

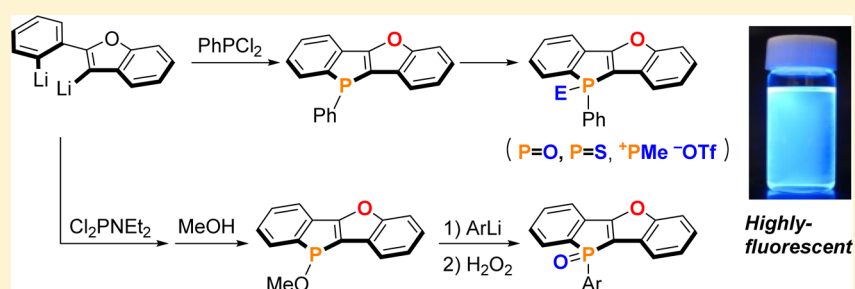
# Synthesis and Properties of Benzophospholo[3,2-*b*]benzofuran Derivatives

Motonobu Takahashi,<sup>†</sup> Koji Nakano,<sup>\*,‡</sup> and Kyoko Nozaki<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

<sup>‡</sup>Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

**S** Supporting Information



**ABSTRACT:** Benzophospholo[3,2-*b*]benzofuran (BPBF) derivatives were studied as a new family of phosphole-containing  $\pi$ -conjugated organic materials. The versatile reactivity of the trivalent phosphorus center of the parent BPBF offered access to a variety of derivatives by simple chemical modifications. The diversity-oriented synthetic route was also developed to allow 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.

## INTRODUCTION

Incorporation of phosphole moiety(s) into the  $\pi$ -conjugated system is a promising strategy for new organic functional materials with novel properties.<sup>1</sup> 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  $\pi$ -electrons efficiently, which causes the very low aromaticity of phosphole.<sup>2</sup> On the other hand, such a tetrahedral geometry allows the effective interaction of the exocyclic P–C  $\sigma^*$  orbital with the endocyclic butadiene  $\pi^*$  orbital, resulting in a low-lying LUMO energy level of phosphole.<sup>3</sup> 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 the phosphole moiety, a variety of phosphole-containing  $\pi$ -conjugated molecules, such as oligophospholes,<sup>4</sup> phosphole-containing polymers,<sup>5</sup> 2,5-diarylphospholes,<sup>6</sup> (di)benzophospholes,<sup>7</sup> dithieno[3,2-*b*;2',3'-*d*]-phospholes,<sup>8</sup> benzophospholo[3,2-*b*]benzophospholes,<sup>9</sup> and zwitterionic benzoborolo[3,2-*b*]benzophospholes,<sup>10</sup> have been developed and found to be promising candidates for high-performance organic functional materials. In particular, a high

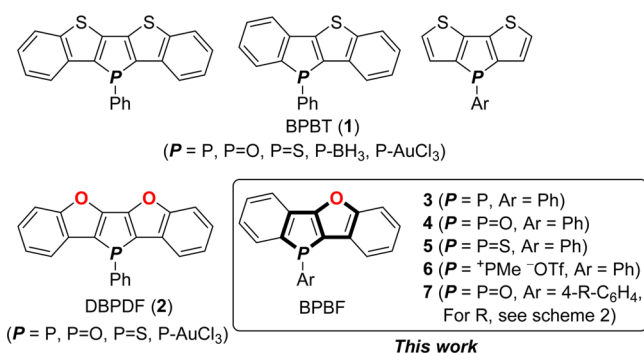
emission property is characteristic in phosphole-containing  $\pi$ -conjugated compounds. For example, 2,5-diarylphospholes have been systematically studied to be applied as an emissive layer for organic light-emitting diodes (OLEDs).<sup>6d,e</sup> Extended  $\pi$ -conjugated systems with a dithienophosphole<sup>8a,b,d</sup> or phospholo[3,2-*b*]phosphole moiety<sup>9</sup> with extended  $\pi$ -conjugated systems have been reported to demonstrate intense fluorescence with moderate to high quantum yields.

