

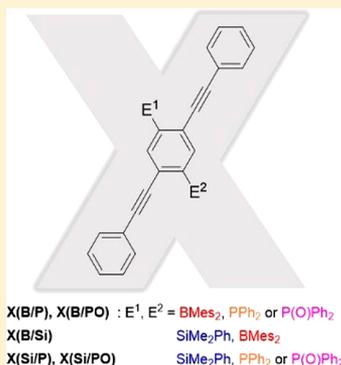
Synthesis and Photophysical Properties of Phenyleneethynylenes Containing a Combination of Two Main Group Element Moieties of B, Si, or P on the Side Chain

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S Supporting Information

ABSTRACT: X-shaped 1,4-phenyleneethynylenes containing a combination of two main group element moieties of B, Si, or P as part of the side chain have been synthesized. The halogen–lithium exchange of 2-bromo-5-dimethylphenylsilyl-1,4-bis(phenylethynyl)benzene followed by addition of fluorodimesitylborane or chlorodiphenylphosphine gave the “X-shaped” B/Si and Si/P, respectively. The P-containing molecule was oxidized to afford a P(=O) derivative. The B/PO moieties were introduced to the 1,4-phenyleneethynylene unit by 3 steps, i.e., the halogen–lithium exchange of 2,5-dibromo-1,4-bis(trimethylsilylethynyl)benzene followed by sequential addition of fluorodimesitylborane and chlorodiphenylphosphine oxide, desilylation, and the Sonogashira coupling with aryl iodides. Then, the reduction of the B/PO gave “X-shaped” B/P derivative. The absorption and fluorescence spectra of the “X-shaped” molecules showed the molecules have two-dimensional conjugation systems, i.e., the π -conjugation of the original π -conjugation backbone and p(B) π – π^* conjugation of B, σ^* – π^* conjugation of Si, and n– π and σ^* – π^* conjugation of P, extended from the π -core. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels are significantly altered because of a lowering of the LUMO level due to p– π^* conjugation for B and σ^* – π^* conjugation for Si and P compared with the parent phenyleneethynylene, which are also supported by density functional theory calculations.

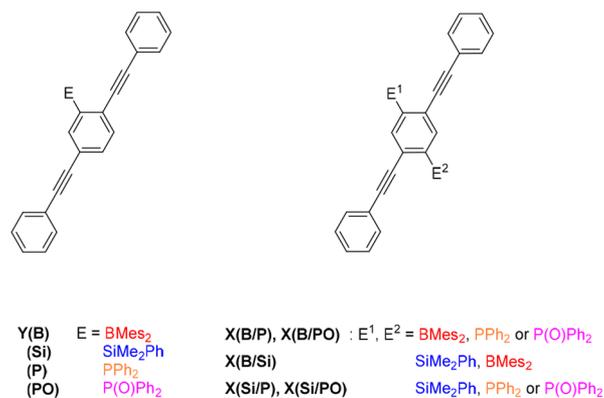


INTRODUCTION

Over the past decades, the design and synthesis of π -conjugated polymers and oligomers have been active areas of research because of their applications as optoelectronic materials, such as organic field-effect transistors and organic electroluminescent devices. In this regard, main group element-containing π -conjugated molecules are interesting.¹ When some types of main group elements, especially those in the group 13, B, 14, Si, and 15, P, are incorporated into the π -conjugated framework, the orbital interactions, p– π^* conjugation for B, σ – π and σ^* – π^* conjugation for Si, and n– π conjugation for P, lead to a reduction in the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps compared with the parent π -system. In addition, chemical modifications such as the oxidation of P can also change the electronic state. This strategy has been employed to control the electro- and optical properties, for example, the absorption or emission wavelengths, and improved the fluorescence quantum yield, as well as the solubility of the polymers. Along this line, some examples of B, Si, and P contained in π -conjugated systems including the main chain type^{2,3} and side group type^{4–6} have been reported.⁷ In addition, incorporation of two main group elements into π -conjugated molecules is also reported.^{8–10}

We also reported the synthesis and optical properties of a series of phenyleneethynylenes containing a main group element moiety of B, Si, or P on the side chain, which could be a simple model of the B, Si, and P contained in π -conjugated systems (Y(B), Y(Si), Y(P), and Y(PO), Chart 1).¹¹

Chart 1. Chemical Structures of 1,4-Phenyleneethynylenes Containing a Combination of Main Group Element Moieties of B, Si, or P as Part of the Side Chain



The HOMO–LUMO energy levels are altered due to a rise of the HOMO level Y(P) or a lowering of the LUMO level (Y(B) and Y(PO)) compared with the parent phenyleneethynylene, which is also supported by molecular orbital calculations. At the same time, the design and synthesis of X-shaped 1,4-phenyleneethynylenes have been extensively studied.^{12,13} In X-shaped 1,4-phenyleneethynylenes, depending upon their substituents,

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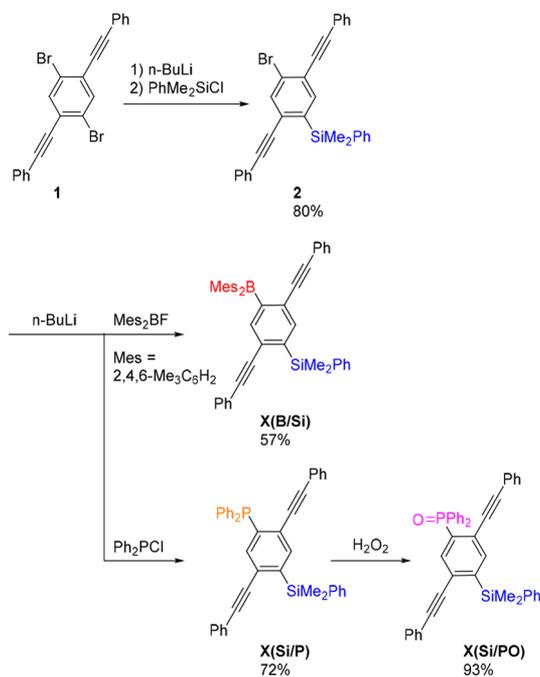
the frontier molecular orbitals are either congruent, i.e., HOMO and LUMO occupy the same real space, or disjointed, i.e., the HOMO is located on one branch of them while the LUMO is located on the second one. Then, we decided to synthesize X-shaped 1,4-phenyleneethynylenes containing a combination of two main group element moieties of B, Si, or P as part of the side chain, because exploiting a combination of two main group element groups could be interesting.

Here, we show the design, synthesis, and optical properties of a series of “X-shaped” phenyleneethynylenes containing two main group element moieties with combinations of B/Si, B/P, and Si/P on the side chain (Chart 1). The “X-shaped” molecules have two-dimensional conjugation systems, i.e., one is the original π -conjugation backbone and the other is the $p-\pi^*$ conjugation of B, $\sigma^*-\pi^*$ conjugation of Si and P, or $n-\pi$ conjugation of P, extended from the π -core. These conjugated molecules with two main group elements across the periodic table could be an alternative example for conjugated systems.

RESULTS AND DISCUSSION

Synthesis. The synthesis of “X-shaped” B/Si, Si/P, and Si/PO is shown in Scheme 1. In this study, the 1,4-phenyleneethynylene

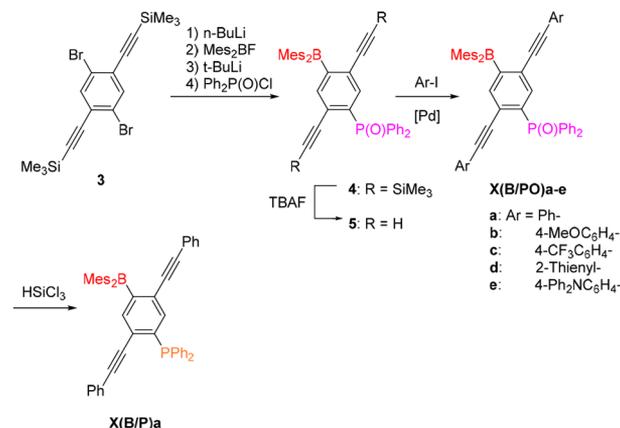
Scheme 1. Synthesis of X(B/Si), X(Si/P), and X(Si/PO)



unit is selected as the parent π -conjugated framework. The reaction of 1,4-dibromo-2,5-bis(phenylethynyl)benzene **1** and butyllithium followed by addition of chlorodimethylphenylsilane gave **2**. The second lithiation followed by addition of fluorodimesitylborane (mesityl = 2,4,6-trimethylphenyl) or chlorodiphenylphosphine gave the “X-shaped” B/Si or Si/P, respectively. The P-containing molecule, X(Si/P), was oxidized with hydrogen peroxide to afford X(Si/PO).

