

# Bithiophene-Fused Benzo[c]phospholes: Novel P,S-Containing Hybrid $\pi$ -Conjugated Systems with Small HOMO–LUMO Energy Gaps

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Bithiophene-fused benzo[c]phospholes were successfully prepared by a Ti<sup>II</sup>-mediated cyclization of dialkynylated bithiophene derivatives. It was revealed that the optical and electrochemical properties of the bithiophene-fused benzo[c]phospholes are deeply related to the  $\pi$ -conjugation modes at the fused bithiophene subunits. Both experimental and theoretical results demonstrate that the appropriately ring-

annulated systems are potential emitters with small HOMO–LUMO energy gaps covering the orange-to-red region due to the efficient  $\pi$ -electron delocalization over the three conjugated heterole rings.

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## Introduction

Phosphole is known as a poorly aromatic heterocyclopentadiene having a low-lying LUMO and a narrow HOMO–LUMO energy gap due to the effective  $\sigma^*-\pi^*$  conjugation.<sup>[1,2]</sup> The optical and electrochemical properties of phospholes, which are derived from the phosphane-linked *cis*-1,3-diene functionality, can be varied widely by chemical modifications at the dienic backbone and at the phosphorus center. In this context, the phosphole-based  $\pi$ -conjugated systems<sup>[3–5]</sup> are promising candidates for use in optoelectronic applications.<sup>[6,7]</sup> In particular, the ring-annulated polycyclic  $\pi$ -conjugated systems such as dibenzo[*b,d*]phospholes and dithieno[*b,d*]phospholes have attracted growing interest, as they possess rigid and elongated  $\pi$  networks that are beneficial for designing efficient light-emitting and electron-conducting materials.<sup>[8,9]</sup> A recent theoretical study on the electronic structures and reactivities of a series of benzo[c]heteroles predicted that benzo[c]phosphole would also be an attractive skeleton for developing novel phosphole-based  $\pi$ -conjugated systems with relatively small HOMO–LUMO energy gaps.<sup>[10]</sup> However, the chemistry of benzo[c]phospholes still remains unveiled due to the lack of a general method for the synthesis of thermally stable derivatives. Namely, the highly reactive *o*-quinonoid character of unsubstituted benzo[c]phosphole has precluded its isolation under ambient conditions.<sup>[11]</sup> With this in mind,

we designed a new class of ring-annulated benzo[c]phospholes that would possess a small *o*-quinonoid character. Herein, we report the first systematic study of the synthesis, structure, and optical and electrochemical properties of three types of bithiophene-fused benzo[c]phospholes. We experimentally demonstrated that changing the bithiophene skeleton dramatically affects the HOMO and LUMO energies as well as the intrinsic emitting properties of the hybrid phosphole–bithiophene-fused  $\pi$  systems.

