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Synthesis and Properties of Benzophospholo[3,2-*b*]benzofuran Derivatives

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ABSTRACT: Benzophospholo[3,2-*b*]benzofuran (BPBF) derivatives were studied as a new family of phosphole-containing π-conjugated organic materials. The versatile reactivity of the trivalent phosphorus center of the parent BPBF offered an access to a variety of derivatives by simple chemical modifications. The diversity-oriented synthetic route was also developed to allow a facile access to BPBFs with a different substituent on the phosphorus center. Photophysical properties were revealed based on UV-vis and photoluminescence spectroscopies and theoretical calculation. The characteristic property of BPBF derivatives is highly-efficient photoluminescence. In particular, phosphole oxide derivatives demonstrated intense blue fluorescence with high quantum yield over 85% even in the solid state.

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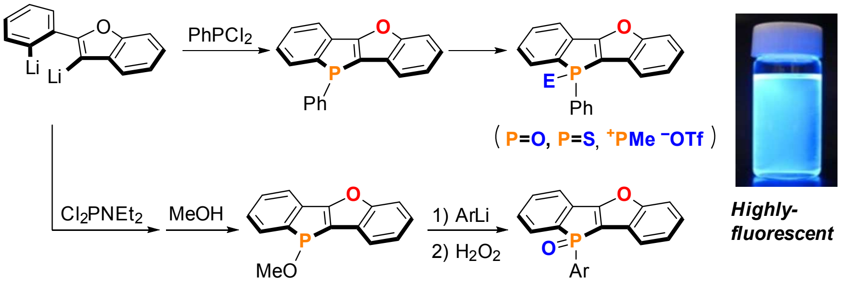


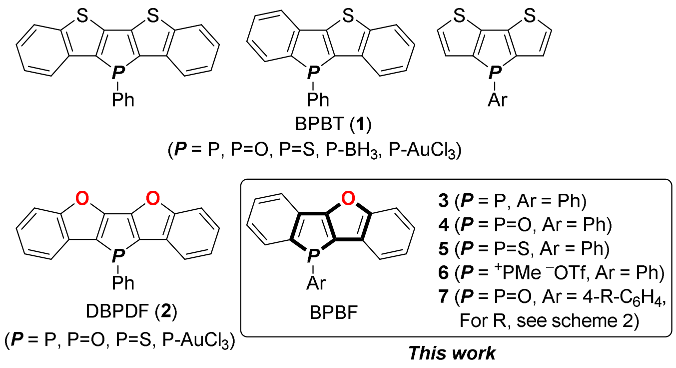
INTRODUCTION

Incorporation of phosphole moiety(s) into the π-conjugated system is a promising strategy for new organic functional materials with novel properties.[1] In contrast to the nitrogen center in pyrrole, the trivalent phosphorus center in a phosphole ring adopts a tetrahedral geometry. Accordingly, the lone pair on the phosphorus center cannot interact with butadiene π-electrons efficiently, which causes the very low aromaticity of phosphole.[2] On the other hand, such a tetrahedral geometry allows the effective interaction of the exocyclic P−C σ^* orbital with the endocyclic butadiene π* orbital, resulting in a low-lying LUMO energy level of phosphole.[3] The tetrahedral geometry of the phosphorus center also gives phosphole an opportunity for easy modification. Oxidation, alkylation, and coordination to a Lewis acid give the corresponding phosphole derivatives with different electronic and steric structures. Based on these attractive features of phosphole moiety, a variety of phosphole-containing π-conjugated molecules have been developed, such as oligophospholes,[4] phosphole-containing polymers,[5] 2,5-diarylphospholes,[6] (di)benzophospholes,[7] dithieno[3,2-*b*;2′,3′-*d*]phospholes,[8] benzophospholo[3,2-*b*]benzophospholes,[9] and zwitterionic benzoborolo[3,2-*b*]benzophospholes,[10] and found to be promising candidates for high-performance organic functional materials. In particular, high emission property is characteristic in phosphole-containing π-conjugated compounds. For example, 2,5-diarylphospholes have been systematically studied to be applied as emissive layer for organic light-emitting diodes (OLEDs).[6d, 6e] Extended π-conjugated systems with a dithienophosphole[8a, 8b, 8d] or phospholo[3,2-*b*]phosphole moiety[9] with extended π-conjugated systems have been reported to demonstrate intense fluorescence with moderate to high quantum yields.

Benzene-,[7] thiophene-,[8] phosphole-,[9] and borole-fused[10] phosphole derivatives have been reported so far. In particular, thiophene-fused derivatives were intensely studied (Chart 1). On the other hand, the furan-fused phosphole derivatives, such as dibenzo[*d*,*d*']phospholo[3,2-*b*:4,5-*b*']difuran **2** (DBPDF) (Chart 1), have been synthesized only in the last few years,[11] and there is a limited information about their structure–property relationship.[11b] Recently, a variety of furan-fused π-conjugated molecules have been synthesized and been applied as organic functional materials.[12] Accordingly, it should make a significant contribution to the field of organic functional materials to investigate π-conjugated furan-fused phosphole derivatives. Here we report the synthesis and properties of benzophospholo[3,2-*b*]benzofuran (BPBF) derivatives **3−7**, π-conjugated molecules with a phospholo[3,2-*b*]furan moiety (Chart 1). The desired BPBFs were successfully synthesized via a conventional synthetic approach for dibenzophospholes. In addition, the diversity-oriented synthetic strategy was also developed in this study, which allows a facile access to BPBFs with a different substituent on the phosphorus center. Furan moiety can be considered as an electron donor,[13] while phosphole can serve as an electron acceptor.[8a, 8b] Accordingly, the

BPBF framework is expected to be an intramolecular donor-acceptor-type π-electron system, inducing a large Stokes shift and high photoluminescence property. Indeed, the present BPBFs demonstrated high fluorescence with high quantum yield even in the solid state.