The next example is X-shaped conjugated molecules with B and P, where B is electro-deficient and shows Lewis acid nature but P is electron-rich and shows Lewis basic nature. This combination could be interesting. Scheme 2 shows the synthesis of “X-shaped” B/PO and B/P. The synthesis route is slightly different from the mentioned above. The reaction of 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene (**3**) and

Scheme 2. Synthesis of X(B/PO)a–d and X(B/P)a



butyllithium followed by sequential addition of fluorodimesitylborane and chlorodiphenylphosphine oxide gave **4**. After desilylation, the Sonogashira coupling of **5** with aryl iodides gave **X(B/PO)**. Using this coupling method, X(B/PO)a–e with a wide variety of aromatic end groups including 4-trifluorophenyl, 4-anisyl-, 2-thienyl, and 4-(*N,N'*-diphenylamino)phenyl were synthesized. Because the B/PO groups as part of the side chain on the 1,4-phenyleneethynylene could act as an electron-withdrawing group (*vide infra*), the electron-donating groups, anisyl, thienyl, and diphenylaminophenyl groups, were introduced to X(B/PO) among others. Furthermore, X(B/P)a was obtained by the reaction of X(B/PO)a with trichlorosilane in good yield. All compounds were fully characterized (also see the Supporting Information).

Optical Properties. The optical properties of “X-shaped” B/Si, B/P, B/PO, Si/P, and Si/PO are of interest. The optical data in solution, along with those of a parent compound, 2,5-bis(phenylethynyl)benzene (BPEB), are summarized in Table 1.

The absorption and fluorescence spectra of X(B/Si) and also BPEB are shown in Figure 1. The spectral features of X(B/Si) are much different from those of BPEB. In the absorption spectra of X(B/Si), an absorption maximum at 323 nm with an absorption shoulder at 360 nm is found. The absorption shoulder is assigned to a cross-conjugated state with orbital contributions from the empty p-orbital on B along the phenyleneethynylene framework. When excited at the absorption edge, X(B/Si) displays a broad emission at around 489 nm with a large Stokes shift (7330 cm⁻¹ in CH₂Cl₂). In hexane, a broad emission is blue-shifted by 30 nm relative to that in CH₂Cl₂. This band is assignable to the intramolecular charge transfer emission, where the dimesitylboryl group could act as a π -acceptor. A peak at 370 nm is found in the excitation spectrum (Figure S1).

Next, the absorption and fluorescence spectra of X(Si/P) and X(Si/PO) in dichloromethane are shown in Figure 2. In the absorption of X(Si/P) are found an absorption maximum at 335 nm and a weak additional absorption band at around 410 nm ($\epsilon = 300 \text{ cm}^{-1} \text{ M}^{-1}$) assignable to the $n-\pi^*$ transition. The absorption at around 400 nm is dependent on the solvent polarity and clearly observed in methanol (Figure S2). When excited at the $n-\pi^*$ transition, X(Si/P) exhibits a broad emission at around 509 nm. The excitation spectrum monitored at this emission shows a peak at 400 nm, which is in good agreement with the $n-\pi^*$ transition in the absorption. It is noted that a structured emission was found at 390 nm when excited at 310 nm. In contrast, X(Si/PO) displays an absorption maximum at 345 nm, which is red-shifted by 25 nm relative to that

Table 1. Optical Data for X(B/Si), X(B/PO), X(B/P), X(Si/P), X(Si/PO), and Model Compounds

compound	absorption ^a		fluorescence ^a				HOMO (eV) ^d	LUMO (eV) ^d	E _g (eV) ^e
	λ_{abs} (nm)	ϵ (cm ⁻¹ M ⁻¹)	λ_{FL} (nm) ^b	Φ_{FL} ^c	Stokes shift (cm ⁻¹)				
X(B/Si)	323	51000	489	0.01	7330	-5.33	-1.95	3.38	
	360	16000							
X(B/PO)a	362	15000	527	0.01	8650	-5.39	-2.07	3.32	
	b	358	23000	520	0.01	8700			
	c	384	21000	521	0.06	6850			
	d	385	15000	537	0.01	7350			
e	440	34000	583	0.65	5570				
X(B/P)a	327, 430 (sh)	36000, 3000	470, ^f 523 ^g	0.01, 0.01	9300, 4100	-5.31	-1.94	3.37	
X(Si/P)	335, 410	45000, 300	509	0.34	4740	-5.35	-1.73	3.62	
X(Si/PO)	345	39000	372, 390	0.81	2100	-5.41	-1.85	3.56	
Y(B) ^e	305, 345	30000, 17000	476	0.08	7890	-5.37	-1.91	3.46	
Y(Si) ^e	326	34700	354, 371	0.29	2030	-5.41	-1.72	3.69	
Y(P) ^e	325, 405 (sh)	28000, 300	500	0.13	4690	-5.37	-1.73	3.64	
Y(PO) ^e	342	34000	383, 405	0.05	1770	-5.46	-1.83	3.63	
BPEB	320	60300	356	0.64	2800	-5.43	-1.74	3.69	

^aIn CH₂Cl₂. ^bExcited at the longest absorption maximum wavelengths. ^cQuantum yield determined with quinine sulfate as a standard. ^dCalculated HOMO–LUMO energy levels at the B3LYP/6-31G* level. ^eFrom ref 11. ^fExcited at 350 nm. ^gExcited at 430 nm

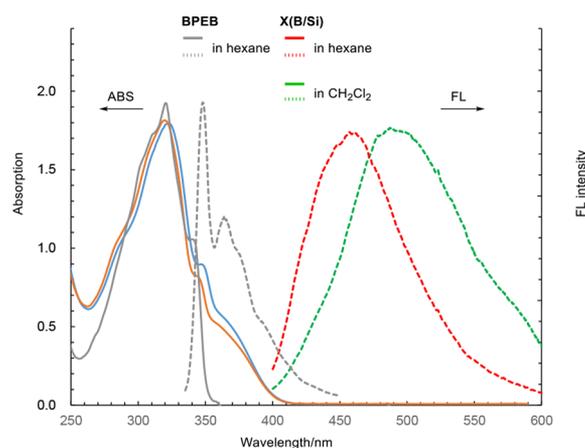


Figure 1. Absorption and fluorescence spectra of X(B/Si) in hexane and dichloromethane and BPEB in hexane.

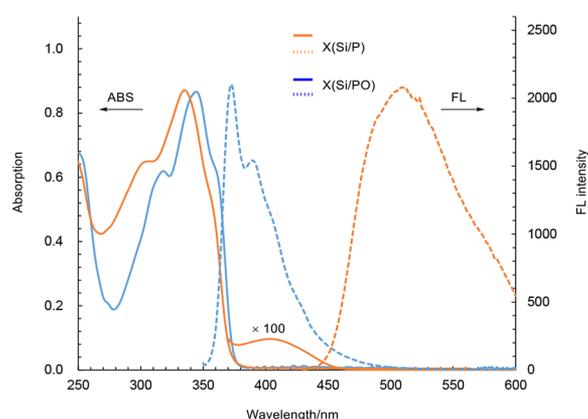


Figure 2. Absorption and fluorescence spectra of X(Si/P) and X(Si/PO) in dichloromethane.

of BPEB because of the strong electron-withdrawing P(=O) moiety.¹⁴ In the fluorescence spectrum, X(Si/PO) shows a structured emission at 390 nm. Noted that the absorption and fluorescence spectra in dichloromethane and THF were not nearly solvent dependent (Figure S3).