## Results and Discussion

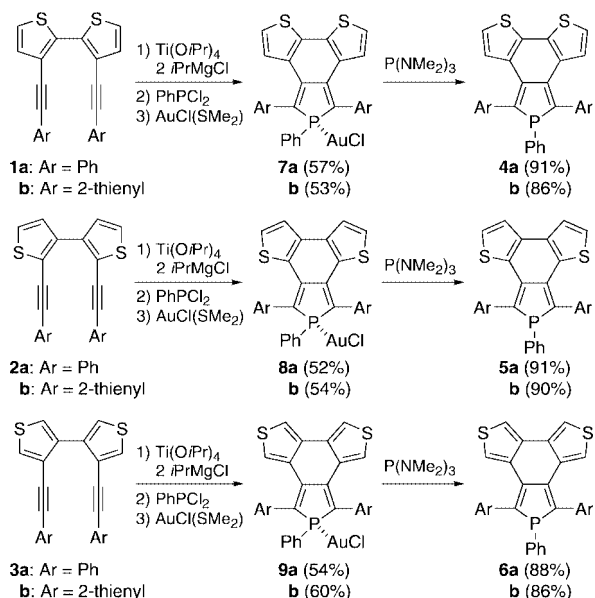
Bithiophene-fused benzo[c]phospholes **4–9** were successfully prepared by the Ti<sup>II</sup>-mediated cyclization<sup>[12]</sup> of dialkynylated bithiophene derivatives **1–3** (Scheme 1). Reaction of **1a**<sup>[13]</sup> with ( $\eta^2$ -propene)Ti(OiPr)<sub>2</sub> generated in situ from Ti(OiPr)<sub>4</sub> and 2 equiv. of *i*PrMgCl,<sup>[14]</sup> followed by treatment with dichloro(phenyl)phosphane, gave a mixture containing target compound **4a** and unreacted **1a**, which were not separable by column chromatography. Therefore, the mixture was subsequently treated with AuCl(SMe<sub>2</sub>) to afford Au<sup>I</sup>-phosphole complex **7a**, which could be easily isolated as a red solid in 57% yield. Treatment of **7a** with an excess amount of P(NMe<sub>2</sub>)<sub>3</sub> in toluene, followed by reprecipitation from MeOH reproduced  $\sigma^3$ -phosphole **4a** in 91% yield in high purity. The 2-thienyl-substituted derivatives (**4b** and **7b**) and the other types of bithiophene-fused benzo[c]phospholes (**5**, **6**, **8**, and **9**) were prepared from the corresponding bithiophene derivatives (**1b**, **2**, and **3**) according to a similar procedure.

Compounds **4–9** are air- and thermally stable solids soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, and toluene, and they were fully characterized by standard spectroscopic techniques. The <sup>31</sup>P NMR peaks of

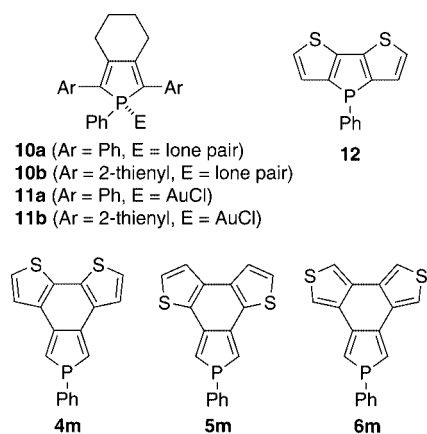
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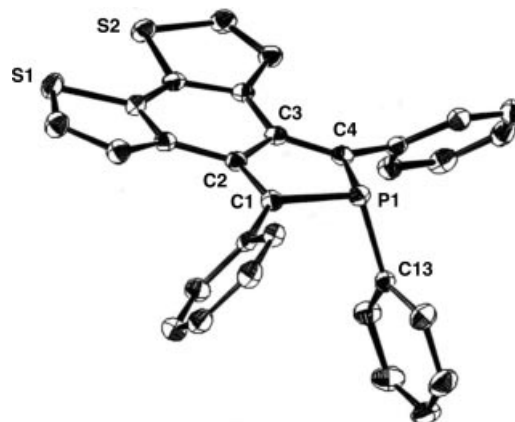

 Scheme 1. Synthesis of bithiophene-fused benzo[c]phospholes **4–9**.

$\sigma^3$ -derivatives **4–6** appeared at  $\delta = 24.2$ – $29.6$  ppm, whereas those of Au complexes **7–9** appeared at  $\delta = 46.5$ – $51.4$  ppm. The observed downfield shifts ( $\Delta\delta = 19.0$ – $23.9$  ppm for **7**, **8**, **9** vs. **4**, **5**, **6**) clearly support that the gold is coordinated to the phosphorus center. The downfield appearances of the  $^{31}\text{P}$  NMR peaks of **4–6** relative to those ( $\delta = 12.7$ – $13.6$  ppm) of Réau's 3,4- $\text{C}_4$ -bridged  $\sigma^3$ -phospholes **10a,b** (Figure 1)<sup>[3c]</sup> are presumably due to  $\pi$  conjugation along the benzo[c]-backbone of the present fused  $\pi$  system.