Chart 1. Structures of thiophene- and furan-fused phospholes

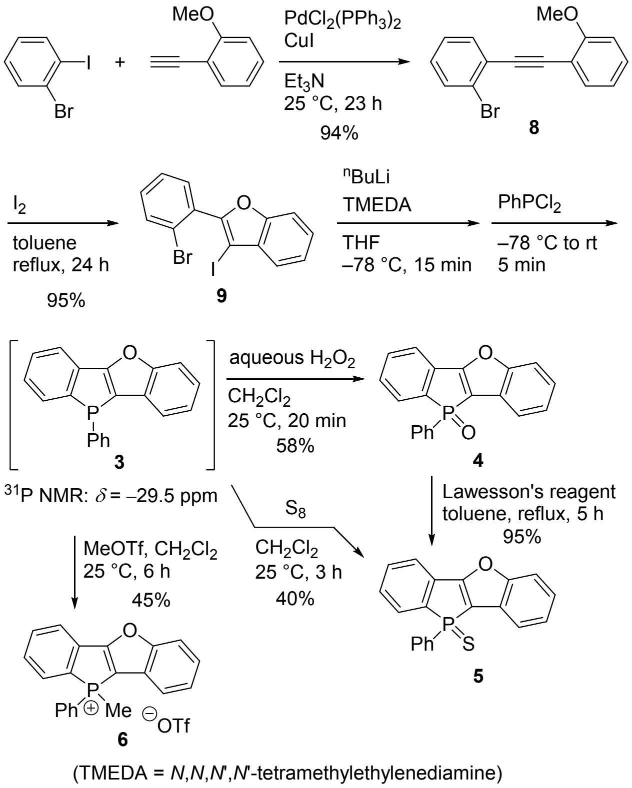


RESULTS AND DISCUSSION

Synthesis of BPBF Derivatives. Synthesis of the target molecules, 10-phenyl-benzophospholo[3,2-*b*]benzofuran derivatives (10-Ph-BPBFs) is described in Scheme 1. One of the most common synthetic strategies for dibenzophosphole moiety is the reaction of dilithiated biaryls with dichlorophosphines.[1f] In addition, the sulfur analog **1**, benzophospholo[3,2-*b*]benzothiophenes (BPBT) (Chart 1) were synthesized via the lithiation of 2-(2-bromophenyl)-3-bromobenzo[*b*]thiophene and the subsequent reaction with dichlorophosphines.[14] Accordingly, we designed 2-(2-bromophenyl)-3-iodobenzo[*b*]furan (**9**) as a starting material for 10-Ph-BPBF **3** which possesses a trivalent phosphorus center and should be a key intermediate for a series of BPBF derivatives **4**−**6** (Scheme 1). Compound **9** was synthesized efficiently by iodine-mediated electrophilic cyclization[15] of diarylethyne **8** which was obtained in high yield from the commercially-available compounds via Sonogashira−Hagihara coupling reaction. The obtained compound **9** was then dilithiated with ^{n}BuLi in the presence of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), and treated with dichlorophenylphosphine. The crude product of **3** after column chromatography (neutral-alumina) under argon atmosphere showed the singlet signal at –29.5 ppm in ^{31}P NMR spectroscopy. The chemical shift was high-field shifted compared to that of the thiophene analog, BPBT **1** (***P*** = P, Chart 1) (–16.5 ppm),[14] while it was low-field shifted compared to that of the related furan-fused phosphole compound, DBPDF **2** (***P*** = P, Chart 1) (–44.0 ppm).[11b] The complete isolation of **3** could not be achieved partially because of its instability under air. Accordingly, the product was isolated as air-stable phosphole oxide derivative **4** by treatment with aqueous H_2O_2 (58% yield from **9**).

The low-field-shifted ^{31}P NMR resonance (21.5 ppm) clearly supported the formation of phosphole oxide derivative **4**. The chemical shift was again high-field shifted compared to that of BPBT oxide **1** (***P*** = P=O, Chart 1) (26.1 ppm),[14] while it was low-field shifted compared to that of DBPDF oxide **2** (***P*** = P=O, Chart 1) (11.9 ppm).[11b]

Scheme 1. Synthesis of 10-Ph-BPBF Derivatives **3**–**6**



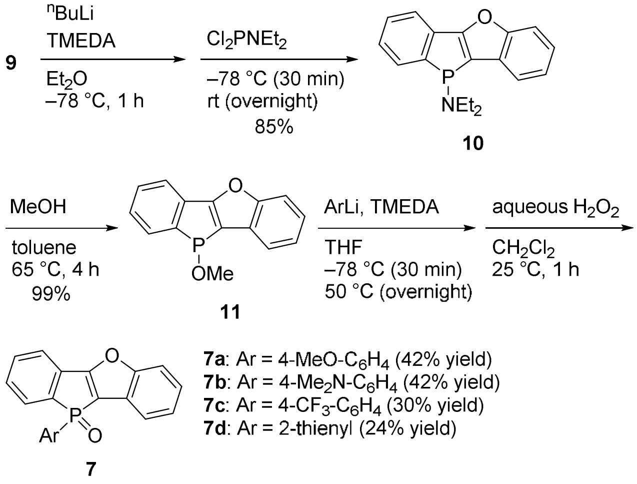
(TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine)

Trivalent phosphole compound **3** was a common precursor for other derivatives (Scheme 1).[8d] As summarized in Scheme 1, oxidation of **3** with S_8 gave phosphole sulfide derivative **5** in 40% yield (from **9**). Phosphole sulfide derivative **5** can be synthesized by treatment of phosphole oxide derivative **4** with Lawesson's reagent (95%) as well. Phosphonium derivative **6** was obtained via the reaction of **3** with methyl triflate in 45% yield (from **9**). These two compounds are also air-stable and can be easily isolated under ambient condition. The ^{31}P NMR spectra of compounds **5** and **6** demonstrated low-field shift (27.8 ppm for **5**, 16.3 ppm for **6**) relative to the parent compound **3**.

We also developed a facile synthetic route to phosphole-fused π-conjugated compounds with a desired substituent on the phosphorus center. The substituent on the phosphorus center would have significant influence on physical properties of phosphole-fused π-conjugated compounds. Accordingly, elucidation of the substituent effects is important to design new phosphole-fused π-conjugated compounds. However, the substituent on the phosphorus center is indeed a phenyl group in most of phosphole-fused π-conjugated compounds, and the reports on the substituent effects have been very limited. Recently, Baumgartner and coworkers synthesized dithieno[3,2-*b*;2′,3′-*d*]phospholes with a variety of substituents on the phosphorus center.[16] Their synthetic approach was the reaction of dilithiobiaryls with aryldichlorophosphines which should be prepared on demand. In our synthetic route, 10-MeO-BPBF **11** is designed as a common intermediate which afford the desired 10-aryl-BPBFs **7** after the reaction with organilithium reagent (Scheme 2). In this route, the substituent on phosphorus center can be introduced in the last step. In addition, a variety of organolithium can be easily prepared from the commercially-available organohalogen compounds. Accordingly, the library of BPBFs with a different substituent on the phosphorus center can be readily prepared.

