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Synthesis and Anion Binding Properties of Multi-phosphonium Triarylboranes: Selective Sensing of Cyanide Ions in Buffered Water at pH 7

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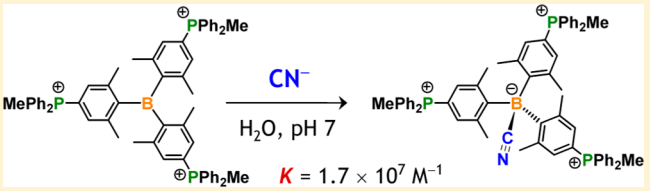
Supporting Information

ABSTRACT: A series of mono-, di-, and triphosphonium-substituted triarylboranes, $[Mes_2BAr^P]I$ ($[\mathbf{2}]I$), $[MesBAr^P_2]I_2$ ($[\mathbf{3}]I_2$), and $[BAr^P_3]I_3$ ($[\mathbf{4}]I_3$) (Ar^P = 4-($MePh_2P$)-2,6-Me_2-C_6H_2), were prepared from the corresponding neutral boranes **2a**–**4a**. The crystal structure of $[\mathbf{4}]I_3$ determined by X-ray diffraction study reveals peripheral decoration of aryl groups with phosphonium moieties. The anion affinity of the cationic boranes for fluoride and cyanide ions was investigated by UV–vis absorption titrations in aqueous solution. The triarylboranes, $[\mathbf{2}]I$–$[\mathbf{4}]I_3$ bind both fluoride and cyanide ions in a DMSO/H_2O (7:3 v/v) mixture with high binding constants (K). Comparison of the K values of triarylboranes for fluoride reveals that fluorophilicity increases with the increasing number of phosphonium moieties: $[\mathbf{2}]^+$ ($K = 2.3 \times 10^1$ M^{-1}) < $[\mathbf{3}]^{2+}$ (3.6×10^5 M^{-1}) < $[\mathbf{4}]^{3+}$ (1.0×10^7 M^{-1}). A similar trend is also observed in the cyanide binding, with K values that are greater by 2–4 orders of magnitude than those in the fluoride binding. These results indicate an apparent additive effect of multiple phosphonium substitutions on the Lewis acidity enhancement of triarylboranes. The triphosphonium borane $[\mathbf{4}]Cl_3$, a water-soluble form of $[\mathbf{4}]I_3$, was further utilized in evaluating the anion affinity in water. While $[\mathbf{4}]^{3+}$ is shown to hardly bind fluoride in buffered water at pH 7, it binds cyanide with a high binding constant (1.7×10^7 M^{-1}).



INTRODUCTION

The detection and quantification of anions such as fluoride and cyanide ions are of great interest owing to the harmful effects of such anions in physiological and environmental systems. Fluoride is added to drinking water and toothpaste for dental health and is also used in treating osteoporosis,[1] but taking excessive fluorides may lead to fluorosis.[2] Cyanide is a toxic anion that inhibits cytochrome *c* oxidase; thus widespread industrial uses of cyanide may raise physiological and environmental concerns.[3] For these reasons, the selective detection of these anions has received considerable attention during the past decade.

Among the receptors for the recognition of fluoride and cyanide ions developed to date, triarylborane compounds are shown to be one of the most effective molecular platforms due to their high affinity toward nucleophilic anions.[4] While most triarylborane receptors have successfully operated in organic media and provided various detection methods,[5] they nonetheless showed a limited binding ability in the presence of water, which interferes with the anion binding, leaving them hardly utilized in water or aqueous solution. In addition, the competitive protonation of cyanide ions in neutral water may complicate cyanide detection. To resolve this issue, many efforts have been devoted to enhancing the Lewis acidity of triarylborane by introducing strong electron-withdrawing groups into the triarylboranes.[6−15] Among such approaches, in particular, the cationic triarylboranes have been shown to largely increase the anion affinity of the boron center enough to operate in aqueous media, due to the Coulombic and inductive effects of cationic groups that assist boron–anion dative interactions.[6,8−14]

For example, as shown in Chart 1, various types of cationic triarylboranes were recently reported by Gabbaï and co-workers. The monoammonium borane $[\mathbf{I}]^+$ selectively binds cyanide ions in DMSO/H_2O (4:6 v/v, pH 7) with a high binding constant ($K = 3.9 \times 10^8$ M^{-1}), while the *ortho*-ammonium derivative $[\mathbf{II}]^+$ is selective for fluoride in the same medium.[14] The sulfonium borane $[\mathbf{III}]^+$ selectively captures cyanide in water at pH 7 by favorable Coulombic effects and the sulfonium–cyanide interaction, leading to fluorescence quenching at the sub-ppm level of cyanide.[8] Fluoride binding studies using a series of monophosphonium boranes ($[\mathbf{IV}]^+$) revealed that they can bind fluoride in H_2O/MeOH (9:1 v/v), and the binding constant increases with their hydrophobicity ($K_{Me} < K_{Et} < K_{nPr} < K_{Ph}$).[10,13] The fluoride ion affinity can also be drastically enhanced by the *ortho*-phosphonium borane $[\mathbf{V}]^+$, which binds fluoride via chelation from the neighboring

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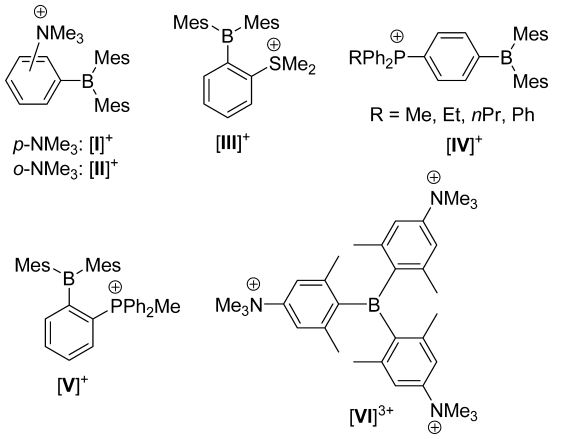
Chart 1



phosphonium and borane moieties.[12] In addition to these monocationic boranes, the Lewis acidity is shown to be enhanced by the introduction of multiple cationic moieties.[9,11] While the mono- and diammonium derivatives fail to bind cyanide in water, the triammonium borane $[\mathbf{VI}]^{3+}$ selectively binds cyanide in water at pH 7.[9]