 Figure 1. 2,5-Diarylphospholes **10** and **11**, dithieno[b,d]phosphole **12**, and bithiophene-fused benzo[c]phosphole models **4m–6m**.

The structures of **4a** and **7a** were further elucidated by X-ray crystallography.<sup>[15]</sup> As shown in Figure 2, the  $\pi$ -conjugated phosphole and bithiophene rings in **4a** are nearly coplanar with moderate C–C/C=C bond length alternations ( $\Delta d = 0.04$ – $0.13$  Å).<sup>[16]</sup> The phosphorus atom is pyramidalized with the sum of the C–P–C bond angles of  $303.2^\circ$ . The planar, fused  $\pi$  structure was also observed for **7a** (Supporting Information, Figure S1), in which the phosphorus atom adopts a distorted tetrahedral geometry ( $\Sigma_{\text{C–P–C}} = 310.9^\circ$ ). The  $\text{C}_\alpha$ – $\text{C}_\beta$  and  $\text{C}_\beta$ – $\text{C}_\beta$  bond lengths of the

phosphole ring in **7a** [1.353(6)–1.374(5) Å and 1.502(7) Å] are close to those in **11a** [1.346(9)–1.350(9) Å and 1.484(9) Å],<sup>[6b]</sup> and the Au–P bond length [2.2283(10) Å] and the P–Au–Cl bond angle [ $177.27(4)^\circ$ ] are within the range of typical values reported for  $\text{Au}^{\text{I}}$ -phosphole complexes.<sup>[17]</sup> In both **4a** and **7a**, the two  $\alpha$ -phenyl groups are twisted from the phosphole ring with dihedral angles of  $53.1$ – $54.7^\circ$  and  $51.8$ – $88.0^\circ$ , respectively.


 Figure 2. ORTEP diagram of **4a** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [ $^\circ$ ]: P1–C1 1.7934(14), P1–C4 1.7958(16), P1–C13 1.8272(15), C1–C2 1.374(2), C2–C3 1.486(2), C3–C4 1.374(2); C1–P1–C4  $92.22(7)$ , C1–P1–C13  $104.97(6)$ , C4–P1–C13  $106.00(7)$ .

To disclose the optical and electrochemical properties of the bithiophene-fused benzo[c]phospholes, we measured UV/Vis absorption and fluorescence spectra and redox potentials of **4–9**, and the results are summarized in Table 1. The UV/Vis absorption spectra of **4a** and **5a** display broad absorption bands attributable to the  $\pi$ – $\pi^*$  transition in the visible region (Figure 3). In the fluorescence spectra, **4a** and **5a** show single emission bands in the orange region with relatively high quantum yields (**4a**,  $\Phi_{\text{F}} = 17.6\%$ ; **5a**,  $\Phi_{\text{F}} = 9.7\%$ ). The absorption and fluorescence maxima of **4a** (462 nm; 600 nm) and **5a** (472 nm; 609 nm) are remarkably

 Table 1. Optical and electrochemical data for **4–9**.