The synthesis of 10-Ar-BPBFs is described in Scheme 2. Compound **9** was dilithiated and treated with Cl_2PNEt_2, affording 10-NEt_2-BPBF **10** (85% yield). The compound **10** is not so air-sensitive and can be purified under air.[17] Then, the obtained **10** was completely converted to 10-MeO-BPBF **11** by the reaction with methanol.[18] Finally, 10-MeO-BPBF **11** was reacted with organolithium reagent and subsequently oxidized with H_2O_2 to give the desired 10-Ar-BPBF oxides **7**.[19] This procedure gave a library of BPBF oxides with electron-donating (4-MeO-C_6H_4, 4-Me_2N-C_6H_4, thienyl) and electron-withdrawing (4-CF_3-C_6H_4) aryl groups on the phosphorus center.

Scheme 2. Synthesis of 10-Ar-BPBFs **7** by using 10-MeO-BPBF **11** as a common intermediate



Photophysical Properties of 10-Phenyl-BPBF Derivatives. Photophysical properties of compounds **4**−**6** were evaluated by UV−vis absorption spectroscopy and photolumenescence spectroscopy. Their spectra are shown in Figure 1, and their photophysical data are summarized in Table 1. Phosphole oxide and sulfide derivatives **4** and **5** gave the almost identical longest absorption maxima around at 340 nm with each other, while the molar absorption coefficient of **4** (ε = 0.77 × 10^4 $M^{-1}\cdot cm^{-1}$ at λ_{abs} = 341 nm) was larger than that of **5** (ε = 0.66 × 10^4 $M^{-1}\cdot cm^{-1}$ at λ_{abs} = 342 nm). Absorption spectrum of phosphonium derivative **6** showed the longest absorption maximum at 351 nm, which was red-shifted compared to those of **4** and **5**.

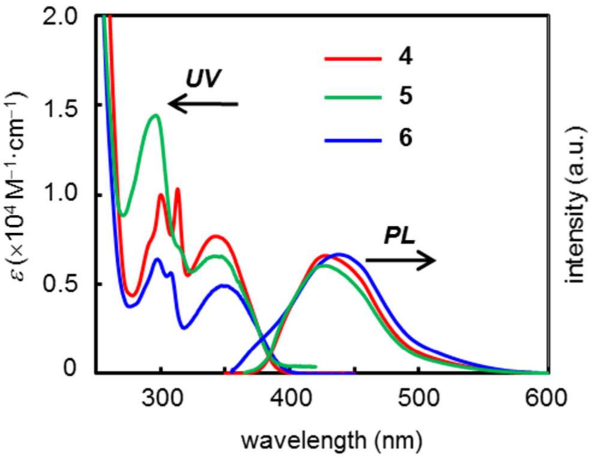


Figure 1. UV−Vis absorption and photoluminescence spectra of BPBFs **4**–**6**.

Table 1. Photophysical Data of BPBFs

	solution				powder	
	λ_{abs} (nm)^a	λ_{em} (nm)^b	Stokes shift	Φ (%)^c	λ_{em} (nm)^d	Φ (%)^c
4	341	428	5960	84	421	87
5	342	426	5770	<1	---^{e}	<1
6	351	439	5710	98	469	50

^{a}In CH_2Cl_2. ^{b}In CH_2Cl_2. Excitation at 340 nm. ^{c}Absolute quantum yield determined by a calibrated integrating sphere system. ^{d}Excitation at 340 nm. ^{e}Emission maximum cannot be detected because of low emission intensity.

The present BPBF derivatives were found to possess high photoluminescence properties. All of the BPBF derivatives showed broad photoluminescence spectra in CH_2Cl_2 with large Stokes shifts of 5700~6000 cm^{-1}. Compounds **4** and **6** exhibited intense blue emission with high quantum yields, which are higher than those of the previously-reported dithienophosphole derivatives[8a, 8b, 8d] and 10-Ph-BPBT derivatives **1**, and are competitive with highly-emissive bis-phosphoryl-bridged stilbene derivatives.[9] In contrast, the low fluorescence intensity with a very low quantum yield was observed for the phosphole sulfide derivative **5**. It is noteworthy that high quantum yields of compounds **4** and **6** were maintained in their solid states. In particular, the quantum yield of the phosphole oxide derivative **4** was 0.87. High emission property of phosphole oxide derivatives **4** in the solid state may be due to the sterically-hindered structure around the tetrahedral phosphorus center.[8d]

Theoretical Study of Photophysical Properties of 10-Phenyl-BPBF Derivatives. Phosphole oxide **4** possess the calculated longest wavelength absorption at 344 nm with large oscillator strength (Table S4 for the selected absorption peaks), which are almost identical to the experimental values (341 nm, Table 1). The calculated longest wavelength absorption of phosphonium derivative **6** (363 nm) was longer than the experimental value, while the red-shifted absorption relative to that of **4** was well demonstrated. These $S_0 \rightarrow S_1$ electron transitions of **4** and **6** are dominated by HOMO−LUMO (π–π^*) transition. On the other hand, the obvious transition for phosphole sulfide **5** is $S_0 \rightarrow S_3$ electron transition (329 nm) dominated by [HOMO−2]−LUMO transition, which would be observed as the experimental longest wavelength absorption maximum (342 nm, Table 1). The lower-energy transitions at 370 nm (HOMO−LUMO) and 350 nm ([HOMO−1]−LUMO) possess much lower oscillator strength,[20] which were not detected as absorption maxima in UV−vis absorption spectroscopy. As shown in Figure 2, the HOMO orbital of compound **4** spreads over the BPBF framework, and the slightly larger distribution is observed in the furan side. In contrast, the LUMO orbital is largely dominated by phosphole oxide moiety. Such distribution in HOMO and LUMO orbitals may be attributed to that furan and phosphole moieties work as electron donor and acceptor, respectively, resulting in intramolecular donor-acceptor-type π-electron systems.[13] This intramolecular donor-acceptor-type interaction is partially supported by solvatochromism of **4**.[21] Increase in solvent polarity caused red-shift in photoluminescence spectra (λ_{em} = 413 nm in hexane [$E_T(30)$ = 30.9], 423 nm in benzene [$E_T(30)$ = 34.5], 423 nm in CH_3CN [$E_T(30)$ = 46.7], 428 nm in $CHCl_3$ [$E_T(30)$ = 39.1], 438 nm in MeOH [$E_T(30)$ = 55.5], $E_T(30)$ = solvent polarity parameter,[22] Figure

3), while significant solvatochromism in the absoption spectra was not observed (λ_{abs} = 336 nm in hexane, 341 nm in benzene, 341 nm in CH_3CN, 343 nm in $CHCl_3$, 343 nm in MeOH, Figure 4).[14] Such an electronic structure may induce large Stokes shifts, which can diminish the self-quenching of photoluminescence to afford high quantum yields.[13, 23]

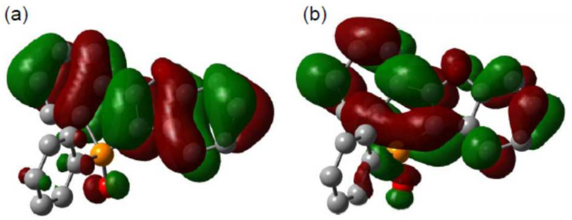


Figure 2. Molecular orbitals of (a) HOMO and (b) LUMO of **4** by the DFT calculation at the B3LYP/6-31G(d) level.