Although the foregoing studies on the cationic boranes successfully demonstrated fluoride or cyanide binding in aqueous solution or water at a low level of concentration, their low stability in such medium, partly due to the increased Lewis acidity, often made it difficult to measure the exact binding constant for the quantification of anions. In particular, the effect of the multiple introductions of a cationic moiety on the increase in the binding constant was not adequately evaluated. For example, multiammonium boranes showed sluggish binding and low affinity in water.[9] To better understand the additive effect of multiple substitutions of the cationic moiety on the Lewis acidity enhancement of triarylboranes and to quantify the resulting increase in the binding constant, we turned our attention to the *para*-phosphonium-substituted boranes, which showed high stability in aqueous medium.[10,13] In this report, we prepared a series of mono-, di-, and triphosphonium-substituted triarylboranes and compared their fluoride and cyanide ion affinities in aqueous solution. The triphosphonium borane was further utilized in evaluating the anion affinity in water. Details of the synthesis, characterization, and anion binding studies of the multi-phosphonium boranes are described.

EXPERIMENTAL SECTION

General Considerations. All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques. Anhydrous grade solvents (Aldrich) were dried by passing them through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric grade DMSO (Aldrich) was used as received. Commercial reagents were used without any further purification after purchasing from Aldrich (chlorodiphenylphosphine (Ph_2PCl), dimesitylboron fluoride (Mes_2BF), MeI, Amberlite IRA-400 chloride form, $BF_3{\cdot}OEt_2$, *n*-BuLi (2.5 M solution in *n*-hexanes), *N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid (HEPES), tetra-*n*-butylammonium fluoride (TBAF), tetra-*n*-butylammonium cyanide (TBACN), KF, NaCN). Buffer solution (HEPES 10 mM in H_2O, pH 7),[16] dimethyl mesitylboronate ($MesB(OMe)_2$),[17] and 2,5-dibromo-*m*-xylene[18] were analogously prepared according to the reported procedures. Deuterated solvents from Cambridge Isotope Laboratories were used. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ^1H, 100.62 MHz for ^{13}C) and a Bruker AM 300 spectrometer (96.29 MHz for ^{11}B, 121.5 MHz for ^{31}P) at ambient temperature. Chemical shifts are given in ppm and are referenced against external Me_4Si (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), and 85% H_3PO_4 (^{31}P). HR EI-MS measurement (JEOL JMS700) was carried out at Korea Basic Science Institute. Elemental analyses were performed on an EA1110 (Fisons Instruments) by the Environmental Analysis Laboratory at KAIST. UV−vis absorption spectra were recorded on a Jasco V-530 spectrophotometer.

Synthesis of (4-Bromo-3,5-dimethylphenyl)-diphenylphosphine (1). A hexane solution of *n*-BuLi (3.6 mL, 9.07 mmol) was added at −78 °C to a solution of 2,5-dibromo-*m*-xylene (2.18 g, 8.25 mmol) in Et_2O (20 mL), and the mixture was stirred for 45 min at this temperature. A solution of chlorodiphenylphosphine (1.48 mL, 8.25 mmol) in THF (5 mL) was slowly added to the mixture. The reaction mixture was stirred for 1 h at −78 °C and allowed slowly to warm to room temperature. After stirring for 4 h, all volatiles were removed under vacuum. The white residue was extracted with *n*-hexane (30 mL) and filtered. After evaporating the solvent, the remaining sticky residue was purified by column chromatography (eluent: hexane/ethyl acetate, 10:1 v/v), which afforded **1** as a colorless oil (2.57 g, 84%). ^1H NMR ($CDCl_3$): δ 2.34 (s, 6H, Me_2Ph), 6.98 (d, J = 7.5 Hz, 2H, Me_2Ph-C*H*), 7.31 (m, 10H, Ph-C*H*). ^{13}C NMR ($CDCl_3$): δ 23.87 (Me_2Ph), 128.52 (d, J_{C-P} = 6.9 Hz), 128.77, 131.51 (d, J_{C-P} = 18 Hz), 133.28 (d, J_{C-P} = 20 Hz), 133.65 (d, J_{C-P} = 19 Hz), 135.53 (d, J_{C-P} = 11 Hz), 136.89 (d, J_{C-P} = 11 Hz), 138.44 (d, J_{C-P} = 7.5 Hz). ^{31}P NMR ($CDCl_3$): δ −5.8. HR EI-MS: m/z calcd for $C_{20}H_{18}BrP$, 368.0329; found, 368.0327.

Synthesis of Dimesityl(4-(diphenylphosphino)-2,6-dimethylphenyl)borane (2a). A hexane solution of *n*-BuLi (0.44 mL, 1.1 mmol) was added at 0 °C to a solution of **1** (0.37 g, 1.0 mmol) in Et_2O (15 mL), and the reaction mixture was stirred for 30 min. After stirring for 1 h at room temperature, a solution of Mes_2BF (0.30 g, 1.0 mmol) in Et_2O (10 mL) was added to the mixture at −78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (20 mL). The combined organic portions were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (eluent: CH_2Cl_2/hexane, 1:8 v/v) afforded **2a** as a white powder (0.24 g, 45%). ^1H NMR ($CDCl_3$): δ 1.92 (s, 6H, Ar-CH_3), 1.96 (s, 6H, Mes-CH_3), 1.97 (s, 6H, Mes-CH_3), 2.24 (s, 6H, Mes-CH_3), 6.72 (s, 4H, Mes-C*H*), 6.79 (d, J = 8.2 Hz, 2H, Ar−C*H*), 7.29 (m, 10H, Ph-C*H*). ^{13}C NMR ($CDCl_3$): δ 21.22 (Mes-CH_3), 22.79, 22.84, 22.88 (Ar-CH_3 and Mes-CH_3), 128.36 (d, J_{C-P} = 7.1 Hz), 128.56, 128.63 (d, J_{C-P} = 3.0 Hz), 132.49 (d, J_{C-P} = 18.2 Hz), 133.67 (d, J_{C-P} = 3.0 Hz), 133.87 (d, J_{C-P} = 3.8 Hz), 137.20 (d, J_{C-P} = 8.3 Hz), 137.54 (d, J_{C-P} = 9.7 Hz), 139.37, 140.19 (d, J_{C-P} = 6.8 Hz), 140.45, 140.67. ^{31}P NMR ($CDCl_3$): δ −5.7. ^{11}B NMR ($CDCl_3$): δ 79.8. Anal. Calcd for $C_{38}H_{40}BP$: C, 84.75; H, 7.49. Found: C, 84.58; H, 7.59.