Figure 3 shows the absorption and fluorescence spectra of X(B/PO)a–e. The controlled samples for 1,4-phenyleneethylenes

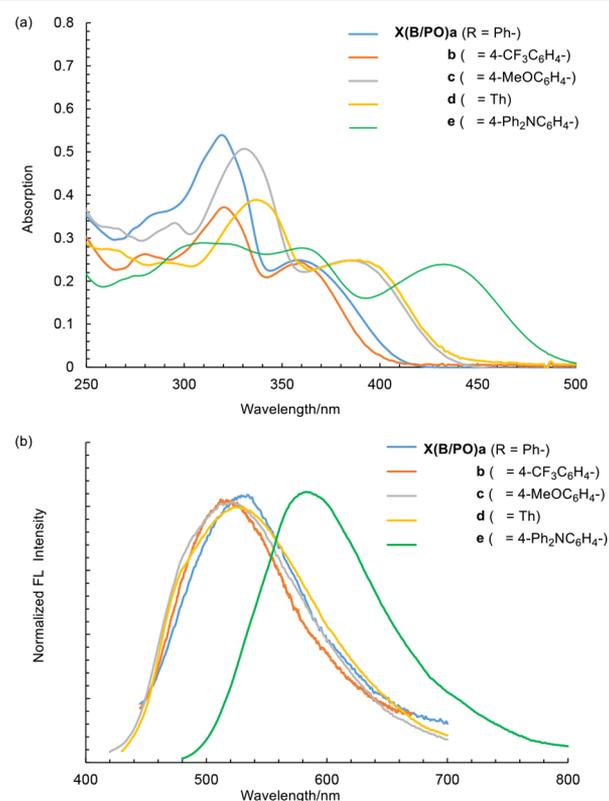


Figure 3. (a) Absorption and (b) fluorescence spectra of X(B/PO)a–e in dichloromethane.

with electron-donating groups as the side chain could also be referred.¹⁵ In the absorption, the phenyl-substituted compound, X(B/PO)a, displays two absorption bands at 322 and 362 nm. The longer absorption band observed at 362 nm is primarily ascribed to the cross-conjugated state with orbital contributions from the empty p-orbital on B with attached π -systems. When substituted with the electron-withdrawing

trifluoromethylphenyl group, $X(B/PO)b$ shows an absorption that is almost the same as that of $X(B/PO)a$. However, when substituted with electron-donating groups, anisyl, thienyl, and diphenylaminophenyl groups, $X(B/PO)c-e$ show red-shifted absorptions compared to that observed for $X(B/PO)a$. In the fluorescence spectra, $X(B/PO)a-d$ show emissions at around 550 nm. $X(B/PO)e$ with the strong electron-donating group shows an emission at around 600 nm. Furthermore, the fluorescence is strongly dependent on the solvent used. For example, Figure 4 shows the solvent-dependent fluorescence spectra of

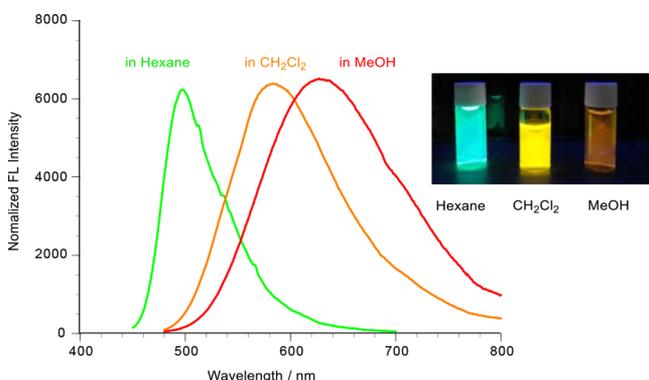


Figure 4. Solvent-dependent fluorescence spectra of $X(B/PO)e$.

$X(B/PO)e$. With increasing the solvent polarity, from hexane and dichloromethane to methanol, the fluorescence shifts to the longer wavelengths, and the color of the solution under UV irradiation is changed from blue to dark orange as shown in the inset in Figure 4. Thus, the absorption and emission of $X(B/PO)$ has a charge-transfer character.

Figure 5 shows the absorption, fluorescence, and excitation spectra of $X(B/P)a$. In the absorption spectrum, $X(B/P)a$

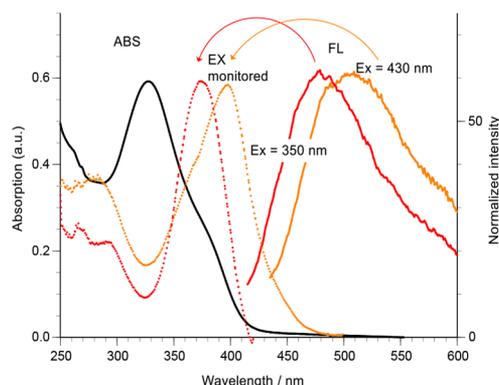


Figure 5. Absorption, fluorescence, and excitation spectra of $X(B/P)a$.

displays an absorption maximum at 327 nm along with an absorption shoulder at around 420 nm, which are associated with the transitions largely arising from the $p-\pi^*$ conjugation with B and the $n-\pi$ conjugation with P extended from the π -core, respectively. In the fluorescence spectra, when excited at 430 nm, this emission at 523 nm is observed. The excitation spectra monitored at this emission shows a peak at around 400 nm, which matches the $n-\pi^*$ transition in the absorption. In contrast, when excited at 350 nm, an emission at 470 nm is observed, and the excitation spectra monitored at this emission shows a peak at around 370 nm as observed in the absorption.

Note that introducing B most often provided significant reducing the quantum yields (~ 0.01). Further study of the detail photophysical process are required.

The conformal films of $X(B/Si)$, $X(B/PO)$, $X(B/P)$, $X(Si/P)$, and $X(Si/PO)$ on a quartz plate were obtained by casting a toluene solution and explored the optical properties in the solid state (Table S1 and Figures S4 and S5). It is noted that in the fluorescence spectrum the emission of the film of $X(B/Si)$ is blue-shifted by 43 nm relative to that observed in solution. $X(Si/PO)$ displays an emission at 399 and 417 nm with a red-shift of 27 nm relative to that in solution, but $X(Si/P)$ shows an emission at around 513 nm likewise in solution. The emissions of the film of $X(B/PO)a-e$ are blue-shifted by 50 nm relative to that observed in solution. However, the absorption of the film of $X(B/P)a$ is almost the same as that observed in solution. Unfortunately, the measurement of the quantum yields in the solid state, whose information are important for further application of the present materials, are not available in our laboratory at this time.

Density Functional Theory (DFT) Calculations. For further understanding of the electronic structures, DFT calculations were performed at the B3LYP/6-31G* level. The molecular orbital (MO) diagrams are shown in Figure 6 and the calculated HOMO and LUMO energy levels are also listed in Table 1.

The HOMO energy levels of the five compounds, $X(B/Si)$, $X(B/P)$, $X(B/PO)$, $X(Si/P)$, and $X(Si/PO)$, are almost similar and distribute on the phenyleneethynylene unit mostly and are slightly raised relative to that of BPEB (-5.43 eV). When substituted with phosphorus on the phenyleneethynylene unit, i.e., in $X(B/P)$ and $X(Si/P)$, the n orbital of the phosphorus center slightly contributes to the HOMO.

However, the effects of substituent are significant on the LUMO energies. For example, in $X(B/Si)$, the LUMO energy level is lowered because of $p(B)\pi-\pi^*$ conjugation and also $\sigma^*(Si-C)-\pi^*$ conjugation (-1.74 eV for BPEB). The LUMO energy level of $X(B/P)$ is stabilized $p(B)\pi-\pi^*$ and $\sigma^*(P-C)-\pi^*$ orbital interactions. When substituted with large electron-withdrawing PO group, the LUMO energy level of $X(B/PO)$ is even more lowered probably because of the increase in the interactions between the $p(B)\pi$ or $\sigma^*(P-C)$ orbitals and adjust π -orbital of the phenyleneethynylene unit. In addition, the LUMO energy level of $X(Si/PO)$ is still lowered, attributable to enhancement of the interactions between the $\sigma^*(Si-C)$ and $P-C$ and adjust π orbitals of the core.

Time-dependent (TD)-DFT calculation data are summarized in Table 2. The TD-DFT calculation of $X(B/Si)$ suggests the absorption band is assignable to the intramolecular charge transfer transition from the HOMO delocalized over the phenyleneethynylene unit to the LUMO and LUMO+1 of the significant contribution of the B moiety. The calculated transition energy (2.95 eV, 421 nm) is similar to the observed value (~ 410 nm). In $X(B/P)$, the absorption originates from the HOMO partially localized on P to LUMO transition along with the HOMO to the LUMO+1 of the important contribution of the B moiety. The absorption of $X(B/PO)$ is associated with the transition from the HOMO to the LUMO and LUMO+1, where the calculated HOMO-LUMO energy gap is 2.89 eV (429 nm). Then, these transitions could involve the intramolecular charge transfer nature. Alternatively, the TD-DFT calculation on $X(Si/P)$ indicates that the absorption originates from the HOMO partially localized on the P to LUMO transition along with the HOMO-1 localized on the P to the LUMO.