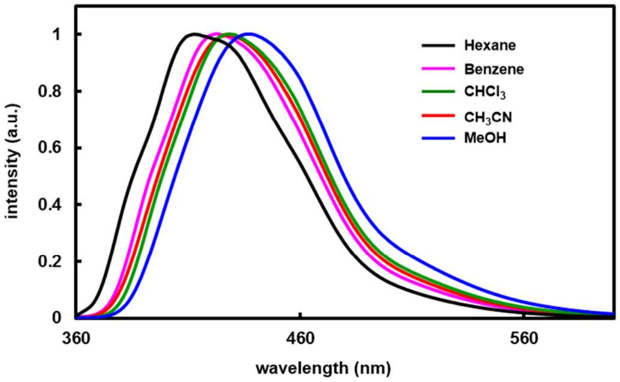


Figure 3. Photoluminescence spectra of BPBF **4** in different solvents.

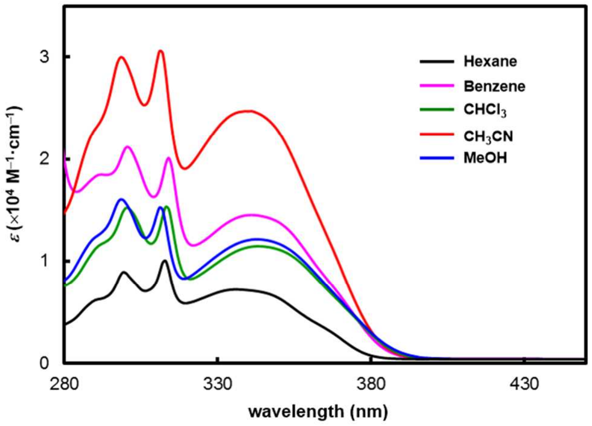


Figure 4. Absorption spectra of BPBF **4** in different solvents.

Effects of the Substituents on Phosphorus Center on Photophysical Properties.

Absorption and fluorescence properties of BPBFs **7** are summarized in Table 2 and Figures 5 and 6. As shown in Figure 5, compound **7a**, **7c**, and **7d** show similar absorption features to compound **4** with absorption maxima at around 300, 310, and 340 nm, while the molar absorption coefficients are depend on the substituents. On the other hand, compound **7b** with 4-(dimethylamino)phenyl group on the phosphorus center shows less resolved absorption spectrum. In the photoluminescence spectra, compound **7a**, **7c**, and **7d** again show similar features with emission at around 430 nm

(Figures 6). In contrast, 4-(dimethylamino)phenyl group induces red-shifted emission. The Stokes shift of 7770 cm^{-1} is largest in the series of BPBF derivatives in this study. Such large Stokes shift should be attributed to intramoleclar charge transfer. The DFT calculation showed that the HOMO of compound **7b** is dominated by 4-(dimethylamino)phenyl moiety (donor) and the LUMO is localized at BPBF moiety (Figure S35). This trend is similar to the reported dithienophospholes with a 4-(diphenylamino)phenyl substituent on the phosphorus center.[24]

Table 2. Photophysical Data of BPBFs **7**

	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Stokes shift (cm^{-1})	Φ (%)[c]
7a	342	428	5880	88
7b	341	464	7770	90
7c	346	433	5810	---
7d	347	428	5450	---

[a] In $CHCl_3$. [b] In $CHCl_3$. Excitation at 315 nm. [c] Absolute quantum yield determined by a calibrated integrating sphere system.

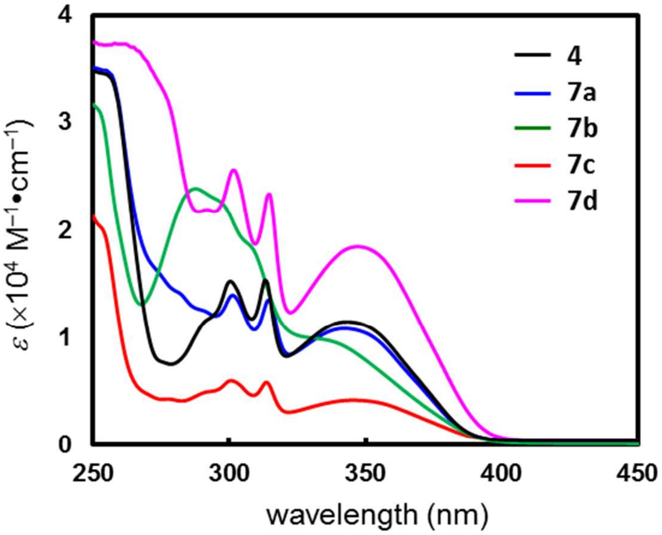


Figure 5. Absorption spectra of BPBFs **4** and **7**.

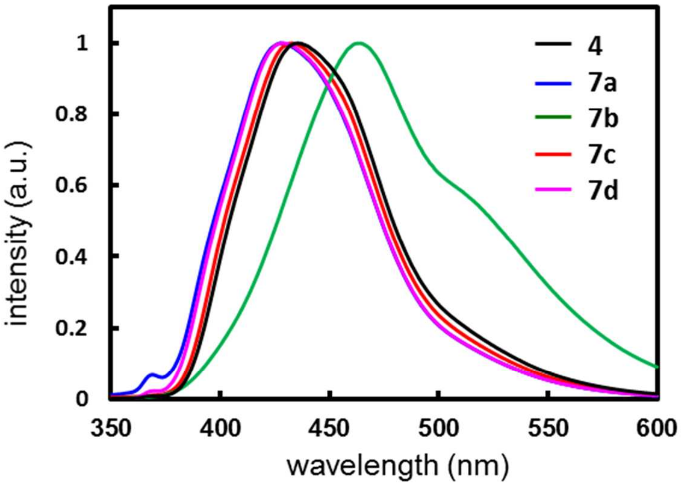


Figure 6. Photoluminescence spectra of BPBFs **4** and **7**.