Synthesis of (4-(Dimesitylboryl)-3,5-dimethylphenyl)-methyldiphenylphosphonium iodide ([2]I). To a solution of **2a** (0.11 g, 0.20 mmol) in Et_2O (10 mL) was added excess MeI (1.02 mL, 2.0 mmol). After stirring overnight at room temperature, the pale yellow precipitate was filtered and washed with Et_2O (3 × 10 mL) and pentane (3 × 10 mL), affording [**2**]I as a pale yellow solid (0.072 g, 52%). ^1H NMR ($CDCl_3$): δ 1.92 (s, 6H, Mes-C*H*), 1.98 (s, 6H, Mes-C*H*), 2.06 (s, 6H, Ar^P-CH_3), 2.24 (s, 6H, Mes-CH_3), 3.15 (d, J = 13.0 Hz, 3H, P-CH_3), 6.74 (s, 4H, Mes-C*H*), 7.14 (d, J = 13.8 Hz, 2H, Ar^P-C*H*), 7.69 (m, 10H, Ph-C*H*). ^{13}C NMR ($CDCl_3$): δ 11.62 (d, J_{C-P} = 56.9 Hz, P-CH_3), 21.18 (Mes-CH_3), 22.93 (Ar^P-CH_3), 22.96 (Mes-CH_3), 118.03 (d, J_{C-P} = 88.0 Hz), 119.09 (d, J_{C-P} = 88.0 Hz), 128.99 (d, J_{C-P} = 4.6 Hz), 130.37 (d, J_{C-P} = 12.9 Hz), 131.03 (d, J_{C-P} = 9.9 Hz), 133.18 (d, J_{C-P} = 9.9 Hz), 135.01 (d, J_{C-P} = 3.8 Hz), 140.07, 140.46, 141.09, 142.43, 142.55. ^{31}P NMR ($CDCl_3$): δ 21.2. ^{11}B NMR ($CDCl_3$): δ 81.4. Anal. Calcd for $C_{39}H_{43}BIP$: C, 68.84; H, 6.37. Found: C, 69.17; H, 6.18.

Synthesis of Bis(4-(diphenylphosphino)-2,6-dimethylphenyl)mesitylborane (3a). To a solution of **1** (0.52 g, 1.41 mmol) in Et_2O (15 mL) was added *n*-BuLi (0.59 mL, 1.48 mmol)

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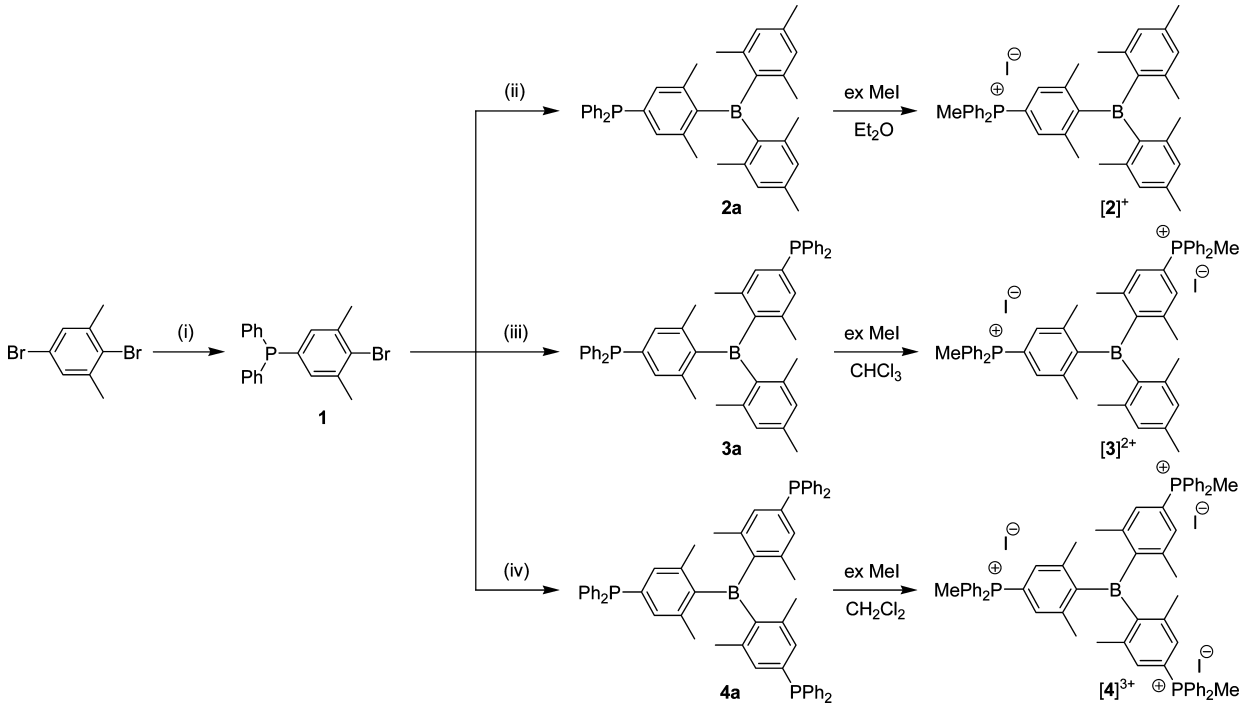
Scheme 1[a]



[a](i) *n*-BuLi, Ph_2PCl, THF/ether, −78 °C, 84%. (ii) *n*-BuLi, Mes_2BF, ether, −78 °C, 45%. (iii) *n*-BuLi, 1/2 $MesB(OMe)_2$, ether, −78 °C, 13%. (iv) *n*-BuLi, 1/3 $BF_3{\cdot}OEt_2$, ether, −78 °C, 50%.