| Compd.    | Absorption <sup>[a]</sup><br>$\lambda_{\text{abs}} / \text{nm}^{[c]}$ | $\log \epsilon$ | Fluorescence <sup>[a]</sup><br>$\lambda_{\text{em}} / \text{nm}^{[d]}$ | $\Phi_{\text{F}} / \%$ <sup>[c]</sup> | Redox potentials <sup>[b]</sup><br>$E_{\text{ox}} / \text{V}^{[f]}$ | $E_{\text{red}} / \text{V}^{[f]}$ |
|-----------|-----------------------------------------------------------------------|-----------------|------------------------------------------------------------------------|---------------------------------------|---------------------------------------------------------------------|-----------------------------------|
| <b>4a</b> | 462                                                                   | 3.89            | 600                                                                    | 17.6                                  | 0.45                                                                | –2.14                             |
| <b>4b</b> | 483                                                                   | 3.94            | 646                                                                    | 2.9                                   | 0.36                                                                | –2.00                             |
| <b>5a</b> | 472                                                                   | 3.66            | 609                                                                    | 9.7                                   | 0.47                                                                | –2.09                             |
| <b>5b</b> | 491                                                                   | 3.69            | 656                                                                    | 2.6                                   | 0.39                                                                | –1.97                             |
| <b>6a</b> | 395 (sh)                                                              | 3.36            | 548                                                                    | 0.64                                  | 0.66                                                                | –2.35                             |
| <b>6b</b> | 409 (sh)                                                              | 3.51            | 582                                                                    | 1.10                                  | 0.56                                                                | –2.18                             |
| <b>7a</b> | 502                                                                   | 3.73            | 661                                                                    | 0.30                                  | 0.83                                                                | –1.63                             |
| <b>7b</b> | 535                                                                   | 3.79            | 710                                                                    | 0.05                                  | 0.66                                                                | –1.55                             |
| <b>8a</b> | 503                                                                   | 3.46            | 675                                                                    | 0.10                                  | 0.86                                                                | –1.62                             |
| <b>8b</b> | 539                                                                   | 3.67            | 720                                                                    | 0.02                                  | 0.70                                                                | –1.50                             |
| <b>9a</b> | 420 (sh)                                                              | 3.15            | 596                                                                    | 0.47                                  | 1.12                                                                | –1.86                             |
| <b>9b</b> | 435 (sh)                                                              | 3.45            | 606                                                                    | 0.67                                  | 0.88                                                                | –1.76                             |

[a] Measured in  $\text{CH}_2\text{Cl}_2$ . [b] Determined by DPV in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M } n\text{Bu}_4\text{NPF}_6$ . [c] The longest absorption maxima. [d] Excited at 440 nm for **4**, **5**, **7**, and **8** and at 420 nm for **6** and **9**. [e] Fluorescence quantum yields relative to **11b** ( $\Phi_{\text{F}} = 12.9\%$ ; ref.<sup>[6b]</sup>). [f] Redox potentials vs.  $\text{Fc}/\text{Fc}^+$  couple.

redshifted relative to those of **10a** (354 nm; 466 nm)<sup>[3c]</sup> and Baumgartner's dithieno[*b,d*]phosphole **12** (338 nm; 415 nm),<sup>[9a]</sup> exhibiting the effective  $\pi$ -extension in the present fused  $\pi$  systems. In marked contrast, **6a** exhibits a weak absorption peak (sh) at 395 nm and is far less emissive ( $\Phi_F = 0.64\%$ ). The Stokes shift of **6a** (7070  $\text{cm}^{-1}$ ) is considerably larger relative to those of **4a** (4980  $\text{cm}^{-1}$ ) and **5a** (4770  $\text{cm}^{-1}$ ). The observed large redshifts in **4a** and **5a** relative to that of **6a** are attributable to the difference in their  $\pi$ -conjugation modes. That is, the  $\pi$  electrons are less efficiently spread over the fused rings for **6a** than for **4a** and **5a**, as all three heterole rings are linked at the respective  $\beta$ -positions in **6a**. Moreover, the small  $\Phi_F$  value of **6a** in comparison with those of **4a** and **5a** may result from the large Stokes shift of **6a**, which accelerates nonradiative decay of the  $S_1$  state of **6a**. The above results demonstrate for the first time that the optical properties of benzo[*c*]phospholes are tunable by chemical modifications at the fused  $\pi$  backbone.