CONCLUSION

In conclusion, a series of BPBF derivatives have been synthesized via simple reaction sequences. The trivalent phosphole derivative, 10-Ph-BPBF was obtained by using the conventional synthetic route and transformed to *P*-functionalized derivatives. In addition, the diversity-oriented synthetic route was developed by using 10-MeO-BPBF as an easily-to-use common intermediate. This synthetic approach would be applied to the synthesis of other dibenzophosphole derivatives and open up the chemistry of phosphole-containing π-conjugated compounds. Photophysical properties of BPBFs were revealed based on UV-vis and photoluminescence spectroscopies and theoretical calculation. The highly electron-donating aryl substituent on phosphorus center were found to induce large Stokes shift, which should be caused by intramolecular charge transfer. The chracteristics of the present BPBF derivatives are large Stokes shift and high emission property even in the solid state, which would be derived from the incorporation of the phosphole moiety into the fused-conjugated system.

EXPERIMENTAL SECTION

General Procedures. NMR spectra were recorded in deuteriochloroform or C_6D_6 on a 500 MHz spectrometer (^{1}H 500 MHz, ^{13}C 126 MHz, ^{31}P 202 MHz) or a 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz, ^{31}P 162 MHz). Chemical shifts are reported in ppm relative to the internal standard peak (0 ppm for Me_4Si) for ^{1}H, the deuterated solvent peak (77.16 ppm for $CDCl_3$) for ^{13}C, and the external standard peak (85% H_3PO_4) for ^{31}P. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. High resolution mass spectra are taken by electrospray ionization-time-of-flight (ESI−TOF) method or by atmospheric pressure chemical ionization-time-of-flight (APCI−TOF) method. UV absorption spectra were recorded on a UV−VIS scanning spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorometer. Absolute quantum yields were determined by calibrated integrating sphere system.

All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box under argon atmosphere or with the standard Schlenk technique under argon. All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator. Column chromatography was performed by using silica gel (spherical neutral, particle size 63-210 μm).

Computational Studies. The DFT and TD–DFT calculations were performed by using the Gaussian 03 program (compounds **4** and **5**)[25] or Gaussian 09 program (compounds **6** and **7b**)[26] at the B3LYP/6–31G(d) level.

Synthetic Procedures. The followings are synthetic procedures for BPBFs in this study.

1-Bromo-2-[(2-methoxyphenyl)ethynyl]benzene (8).[27] A flame-dried 250-mL Schlenk tube containing a magnetic stirring bar was charged with 2-ethynylanisole (2.78 g, 21 mmol), 1-bromo-2-iodobenzene (5.67 g, 20 mmol), $PdCl_2(PPh_3)_2$ (282 g, 0.40 mmol), CuI (38 g, 0.20 mmol), Et_3N (50 mL) under argon atmosphere. After degassed by freeze-pump-thaw cycles (three times), the mixture was stirred under argon atmosphere at 25 °C for 23 h. White precipitate was filtered off with Et_2O, and the filtrated was concentrated under reduced pressure. The resulting residue was purified by silica-gel column chromatography (Hex/AcOEt = 8/1, R_f = 0.43) to give the title compound as a pale-yellow oil (5.39 g, 94% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.55 (dd, J = 7.6, 1.8 Hz, 1H), 7.35–7.31 (m, 1H), 7.28 (td, J = 7.6, 1.1 Hz, 1H), 7.16 (td, J = 7.7, 1.8 Hz, 1H), 6.95 (td, J = 7.5, 0.8 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 3.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 133.7, 133.3, 132.4, 130.2, 129.3, 127.0, 125.8, 125.5, 120.5, 112.2, 110.9, 92.0, 90.6, 55,9.

3-Iodo-2-(2-bromophenyl)benzo[*b*]furan (9).[12k] A flame-dried 200-mL round-bottom flask containing a magnetic stirring bar was charged with **8** (1.0 g, 3.5 mmol), iodine (3.6 g, 14 mmol), and toluene (30 mL). After the mixture was stirred under reflux for 24 h in the dark, saturated aqueous sodium thiosulfate solution (100 mL) was added to the mixture. The resulting mixture was stirred at 25 °C for 30 min, and the organic layer was separated. The aqueous layer was extracted with toluene (20 mL × 3), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting reside was purified by silica-gel column chromatography (hexane as an eluent, R_f = 0.30) to give the title compound as a colorless oil (1.32 g, 95%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.1, 1.3 Hz, 1H), 7.57 (dd, J = 7.6, 1.8 Hz, 1H), 7.53–7.51 (m, 1H), 7.50–7.48 (m, 1H), 7.45 (td, J =

7.6, 1.1 Hz, 1H), 7.41 (td, J = 7.6, 1.4 Hz, 1H), 7.38–7.35 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 154.5, 133.5, 133.1, 131.5, 131.5, 131.2, 127.3, 125.9, 124.2, 123.7, 121.9, 111.6, 66.4. Anal. Calcd for $C_{14}H_8BrIO$ (%): C, 42.14; H, 2.02. Found (%): C, 41.98; H, 2.12.

10-Phenylbenzophospholo[3,2-*b*]benzofuran (3). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with **9** (200 mg, 0.5 mmol), Et_2O (10 mL), and *N,N,N′,N′*-tetramethylethylenediammine (TMEDA, 30 μL, 2.0 mmol) under argon atmosphere. The mixture was stirred for 30 min at −78 °C, and *n*-butyllithium (0.67 mL of 1.67 M solution in hexane, 1.1 mmol) was added dropwise to the mixture at −78 °C. After stirred at the same temperature for 15 min, $PPhCl_2$ (90 μL, 0.66 mmol) was added in one portion to the reaction mixture. The reaction mixture was allowed to warm quickly to 25 °C (over 5 min) and concentrated under reduced pressure. The residue was dissolved with CH_2Cl_2 (50 mL) and passed through a short pad of neutral alumina under argon atmosphere. The filtrate was concentrated under reduced pressure and further purified by neutral-alumina column chromatography under argon atmosphere (CH_2Cl_2/hexane = 2/1 as an eluent, R_f = 0.40) to provide **3** as a pale yellow solid (86 mg, 57 % yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J_{HH} = 7.6 Hz, 1H), 7.69–7.66 (m, 1H), 7.62–7.59 (m, 2H), 7.45–7.42 (m, 3H), 7.33–7.23 (m, 6H);

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.5 (d, J_{CP} = 8.6 Hz), 159.1 (d, J_{CP} = 4.8 Hz), 146.9 (d, J_{CP} = 7.7 Hz), 134.0 (d, J_{CP} = 16.3 Hz), 133.2 (s), 132.5 (d, J_{CP} = 20.1 Hz), 130.8 (d, J_{CP} = 20.1 Hz), 129.6 (s), 128.9 (d, J_{CP} = 7.7 Hz), 128.7 (s), 128.3 (d, J_{CP} = 13.4 Hz), 127.3 (d, J_{CP} = 7.7 Hz), 124.6 (s), 123.8 (s), 120.9 (s), 120.1 (s), 118.1 (d, J_{CP} = 5.8 Hz), 112.4 (s); $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ –29.5 (s).