at 0 °C, and the mixture was stirred for 30 min at this temperature. After stirring for 1 h at room temperature, a solution of $MesB(OMe)_2$ (0.11 g, 0.56 mmol) in Et_2O (10 mL) was added to the mixture at −78 °C. The reaction mixture was allowed slowly to warm to room temperature and stirred overnight. After quenching with saturated aqueous NH_4Cl (30 mL), the organic layer was separated and the aqueous layer was extracted with Et_2O (20 mL). The combined organic portions were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (eluent: CH_2Cl_2/hexane, 1:5 v/v) afforded **3a** as a white powder (0.052 g, 13%). ^{1}H NMR ($CDCl_3$): δ 1.99 (s, 6H, Ar-CH_3), 2.03 (s, 6H, Ar-CH_3), 2.14 (s, 6H, Mes-CH_3), 2.30 (s, 3H, Mes-CH_3), 6.82 (s, 2H, Mes-C*H*), 6.89 (d, J = 12.0 Hz, 2H, Ar-C*H*), 7.17 (d, J = 3.8 Hz, 2H, Ar-C*H*), 7.29 (m, 20H, Ph-C*H*). ^{13}C NMR ($CDCl_3$): δ 21.22 (Mes-CH_3), 23.50, 23.54, 23.64, 23.82 (Ar-CH_3 and Mes-CH_3), 127.68, 128.38 (d, J_{C-P} = 7.6 Hz), 128.42 (d, J_{C-P} = 5.3 Hz), 128.58, 131.63, 131.82, 132.03 (d, J_{C-P} = 6.2 Hz), 132.18, 133.71, 133.91, 136.10 (d, J_{C-P} = 3.8 Hz), 136.22, 137.23, 137.34 139.06, 140.36 (d, J_{C-P} = 6.8 Hz), 141.14, 144.45, 144.60, 144.88. ^{31}P NMR ($CDCl_3$): δ −14.1, −5.4. ^{11}B signal was not observed. Anal. Calcd for $C_{49}H_{47}BP_2$: C, 83.05; H, 6.68. Found: C, 82.59; H, 6.87.

Synthesis of 1,1′-Mesitylboranediylbis((3,5-dimethylphenyl)methyldiphenylphosphonium) Diiodide ([3]I$_2$). To a solution of **3a** (0.032 g, 0.045 mmol) in $CHCl_3$ (3 mL) was added excess MeI (0.67 mL, 1.35 mmol). After stirring overnight at room temperature, the resulting solution was treated with Et_2O (20 mL), which precipitated out a pale yellow solid. Filtration followed by washing with Et_2O (3 × 10 mL) and pentane (3 × 10 mL) afforded [3]I_2 as a pale yellow solid (0.037 g, 84%). ^{1}H NMR ($CDCl_3$): δ 2.02 (s, 6H, Mes-CH_3), 2.12 (s, 6H, Ar^P-CH_3), 2.15 (s, 6H, Ar^P-CH_3), 2.28 (s, 3H, Mes-CH_3), 3.13 (d, J = 13.2 Hz, 3H, P-CH_3), 3.24 (d, J = 12.7 Hz, 3H, P-CH_3), 6.84 (s, 2H, Mes-C*H*), 7.27 (d, J = 5.0 Hz, 2H, Ar^P-C*H*), 7.35 (d, J = 14.0 Hz, 2H, Ar^P-C*H*), 7.71 (m, 20H, Ph-C*H*). ^{13}C NMR (CD_3OD): δ 9.00 (d, J_{C-P} = 57.9 Hz, P-CH_3), 14.44 (d, J_{C-P} = 57.2 Hz, P-CH_3), 21.35 (Mes-CH_3), 23.78, 24.18, 24.85, 24.91 (Ar^P-CH_3 and Mes-CH_3), 121.17 (d, J_{C-P} = 89.2 Hz), 121.51 (d, J_{C-P} = 82.3 Hz), 123.72 (d, J_{C-P} = 86.2 Hz), 130.13, 131.42 (d, J_{C-P} = 12.9 Hz), 131.44 (d, J_{C-P} = 12.9 Hz), 131.46 (d, J_{C-P} = 12.9 Hz), 131.81 (d, J_{C-P} = 12.9 Hz), 132.48 (d, J_{C-P} = 9.9 Hz), 133.79 (d, J_{C-P} = 10.6 Hz), 134.44 (d, J_{C-P} = 10.6 Hz), 134.49 (d, J_{C-P} = 10.6 Hz), 136.01 (d, J_{C-P} = 3.0 Hz), 136.15 (d, J_{C-P} = 3.8 Hz), 138.71 (d, J_{C-P} = 11.4 Hz), 140.07, 142.79, 143.23, 143.40 (d, J_{C-P} = 12.9 Hz), 146.04 (d, J_{C-P} = 10.4 Hz). ^{31}P NMR ($CDCl_3$): δ 19.3, 21.6. ^{11}B signal was not observed. Anal. Calcd for $C_{51}H_{53}BI_2P_2$: C, 61.72; H, 5.38. Found: C, 61.94; H, 5.39.

Synthesis of Tris(4-(diphenylphosphino)-2,6-dimethylphenyl)borane (4a). To a solution of **1** (1.93 g, 5.20 mmol) in Et_2O (20 mL) was added *n*-BuLi (2.1 mL, 5.25 mmol) at 0 °C, and the mixture was stirred for 30 min at this temperature. After stirring for 1 h at room temperature, the mixture was cooled to −78 °C. $BF_3{\cdot}OEt_2$ (0.2 mL, 1.58 mmol) was added to the mixture and then allowed to warm to room temperature. After stirring for 24 h, the reaction was quenched with saturated aqueous NH_4Cl (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (20 mL). The combined organic portions were dried over $MgSO_4$ and concentrated under reduced pressure. Recrystallization of the residue from *n*-hexane at −20 °C afforded **2** as a white solid (2.28 g, 50%). Single crystals suitable for X-ray diffraction study were grown from cooling of a THF/MeOH solution of **4a**. ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 18H, Ar-CH_3), 6.82 (d, J = 8.1 Hz, 6H, Ar-C*H*), 7.31 (m, 30H, Ph-C*H*). ^{13}C NMR ($CDCl_3$): δ 22.95 (Ar-CH_3), 128.45 (d, J_{C-P} = 6.9 Hz), 128.67, 132.67 (d, J_{C-P} = 18 Hz), 133.81 (d, J_{C-P} = 19 Hz), 136.95 (d, J_{C-P} = 11 Hz), 138.60 (d, J_{C-P} = 11 Hz), 140.35 (d, J_{C-P} = 6.4 Hz), 146.89. ^{31}P NMR ($CDCl_3$): δ −5.5. ^{11}B signal was not observed. Anal. Calcd for $C_{60}H_{54}BP_3$: C, 82.00; H, 6.19. Found: C, 81.76; H, 6.17.