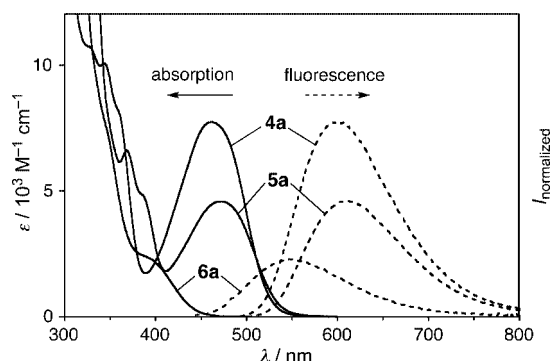


Figure 3. UV/Vis absorption (solid line) and fluorescence (dashed line) spectra of **4a**, **5a**, and **6a** in  $\text{CH}_2\text{Cl}_2$ .

It is well known that the chemical functionalizations at the  $\alpha$ -carbon atoms and the phosphorus atom affect optical and electrochemical properties of the phosphole ring.<sup>[2]</sup> The  $\alpha$ -2-thienyl-substituted derivatives **4b**, **5b**, and **6b** exhibit absorption and emission maxima at longer wavelengths than do the corresponding  $\alpha$ -phenyl derivatives, although the bathochromic shifts ( $\Delta\lambda_{\text{abs}} = 14\text{--}21\text{ nm}$ ;  $\Delta\lambda_{\text{em}} = 34\text{--}47\text{ nm}$ : 2-thienyl vs. phenyl) are smaller than those reported for **10b** versus **10a** (Supporting Information, Figure S2a).<sup>[3c]</sup> The P coordination to the  $\text{AuCl}$  salt induces more pronounced effects on the optical properties, that is, the larger bathochromic shifts in absorption and emission spectra ( $\Delta\lambda_{\text{abs}} = 25\text{--}52\text{ nm}$ ;  $\Delta\lambda_{\text{em}} = 24\text{--}66\text{ nm}$ ) and the considerable decrease in emission efficiency (Supporting Information, Figure S2b). Note that the fluorescence of chromophores **4** and **5** covers the orange-to-red region ( $\lambda_{\text{em}} = 600\text{--}656\text{ nm}$ ).

The electrochemical redox processes of **4–9** were found to be irreversible, and the redox potentials listed in Table 1 were determined by means of differential pulse voltammetry (DPV). The first oxidation potentials ( $E_{\text{ox}}$ ) and the first reduction potentials ( $E_{\text{red}}$ ) of **4a** are 0.45 and  $-2.14\text{ V}$  (vs. ferrocene/ferrocenium), respectively, both of which are comparable to the respective potentials of **5a** ( $E_{\text{ox}} = 0.47\text{ V}$ ;  $E_{\text{red}} = -2.09\text{ V}$ ). By contrast, **6a** showed more positive  $E_{\text{ox}}$

(0.66 V) and more negative  $E_{\text{red}}$  ( $-2.35\text{ V}$ ) relative to those of **4a** and **5a**, showing that the HOMO–LUMO energy gaps of **4a** and **5a** ( $\Delta E = 2.56\text{--}2.59\text{ V}$ ) are much smaller than that of **6a** ( $\Delta E = 3.01\text{ V}$ ). This is in good agreement with the results obtained from the absorption and fluorescence spectra (vide supra).

The complexation at the phosphorus center shifted the redox potentials to the positive direction (**7**, **8**, **9** vs. **4**, **5**, **6**). Noticeably, the shifts of the reduction potentials ( $\Delta E_{\text{red}} = 0.42\text{--}0.51\text{ V}$ ) are somewhat larger than those of the oxidation potentials ( $\Delta E_{\text{ox}} = 0.30\text{--}0.46\text{ V}$ ), indicating that the LUMO is lowered more largely than the HOMO by the complexation. On the other hand, the replacement of the  $\alpha$ -substituents at the phosphole ring from phenyl to 2-thienyl shifted the oxidation and reduction potentials to the negative and positive directions, respectively, thereby narrowing the HOMO–LUMO energy gaps by 0.20–0.34 V.