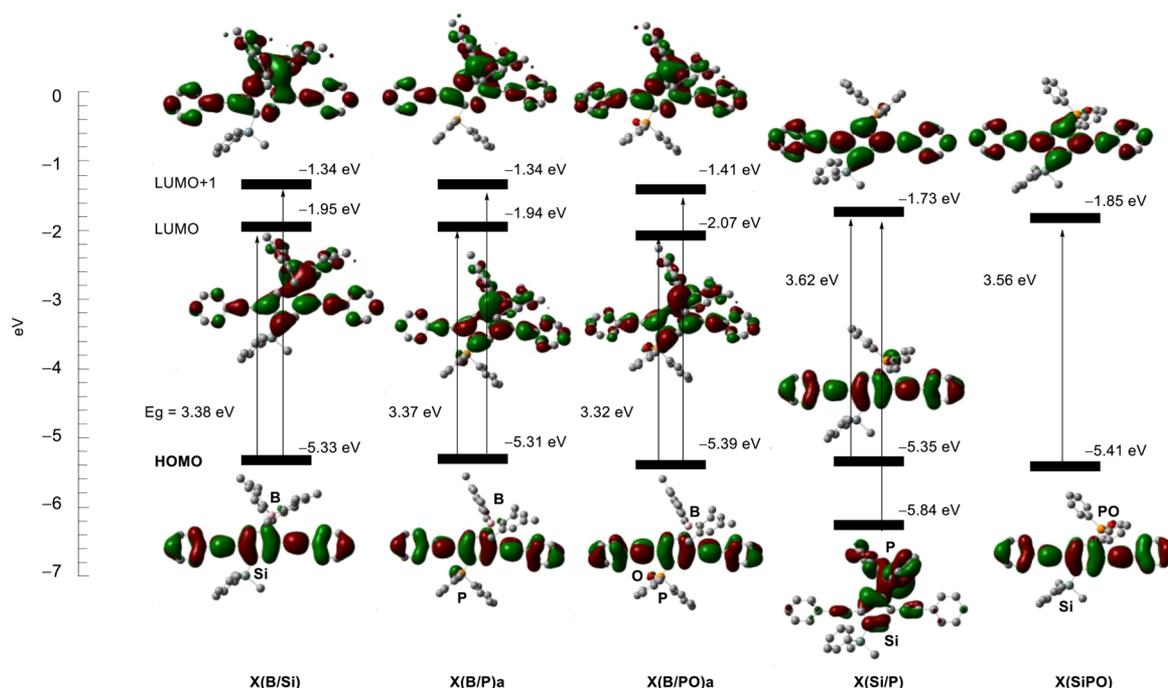


Figure 6. MO diagrams of X(B/Si), X(B/PO)a, X(B/P)a, X(Si/P), and X(Si/PO) (B3LYP/6-31G*).

Table 2. Selected Excitation Energies of X(B/Si), X(Si/P), X(Si/PO), and Model Compounds Assigned by TD-DFT Calculations (B3LYP/6-31G*//B3LYP/6-31G*)

compound	energy (eV)	λ_{calc} (nm)	f^{osc}	transition
X(B/Si)	2.95	421	0.3561	HOMO \rightarrow LUMO (0.67768) HOMO \rightarrow LUMO+1 (-0.1711)
	3.31	375	0.0668	HOMO-1 \rightarrow LUMO (0.68855) HOMO-1 \rightarrow LUMO+1 (-0.11397)
				HOMO \rightarrow LUMO (0.68274) HOMO \rightarrow LUMO+1 (-0.1711)
X(B/PO)a	2.89	429	0.3571	HOMO \rightarrow LUMO (0.68274) HOMO \rightarrow LUMO+1 (-0.1711)
X(B/P)a	2.94	422	0.3404	HOMO \rightarrow LUMO (0.68274) HOMO \rightarrow LUMO+1 (-0.1711)
X(Si/P)	3.31	375	1.0285	HOMO \rightarrow LUMO (0.67812) HOMO-1 \rightarrow LUMO (0.16923)
	3.52	353	0.3713	HOMO \rightarrow LUMO (0.66946) HOMO-1 \rightarrow LUMO (-0.17652)
				HOMO \rightarrow LUMO (0.69959)
X(Si/PO)	3.28	378	1.3232	HOMO \rightarrow LUMO (0.69959)

^aOscillator strength.

The calculated HOMO–LUMO energy gaps are 3.62 eV for X(Si/P) and 3.56 eV for X(Si/PO), which are similar to the observed absorption (335 nm (3.70 eV) for X(Si/P) and 345 nm (3.59 eV) for X(Si/PO)).

As mentioned above, we have reported the synthesis and optical properties of a series of “Y-shaped” phenyleneethynyls containing a main group element moiety of B, Si, or P on the side chain, which could be a model of the “X-shaped” Si/B, Si/P, and Si/PO (Chart 1).¹¹ The optical properties are listed for references in Table 1. The absorption and emission maxima of X-shaped molecules are a red-shifted (5–15 nm) compared with that of Y(B), Y(P), and Y(PO), along with high molar absorptivity. The calculated HOMO–LUMO energy gaps of X(B/Si), X(B/PO), X(B/P), X(Si/P), and X(Si/PO) are narrower than those of the Y-shaped molecules. For example, when compared to the electronic states of Y(Si), the substitution effects of the B and P moieties on the HOMO and LUMO are significant. In X(B/Si), X(B/P), and X(B/PO),

the dimethylboryl group especially stabilize the LUMO by 0.23, 0.22, and 0.35 eV, respectively ($E_{\text{LUMO}} = -1.72$ eV for Y(Si)), where the vacant p orbital of the B center apparently contributes. The diphenylphosphinyl group slightly raises the HOMO energy levels in X(Si/P) and X(B/P) owing to the $n-\pi$ interaction. In addition, the LUMOs of X(B/Si), X(Si/P), and X(Si/PO) show the marginally orbital interactions of the silyl group.

Thus, the “X-shaped” conjugation path is clearly observed for the LUMOs of the B/Si, B/P, B/PO, and Si/P derivatives and the HOMO–1 of the Si/P derivative according to DFT calculations although the role of the silyl group appears to be limited in comparison to the other substituents.

CONCLUSIONS

We have demonstrated the design and synthesis of “X-shaped” B/Si/P conjugated molecules. The electronic states could be controlled by incorporation of B, Si, P, and P(=O) groups compared with the parent π -system, owing to a rise of the

HOMO level (P) or a lowering of the LUMO level (B and P=O), which are also supported by the DFT calculations. We believe these results have furnished an alternative example of main group element-containing π -conjugated molecules to control optical properties. A variety of the structural designs, for example, side- and end-group-type “X-shaped” conjugation systems and the combination of the main group elements and aromatic groups and also further chemical modifications of B and P moieties could be possible. Further study along this line is in progress.

EXPERIMENTAL SECTION

Measurements. ^1H , ^{11}B , ^{13}C , ^{19}F , and ^{29}Si NMR spectra were recorded using a Bruker DPX 300 FT-NMR spectrometer at 300, 96.3, 75.4, 282, and 60 MHz, respectively. ^{11}B and ^{31}P NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at 128 and 162 MHz, respectively. ^1H and ^{13}C chemical shifts (ppm) were referenced to solvent residues. ^{11}B , ^{19}F , ^{29}Si , and ^{31}P NMR chemical shifts (ppm) were referenced to external $\text{BF}_3\cdot\text{Et}_2\text{O}$, CFCl_3 , Me_4Si , and 85% H_3PO_4 (aqueous), respectively. GC–MS were obtained using a Shimadzu GC–MS 17A/QP-5000 mass spectrometer. High-resolution and fast atom bombardment (FAB, matrix: 3-nitrobenzyl alcohol) mass spectra were obtained with a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. Melting points were measured on a micromelting point apparatus (As-one IA9100). UV–vis spectra were recorded using an Agilent 8453 spectrometer. Fluorescence spectra were recorded using a Hitachi F 4500 spectrometer. Fluorescence quantum yield was determined with quinine sulfate as a standard. Elemental analysis was performed at the Center for Advanced Materials Analysis, Technical Department, Tokyo Tech.

Materials. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry nitrogen gas. All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification, unless otherwise noted below. Toluene, diethyl ether, and THF were dried and distilled from sodium/benzophenone just before use. Fluorodimesitylborane,¹⁶ 2,5-dibromo-1,4-bis(phenylethynyl)benzene (1),¹⁷ 2-bromo-5-dimethylphenylsilyl-1,4-bis(phenylethynyl)benzene (2),¹¹ and 2-bromo-5-dimesitylboryl-1,4-bis(trimethylsilylethynyl)benzene (3)¹⁸ were prepared using literature procedures.