Benzene-,<sup>7</sup> thiophene-,<sup>8</sup> phosphole-,<sup>9</sup> and borole-fused<sup>10</sup> 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 past few years,<sup>11</sup> and there is a limited information about their structure–property relationships.<sup>11b</sup> Recently, a variety of furan-fused  $\pi$ -conjugated molecules have been synthesized and been applied as organic functional materials.<sup>12</sup> Accordingly, it should make a significant contribution to the field of organic functional materials to investigate  $\pi$ -conjugated furan-fused phosphole derivatives. Here we report the synthesis and properties of benzophospholo[3,2-*b*]benzofuran (BPBF) de-

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Chart 1. Structures of Thiophene- And Furan-Fused Phospholes

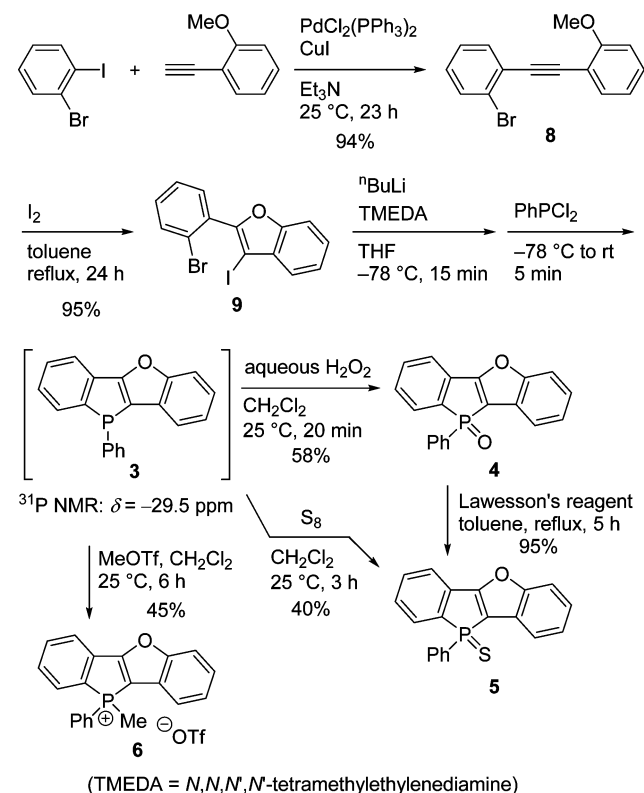


derivatives 3–7,  $\pi$ -conjugated molecules with a phospholo[3,2-*b*]furan moiety (Chart 1). The desired BPBFs were successfully synthesized via a conventional synthetic approach for dibenzophospholes. In addition, the diversity-oriented synthetic strategy was also developed in this study, which allows facile access to BPBFs with a different substituent on the phosphorus center. The furan moiety can be considered an electron donor,<sup>13</sup> while phosphole can serve as an electron acceptor.<sup>8a,b</sup> Accordingly, the BPBF framework is expected to be an intramolecular donor–acceptor-type  $\pi$ -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.

## 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.<sup>1f</sup> 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.<sup>14</sup> 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<sup>15</sup> 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 <sup>n</sup>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 <sup>31</sup>P NMR spectroscopy. The chemical shift was high-field shifted compared with that of the thiophene analog, BPBT 1 (P = P, Chart 1) (–16.5 ppm),<sup>14</sup> while it was low-field shifted compared with that of the related furan-fused phosphole compound, DBPDF 2 (P = P, Chart 1) (–44.0 ppm).<sup>11b</sup> 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<sub>2</sub>O<sub>2</sub> (58% yield from 9). The low-field-shifted <sup>31</sup>P NMR resonance (21.5 ppm) clearly supported the formation of

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



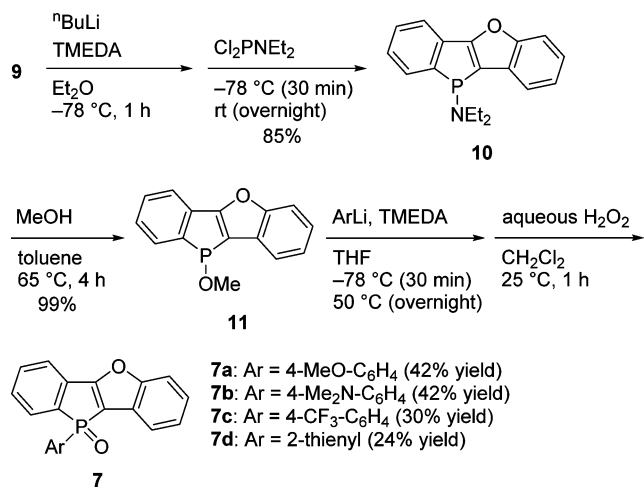
phosphole oxide derivative 4. The chemical shift was again high-field shifted compared with that of BPBT oxide 1 (P = P=O, Chart 1) (26.1 ppm),<sup>14</sup> while it was low-field shifted compared with that of DBPDF oxide 2 (P = P=O, Chart 1) (11.9 ppm).<sup>11b</sup>