10-Phenylbenzophospholo[3,2-*b*]benzofuran oxide (4). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with **3**, which was prepared from 200 mg of **9** (0.50 mmol) according to the procedure described above, and CH_2Cl_2 (10 mL) under argon atomosphere. H_2O_2 (0.80 mL, 35% aqueous solution) was added in one portion. After the resulting mixture was stirred 25 °C for 20 min, saturated aqueous $Na_2S_2O_3$ (3 mL) was slowly added to the reaction mixture. Organic layer was separated, and the aqueous layer was extracted with AcOEt (20 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by silica-gel column chromatography (AcOEt/hexane = 2/1 as an eluent, R_f = 0.38) to give the title compound as a colorless solid (92 mg, 58% yield from **9**): mp 160−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J_{HP} = 13.5, J_{HH} = 7.3 Hz, 2H), 7.72–7.66 (m, 2H), 7.62–7.59 (m, 2H), 7.56–7.51 (m, 2H), 7.44–7.38 (m, 3H), 7.36–7.32 (m, 1H), 7.28 (t, J_{HH} =

6.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$) δ 168.0 (d, J_{CP} = 36.4 Hz), 159.4 (d, J_{CP} = 10.5 Hz), 138.7 (d, J_{CP} = 106.4 Hz), 133.0 (d, J_{CP} = 12.5 Hz), 132.8 (d, J_{CP} = 1.9 Hz), 132.7 (d, J_{CP} = 2.9 Hz), 131.1 (d, J_{CP} = 11.5 Hz), 130.2 (d, J_{CP} = 11.5 Hz), 130.02 (d, J_{CP} = 8.6 Hz), 129.98 (d, J_{CP} = 110.2 Hz), 129.1 (d, J_{CP} = 13.4 Hz), 125.7 (s), 125.4 (d, J_{CP} = 7.7 Hz), 124.9 (s), 121.5 (s), 120.1 (d, J_{CP} = 8.6 Hz), 112.5 (s), 112.3 (d, J_{CP} = 121.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$) δ 21.5 (s). Anal. Calcd for $C_{20}H_{13}O_2P$ (%): C, 75.95; H, 4.34. Found (%): C, 75.75; H, 4.34.

10-Phenylbenzophospholo[3,2-*b*]benzofuran sulfide (5). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with **3**, which was prepared from 200 mg of **9** (0.50 mmol) according to the procedure described above, and CH_2Cl_2 (10 mL) under argon atmosphere. An excess sulfur S_8 (320 mg, 10 mmol) was added in one portion, and the reaction mixture was stirred 25 °C for 3 h. After the reaction mixture was concentrated under reduced pressure, the resulting crude residue was purified by silica-gel column chromatography (CHCl$_3$/hexane = 3/2 as an eluent, R_f = 0.35) to give the title compound as a colorless solid (67 mg, 40% yield from **9**): mp 168−170 °C; ^1H NMR (500 MHz, CDCl$_3$) δ 7.86 (dd, J_{HP} = 15.0, J_{HH} = 7.4 Hz, 2H), 7.72–7.68 (m, 2H), 7.63–7.60 (m, 2H), 7.56–7.53 (m, 1H), 7.49–7.46 (m, 1H), 7.43–7.34 (m, 4H), 7.29 (t, J = 7.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 166.0 (d, J_{CP}

= 31.7 Hz), 159.4 (d, J_{CP} = 11.5 Hz), 142.4 (d, J_{CP} = 88.3 Hz), 132.4 (d, J_{CP} = 2.9 Hz), 132.2 (s), 130.9 (d, J_{CP} = 12.5 Hz), 130.23 (d, J_{CP} = 12.5 Hz), 130.22 (d, J_{CP} = 86.4 Hz), 129.6 (d, J_{CP} = 10.6 Hz), 129.0 (d, J_{CP} = 13.4 Hz), 125.8 (s), 125.1 (d, J_{CP} = 8.6 Hz), 124.9 (s), 121.0 (s), 120.3 (d, J_{CP} = 7.7 Hz), 114.0 (d, J_{CP} = 105.6 Hz), 112.6 (s); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 27.8 (s). Anal. Calcd for $C_{20}H_{13}OPS$ (%): C, 72.28; H, 3.94. Found (%): C, 72.15; H, 4.05.

Transformation of 4 into 5 by Lawesson's reagent. A flame-dried 50-mL round-bottom flask containing a magnetic stirring bar was charged with **4** (158 mg, 0.5 mmol), Lawesson's reagent (810 mg, 2.0 mmol), and toluene (20 mL). After stirring under reflux for 5 h, the reaction mixture was concentrated under reduced pressure. The resulting crude residue was purified by silica-gel column chromatography ($CHCl_3$/hexane = 2/1 as an eluent, R_f = 0.33) to give **5** as a colorless solid (158 mg, 95% yield).

10-Methyl-10-phenylbenzophospholo[3,2-*b*]benzofuran-10-ium trifluoromethansulfonate (6). A flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with **3**, which was prepared from 100 mg of **9** (0.25 mmol) according to the procedure described above, and CH_2Cl_2 (8 mL) under argon atmosphere. Methyl triflate (110 μL, 1.1 mmol) was added in one portion, and the reaction mixture was stirred 25 °C for 6 h. After the reaction mixture was concentrated under reduced pressure, the title compound was obtained by reprecipitation from acetone as a colorless solid (52 mg, 45% yield from **9**): mp 179.5−181.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J_{HP} = 11.7 Hz, J_{HH} = 7.7 Hz, 1H), 8.08 (dd, J_{HP} = 15.1 Hz, J_{HH} = 7.4 Hz, 2H), 7.92 (dd, J_{HP} = 3.4 Hz, J_{HH} = 7.5 Hz, 1H), 7.86–7.62 (m, 7H), 7.55–7.47 (m, 2H), 2.95 (d, J_{HP} = 15.0 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 169.7 (d, J_{CP} = 31.7 Hz), 159.8 (d, J_{CP} = 11.5 Hz), 135.9 (d, J_{CP} = 2.9 Hz), 135.5 (d, J_{CP} = 1.9 Hz), 134.0 (d, J_{CP} = 9.6 Hz), 133.0 (d, J_{CP} = 11.5 Hz), 132.6 (d, J_{CP} = 12.5 Hz), 132.3 (d, J_{CP} = 12.5 Hz), 130.8 (d, J_{CP} = 14.4 Hz), 128.6 (d, J_{CP} = 91.2 Hz), 127.6 (s), 126.6 (s), 123.8 (d, J_{CP} = 9.6 Hz), 122.3 (d, J_{CP} = 8.6 Hz), 121.3 (s), 120.9 (q, J_{CF} = 320.5 Hz, one of the signals of the quartet overlaps with the doublet at 122.3 ppm), 116.3 (d, J_{CP} = 90.2 Hz), 113.3 (s), 100.9 (d, J_{CP} = 113.2 Hz), 7.7 (d, J_{CP} = 53.7 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 16.3 (s). HRMS–ESI$^+$ (*m*/*z*) calcd for $C_{21}H_{16}OP$ {$[M–OSO_2CF_3]^+$} 315.0939, found315.0940.