Synthesis of 1,1′,1″-Boranetriyltris((3,5-dimethylphenyl)-methyldiphenylphosphonium) Triiodide ([4]I$_3$). To a solution of **4a** (70 mg, 0.080 mmol) in CH_2Cl_2 (15 mL) was added excess MeI (0.05 mL, 0.8 mmol). The mixture was stirred overnight at room temperature. After removal of all volatiles, the residue was suspended in a CH_3CN/Et_2O mixed solvent. The insoluble part was collected by filtration and washed with Et_2O to afford [4]I_3 as a pale yellow solid (70 mg, 68%). Single crystals suitable for X-ray diffraction study were grown from vapor diffusion of pentane into a CH_3CN/THF solution of [4]I_3. ^{1}H NMR (CD_3OD): δ 2.16 (s, 18H, Ar^P-CH_3), 3.02 (d, J =

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12 Hz, 9H, P-CH_3), 7.42 (d, J = 12 Hz, 6H, Ar^P-CH), 7.75 (m, 24H, Ph-CH), 7.87 (m, 6H, Ph-CH). ^{13}C NMR (CD_3OD): δ 8.93 (d, J_{C-P} = 57 Hz, P-CH_3), δ 23.68 (Ar^P-CH_3), 120.75 (d, J_{C-P} = 88 Hz), 123.35 (d, J_{C-P} = 87 Hz), 131.45 (d, J_{C-P} = 13 Hz), 133.44 (d, J_{C-P} = 10 Hz), 134.50 (d, J_{C-P} = 10 Hz), 136.18 (d, J_{C-P} = 3.0 Hz), 143.91 (d, J_{C-P} = 13 Hz), 152.35. ^{31}P NMR (CD_3OD): δ 21.9. ^{11}B signal was not observed. Anal. Calcd for $C_{63}H_{63}BI_3P_3$: C, 58.00; H, 4.87. Found: C, 57.61; H, 5.16.

Synthesis of 1,1′,1″-Boranetriyltris((3,5-dimethylphenyl)-methyldiphenylphosphonium) Trichloride ([4]Cl$_3$). [4]I_3 (70 mg, 0.054 mmol) and Amberite IRA-400(Cl) ion-exchange resin (1.34 g) were mixed in MeOH/water (1:1 v/v, 10 mL) and stirred for 12 h. The resin was removed by filtration, and the procedure was repeated three times. In the last cycle, 1 mL of HCl solution (2.0 M) was added. Evaporation of the filtrate and drying under vacuum at 80 °C overnight yielded [4]Cl_3 as a white solid (40 mg, 72%). ^{1}H NMR (CD_3OD): δ 2.16 (s, 18H, Ar^P-CH_3), 3.02 (d, J = 16 Hz, 9H, P-CH_3), 7.43 (d, J = 12 Hz, 6H, Ar^P-CH), 7.77 (m, 24H, Ph-CH), 7.88 (m, 6H, Ph-CH). ^{13}C NMR (CD_3OD): δ 8.56 (d, J_{C-P} = 57 Hz, P-CH_3), δ 23.41 (Ar^P-CH_3), 120.76 (d, J_{C-P} = 88 Hz), 123.66 (d, J_{C-P} = 87 Hz), 131.46 (d, J_{C-P} = 13 Hz), 133.41 (d, J_{C-P} = 10 Hz), 134.44 (d, J_{C-P} = 11 Hz), 136.28 (d, J_{C-P} = 3.0 Hz), 143.93 (d, J_{C-P} = 13 Hz), 152.29. ^{31}P NMR (CD_3OD): δ 22.1. ^{11}B signal was not observed. Anal. Calcd for $C_{63}H_{63}BCl_3P_3\cdot(H_2O)_3$: C, 69.78; H, 6.41. Found: C, 69.45; H, 6.10.

UV−Vis Titration Experiments. UV−vis titrations of anions were performed in DMSO/H_2O (7:3 v/v) or in buffered water (10 mM HEPES, pH 7) with a 1 cm quartz cuvette at ambient temperature. Typically, a solution of cationic borane (3.0 mL, 5 × 10^{-5} M) was titrated with incremental amounts of anions. The absorbance data obtained were fitted to a 1:1 binding isotherm. The pK_a of HCN in DMSO/H_2O (7:3 v/v, pH 7) was measured to be 9.5 (potentiometric titration of NaCN with HCl) and used in the determination of the cyanide binding constant.[14] The detailed conditions are given in the figure captions.

X-ray Crystallography. Single crystals of **4a** and [4]I_3 were coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurement was performed on a Bruker SMART Apex II CCD area detector diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL/PC package. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. For [4]I_3, disordered solvent molecules were removed by the squeeze operation in PLATON. The detailed crystallographic data are given in Table S1 (see Supporting Information).