Synthesis of X(B/Si). A solution of 1.67 M *n*-butyllithium in hexane (1.05 mL, 1.75 mmol) was added to a solution of 2-bromo-5-dimethylphenylsilyl-1,4-bis(phenylethynyl)benzene (2) (0.71 g, 1.46 mmol) in THF (5 mL) at -78°C . After stirring at -78°C for 1 h, fluorodimesitylborane (0.51 g, 1.90 mmol) in THF (2.5 mL) was added to the mixture at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 28 h. After addition of water, the product was extracted with ether (30 mL), and the organic layer was washed with saturated NH_4Cl (aqueous) and saturated NaCl (aqueous), and dried over anhydrous Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed on silica gel (hexane/dichloromethane = 5/1, R_f = 0.7) to give X(B/Si) (0.55 g, 0.83 mmol, 57% yield). Pale yellow powder. Mp = 144.5–145.2 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 0.68 (s, 6H, SiMe), 2.01 (s, 12H, *o*-Me \times 4), 2.24 (s, 6H, *p*-Me \times 2), 6.74 (s, 4H, *m*-CH (Mes)), 6.97–7.00 (m, 2H, *p*-CH (Ar)), 7.17–7.21 (m, 4H, *m*-CH (Ar)), 7.31–7.34 (m, 5H, *o*,*m*-CH (Ar) + *p*-CH (SiAr)), 7.44 (s, 1H, C_6HH), 7.52–7.56 (m, 4H, *o*-CH (Ar)), 7.62 (s, 1H, C_6HH). ^{13}C NMR (CDCl_3 , 75 MHz) δ –2.0 (SiMe), 21.2 (*o*-Me \times 4), 23.3 (*p*-Me \times 2), 90.1 (ethynyl), 91.3 (ethynyl), 93.0 (ethynyl), 94.0 (ethynyl), 123.0, 123.2, 125.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 129.1, 131.2, 131.57, 131.63, 134.3, 137.4, 137.6, 139.2, 139.4, 140.9, 142.2, several peaks overlapped. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 73.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 60 MHz) δ –7.2. HR–MS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{48}\text{H}_{45}\text{BSi}$ ($[\text{M}]^+$) m/z 660.3384, found 660.3387. Elemental analysis calculated (%) for $\text{C}_{48}\text{H}_{45}\text{BSi}$: C, 87.25; H, 6.86. Found: C, 86.90; H, 6.90.

Synthesis of X(Si/P). A solution of 1.67 M *n*-butyllithium in hexane (1.31 mL, 2.19 mmol) was added to a solution of

2-bromo-5-dimethylphenylsilyl-1,4-bis(phenylethynyl)benzene (2) (0.89 g, 1.82 mmol) in THF (5 mL) at -78°C . After stirring at -78°C for 1 h, chlorodiphenylphosphine (0.39 mL, 2.18 mmol) was added to the mixture at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 26 h. The volatiles were removed under reduced pressure; then, toluene (20 mL) was added to the residue. After filtration and removal of the solvent, the residue was chromatographed on silica gel (hexane/dichloromethane = 5/1, R_f = 0.47) to give X(Si/P) (0.75 g, 1.32 mmol, 72% yield). Yellow powder. Mp = 123.5–125.9 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 0.67 (s, 6H, SiMe), 6.97 (d, $^3J_{\text{P-H}}$ = 3.9 Hz, 1H, C_6HH), 7.10–7.23 (m, 8H, Ar), 7.31–7.39 (m, 15H, Ar), 7.53–7.57 (m, 2H, *o*-CH (SiAr)), 7.64 (d, $^4J_{\text{P-H}}$ = 3.9 Hz, 1H, C_6HH). ^{13}C NMR (CDCl_3 , 75 MHz) δ –2.1 (SiMe), 88.8 (d, $^3J_{\text{P-C}}$ = 6.9 Hz, ethynyl), 90.9 (ethynyl), 94.4 (ethynyl), 98.1 (ethynyl), 122.8, 122.9, 126.5 (d, $^2J_{\text{P-C}}$ = 26.3 Hz, P(*o*-C)), 127.8, 128.1 (d, $^3J_{\text{P-C}}$ = 8.7 Hz, P(*m*-C)), 128.4, 128.5, 128.6, 128.7, 129.0, 129.1, 131.3 (d, $^2J_{\text{P-C}}$ = 17.7 Hz, P(*o*-C)), 134.1, 134.3, 134.5, 135.6, 135.8 (d, $^3J_{\text{P-C}}$ = 6.3 Hz, P(*m*-C)), 137.4, 138.8, 140.3, 142.0 (d, $^1J_{\text{P-C}}$ = 14.6 Hz, P(*ipso*-C)), several peaks overlapped. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ –7.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 60 MHz) δ –4.7. HR–MS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{42}\text{H}_{33}\text{PSi}$ ($[\text{M}]^+$) m/z 596.2089, found 596.2089. Elemental analysis calculated (%) for $\text{C}_{42}\text{H}_{33}\text{PSi}$: C, 84.53; H, 5.57. Found: C, 84.25; H, 5.59.

Synthesis of X(Si/PO). A mixture of X(Si/P) (510 mg, 0.85 mmol) and 30% H_2O_2 (0.08 mL, 0.93 mmol) in dichloromethane (30 mL) was stirred at room temperature for 2.5 h. The reaction mixture was washed with water (30 mL \times 2), saturated NH_4Cl (aqueous) (40 mL), and saturated NaCl (aqueous) (30 mL); the organic layer was dried over anhydrous MgSO_4 . After filtration and removal of the solvent, the residue was chromatographed on silica gel (hexane/ethyl acetate = 2/1, R_f = 0.23) to give X(Si/PO) (280 mg, 0.45 mmol, 53% yield). Yellow powder. Mp = 197.1–198.0 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 0.70 (s, 6H, SiMe), 6.96–6.99 (m, 2H, *p*-CH (Ar)), 7.16–7.58 (m, 19H, Ar), 7.68 (d, $^3J_{\text{P-H}}$ = 4.2 Hz, 1H, C_6HH), 7.78–7.85 (m, 4H, *o*-CH (Ar)), 8.11 (d, $^4J_{\text{P-H}}$ = 12.9 Hz, 1H, C_6HH). ^{13}C NMR (CDCl_3 , 75 MHz) δ –2.3 (SiMe), 88.9 (d, $^3J_{\text{P-C}}$ = 5.2 Hz, ethynyl), 90.2 (ethynyl), 95.6 (ethynyl), 98.7 (ethynyl), 122.3, 122.7, 124.3, 127.9, 128.0, 128.3, 128.5, 128.6, 128.8 (d, $^3J_{\text{P-C}}$ = 12.2 Hz, P(*m*-C)), 129.3, 131.2, 131.9 (d, $^4J_{\text{P-C}}$ = 2.8 Hz, P(*p*-C)), 132.2 (d, $^3J_{\text{P-C}}$ = 10.1 Hz, P(*m*-C)), 132.6, 134.3, 134.6 (d, $^1J_{\text{P-C}}$ = 99.2 Hz, P(*ipso*-C)), 136.7, 137.4 (d, $^2J_{\text{P-C}}$ = 9.0 Hz, P(*o*-C)), 140.5 (d, $^2J_{\text{P-C}}$ = 8.8 Hz, P(*o*-C)), 144.6 (d, $^4J_{\text{P-C}}$ = 2.1 Hz, P(*p*-C)), several peaks overlapped. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 28.0. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 60 MHz) δ –6.2. HR–MS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{42}\text{H}_{33}\text{OPSi}$ ($[\text{M}]^+$) m/z 612.2038, found 612.2031. Elemental analysis calculated (%) for $\text{C}_{42}\text{H}_{33}\text{OPSi}$: C, 82.32; H, 5.43. Found: C, 76.22; H, 4.00. Low carbon and hydrogen values were obtained even after multiple analysis attempts using different batches of samples, suggesting incomplete combustion occurs with this compound. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

Synthesis of 2-Dimesitylboryl-5-diphenylphosphoryl-1,4-bis(trimethylsilylethynyl)benzene (4). To a solution of 2,5-dibromo-1,4-bis(trimethylsilylethynyl)benzene (3) (4.04 g, 9.42 mmol) in ether (80 mL) was added a solution of 1.65 M *n*-butyllithium in hexane (6.8 mL, 11.3 mmol) in ether (100 mL) at -78°C . After stirring for 1 h, fluorodimesitylborane (3.04 g, 11.3 mmol) was added to the mixture at -78°C . The reaction mixture was allowed to come room temperature and stirred for 6 h. After addition of saturated NH_4Cl (aqueous) (150 mL), the product was extracted with methyl *t*-butyl ether, and the organic layer was dried over anhydrous Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed over silica gel (hexane/dichloromethane = 2/1, R_f = 0.73) to give 2-bromo-5-dimesitylboryl-1,4-bis(trimethylsilylethynyl)benzene (4.82 g, 8.07 mmol, 86% yield). White powder. Mp = 113–115 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ –0.04 (s, 9H, SiMe_3), 0.23 (s, 9H, SiMe_3), 1.94 (s, 12H, *o*-Me), 2.26 (s, 12H, *p*-Me), 6.73 (s, 4H, *m*-CH), 7.31 (s, 1H, C_6H_2), 7.69 (s, 1H, C_6H_2). ^{13}C NMR (CDCl_3 , 75 MHz) δ –0.5 (SiMe_3), –0.2 (SiMe_3), 21.3 (*o*-Me), 23.3 (*p*-Me), 100.9 (ethynyl),