10-Diethylaminobenzophospholo[3,2-*b*]benzofuran (10). A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with **9** (800 mg, 2.0 mmol), Et_2O (30 mL), and *N,N,N′,N′*-tetramethylethylenediammine (TMEDA, 1.20 mL, 8.0 mmol) under argon atmosphere. The mixture was cooled to −78 °C, and *n*-butyllithium (1.69 mL of 2.6 M solution in hexane, 4.4 mmol) was added dropwise to the mixture at −78 °C. After stirred at the same temperature for 1 h, Cl_2PNEt_2 (0.39 mL, 2.6 mmol) was added dropwise to the mixture at −78 °C. The resulting mixture was stirred for 30 min at the same temperature and allowed to warm quickly to ambient temperature. After stirring overnight, the reaction mixture was passed through a short pad of neutral alumina with Et_2O wash. The filtrate was concentrated, and hexane (20 mL) was added. The resulting suspension was filtered and concentrated to give 10-NEt_2-BPBF **10** as a yellow oil (504 mg, 85% yield). ^1H NMR (500 MHz, C_6D_6) δ, 7.70 (d, J_{HH} = 7.6 Hz, 1H), 7.66–7.61 (m, 2H), 7.42 (d, J_{HH} = 7.9 Hz, 1H), 7.13–7.02 (m, 4H), 2.82–2.75 (m, 4H), 0.89 (t, J_{HH} = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.6 (d, J_{CP} = 12.0 Hz), 159.7 (d, J_{CP} = 3.6 Hz), 147.5 (d, J_{CP} = 8.4 Hz), 133.3 (d, J_{CP} = 3.6 Hz), 130.9 (d, J_{CP} = 20.4 Hz), 129.2 (d, J_{CP} = 13.7 Hz), 129.1, 127.4 (d, J_{CP} = 7.2 Hz), 124.6, 124.0, 121.2, 119.7 (d, J_{CP} = 15.6 Hz), 119.6, 112.5, 44.7 (d, J_{CP} = 14.4 Hz), 15.3 (d, J_{CP} = 3.67 Hz),$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 28.6 (s).

10-Methoxybenzophospholo[3,2-*b*]benzofuran (11). A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with **10** (492 mg, 1.67 mmol), toluene (3 mL), and methanol (3 mL) under argon atmosphere. The resulting mixture was stirred at 65 °C for 4 h. Concentration of the mixture gives

10-MeO-BPBF **11** as a yellow oil (420 mg, 99% yield). ^{1}H NMR (400 MHz, C_6D_6) δ, 7.50–7.40 (m, 3H), 7.32–7.29 (m, 1H), 7.00–6.93 (m, 3H), 6.90–6.84 (m, 1H), 2.86 (d, J_{PH} = 8.3 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 166.0 (d, J_{CP} = 6.0 Hz), 159.6 (d, J_{CP} = 4.8 Hz), 143.7 (d, J_{CP} = 24.0 Hz), 133.9, 131.8 (d, J_{CP} = 22.8 Hz), 130.4, 128.9 (d, J_{CP} = 14.4 Hz), 128.4 (d, J_{CP} = 6.0 Hz), 124.9, 124.4, 121.5, 119.6, 117.3 (d, J_{CP} = 30.0 Hz), 112.4, 53.8 (d, J_{CP} = 14.4 Hz); ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 80.6 (s).

General Procedure for the Synthesis of 10-Arylphospholo[3,2-*b*]benzofuran (7). The flame-dried 20 mL Schlenk tube containing a magnetic stirring bar was charged with haloarene (1.0 mmol), THF (2.0 mL), and TMEDA (0.30 mL, 2.0 mmol) under argon atmosphere. The mixture was cooled to −78 °C, and *n*-butyllithium (0.38 mL of 2.6 M solution in hexane, 1.0 mmol) was added dropwise to the mixture at −78 °C. After stirred at the same temperature for 1 h, the THF solution of **11** (1.0 mL of 0.50 M) was added dropwise at −78 °C. After stirred at the same temperature for 30 min, the reaction mixture was allowed to warm to 50 °C and stirred at 50 °C for overnight. The reaction mixture was concentrated under reduced pressure, and the residue was suspended with Et_2O (10 mL) under argon atmosphere. The resulting suspension was passed through a short pad of neutral alumina with Et_2O wash, and the filtrate was concentrated. The resulting residue was dissolved in CH_2Cl_2 (5 mL), and H_2O_2 (1.0

mL, 35% aqueous solution) was added in one portion. After the resulting mixture was stirred 25 °C for 1 h, water (5 mL) was added. The organic layer was separated, washed with saturated aqueous $Na_2S_2O_3$ (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting reside was purified by silica-gel column chromatography.

10-(4-Methoxyphenyl)benzophospholo[3,2-*b*]benzofuran oxide (7a). The crude residue was obtained by using 1-bromo-4-methoxybenzene (0.13 mL, 1.0 mmol). The resulting residue was purified by silica-gel column chromatography (AcOEt/hexane = 5/1 as an eluent, $R_f = 0.28$) as a pale yellow solid (70 mg, 42% yield). mp 138.0–140.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.64 (m, 4H), 7.61–7.59 (m, 2H), 7.53 (t, J_{HH} = 7.6 Hz, 1H), 7.41–7.32 (m, 2H), 7.29 (d, J_{HH} = 8.0 Hz, 1H), 6.92 (dd, J_{HP} = 2.3 Hz, J_{HH} = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.9 (d, J_{CP} = 35.5 Hz), 163.3 (d, J_{CP} = 2.9 Hz), 159.4 (d, J_{CP} = 10.5 Hz), 139.21 (d, J_{CP} = 106.4 Hz), 133.0 (d, J_{CP} = 13.4 Hz), 132.9 (d, J_{CP} = 12.5 Hz), 132.7 (d, J_{CP} = 1.9 Hz), 130.2 (d, J_{CP} = 11.5 Hz), 129.8 (d, J_{CP} = 8.6 Hz), 125.6 (s), 125.5 (d, J_{CP} = 7.7 Hz), 124.9 (s), 121.6 (s), 120.5 (d, J_{CP} = 116.9 Hz), 120.0 (d, J_{CP} = 8.6 Hz), 114.8 (d, J_{CP} = 13.4 Hz), 112.5 (d, J_{CP} = 121.7 Hz), 112.5 (s); ^{31}P{1H} NMR (162 MHz, $CDCl_3$) δ 21.6 (s). HRMS–ESI$^+$ (*m*/*z*) calcd for $C_{21}H_{15}O_3PNa$ [{M+Na}$^+$] 369.0657, found 369.0650.