Trivalent phosphole compound 3 was a common precursor for other derivatives (Scheme 1).<sup>8d</sup> As summarized in Scheme 1, oxidation of 3 with S<sub>8</sub> 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 <sup>31</sup>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  $\pi$ -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  $\pi$ -conjugated compounds. Accordingly, elucidation of the substituent effects is important to design new phosphole-fused  $\pi$ -conjugated compounds. However, the substituent on the phosphorus center is indeed a phenyl group in most of phosphole-fused  $\pi$ -conjugated compounds, and the reports on the substituent effects have been very limited. Recently, Baumgartner and co-workers synthesized dithieno-[3,2-*b*;2',3'-*d'*]phospholes with a variety of substituents on the phosphorus center.<sup>16</sup> 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 organolithium reagent (Scheme 2). In this route, the substituent on

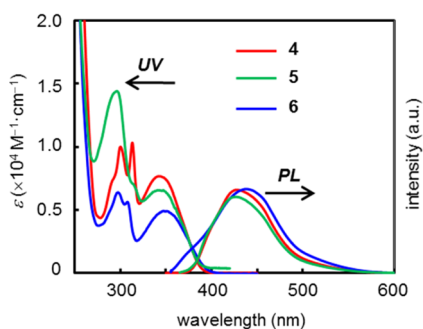
### Scheme 2. Synthesis of 10-Ar-BPBFs **7** by Using 10-MeO-BPBF **11** as a Common Intermediate



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<sub>2</sub>PNEt<sub>2</sub>, affording 10-NEt<sub>2</sub>-BPBF, **10** (85% yield). The compound **10** is not so air-sensitive and can be purified under air.<sup>17</sup> Then, the obtained **10** was completely converted to 10-MeO-BPBF, **11**, by the reaction with methanol.<sup>18</sup> Finally, 10-MeO-BPBF, **11**, was reacted with organolithium reagent and subsequently oxidized with H<sub>2</sub>O<sub>2</sub> to give the desired 10-Ar-BPBF oxides **7**.<sup>19</sup> This procedure gave a library of BPBF oxides with electron-donating (4-MeO-C<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>, thienyl) and electron-withdrawing (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>) aryl groups on the phosphorus center.

**Photophysical Properties of 10-Phenyl-BPBF Derivatives.** Photophysical properties of compounds **4–6** were evaluated by UV–vis absorption spectroscopy and photoluminescence 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 almost identical longest absorption maxima around at 340 nm with



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

**Table 1.** Photophysical Data of BPBFs

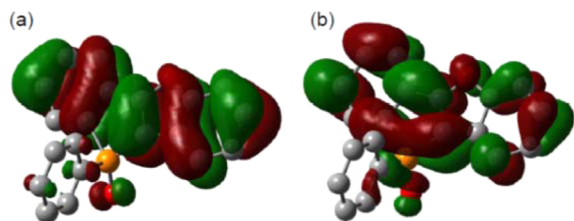
|          | solution                                 |   |                                  | $\Phi$ (%) <sup>c</sup> | powder                                  |                         |
|----------|--|---|----------------------------------|-------------------------|---|-------------------------|
|          | $\lambda_{\text{abs}}$ (nm) <sup>a</sup> | $\lambda_{\text{em}}$ (nm) <sup>b</sup> | Stokes shift (cm <sup>-1</sup> ) |                         | $\lambda_{\text{em}}$ (nm) <sup>d</sup> | $\Phi$ (%) <sup>c</sup> |
| <b>4</b> | 341                                      | 428                                     | 5960                             | 84                      | 421                                     | 87                      |
| <b>5</b> | 342                                      | 426                                     | 5770                             | <1                      | <i>e</i>                                | <1                      |
| <b>6</b> | 351                                      | 439                                     | 5710                             | 98                      | 469                                     | 50                      |

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>In CH<sub>2</sub>Cl<sub>2</sub>. Excitation at 340 nm. <sup>c</sup>Absolute quantum yield determined by a calibrated integrating sphere system. <sup>d</sup>Excitation at 340 nm. <sup>e</sup>Emission maximum cannot be detected because of low emission intensity.

each other, while the molar absorption coefficient of **4** ( $\epsilon = 0.77 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$  at  $\lambda_{\text{abs}} = 341 \text{ nm}$ ) was larger than that of **5** ( $\epsilon = 0.66 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$  at  $\lambda_{\text{abs}} = 342 \text{ nm}$ ). Absorption spectrum of phosphonium derivative **6** showed the longest absorption maximum at 351 nm, which was red-shifted compared with those of **4** and **5**.

