethyl acetate (8:2) ($R_\mathrm{f}=0.4$) and isolated as a dark red powder (0.45 g, 55 %). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): $\delta=6.56$ (d, 4H; $^{3}J(\mathrm{H,H})=3.5$ Hz, $\mathrm{H_{thienyl}}$), 6.91 (dd, 4H; $^{3}J(\mathrm{H,H})=3.5$ Hz, $^{3}J(\mathrm{H,H})=5.1$ Hz, $\mathrm{H_{thienyl}}$), 7.02 (m, 4H; $\mathrm{H_{thienyl}}$), 7.09 (dd, 4H; $^{3}J(\mathrm{H,H})=3.6$ Hz, $^{3}J(\mathrm{H,H})=5.1$ Hz, $\mathrm{H_{thienyl}}$), 7.30 (d, 4H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $\mathrm{H_{thienyl}}$), 7.34 ppm (d, 4H; $^{3}J(\mathrm{H,H})=5.1$ Hz, $\mathrm{H_{thienyl}}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.46 MHz, $\mathrm{CDCl_3}$): $\delta=126.7$ (s, $\mathrm{CH_{thienyl}}$), 126.8 (s, $\mathrm{CH_{thienyl}}$), 127.0 (s, $\mathrm{CH_{thienyl}}$), 127.1 (s, $\mathrm{CH_{thienyl}}$), 127.4 (t-like, $J(\mathrm{P,C})=11.5$ Hz and 11.5 Hz, $\mathrm{CH_{thienyl}}$), 129.2 (d, $^{1}J(\mathrm{P,C})=86.5$ Hz, $\mathrm{PC_\alpha}$), 129.5 (s, $\mathrm{CH_{thienyl}}$), 136.6 (s, $\mathrm{C_{thienyl}}$), 138.4 (t-like, $J(\mathrm{P,C})=11.5$ Hz and 11.5 Hz, $\mathrm{C_{thienyl}}$), 139.8 ppm (m, $\mathrm{PC_\beta}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 121.5 MHz): $\delta=-0.8$ ppm (s); HR-MS (ESI) : *m*/*z*: 821.9112 $[M]^+$; $\mathrm{C_{40}H_{24}P_2S_8}$ calcd: 821.91190; elemental analysis calcd (%) for $\mathrm{C_{40}H_{24}P_2S_8}$ (823.095): C 58.37, H 2.94, S 31.16; found: C 58.21, H 3.06, S 31.08.

1,1′-[2,3,4,5-Tetra(3-thienyl)]bisphosphole (5b): A solution of BuLi in hexanes (1.6 M, 0.656 mL; 1.05 mmol) was added dropwise at −78 °C to a solution of $[\mathrm{Cp_2ZrCl_2}]$ (0.146 g, 0.5 mmol) and 1,2-di(thiophene-3-yl)-ethyne (0.190 g, 1 mmol) in THF (10 mL). After stirring overnight, the solution turned deep red and neat $\mathrm{PBr_3}$ (0.95 mL, 1 mmol) was added at −78 °C. The solution was stirred for four days at room temperature and turned light red. The solution was then filtered through basic alumina (THF, $R_\mathrm{f}=0.8$) and all volatile materials were removed under vacuum. The precipitate was washed several times with pentane and isolated as a red solid (0.205 g, 50 %). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta=6.48$ (d, 4H; $^{3}J(\mathrm{H,H})=4.55$ Hz, $\mathrm{H_{thienyl}}$), 6.61 (m, 4H; $\mathrm{H_{thienyl}}$), 6.72 (m, 4H; $\mathrm{H_{thienyl}}$), 7.08 (m, 8H; $\mathrm{H_{thienyl}}$), 7.20 ppm (m, 4H; $\mathrm{H_{thienyl}}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.46 MHz, $\mathrm{CD_2Cl_2}$): $\delta=124.3$ (t-like, $J(\mathrm{P,C})=5.5$ Hz and 5.5 Hz, $\mathrm{CH_{thienyl}}$) 126.1 (s, $\mathrm{CH_{thienyl}}$), 126.4 (s, $\mathrm{CH_{thienyl}}$), 126.5 (s, $\mathrm{CH_{thienyl}}$), 130.0 (t-like, $J(\mathrm{P,C})=4.1$ Hz and 4.0 Hz, $\mathrm{CH_{thienyl}}$), 130.9 (s, $\mathrm{CH_{thienyl}}$), 131.0 (d, $J(\mathrm{P,C})=87.2$ Hz, $\mathrm{C_\alpha}$), 139.0 (t-like, $J(\mathrm{P,C})=9.9$ Hz and 10.0 Hz, $\mathrm{C_{thienyl}}$), 139.6 (s, $\mathrm{C_{thienyl}}$), 144.5 ppm (m, $\mathrm{C_\beta}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 121.5 MHz): $\delta=-7.4$ ppm (s); HR-MS (*m*NBA, FAB) : *m*/*z*: 844.9031 $[M+\mathrm{Na}]^+$; $\mathrm{C_{40}H_{24}P_2S_8{+}Na}$ calcd: 844.90167; elemental analysis calcd (%) for $\mathrm{C_{40}H_{24}P_2S_8}$ (823.095): C 58.37, H 2.94, S 31.16; found: C 58.55, H 3.00, S 31.35.