To gain more insight into the electronic structures of bithiophene-fused benzo[*c*]phospholes, we carried out DFT calculations at the B3LYP/6-31G\* level on  $\alpha$ -unsubstituted model compounds **4m**, **5m**, and **6m**.<sup>[18]</sup> As visualized in Figure 4, the frontier orbitals of **4m** and **5m** are derived from the typical frontier orbitals of both the phosphole and bithiophene moieties, and they are spread over the entire  $\pi$ -conjugated plane. The HOMOs hold antibonding characters between the adjacent heterole subunits, whereas the LUMOs represent interring bonding interactions. On the other hand, the frontier orbitals of **6m** differ from those of **4m** and **5m**. For instance, the LUMO of **6m** represents almost no bonding interactions among the three heterole rings. As a consequence, the calculated HOMO–LUMO separations of **4m** (3.21 eV) and **5m** (3.20 eV) are much smaller than that of **6m** (3.95 eV).<sup>[19]</sup> This agrees well with the experimentally observed results. As illustrated in Figure 4, the  $\sigma^*(\text{P-C}_{\text{Ph}})$  orbital contributes to the LUMO to some degree, which explains the more pronounced effects of the complexation on the LUMOs relative to their HOMOs.

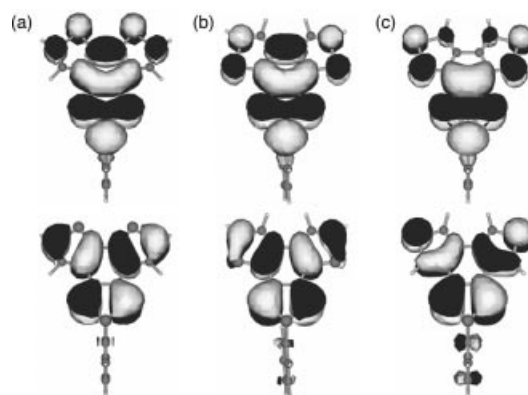


Figure 4. HOMO (lower) and LUMO (upper) of **4m** (a), **5m** (b), and **6m** (c).

## Conclusions

We successfully applied the  $\text{Ti}^{\text{II}}$ -mediated cyclization protocol to the preparation of three types of bithiophene-fused



benzo[*c*]phospholes, which are the first examples of thermally and chemically stable benzo[*c*]phospholes. It was revealed that the optical and electrochemical properties of the bithiophene-fused benzo[*c*]phospholes strongly depend on the  $\pi$ -conjugation modes of the fused rings. Both experimental and theoretical results demonstrate that the appropriately fused  $\pi$  systems are potential emitters with small HOMO–LUMO energy gaps reaching into the near-infrared region. The chemical functionalization at the annulated bithiophene moieties will allow us to further extend the two-dimensional  $\pi$  networks. In this regard, the bithiophene-fused benzo[*c*]phospholes are highly promising building blocks for tailoring P,S-containing hybrid  $\pi$ -conjugated materials toward optoelectronic applications.