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic procedures toward neutral mono-, di-, and triphosphinoboranes Mes_2BAr (**2a**), $MesBAr_2$ (**3a**), and BAr_3 (**4a**) (Ar = 4-(Ph_2P)-2,6-Me_2-C_6H_2) and their cationic derivatives, [Mes_2BAr^P]I ([**2**]I), [$MesBAr^P{}_2$]I_2 ([**3**]I_2), and [$BAr^P{}_3$]I_3 ([**4**]I_3) (Ar^P = 4-($MePh_2P$)-2,6-Me_2-C_6H_2), are shown in Scheme 1. Selective lithiation at the C-5 position of 2,5-dibromo-*m*-xylene with *n*-BuLi in ether followed by reaction with Ph_2PCl in THF/ether produced (4-bromo-3,5-dimethylphenyl)diphenylphosphine (**1**) in high yield (84%). The neutral borane compounds **2a**−**4a** were obtained by reaction of a lithium salt derived from **1** with 1 equiv of Mes_2BF, a half equiv of $MesB(OMe)_2$, and one-third equiv of $BF_3\cdot OEt_2$ in ether at −78 °C, respectively, in moderate to low yield (45% for **2a**, 13% for **3a**, and 50% for **4a**). The formation of **2a**−**4a** was characterized by multinuclear NMR spectroscopy and elemental analysis. While ^{1}H and ^{13}C NMR spectra showed the expected resonances corresponding to the mesityl and 2,6-dimethylphenyl moieties, the C−H protons of the Ar group appear as doublets due to the coupling between ^{31}P and ^{1}H nuclei. The ^{31}P signals detected at ca. δ −5 ppm are consistent with the presence of a neutral phosphine group. In particular, while the three Ar groups in **4a** are chemically equivalent in solution, the two Ar groups in **3a** are shown to be different in chemical environment, judging from the two sets of methyl and C−H proton signals of the Ar groups, as well as two ^{31}P resonances at δ −5 and −14 ppm. Although the ^{11}B NMR signals for di- and trisubstituted **3a** and **4a** were not observed despite a prolonged acquisition time, the signal for **2a** at δ 80 ppm confirms the presence of the trigonal boron atom. Furthermore an X-ray diffraction study revealed the molecular structure of **4a** (Figure 1 and Table S1). The

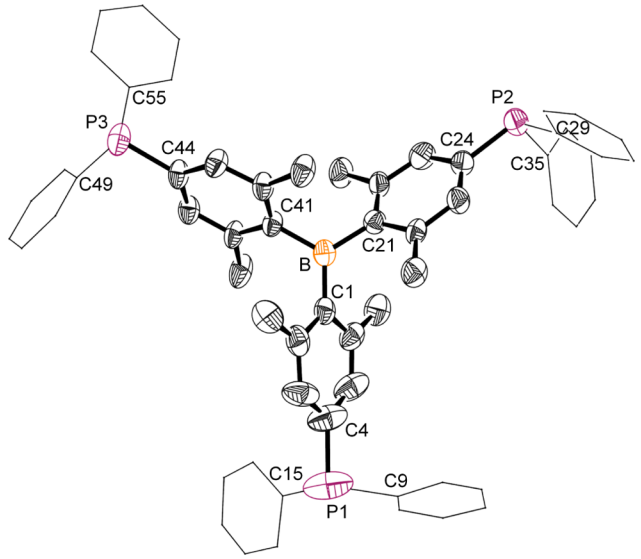

Figure 1. Crystal structure of **4a** (30% ellipsoid). H atoms and one THF molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): B−C(1) 1.558(12), B−C(21) 1.589(11), B−C(41) 1.605(11), P(1)−C(4) 1.815(13), P(2)−C(24), 1.842(9), P(3)−C(44) 1.847(8); C(1)−B−C(21) 121.6(7), C(1)−B−C(41) 119.4(7), C(21)−B−C(41) 118.9(8), C(4)−P(1)−C(9) 99.4(8), C(4)−P(1)−C(15) 101.7(6), C(24)−P(2)−C(29) 103.8(5), C(24)−P(2)−C(35) 100.3(5), C(44)−P(3)−C(49) 102.5(4), C(44)−P(3)−C(55) 102.9(5).

central boron atom adopts a trigonal planar geometry ($\sum_{(C-B-C)}$ = 359.9°), and the Ph_2P moieties are attached at the *para*-positions of the Ar groups. The three Ar groups form a propeller-like conformation probably due to steric repulsion between the six *ortho*-methyl groups around the boron atom.

The neutral boranes **2a**−**4a** were converted into the corresponding iodide salts of methylated phosphonium boranes [**2**]I−[**4**]I_3 by treating them with excess MeI in different solvents (Scheme 1). The identity of the cationic borane salts has been characterized by multinuclear NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra showed the methyl proton resonances at ca. δ 3 ppm as a doublet, indicating methylation on the phosphorus atom. The presence of a four-coordinated phosphonium moiety was also confirmed by the ^{31}P signals at ca. δ 21 ppm. As similarly observed in the neutral boranes, the C−H protons of the Ar^P group in [**2**]$^+$−[**4**]$^{3+}$ appear as doublets and the two Ar^P groups in [**3**]$^{2+}$ are in a different chemical environment, giving rise to the two sets of methyl and C−H proton signals of the Ar^P groups, as well as

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two ^{31}P resonances at δ 19 and 22 ppm (Figures S1–S3). It was shown that theses signals do not coalesce at elevated temperatures, up to 100 °C (Figure S2). Although the ^{11}B NMR signals for the multiphosphonium boranes $[3]^{2+}$ and $[4]^{3+}$ were not observed, the monophosphonium borane $[2]^{+}$ showed the ^{11}B signal at δ 81 ppm, confirming the presence of the trigonal boron atom. Among the cationic boranes, the crystal structure of $[4]I_3$ was unequivocally determined by the X-ray diffraction method (Figure 2 and Table S1). As similarly