Compound 6b: A solution of 1-phenyl-2,3,4,5-tetra(3-thienyl)thiooxophosphole (**3b**; 0.150 g, 0.3 mmol) in toluene (500 mL) containing a catalytic amount of iodine was stirred and irradiated overnight by using a Heraeus TQ 150 mercury vapor lamp. Then all the volatile materials were removed under vacuo and the resulting precipitate was chromatographed on silica gel ($\mathrm{CH_2Cl_2}$, $R_\mathrm{f}=0.7$). Compound **6b** was obtained as a brownish solid (0.020 g, 10 % yield). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): $\delta=7.37$ (m, 2H; $\mathrm{H}_{\mathit{meta},\mathrm{phenyl}}$), 7.48 (m, 1H; $\mathrm{H}_{\mathit{para},\mathrm{phenyl}}$), 7.54 (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$), 7.67 (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$), 7.76 (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$), 7.86 (dd, 2H; $J(\mathrm{H,H})=7.6$ Hz ,$J(\mathrm{P,H})=14.5$ Hz, 2H; $\mathrm{H}_{\mathit{ortho},\mathrm{phenyl}}$), 8.09 ppm (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$; 75.46 MHz): $\delta=122.1$ (d, $J(\mathrm{P,C})=3.2$ Hz, $\mathrm{CH_{thienyl}}$), 125.6 (s, $\mathrm{CH_{thienyl}}$), 125.9 (d, $J(\mathrm{P,C})=130.7$ Hz, $\mathrm{C_\alpha}$), 126.0 (s, $\mathrm{CH_{thienyl}}$), 128.0 (s, $\mathrm{CH_{thienyl}}$), 128.9 (d, $J(\mathrm{P,C})=13.1$ Hz, $\mathrm{CH}_{\mathit{meta},\mathrm{phenyl}}$), 131.1 (d, $J(\mathrm{P,C})=12.2$ Hz, $\mathrm{CH}_{\mathit{ortho},\mathrm{phenyl}}$), 130.4 (d, $J(\mathrm{P,C})=69.6$ Hz, $\mathrm{C}_{\mathit{ipso},\mathrm{phenyl}}$),132.0 (d, $J(\mathrm{P,C})=11.4$ Hz, $\mathrm{C_{thienyl}}$), 132.3 (d, $J(\mathrm{P,C})=2.8$ Hz, $\mathrm{CH}_{\mathit{para},\mathrm{phenyl}}$), 135.5 (d, $J(\mathrm{P,C})=5.2$ Hz, $\mathrm{C_{thienyl}}$), 135.6 (d, , $\mathrm{J(P,C)}=5.1$ Hz, $\mathrm{C_{thienyl}}$), 136.7 (d, $J(\mathrm{P,C})=19.3$ Hz, $\mathrm{C_{thienyl}}$), 140.1 ppm (d, $J(\mathrm{P,C})=2.5$ Hz, $\mathrm{C_\beta}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+41.6$ ppm (s); HR-MS (EI): *m*/*z*: 515.9325 $[M]^+$; $\mathrm{C_{26}H_{13}PS_5}$ calcd: 515.93585; elemental analysis calcd (%) for $\mathrm{C_{26}H_{13}PS_5}$ (516.686): C 60.44, H 2.54, S 31.03; found: C 60.15, H 2.78, S 31.32.