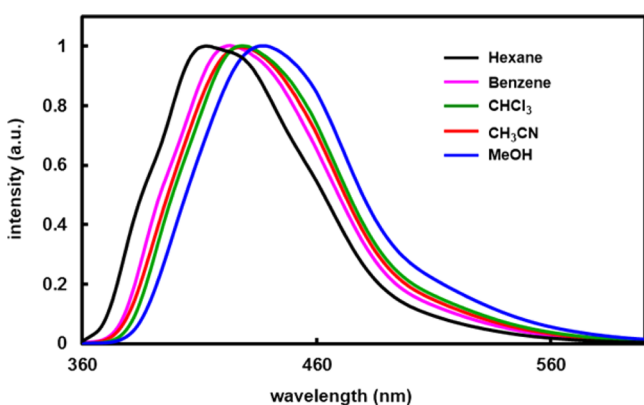
The present BPBF derivatives were found to possess high photoluminescence properties. All of the BPBF derivatives showed broad photoluminescence spectra in CH<sub>2</sub>Cl<sub>2</sub> with large Stokes shifts of 5700–6000 cm<sup>-1</sup>. Compounds **4** and **6** exhibited intense blue emission with high quantum yields, which are higher than those of the previously reported dithienophosphole derivatives<sup>8a,b,d</sup> and 10-Ph-BPBT derivatives **1**, and are competitive with highly emissive bis-phosphoryl-bridged stilbene derivatives.<sup>9</sup> 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 properties of phosphole oxide derivatives **4** in the solid state may be due to the sterically hindered structure around the tetrahedral phosphorus center.<sup>8d</sup>

**Theoretical Study of Photophysical Properties of 10-Phenyl-BPBF Derivatives.** Phosphole oxide **4** possesses the calculated longest absorption wavelength 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 absorption wavelength 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<sub>0</sub> → S<sub>1</sub> electron transitions of **4** and **6** are dominated by HOMO–LUMO ( $\pi$ – $\pi^*$ ) transition. On the other hand, the obvious transition for phosphole sulfide **5** is S<sub>0</sub> → S<sub>3</sub> 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), which were not detected as absorption maxima in UV–vis absorption spectroscopy, possess much lower oscillator strength<sup>20</sup>. 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 the phosphole oxide moiety. Such distribution in HOMO and LUMO orbitals may be attributed to the furan and phosphole moieties working as electron donor and acceptor, respectively, resulting in intramolecular donor–acceptor-type  $\pi$ -electron systems.<sup>13</sup> This intramolecular donor–acceptor-type interac-



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

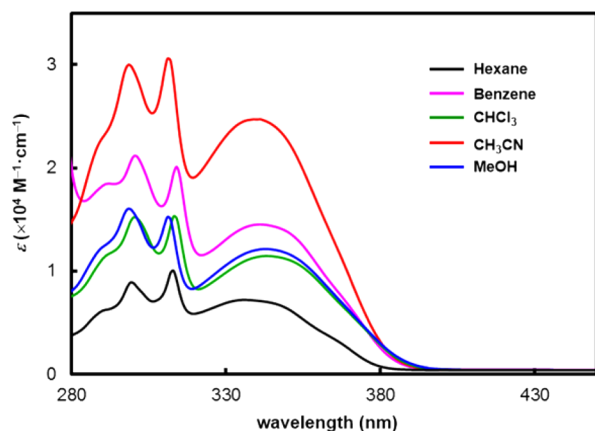
tion is partially supported by solvatochromism of **4**.<sup>21</sup> Increase in solvent polarity caused a red-shift in the photoluminescence spectra ( $\lambda_{em} = 413$  nm in hexane [ $E_T(30) = 30.9$ ], 423 nm in benzene [ $E_T(30) = 34.5$ ], 423 nm in  $\text{CH}_3\text{CN}$  [ $E_T(30) = 46.7$ ], 428 nm in  $\text{CHCl}_3$  [ $E_T(30) = 39.1$ ], 438 nm in MeOH [ $E_T(30) = 55.5$ ],  $E_T(30) =$  solvent polarity parameter,<sup>22</sup> Figure 3), while