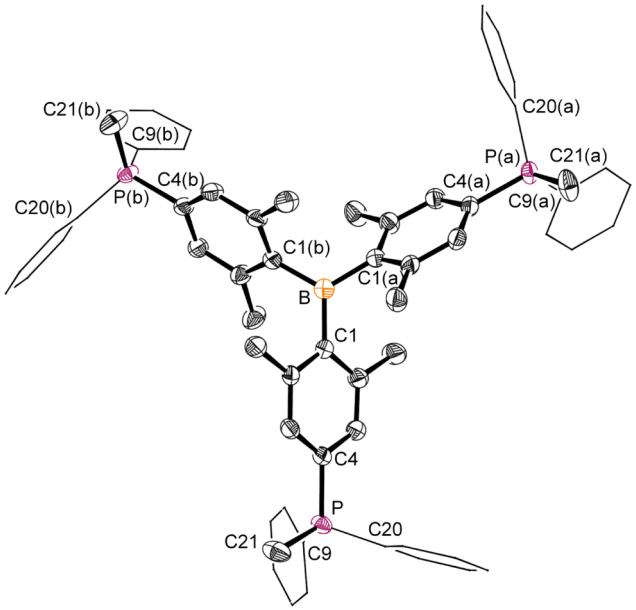


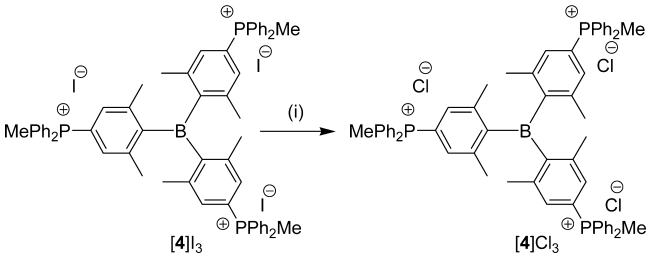
Figure 2. Crystal structure of $[4]^{3+}$ in $[4]I_3$ (50% ellipsoid). H atoms and iodides were omitted for clarity. Selected bond lengths (Å) and angles (deg): B–C(1) 1.584(5), P–C(4) 1.792(5), P–C(21) 1.775(6); C(1)–B–C(1a) 120.0, C(4)–P–C(9) 108.2(2), C(4)–P–C(20) 107.4(2), C(4)–P–C(21) 111.0(3).

noted in neutral **4a**, the three $MePh_2P$ moieties are appended at the *para*-positions of the Ar^P groups, which form a propeller-like conformation around the trigonal boron atom. Since $[4]I_3$ crystallizes in the rhombohedral crystal system, the C_3-axis perpendicular to the trigonal boron center is clearly observed.

Although the iodide salts of cationic boranes $[2]I$–$[4]I_3$ are highly soluble in alcohol and partially in aqueous solution, they are poorly soluble in water, limiting their use in the anion binding in water. Thus, the chloride salt of triphosphonium borane $[4]Cl_3$ was prepared by repeated treatments of $[4]I_3$ with a chloride-exchange resin (Scheme 2).[19] It was found that $[4]Cl_3$ freely dissolves in water, and the spectroscopic features are essentially identical to those for $[4]I_3$.

Anion Binding Studies. To investigate anion binding properties and an additive effect of multiple cationic moieties on the Lewis acidity enhancement of triarylborane, UV–vis titration experiments with fluoride were first carried out using $[2]I$–$[4]I_3$ in a DMSO/H_2O (7:3 v/v) mixture. The choice of DMSO/H_2O (7:3 v/v) was to differentiate between the binding constants of the cationic boranes within a measurable range by absorption titration (*vide infra*). The phosphonium boranes $[2]I$, $[3]I_2$, and $[4]I_3$ feature low-energy absorption bands in the region 300–375 nm (Figure 3). Upon addition of incremental amounts of fluoride, all absorption bands are gradually quenched as a result of fluoride binding to the boron center. The fluoride binding constants (K) estimated from the

Scheme 2[a].



[a](i) Amberite IRA-400(Cl) ion-exchange resin, MeOH/H_2O, 25 °C, 72%.

1:1 binding isotherms are equal to $K = 2.3 \times 10^1$ M^{-1} for $[2]^+$, 3.6×10^5 M^{-1} for $[3]^{2+}$, and 1.0×10^7 M^{-1} for $[4]^{3+}$. Comparison of these K values reveals a drastic increase of fluorophilicity with the increasing number of phosphonium moieties; the K value increases by 4 and 6 orders of magnitude on going from mono- to dication and to trication, respectively (insets in Figure 3). These results indicate that the introduction of multiple phosphonium moieties into the triarylborane has an apparent additive effect on the Lewis acidity enhancement of the triarylborane probably due to the increased Coulombic and inductive effects of the phosphonium groups.[9,15]

Next, cyanide ion affinities of the phosphonium boranes $[2]I$ and $[3]I_2$ were investigated and compared with their fluoride ion affinities. UV–vis titrations were carried out in buffered DMSO/H_2O (7:3 v/v, 10 mM HEPES, pH 7) solution. Due to competitive protonation of cyanide in aqueous solution, the pK_a of HCN in DMSO/H_2O (7:3 v/v) was first measured, which afforded a pK_a of 9.5, and was used in the determination of the cyanide binding constant.[14] The low-energy absorption bands in the region 300–375 nm for $[2]I$ and $[3]I_2$ are gradually quenched upon the addition of incremental amounts of cyanide (Figure 4). On the basis of the 1:1 binding isotherms, the cyanide binding constants (K) were calculated to be $K = 5.8 \times 10^4$ M^{-1} for $[2]^+$ and 5.7×10^7 M^{-1} for $[3]^{2+}$, respectively (insets in Figure 4).

These results indicate that both $[2]^+$ and $[3]^{2+}$ have a high affinity for cyanide in the DMSO/H_2O (7:3 v/v) mixture. The K values of $[2]^+$ and $[3]^{2+}$ for cyanide are shown to be greater by 4 and 2 orders of magnitude than those for fluoride, respectively. An increase of cyanide ion affinity by 3 orders of magnitude for dicationic $[3]^{2+}$ compared with that for monocationic $[2]^+$ is also consistent with that observed in the fluoride binding studies, indicating an additive effect of the cationic moiety on the Lewis acidity enhancement of the triarylborane. Because neutral triarylboranes such as Mes_3B do not form any detectable quantities of cyanoborate or fluoroborate complexes in aqueous solution, these results clearly demonstrate that the introduction of multiple phosphonium moieties into the triarylborane significantly enhances the Lewis acidity of the boron atom, the extent of which also increases with the increasing number of phosphonium moieties.