Compound 7b: A solution of 1-phenyl-2,3,4,5-tetra(3-thienyl)oxophosphole (**4b**; 0.105 g, 0.2 mmol) in toluene (240 mL) containing a catalytic amount of iodine was stirred and irradiated overnight by using a Heraeus TQ 150 mercury vapor lamp. Then all the volatile materials were removed under vacuo and the resulting precipitate was chromatographed on silica gel (ethyl acetate, $R_\mathrm{f}=0.5$). Compound **7b** was obtained as a brownish solid (0.027 g, 26 % yield). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta=7.36$ (m, 3H; $\mathrm{H}_{\mathit{meta},\mathrm{phenyl}}$ and $\mathrm{H}_{\mathit{para},\mathrm{phenyl}}$), 7.50 (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$), 7.62 (d, 2H; $^{3}J(\mathrm{H,H})=5.3$ Hz, $\mathrm{H_{thienyl}}$), 7.64 (d, 2H; $^{3}J(\mathrm{H,H})=5.6$ Hz, $\mathrm{H_{thienyl}}$), 7.76 (ddd, 2H; $J(\mathrm{H,H})=1.5$ Hz, $J(\mathrm{H,H})=6.9$ Hz, $J(\mathrm{P,H})=13.2$ Hz, 2H; $\mathrm{H}_{\mathit{ortho},\mathrm{phenyl}}$), 8.01 ppm (d, 2H; $^{3}J(\mathrm{H,H})=5.6$ Hz, $\mathrm{H_{thienyl}}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$; 75.46 MHz): $\delta=122.8$ (d, $J(\mathrm{P,C})=2.8$ Hz, $\mathrm{CH_{thienyl}}$), 125.3 (s, $\mathrm{CH_{thienyl}}$), 124.2 (d, $J(\mathrm{P,C})=106.6$ Hz, $\mathrm{C_\alpha}$), 125.7 (s, $\mathrm{CH_{thienyl}}$), 127.8 (s, $\mathrm{CH_{thienyl}}$), 128.9 (d, $J(\mathrm{P,C})=12.6$ Hz, $\mathrm{CH}_{\mathit{meta},\mathrm{phenyl}}$), 129.3 (d, $J(\mathrm{P,C})=76.0$ Hz, $\mathrm{C}_{\mathit{ipso},\mathrm{phenyl}}$), 131.1 (d, $J(\mathrm{P,C})=11.1$ Hz, $\mathrm{CH}_{\mathit{ortho},\mathrm{phenyl}}$), 131.7 (d, $J(\mathrm{P,C})=12.1$ Hz, $\mathrm{C_{thienyl}}$), 132.3 (d, $J(\mathrm{P,C})=2.9$ Hz, $\mathrm{CH}_{\mathit{para},\mathrm{henyl}}$), 135.1 (d, $J(\mathrm{P,C})=11.5$ Hz, $\mathrm{C_{thienyl}}$), 136.3 (d, $J(\mathrm{P,C})=10.6$ Hz, $\mathrm{C_{thienyl}}$), 137.3 (d, $J(\mathrm{P,C})=22.5$ Hz, $\mathrm{C_{thienyl}}$), 140.4 ppm (d, $J(\mathrm{P,C})=2.2$ Hz, $\mathrm{C_\beta}$); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 121.5 MHz): $\delta=+33.6$ (s); HR-MS (ESI): *m*/*z*: 500.9655 $[M+\mathrm{H}]^+$; $\mathrm{C_{26}H_{14}POS_4}$ calcd: 500.96652; elemental analysis calcd (%) for $\mathrm{C_{26}H_{13}POS_4}$ (501.629): C 62.25, H 2.81, S 25.57; found: C 62.30, H 2.68, S 25.87.

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