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

significant solvatochromism in the absorption spectra was not observed ( $\lambda_{abs} = 336$  nm in hexane, 341 nm in benzene, 341 nm in  $\text{CH}_3\text{CN}$ , 343 nm in  $\text{CHCl}_3$ , 343 nm in MeOH, Figure 4).<sup>14</sup> Such an electronic structure may induce large Stokes shifts, which can diminish the self-quenching of photoluminescence to afford high quantum yields.<sup>13,23</sup>

**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, compounds **7a**, **7c**, and **7d** show

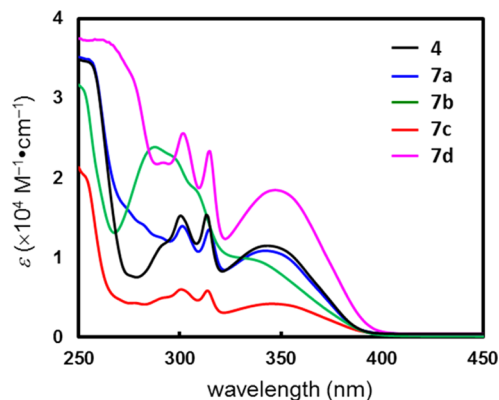


**Figure 4.** Absorption spectra of BPBF **4** in different solvents.

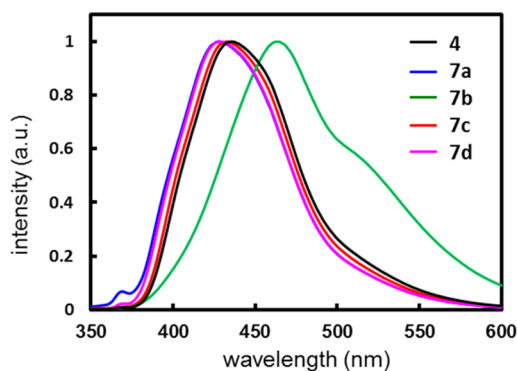
**Table 2.** Photophysical Data of BPBFs **7**

|           | $\lambda_{abs}$ (nm) <sup>a</sup> | $\lambda_{em}$ (nm) <sup>b</sup> | Stokes shift ( $\text{cm}^{-1}$ ) | $\Phi(\%)$ <sup>c</sup> |
|-----------|-----------------------------------|----------------------------------|-----------------------------------|-------------------------|
| <b>7a</b> | 342                               | 428                              | 5880                              | 88                      |
| <b>7b</b> | 341                               | 464                              | 7770                              | 90                      |
| <b>7c</b> | 346                               | 433                              | 5810                              |                         |
| <b>7d</b> | 347                               | 428                              | 5450                              |                         |

<sup>a</sup>In  $\text{CHCl}_3$ . <sup>b</sup>In  $\text{CHCl}_3$ . Excitation at 315 nm. <sup>c</sup>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**.

similar absorption features to compound **4** with absorption maxima at around 300, 310, and 340 nm, while the molar absorption coefficients depend on the substituents. On the other hand, compound **7b** with 4-(dimethylamino)phenyl group on the phosphorus center shows a less resolved absorption spectrum. In the photoluminescence spectra, compounds **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  $7770 \text{ cm}^{-1}$  is the largest in the series of BPBF derivatives in this study. Such a large Stokes shift should be attributed to intramolecular charge transfer. The DFT calculation showed that the HOMO of compound **7b** is dominated by the 4-(dimethylamino)phenyl moiety (donor) and the LUMO is localized at the BPBF moiety (Figure S35, Supporting Information). This trend is similar to the reported dithienophospholes with a 4-(diphenylamino)phenyl substituent on the phosphorus center.<sup>24</sup>

## 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 easy-to-use common intermediate. This synthetic approach could be applied to the synthesis of other dibenzophosphole derivatives and open up the chemistry of phosphole-containing  $\pi$ -conjugated compounds. Photophysical properties of BPBFs were revealed based on UV-vis and photoluminescence spectroscopies and theoretical calculation. The highly electron-donating aryl substituents on phosphorus center were found to induce large Stokes shift, which should be caused by intramolecular charge transfer. The characteristics of the present BPBF derivatives are large Stokes shift and high emission properties 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 ( $^1H$  500 MHz,  $^{13}C$  126 MHz,  $^{31}P$  202 MHz) or a 400 MHz spectrometer ( $^1H$  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  $^1H$ , 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- or moisture-sensitive compounds were carried out in a glovebox 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 reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on 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  $\mu m$ ).