101.5 (ethynyl), 102.8 (ethynyl), 103.0 (ethynyl), 124.7, 127.7, 127.9, 128.3, 136.9, 137.8, 139.5, 140.9. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 72.3. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 60 MHz) δ -17.7, -16.6. The physical and spectral characteristics of the obtained are identical with those described in the literature.¹⁸

Next, to a solution of 2-bromo-5-dimesitylboryl-1,4-bis(trimethylsilyl)ethynylbenzene (6.41 g, 10.7 mmol) in THF (80 mL) was added a solution of 1.55 M *t*-butyllithium in pentane (13.8 mL, 21.4 mmol) at -78°C . After stirring for 1.5 h at the temperature, diphenylphosphoryl chloride (5.06 g, 21.4 mmol) in THF (20 mL) was added to the mixture at -78°C . The reaction mixture was allowed to come to room temperature and stirred for 22 h. After addition of H_2O (10 mL), the product was extracted with ether (50 mL), and the organic layer was washed with saturated NaHCO_3 (aqueous) (30 mL) and saturated NaCl (aqueous) (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed over silica gel (hexane/ethyl acetate = 2/1, R_f = 0.27) to give **4** (6.44 g, 8.96 mmol, 84% yield). White powder. Mp = 237.5–239.8 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ -0.09 (s, 9H, SiMe), -0.08 (s, 9H, SiMe), 1.96 (s, 12H), 2.26 (s, 6H), 6.74 (s, 6H), 7.42–7.46 (m, 5H, Ar + C_6HH), 7.50–7.55 (m, 2H, Ar), 7.69–7.76 (m, 4H, Ar), 7.85 (d, $^4J_{\text{P-H}}$ = 13.2 Hz, 1H, C_6HH). ^{13}C NMR (CDCl_3 , 75 MHz) δ -0.7 (SiMe), -0.5 (SiMe), 21.3 (Me), 23.4 (Me), 101.2 (ethynyl), 103.3 (d, $^3J_{\text{P-C}}$ = 5.3 Hz, ethynyl), 103.5 (ethynyl), 104.7 (ethynyl), 124.8 (d, $^2J_{\text{P-C}}$ = 6.0 Hz, P(*o*-C)), 126.2 (d, $^3J_{\text{P-C}}$ = 12.0 Hz, P(*m*-C)), 128.3, 128.4, 131.8, (d, $^4J_{\text{P-C}}$ = 3.0 Hz, P(*p*-C)), 132.0 (d, $^1J_{\text{P-C}}$ = 106.5 Hz, P(*ipso*-C)), 132.2 (d, $^3J_{\text{P-C}}$ = 9.8 Hz, P(*m*-C)), 135.2 (d, $^1J_{\text{P-C}}$ = 99.0 Hz, P(*ipso*-C)), 138.4 (d, $^2J_{\text{P-C}}$ = 5.3 Hz, P(*o*-C)), 138.5 (d, $^4J_{\text{P-C}}$ = 3.8 Hz, P(*o*-C)), 139.7, 141.0, several peaks overlapped. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 28.2. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 72.8. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 60 MHz) δ -17.8, -17.3. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{46}\text{H}_{33}\text{BOPSi}_2$ (^{11}B , $[\text{M} + \text{H}]^+$) m/z 719.3465, found 719.3464. Elemental analysis calculated (%) for $\text{C}_{46}\text{H}_{33}\text{BOPSi}_2$: C, 76.86; H, 7.29. Found: C, 75.43; H, 7.06. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

Synthesis of 2-Dimesitylboryl-5-diphenylphosphoryl-1,4-bis(ethynyl)benzene (5). A solution of 1 M TBAF in THF (60 mL, 60 mmol) was added to **4** (2.03 g, 2.82 mmol) at room temperature, and the mixture was stirred for 3 h. After addition of H_2O (60 mL) and dichloromethane (20 mL), the aqueous layer was washed with dichloromethane (10 mL \times 2). The combined organic layer was dried over Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.77) to give **5** (0.73 g, 1.28 mmol, 85% yield). Pale yellow powder. Mp = 189.4–190.5 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 1.96 (s, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me), 2.78 (s, 1H, ethynyl), 3.01 (s, 1H, ethynyl), 6.73 (s, 4H, *m*-CH(Mes)), 7.41–7.53 (m, 7H, *m,p*-CH(Ar) + C_6HH), 7.58 (d, $^3J_{\text{P-H}}$ = 13.2 Hz, 2H), 7.65–7.72 (m, 4H, *o*-CH(Ph)). ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.2 (*p*-Me), 23.2 (*o*-Me), 81.4 (d, $^4J_{\text{P-C}}$ = 5.8 Hz, ethynyl), 81.8 (ethynyl), 83.1 (ethynyl), 86.5 (ethynyl), 124.5 (d, $^4J_{\text{P-C}}$ = 5.8 Hz, P(*p*-C)), 125.4 (d, $^3J_{\text{P-C}}$ = 12.6 Hz, P(*m*-C)), 128.2, 128.3, 128.5, 131.6 (d, $^1J_{\text{P-C}}$ = 98.6 Hz, P(*ipso*-C)), 137.7 (d, $^2J_{\text{P-C}}$ = 10.1 Hz, P(*o*-C)), 139.2 (d, $^2J_{\text{P-C}}$ = 8.6 Hz, P(*o*-C)), 139.8, 140.9, several peaks overlapped. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 28.7. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 72.3. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{40}\text{H}_{37}\text{BOP}$ (^{11}B , $[\text{M} + \text{H}]^+$) m/z 575.2675, found 575.2682. Elemental analysis calculated (%) for $\text{C}_{40}\text{H}_{37}\text{BOP}$: C, 83.63; H, 6.32. Found: C, 81.91; H, 6.42. Satisfactory elemental analysis data could not be obtained. The NMR spectra are provided in the Supporting Information as alternative characterization data.

Synthesis of X(B/PO)a. A mixture of **5** (290 mg, 0.50 mmol), iodobenzene (0.25 mL, 2.24 mmol), $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.052 mmol), and CuI (55 mg, 0.29 mmol) in THF/*i*-Pr₂EtN (v. 3/1, 5 mL) was stirred at 50 $^\circ\text{C}$ for 15 h. After addition of dichloromethane (30 mL) and saturated NH_4Cl (aqueous) (30 mL), the aqueous layer was washed with dichloromethane (5 mL \times 2). The combine organic layer was dried over anhydrous Na_2SO_4 . After filtration and removal of the

solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.77) to give X(B/PO)a (320 mg, 0.45 mmol, 89% yield). Yellow powder. Mp = 262.3–263.5 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 2.03 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 6.77 (s, 4H, *m*-CH (Mes)), 6.96–7.20 (m, 10H, Ph), 7.40–7.54 (m, 7H, C_6HH + *m,p*-CH (Ar)), 7.76–7.82 (m, 4H, *o*-CH (Ar)), 7.90 (d, $^3J_{\text{P-H}}$ = 13.2 Hz, C_6HH). ^{13}C NMR (CDCl_3 , 75 MHz) δ 21.2 (*p*-Me), 23.3 (*o*-Me), 88.7 (d, $^3J_{\text{P-C}}$ = 5.6 Hz, ethynyl), 89.0 (ethynyl), 95.3 (ethynyl), 98.6 (ethynyl), 122.3, 122.7, 125.0 (d, $^4J_{\text{P-C}}$ = 6.2 Hz, P(*p*-C)), 126.2 (d, $^3J_{\text{P-C}}$ = 12.6 Hz, P(*m*-C)), 127.8, 128.0, 128.2, 128.3, 128.5, 128.6, 131.3, 131.5, 131.85 (d, $^4J_{\text{P-C}}$ = 2.3 Hz, P(*p*-C)), 131.91 (d, $^1J_{\text{P-C}}$ = 105.8 Hz, P(*ipso*-C)), 132.0 (d, $^3J_{\text{P-C}}$ = 10.0 Hz, P(*m*-C)), 135.2 (d, $^1J_{\text{P-C}}$ = 99.2 Hz, P(*ipso*-C)), 137.7 (d, $^2J_{\text{P-C}}$ = 9.7 Hz, P(*o*-C)), 138.4 (d, $^2J_{\text{P-C}}$ = 8.7 Hz, P(*o*-C)), 139.6, 140.9. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 28.5. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 72.3. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{52}\text{H}_{45}\text{BOP}$ (^{11}B , $[\text{M} + \text{H}]^+$) m/z 727.3261, found 727.3253. Elemental analysis calculated (%) for $\text{C}_{52}\text{H}_{45}\text{BOP}$: C, 85.95; H, 6.10. Found: C, 84.48; H, 6.13. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. The NMR spectra are provided in the Supporting Information as alternative characterization data.