## Experimental Section

**7a:** To a mixture of **1a** (110 mg, 0.30 mmol),  $\text{Ti}(\text{O}i\text{Pr})_4$  (0.088 mL, 0.30 mmol), and  $\text{Et}_2\text{O}$  (9 mL) was added a solution of  $i\text{PrMgCl}$  (2.0 M in ether, 0.30 mL, 0.60 mmol) at  $-60^\circ\text{C}$ . The resulting mixture was stirred for 3 h at  $-40^\circ\text{C}$ , followed by the addition of  $\text{PhPCl}_2$  (0.041 mL, 0.30 mmol) at this temperature. The resulting suspension was warmed to  $0^\circ\text{C}$  and stirred for 1 h. After stirring for an additional 3 h at room temperature, the mixture was subjected to short silica gel column chromatography ( $\text{CH}_2\text{Cl}_2$ ). The orange fraction was then collected and treated with  $\text{AuCl}(\text{SMe}_2)$  (90 mg, 0.30 mmol). The color of the solution turned to red in a few seconds, and the mixture was concentrated under reduced pressure. The solid residue was subjected to silica gel column chromatography ( $\text{CH}_2\text{Cl}_2$ /hexane). The red fraction was collected, evaporated, and washed with MeOH to give **7a** as a red solid (120 mg, 57%). M.p.  $215^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 6.56 (d,  $J$  = 5.2 Hz, 2 H), 7.01 (d,  $J$  = 5.2 Hz, 2 H), 7.05 (br., 2 H), 7.27 (br., 2 H), 7.32–7.42 (m, 4 H), 7.42–7.60 (m, 5 H), 7.79 (br., 2 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = +46.5 ppm. MS (MALDI-TOF):  $m/z$  = 707  $[\text{M}]^+$ . HRMS (FAB): calcd. for  $\text{C}_{30}\text{H}_{19}\text{AuClPS}_2$   $[\text{M}]^+$  706.0020; found 706.0016.

**4a:**  $\text{P}(\text{NMe}_2)_3$  (32  $\mu\text{L}$ , 0.18 mmol) was added to a toluene solution (5 mL) containing **7a** (42 mg, 0.060 mmol). After stirring at room temperature for 10 min, the mixture was concentrated under reduced pressure. The residue was washed with MeOH to give **4a** as an orange solid (26 mg, 91%). M.p.  $175^\circ\text{C}$  (dec).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 6.85 (d,  $J$  = 5.2 Hz, 2 H), 7.02 (d,  $J$  = 5.2 Hz, 2 H), 7.10–7.24 (m, 5 H), 7.25–7.40 (m, 10 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 122.8, 126.3, 127.4, 128.5 (d,  $J_{\text{PC}}$  = 9.9 Hz), 128.8, 128.9 (d,  $J_{\text{PC}}$  = 9.1 Hz), 129.9 (d,  $J_{\text{PC}}$  = 7.4 Hz), 130.3 (d,  $J_{\text{PC}}$  = 1.7 Hz), 132.6 (d,  $J_{\text{PC}}$  = 3.3 Hz), 134.7 (d,  $J_{\text{PC}}$  = 1.6 Hz), 134.9 (d,  $J_{\text{PC}}$  = 19.0 Hz), 136.2 ( $J$  = 14.9 Hz), 138.0 (d,  $J_{\text{PC}}$  = 14.9 Hz), 146.1 (d,  $J_{\text{PC}}$  = 3.3 Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = +24.6 ppm. MS (MALDI-TOF):  $m/z$  = 474  $[\text{M}]^+$ . HRMS (FAB): calcd. for  $\text{C}_{30}\text{H}_{19}\text{PS}_2$   $[\text{M}]^+$  474.0666; found 474.0672.

**Supporting Information** (see footnote on the first page of this article): Experimental details, characterization data, and DFT computational results.

## Acknowledgments

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- These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [16] The dihedral angles between the phosphole ring and the two thiophene rings are 6.0–8.8° for **4a** and 3.3–7.7° for **7a**. The phosphorus atom is slightly deviated from the mean plane of the benzo[c]phosphole skeleton by 0.14 Å for **4a** and 0.06 Å for **7a**.
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- [18] The calculated structural parameters of **4m** are in good accordance with the experimentally determined parameters of **4a**, suggesting that **4m** is a good model for discussing the electronic structure of **4a**. The structural parameters of **4m**, **5m**, and **6m** are summarized in Figure S4 in the Supporting Information.
- [19] The HOMO and LUMO energies (in eV) are as follows: **4m** (–5.10, –1.89), **5m** (–5.16, –1.96), **6m** (–5.55, –1.60).

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