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

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

**1-Bromo-2-[(2-methoxyphenyl)ethynyl]benzene (8).**<sup>27</sup> 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), and  $Et_3N$  (50 mL) under argon atmosphere. After being degassed by freeze-pump-thaw cycles (three times), the mixture was stirred under argon atmosphere at 25 °C for 23 h. A white precipitate was filtered off with  $Et_2O$ , and the filtrate 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):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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);  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  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).**<sup>12k</sup> 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  $\times$  3), and the combined organic layers were dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. The resulting residue 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%):  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA, 30  $\mu L$ , 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 the mixture was stirred at the same temperature for 15 min,  $PPhCl_2$  (90  $\mu L$ , 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,  $CDCl_3$ )  $\delta$  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);  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  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);  $^{31}P\{^1H\}$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  –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 atmosphere.  $H_2O_2$  (0.80 mL, 35% aqueous solution) was added in one portion. After the resulting mixture was stirred at 25 °C for 20 min, saturated aqueous  $Na_2S_2O_3$  (3 mL) was slowly added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with AcOEt (20 mL  $\times$  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;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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,  $CDCl_3$ )  $\delta$  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<sub>2</sub>Cl<sub>2</sub> (10 mL) under argon atmosphere. An excess sulfur S<sub>8</sub> (320 mg, 10 mmol) was added in one portion, and the reaction mixture was stirred at 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<sub>3</sub>/hexane = 3/2 as an eluent, R<sub>f</sub> = 0.35) to give the title compound as a colorless solid (67 mg, 40% yield from **9**): mp 168–170 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (dd, J<sub>HP</sub> = 15.0, J<sub>HH</sub> = 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); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 166.0 (d, J<sub>CP</sub> = 31.7 Hz), 159.4 (d, J<sub>CP</sub> = 11.5 Hz), 142.4 (d, J<sub>CP</sub> = 88.3 Hz), 132.4 (d, J<sub>CP</sub> = 2.9 Hz), 132.2 (s), 130.9 (d, J<sub>CP</sub> = 12.5 Hz), 130.23 (d, J<sub>CP</sub> = 12.5 Hz), 130.22 (d, J<sub>CP</sub> = 86.4 Hz), 129.6 (d, J<sub>CP</sub> = 10.6 Hz), 129.0 (d, J<sub>CP</sub> = 13.4 Hz), 125.8 (s), 125.1 (d, J<sub>CP</sub> = 8.6 Hz), 124.9 (s), 121.0 (s), 120.3 (d, J<sub>CP</sub> = 7.7 Hz), 114.0 (d, J<sub>CP</sub> = 105.6 Hz), 112.6 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>) δ 27.8 (s). Anal. Calcd for C<sub>20</sub>H<sub>13</sub>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<sub>3</sub>/hexane = 2/1 as an eluent, R<sub>f</sub> = 0.33) to give **5** as a colorless solid (158 mg, 95% yield).

**10-Methyl-10-phenylbenzophospholo[3,2-*b*]benzofuran-10-ium Trifluoromethanesulfonate (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<sub>2</sub>Cl<sub>2</sub> (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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.50 (dd, J<sub>HP</sub> = 11.7 Hz, J<sub>HH</sub> = 7.7 Hz, 1H), 8.08 (dd, J<sub>HP</sub> = 15.1 Hz, J<sub>HH</sub> = 7.4 Hz, 2H), 7.92 (dd, J<sub>HP</sub> = 3.4 Hz, J<sub>HH</sub> = 7.5 Hz, 1H), 7.86–7.62 (m, 7H), 7.55–7.47 (m, 2H), 2.95 (d, J<sub>HP</sub> = 15.0 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) δ 169.7 (d, J<sub>CP</sub> = 31.7 Hz), 159.8 (d, J<sub>CP</sub> = 11.5 Hz), 135.9 (d, J<sub>CP</sub> = 2.9 Hz), 135.5 (d, J<sub>CP</sub> = 1.9 Hz), 134.0 (d, J<sub>CP</sub> = 9.6 Hz), 133.0 (d, J<sub>CP</sub> = 11.5 Hz), 132.6 (d, J<sub>CP</sub> = 12.5 Hz), 132.3 (d, J<sub>CP</sub> = 12.5 Hz), 130.8 (d, J<sub>CP</sub> = 14.4 Hz), 128.6 (d, J<sub>CP</sub> = 91.2 Hz), 127.6 (s), 126.6 (s), 123.8 (d, J<sub>CP</sub> = 9.6 Hz), 122.3 (d, J<sub>CP</sub> = 8.6 Hz), 121.3 (s), 120.9 (q, J<sub>CP</sub> = 320.5 Hz, one of the signals of the quartet overlaps with the doublet at 122.3 ppm), 116.3 (d, J<sub>CP</sub> = 90.2 Hz), 113.3 (s), 100.9 (d, J<sub>CP</sub> = 113.2 Hz), 7.7 (d, J<sub>CP</sub> = 53.7 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>) δ 16.3 (s). HRMS–ESI<sup>+</sup> (*m/z*) calcd for C<sub>21</sub>H<sub>16</sub>OP [[M–OSO<sub>2</sub>CF<sub>3</sub>]<sup>+</sup>] 315.0939, found 315.0940.