Synthesis of X(B/PO)b. A mixture of **5** (230 mg, 0.48 mmol), 4-trifluoroiodobenzene (0.3 mL, 2.10 mmol), $\text{Pd}(\text{PPh}_3)_4$ (56 mg, 0.049 mmol), and CuI (56 mg, 0.29 mmol) in THF/*i*-Pr₂EtN (v. 3/1, 5 mL) was stirred at room temperature for 10 min and then at 50 $^\circ\text{C}$ for 24 h. After addition of dichloromethane (20 mL) and saturated NH_4Cl (aqueous) (20 mL), the aqueous layer was washed with dichloromethane (5 mL \times 2). The combine organic layer was dried over anhydrous Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.90) to give X(B/PO)b (280 mg, 0.33 mmol, 69% yield). White powder. Mp = 211.8–213.9 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 2.01 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 6.77 (s, 4H, *m*-CH (Mes)), 7.03–7.34 (m, 6H, *o,m*-CH ($p\text{-CF}_3\text{C}_6\text{H}_4$)), 7.43–7.53 (m, 9H, C_6HH + *m,p*-CH (Ar) + *m*-CH ($p\text{-CF}_3\text{C}_6\text{H}_4$)), 7.57 (d, $^3J_{\text{P-H}}$ = 4.2 Hz, C_6HH), 7.72–7.80 (m, 4H, *o*-CH (Ar)). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 21.2 (*p*-Me), 23.4 (*o*-Me), 90.6 (d, $^3J_{\text{P-C}}$ = 5.4 Hz, ethynyl), 91.0 (ethynyl), 93.9 (ethynyl), 97.2 (ethynyl), 124.8 (quart, $^3J_{\text{F-C}}$ = 3.7 Hz, $p\text{-CF}_3\text{C}_6\text{H}_4$), 125.0 (quart, $^3J_{\text{F-C}}$ = 4.1 Hz, $p\text{-CF}_3\text{C}_6\text{H}_4$), 125.6 (d, $^4J_{\text{P-C}}$ = 3.8 Hz, P(*p*-C)), 125.9 (d, $^3J_{\text{P-C}}$ = 12.4 Hz, P(*m*-C)), 127.2 (quart, $^1J_{\text{F-C}}$ = 259.5 Hz, $p\text{-CF}_3\text{C}_6\text{H}_4$), 128.5, 128.6, 128.7, 129.8 (quart, $^2J_{\text{F-C}}$ = 30.3 Hz, $p\text{-CF}_3\text{C}_6\text{H}_4$), 130.0, 131.60, 131.61 (d, $^1J_{\text{P-C}}$ = 106.3 Hz, P(*ipso*-C)), 131.8, 132.0 (d, $^3J_{\text{P-C}}$ = 9.4 Hz, P(*m*-C)), 132.1 (d, $^4J_{\text{P-C}}$ = 2.8 Hz, P(*p*-C)), 135.8 (d, $^1J_{\text{P-C}}$ = 98.8 Hz, P(*ipso*-C)), 137.8 (d, $^2J_{\text{P-C}}$ = 10.1 Hz, P(*o*-C)), 138.7 (d, $^2J_{\text{P-C}}$ = 8.4 Hz, P(*o*-C)), 139.9, 141.0, several peaks overlapped. ^{19}F NMR (CDCl_3 , 282 MHz) δ -62.8, -62.8. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ 75.1. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 28.8. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for $\text{C}_{54}\text{H}_{43}\text{BF}_6\text{OP}$ (^{11}B , $[\text{M} + \text{H}]^+$) m/z 863.3049, found 863.3054. Elemental analysis calculated (%) for $\text{C}_{54}\text{H}_{43}\text{BF}_6\text{OP}$: C, 75.18; H, 4.91. Found: C, 71.58; H, 4.85. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. The NMR spectra are provided in the Supporting Information as alternative characterization data.

Synthesis of X(B/PO)c. A mixture of **5** (290 mg, 0.50 mmol), 4-iodoanisole (490 mg, 2.11 mmol), $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.050 mmol), and CuI (55 mg, 0.29 mmol) in THF/*i*-Pr₂EtN (v. 3/1, 5 mL) was stirred at room temperature for 10 min and then at 50 $^\circ\text{C}$ for 22 h. After addition of dichloromethane (30 mL) and saturated NH_4Cl (aqueous) (30 mL), the aqueous layer was washed with dichloromethane (5 mL \times 2). The combine organic layer was dried over anhydrous Na_2SO_4 . After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.57) to give X(B/PO)c (280 mg, 0.36 mmol, 71% yield). Yellow powder. Mp = 189.4–190.5 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 300 MHz) δ 2.01 (s, 12H, *o*-Me \times 4), 2.25 (s, 6H, *p*-Me \times 2), 3.75 (s, 3H, OMe), 3.76 (s, 3H, OMe), 6.68–6.71 (m, 4H, *m*-CH (*p*-An)), 6.76 (s, 4H, *m*-CH (Mes)), 6.89–6.98 (m, 4H, *o*-CH (An)), 7.38–7.52 (m, 7H, C_6HH + *m,p*-CH

(Ph)), 7.73–7.82 (m, 4H, *o*-CH (Ar)), 7.84 (d, $^3J_{\text{P-H}} = 13.2$ Hz, C₆HH). ^{13}C NMR (CDCl₃, 75 MHz) δ 21.2 (*p*-Me), 23.3 (*o*-Me), 55.2(0) (OMe), 55.2(3) (OMe), 87.8 (d, $^3J_{\text{P-C}} = 5.5$ Hz, ethynyl), 88.0 (ethynyl), 95.4 (ethynyl), 98.8 (ethynyl), 113.5 (*m*-C (*p*-An)), 113.6 (*m*-C (*p*-An)), 114.5 (*ipso*-C (*p*-An)), 115.0 (*ipso*-C (*p*-An)), 125.5 (d, $^4J_{\text{P-C}} = 6.6$ Hz, P(*p*-C)), 128.3, 128.5, 131.8 (d, $^4J_{\text{P-C}} = 2.6$ Hz, P(*p*-C)), 132.07 (d, $^1J_{\text{P-C}} = 105.8$ Hz, P(*ipso*-C)), 132.09 (d, $^3J_{\text{P-C}} = 9.9$ Hz, P(*m*-C)), 132.9 (*o*-C (*p*-An)), 133.1 (*o*-C (*p*-An)), 134.9 (d, $^1J_{\text{P-C}} = 99.5$ Hz, P(*ipso*-C)), 137.6 (d, $^2J_{\text{P-C}} = 9.8$ Hz, P(*o*-C)), 138.2 (d, $^2J_{\text{P-C}} = 9.1$ Hz, P(*o*-C)), 139.5, 140.9, 159.5 (*p*-C (*p*-An)), 159.8 (*p*-C (*p*-An)), several peaks overlapped. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl₃, 128 MHz) δ 74.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ 28.7. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for C₅₄H₄₉BO₃P (^{11}B , [M + H]⁺) *m/z* 787.3512, found 787.3515. Elemental analysis calculated (%) for C₅₄H₄₈BO₃P: C, 82.44; H, 6.15. Found: C, 82.11; H, 6.44.