10-[4-(Dimethylamino)phenyl]benzophospholo[3,2-*b*]benzofuran oxide (7b). The crude residue was obtained by using 1-bromo-4-(dimethylamino)benzene (200 mg, 1.0 mmol). The resulting residue was purified by silica-gel column chromatography (AcOEt/hexane = 5/1 as an eluent, $R_f = 0.23$) as a pale yellow solid (76 mg, 42% yield): mp 225-230 °C (decompose); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.57 (m, 6H), 7.47 (t, J_{HH} = 7.6 Hz, 1H), 7.39–7.24 (m, 3H), 6.65 (dd, J_{HH} = 8.7, 2.3 Hz, 2H), 2.96 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6 (d, J_{CP} = 35.5 Hz), 159.3 (d, J_{CP} = 10.5 Hz), 153.1 (d, J_{CP} = 1.9 Hz), 139.8 (d, J_{CP} = 106.4 Hz), 132.7 (d, J_{CP} = 12.5 Hz), 132.4 (d, J_{CP} = 12.5 Hz), 132.3, 130.0 (d, J_{CP} = 11.5 Hz), 129.6 (d, J_{CP} = 8.6 Hz), 125.7 (d, J_{CP} = 7.7 Hz), 125.4, 124.7, 121.6, 119.8 (d, J_{CP} = 8.6 Hz), 113.5 (d, J_{CP} = 40.3 Hz), 112.33 (d, J_{CP} = 39.3 Hz), 112.30, 111.9 (d, J_{CP} = 13.4 Hz), 40.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 22.6. HRMS–APCI$^+$ (*m*/*z*) calcd for $C_{22}H_{19}NO_2P$ [$\{M+H\}^+$] 360.1153, found 360.1149.

10-[4-(Trifluoromethyl)phenyl]benzophospholo[3,2-*b*]benzofuran oxide (7c). The crude residue was obtained by using 1-bromo-4-(trifluoromethyl)benzene (0.14 mL, 1.0 mmol). The resulting residue was purified by silica-gel column chromatography (AcOEt/hexane = 5/1 as an eluent, $R_f = 0.55$) as a pale yellow solid (58 mg, 30% yield): mp 191.5−193.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J_{HH} = 7.8

Hz, 1H), 7.91 (d, J_{HH} = 8.2 Hz, 1H), 7.71–7.67 (m, 4H), 7.63–7.58 (m, 3H), 7.45–7.41 (m, 1H), 7.37 (t, J_{HH} = 7.8 Hz, 1H), 7.30 (d, J_{HH} = 7.6 Hz, 1H); $^{13}C\{^1H\}$. NMR (101 MHz, $CDCl_3$) δ 168.3 (d, J_{CP} = 37.4 Hz), 159.4 (d, J_{CP} = 10.5 Hz), 137.8 (d, J_{CP} = 108.3 Hz), 134.6 (d, J_{CP} = 107.4 Hz), 134.4 (dq, J_{CP} = 2.9 Hz, J_{CF} = 25.4 Hz), 133.3, 133.0 (d, J_{CP} = 13.4 Hz), 131.7 (d, J_{CP} = 11.5 Hz), 130.5 (d, J_{CP} = 11.5 Hz), 130.2 (d, J_{CP} = 8.6 Hz), 126.0 (q, J_{CP} = 3.8 Hz), 125.9 (q, J_{CP} = 3.8 Hz), 125.6 (d, J_{CP} = 86.3 Hz), 125.1 (d, J_{CP} = 9.6 Hz), 123.6 (q, J_{CF} = 204.6 Hz), 121.4, 120.4 (d, J_{CP} = 8.6 Hz), 112.6, 111.63 (d, J_{CP} = 123.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 19.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2. HRMS–APCI$^+$ (m/z) calcd for $C_{21}H_{13}F_3O_2P$ [$\{M+H\}^+$] 385.0605, found 385.0614.

10-Thienylbenzophospholo[3,2-*b*]benzofuran oxide (7d). The crude residue was obtained by using thiophene (79 μL, 1.0 mmol). The resulting residue was purified by silica-gel column chromatography (AcOEt/hexane = 5/1 as an eluent, R_f = 0.38) as a pale yellow solid (39 mg, 24% yield): mp 163.3−165.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J_{HP} = 11.5 Hz, J_{HH} = 7.3 Hz, 1H), 7.71–7.69 (m, 1H), 7.66–7.63 (m, 3H), 7.61–7.58 (m, 1H), 7.57–7.52 (m, 1H), 7.45–7.40 (m, 1H), 7.38–7.30 (m, 2H), 7.14–7.11 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.7 (d, J_{CP} = 39.3 Hz), 159.3 (d, J_{CP} = 11.5 Hz), 138.4 (d, J_{CP} = 113.1 Hz), 136.1 (d, J_{CP} = 11.5 Hz), 133.7 (d, J_{CP} = 5.6

Hz), 133.0, 132.3 (d, J_{CP} = 14.4 Hz), 130.9 (d, J_{CP} = 121.7 Hz), 130.3 (d, J_{CP} = 11.5 Hz), 129.8 (d, J_{CP} = 8.6 Hz), 128.6 (d, J_{CP} = 14.4 Hz), 125.7, 125.0 (d, J_{CP} = 8.6 Hz), 125.0, 121.5, 120.2 (d, J_{CP} = 9.6 Hz), 112.5, 112.3 (d, J_{CP} = 129.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 13.1. HRMS–ACPI^{+} (*m*/*z*) calcd for $C_{18}H_{12}O_2PS$ [{M+H}$^{+}$] 323.0296, found 323.0299.

ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for synthesized compounds, DFT and TD−DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

The authors declare no competing financial interest.

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