**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<sub>3</sub>O (30 mL), and N,N,N',N'-tetramethylethylenediamine (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 the mixture was stirred at the same temperature for 1 h, Cl<sub>2</sub>PNET<sub>2</sub> (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<sub>2</sub>O wash. The filtrate was concentrated, and hexane (20 mL) was added. The resulting suspension was filtered and concentrated to give 10-NEt<sub>2</sub>-BPBF, **10**, as a yellow oil (504 mg, 85% yield). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ, 7.70 (d, J<sub>HH</sub> = 7.6 Hz, 1H), 7.66–7.61 (m, 2H), 7.42 (d, J<sub>HH</sub> = 7.9 Hz, 1H), 7.13–7.02 (m, 4H), 2.82–2.75 (m, 4H), 0.89 (t, J<sub>HH</sub> = 7.2 Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (126

MHz, CDCl<sub>3</sub>) δ 163.6 (d, J<sub>CP</sub> = 12.0 Hz), 159.7 (d, J<sub>CP</sub> = 3.6 Hz), 147.5 (d, J<sub>CP</sub> = 8.4 Hz), 133.3 (d, J<sub>CP</sub> = 3.6 Hz), 130.9 (d, J<sub>CP</sub> = 20.4 Hz), 129.2 (d, J<sub>CP</sub> = 13.7 Hz), 129.1, 127.4 (d, J<sub>CP</sub> = 7.2 Hz), 124.6, 124.0, 121.2, 119.7 (d, J<sub>CP</sub> = 15.6 Hz), 119.6, 112.5, 44.7 (d, J<sub>CP</sub> = 14.4 Hz), 15.3 (d, J<sub>CP</sub> = 3.67 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>) 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). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) 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<sub>PH</sub> = 8.3 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 166.0 (d, J<sub>CP</sub> = 6.0 Hz), 159.6 (d, J<sub>CP</sub> = 4.8 Hz), 143.7 (d, J<sub>CP</sub> = 24.0 Hz), 133.9, 131.8 (d, J<sub>CP</sub> = 22.8 Hz), 130.4, 128.9 (d, J<sub>CP</sub> = 14.4 Hz), 128.4 (d, J<sub>CP</sub> = 6.0 Hz), 124.9, 124.4, 121.5, 119.6, 117.3 (d, J<sub>CP</sub> = 30.0 Hz), 112.4, 53.8 (d, J<sub>CP</sub> = 14.4 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) 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 the mixture was 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 being stirred at the same temperature for 30 min, the reaction mixture was allowed to warm to 50 °C and stirred at 50 °C overnight. The reaction mixture was concentrated under reduced pressure, and the residue was suspended with Et<sub>2</sub>O (10 mL) under argon atmosphere. The resulting suspension was passed through a short pad of neutral alumina with Et<sub>2</sub>O wash, and the filtrate was concentrated. The resulting residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and H<sub>2</sub>O<sub>2</sub> (1.0 mL, 35% aqueous solution) was added in one portion. After the resulting mixture was stirred at 25 °C for 1 h, water (5 mL) was added. The organic layer was separated, washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue 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<sub>f</sub> = 0.28) as a pale yellow solid (70 mg, 42% yield): mp 138.0–140.