Synthesis of X(B/PO)d. A mixture of **5** (270 mg, 0.47 mmol), 2-iodothiophene (0.20 mL, 2.0 mmol), Pd(PPh₃)₄ (59 mg, 0.051 mmol), and CuI (54 mg, 0.28 mmol) in THF/*i*-Pr₂EtN (v. 3/1, 5 mL) was stirred at room temperature for 10 min and then at 50 °C for 21 h. After addition of dichloromethane (20 mL) and saturated NH₄Cl (aqueous) (20 mL), the aqueous layer was washed with dichloromethane (5 mL × 2). The combine organic layer was dried over anhydrous Na₂SO₄. After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.63) to give X(B/PO)d (270 mg, 0.36 mmol, 76% yield). Yellow powder. Mp = 265.9–267.5 °C. ^1H NMR (CDCl₃, 300 MHz) δ 2.02 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 6.78 (s, 4H, *m*-CH (Mes)), 6.83–6.88 (m, 4H, 4,5-CH (thienyl)), 7.18 (dd, $J_{\text{H-H}} = 4.7$ and 1.2 Hz, 1H, 3-CH (thienyl)), 7.20 (dd, $J_{\text{H-H}} = 4.5$, 1.2 Hz, 1H, 3-CH (thienyl)), 7.40–7.54 (m, 7H, C₆HH + *m*,*p*-CH (Ar)), 7.74–7.81 (m, 4H, *o*-CH (Ar)), 7.95 (d, $^3J_{\text{P-H}} = 13.2$ Hz, 1H, C₆HH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 75 MHz) δ 21.3 (*m*-Me), 23.3 (*p*-Me), 88.8 (ethynyl), 92.1 (ethynyl), 92.4 (d, $^3J_{\text{P-C}} = 5.4$ Hz, ethynyl), 92.7 (ethynyl), 122.2, 122.8, 124.4 (d, $^4J_{\text{P-C}} = 6.3$ Hz, P(*p*-C)), 126.1 (d, $^3J_{\text{P-C}} = 12.5$ Hz, P(*m*-C)), 126.8, 126.9, 127.8, 128.2, 128.4, 128.6, 131.7 (d, $^1J_{\text{P-C}} = 106.1$ Hz, P(*ipso*-C)), 131.9 (d, $^4J_{\text{P-C}} = 2.8$ Hz, P(*p*-C)), 132.1 (d, $^3J_{\text{P-C}} = 10.1$ Hz, P(*m*-C)), 132.5, 135.1 (d, $^1J_{\text{P-C}} = 98.7$ Hz, P(*ipso*-C)), 137.5 (d, $^2J_{\text{P-C}} = 9.5$ Hz, P(*o*-C)), 138.1 (d, $^2J_{\text{P-C}} = 8.6$ Hz, P(*o*-C)), 139.7, 140.8, several peaks overlapped. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl₃, 128 MHz) δ 72.6. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ 28.2. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for C₄₈H₄₁BOPS₂ (^{11}B , [M + H]⁺) *m/z* 740.2508, found 740.2477. Elemental analysis calculated (%) for C₄₈H₄₀BOPS₂: C, 78.04; H, 5.46. Found: C, 77.14; H, 5.47. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. The NMR spectra are provided in the Supporting Information as alternative characterization data.

Synthesis of X(B/PO)e. A mixture of **5** (290 mg, 0.50 mmol), 4-iodotriphenylamine (730 mg, 2.0 mmol), Pd(PPh₃)₄ (58 mg, 0.050 mmol), and CuI (48 mg, 0.25 mmol) in THF/*i*-Pr₂EtN (v. 3/1, 6 mL) was stirred at room temperature for 10 min and then at 50 °C for 26 h. After addition of dichloromethane (20 mL) and saturated NH₄Cl (aqueous) (30 mL), the aqueous layer was washed with dichloromethane (10 mL × 4). The combined organic layer was dried over anhydrous Na₂SO₄. After filtration and removal of the solvent, the residue was chromatographed over silica gel (ethyl acetate, R_f = 0.83) to give X(B/PO)e (440 mg, 0.42 mmol, 83% yield). Pale yellow powder. Mp = 264.9–266.5 °C. ^1H NMR (CDCl₃, 300 MHz) δ 2.04 (s, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me), 6.76 (s, 4H, *m*-CH), 6.79–6.85 (m, 8H, Ar), 7.02–7.08 (m, 12H, Ar), 7.19–7.28 (m, 8H, C₆H₄), 7.40–7.50 (m, 7H, C₆HH Ph), 7.76–7.82 (m, 4H, *o*-CH(Ar)), 7.89 (d, $^3J_{\text{P-H}} = 13.2$ Hz, 1H, C₆HH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 75 MHz) δ 21.2 (*p*-Me), 23.3 (*o*-Me), 88.4 (d, $^3J_{\text{P-C}} = 5.3$ Hz, ethynyl), 88.7 (ethynyl), 95.8 (ethynyl), 99.2 (ethynyl), 115.0, 115.8, 121.5, 121.9, 123.5, 123.6, 124.9, 125.1, 126.3 (d, $^3J_{\text{P-C}} = 12.8$ Hz, P(*m*-C)), 128.3, 128.5, 129.3, 129.4, 131.8 (d, $^4J_{\text{P-C}} = 2.4$ Hz, P(*p*-C)), 132.09 (d, $^1J_{\text{P-C}} = 105.8$ Hz, P(*ipso*-C)), 132.11 (d, $^3J_{\text{P-C}} = 10.0$ Hz, P(*m*-C)), 132.3, 132.5, 134.7 (d, $^1J_{\text{P-C}} = 99.5$ Hz, P(*ipso*-C)), 137.7 (d, $^2J_{\text{P-C}} = 9.6$ Hz, P(*o*-C)), 138.4 (d, $^3J_{\text{P-C}} = 8.9$ Hz, P(*o*-C)), 139.5, 140.9, 142.1, 147.0,

147.1, 147.8, 148.1, several peaks overlapped. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl₃, 128 MHz) δ 78.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ 28.7. HRMS (FAB, matrix = 3-nitrobenzyl alcohol/NaCl) calcd for C₇₆H₆₂BN₂OPNa (^{11}B , [M + Na]⁺) *m/z* 1083.4590, found 1083.4637. Satisfactory elemental analysis data could not be obtained. The NMR spectra are provided in the Supporting Information as alternative characterization data.

Synthesis of X(B/P)a. A toluene-*d*₈ solution (0.30 mL) of X(B/P)a (44.2 mg, 0.061 mmol) and trichlorosilane (0.03 mL, 0.297 mmol) was heated at 100 °C for 23 h. After evaporation, to the residue was added chloroform-*d* (0.50 mL), and the soluble part was subjected to the NMR measurement. After evaporation under reduced pressure, X(B/P)a was obtained (25.9 mg, 0.036 mmol, 60% yield). Yellow powder. Mp = 192.8–195.6 °C. ^1H NMR (CDCl₃, 300 MHz) δ 2.08 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 6.78 (s, 4H, *m*-CH (Mes)), 6.92–6.95 (m, 2H, *p*-CH (Ph)), 7.06 (d, $^3J_{\text{P-H}} = 4.5$ Hz, 1H, C₆HH), 7.16–7.37 (m, 17H, C₆HH + Ph), 7.61–7.73 (m, 2H). ^{13}C NMR (CDCl₃, 75 MHz) δ 21.2 (*p*-Me), 23.3 (*o*-Me), 90.1 (ethynyl), 93.3 (ethynyl), 123.2, 125.9, 126.7, 127.0, 127.7, 128.4, 128.5, 128.7, 128.8, 129.1, 130.88 (d, $^2J_{\text{P-C}} = 26.9$ Hz, P(*o*-C)), 130.93 (d, $^2J_{\text{P-C}} = 25.4$ Hz, P(*o*-C)), 131.5, 134.0, 134.3, 135.3 (d, $^3J_{\text{P-C}} = 8.3$ Hz, P(*m*-C)), 137.2 (d, $^3J_{\text{P-C}} = 6.4$ Hz, P(*m*-C)), 138.0 (d, $^1J_{\text{P-C}} = 14.4$ Hz, P(*ipso*-C)), 139.1, 140.7 (d, $^1J_{\text{P-C}} = 20.3$ Hz, P(*ipso*-C)), 140.9, 142.6, several peaks overlapped. $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl₃, 128 MHz) δ 72.3. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 162 MHz) δ -12.78. HRMS (FAB, matrix = 3-nitrobenzyl alcohol) calcd for C₅₂H₄₅BP (^{11}B , [M + H]⁺) *m/z* 712.3430, found 712.3388. Satisfactory elemental analysis data could not be obtained. The NMR spectra are provided in the Supporting Information as alternative characterization data.

DFT and TD-DFT Calculations. The geometries and electronic structures of the molecules were calculated using DFT with B3LYP/6-31G*//B3LYP/6-31G* as the basis set of the Gaussian program.¹⁹

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00768.

Detail of photophysical properties and NMR spectra for all new compounds(PDF)

Computed Cartesian coordinates of X(B/Si), X(B/PO)a, X(B/P)a, X(Si/P), and X(Si/PO) (XYZ)

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Notes

The authors declare no competing financial interest.

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