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75–7.64 (m, 4H), 7.61–7.59 (m, 2H), 7.53 (t, J<sub>HH</sub> = 7.6 Hz, 1H), 7.41–7.32 (m, 2H), 7.29 (d, J<sub>HH</sub> = 8.0 Hz, 1H), 6.92 (dd, J<sub>HP</sub> = 2.3 Hz, J<sub>HH</sub> = 8.8 Hz, 2H), 3.80 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 167.9 (d, J<sub>CP</sub> = 35.5 Hz), 163.3 (d, J<sub>CP</sub> = 2.9 Hz), 159.4 (d, J<sub>CP</sub> = 10.5 Hz), 139.21 (d, J<sub>CP</sub> = 106.4 Hz), 133.0 (d, J<sub>CP</sub> = 13.4 Hz), 132.9 (d, J<sub>CP</sub> = 12.5 Hz), 132.7 (d, J<sub>CP</sub> = 1.9 Hz), 130.2 (d, J<sub>CP</sub> = 11.5 Hz), 129.8 (d, J<sub>CP</sub> = 8.6 Hz), 125.6 (s), 125.5 (d, J<sub>CP</sub> = 7.7 Hz), 124.9 (s), 121.6 (s), 120.5 (d, J<sub>CP</sub> = 116.9 Hz), 120.0 (d, J<sub>CP</sub> = 8.6 Hz), 114.8 (d, J<sub>CP</sub> = 13.4 Hz), 112.5 (d, J<sub>CP</sub> = 121.7 Hz), 112.5 (s); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>) δ 21.6 (s). HRMS–ESI<sup>+</sup> (*m/z*) calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>PNa [[M+Na]<sup>+</sup>] 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<sub>f</sub> = 0.23) as a pale yellow solid (76 mg, 42% yield): mp 225–230 °C (decompose); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71–7.57 (m, 6H), 7.47 (t, J<sub>HH</sub> = 7.6 Hz, 1H), 7.39–7.24 (m, 3H), 6.65 (dd, J<sub>HH</sub> = 8.7, 2.3 Hz, 2H), 2.96 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 167.6 (d, J<sub>CP</sub> = 35.5 Hz), 159.3 (d, J<sub>CP</sub> = 10.5 Hz), 153.1 (d, J<sub>CP</sub> = 1.9 Hz), 139.8 (d, J<sub>CP</sub> = 106.4 Hz), 132.7 (d, J<sub>CP</sub> = 12.5 Hz), 132.4 (d, J<sub>CP</sub> = 12.5 Hz), 132.3, 130.0 (d, J<sub>CP</sub> = 11.5 Hz), 129.6 (d, J<sub>CP</sub> = 8.6 Hz), 125.7 (d, J<sub>CP</sub> = 7.7 Hz), 125.4, 124.7, 121.6, 119.8 (d, J<sub>CP</sub> = 8.6 Hz), 113.5 (d, J<sub>CP</sub> = 40.3 Hz), 112.33 (d, J<sub>CP</sub>

= 39.3 Hz), 112.30, 111.9 (d,  $J_{CP}$  = 13.4 Hz), 40.0;  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  22.6. HRMS-APCI $^+$  ( $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{P}$  [ $\{\text{M}+\text{H}\}^+$ ] 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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J_{\text{HH}}$  = 7.8 Hz, 1H), 7.91 (d,  $J_{\text{HH}}$  = 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,  $J_{\text{HH}}$  = 7.8 Hz, 1H), 7.30 (d,  $J_{\text{HH}}$  = 7.6 Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  19.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.2. HRMS-APCI $^+$  ( $m/z$ ) calcd for  $\text{C}_{21}\text{H}_{13}\text{F}_3\text{O}_2\text{P}$  [ $\{\text{M}+\text{H}\}^+$ ] 385.0605, found 385.0614.

**10-Thienylbenzophospholo[3,2-*b*]benzofuran Oxide (7d).** The crude residue was obtained by using thiophene (79  $\mu\text{L}$ , 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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (dd,  $J_{\text{HP}}$  = 11.5 Hz,  $J_{\text{HH}}$  = 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);  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  13.1. HRMS-APCI $^+$  ( $m/z$ ) calcd for  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{PS}$  [ $\{\text{M}+\text{H}\}^+$ ] 323.0296, found 323.0299.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for synthesized compounds and DFT and TD-DFT calculation results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [k\\_nakano@cc.tuat.ac.jp](mailto:k_nakano@cc.tuat.ac.jp)

\*E-mail: [nozaki@chembio.t.u-tokyo.ac.jp](mailto:nozaki@chembio.t.u-tokyo.ac.jp)

### Notes

The authors declare no competing financial interest.

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