Encouraged by these results, we decided to attempt anion binding studies in real physiological systems, such as in water by use of triphosphonium borane. The water-soluble chloride salt $[4]Cl_3$ was used in the UV–vis titration experiments. Compound $[4]Cl_3$ features a low-energy absorption band centered at 318 nm (log ε = 4.13) in buffered H_2O (10 mM HEPES, pH 7) (Figure 5). Addition of cyanide ions to a

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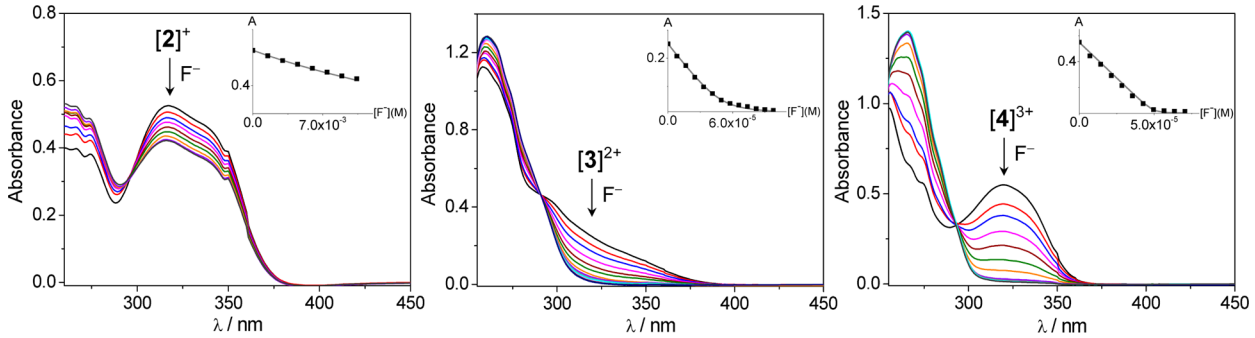

Figure 3. Spectral changes in the UV−vis absorption of a solution of [**2**]I (left), [**3**]I_2 (middle), and [**4**]I_3 (right) in DMSO/H_2O (7:3 v/v, 5.0 × 10^{-5} M) upon addition of TBAF ((0−1.0) × 10^{-2} M for [**2**]I, (0−9.8) × 10^{-5} M for [**3**]I_2, (0−7.0) × 10^{-5} M for [**4**]I_3). The inset shows the absorbance at 317, 319, and 320 nm, respectively, as a function of [F^-]. The line corresponds to the binding isotherm calculated with K = 2.3 × 10^1 M^{-1} for [**2**]I, 3.6 × 10^5 M^{-1} for [**3**]I_2, and 1.0 × 10^7 M^{-1} for [**4**]I_3.

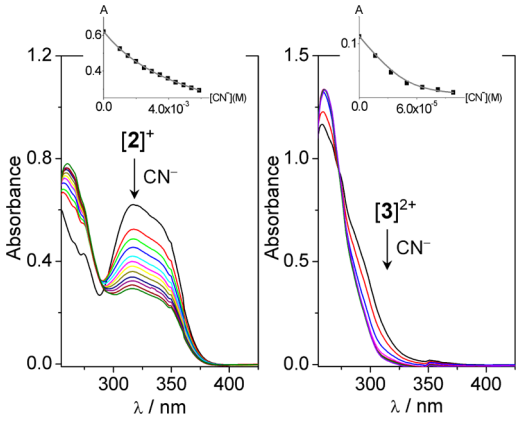

Figure 4. Spectral changes in the UV−vis absorption of a solution of [**2**]I (left) and [**3**]I_2 (right) in buffered DMSO/H_2O (7:3 v/v, 5.0 × 10^{-5} M, 10 mM HEPES, pH 7) upon addition of TBACN ((0−5.9) × 10^{-3} M for [**2**]I, (0−9.8) × 10^{-5} M for [**3**]I_2). The inset shows the absorbance at 318 nm as a function of [CN^-]. The line corresponds to the binding isotherm calculated with K = 5.8 × 10^4 M^{-1} for [**2**]I and 5.7 × 10^7 M^{-1} for [**3**]I_2.

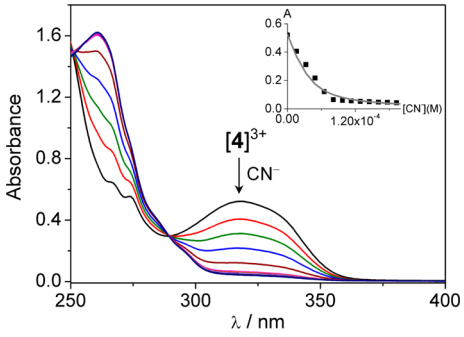

Figure 5. Spectral changes in the UV−vis absorption of a solution of [**4**]Cl_3 in buffered H_2O (3.9 × 10^{-5} M, 10 mM HEPES, pH 7) upon addition of NaCN ((0−1.93) × 10^{-4} M). The inset shows the absorbance at 318 nm as a function of [CN^-]. The line corresponds to the binding isotherm calculated with K = 1.7 × 10^7 M^{-1}.

buffered H_2O solution of [**4**]Cl_3 led to a gradual decrease in the intensity of the absorption band, as similarly observed in the fluoride binding of [**4**]I_3 in DMSO/H_2O (7:3 v/v). This phenomenon reflects conversion of triphosphonium borane into the corresponding triphosphonium cyanoborate [**4**CN]$^{2+}$, whose stability constant is equal to K = 1.7 × 10^7 M^{-1}. In contrast, the absorption spectrum of [**4**]Cl_3 in water (10 mM HEPES, pH 7) is very slightly affected in the presence of fluoride ions, resulting in the absorption quenching of less than 4% upon the addition of up to 16 equiv of fluoride (Figure 6, left). Finally, because hydroxide ions may potentially bind to a boron center of phosphonium borane in water at pH 7,[10] we monitored the absorbance of [**4**]Cl_3 in the presence of hydroxide ions (Figure 6, right). However, the absorption band of [**4**]Cl_3 remains unaffected upon the addition of up to 16 equiv of hydroxide in buffered H_2O solution. The steric protection provided by the six *ortho*-methyl groups to the boron center is most likely responsible for the lack of hydroxide binding. These results thus attest that the triphosphonium borane [**4**]Cl_3 can act as a selective receptor for cyanide ions in water at neutral pH.

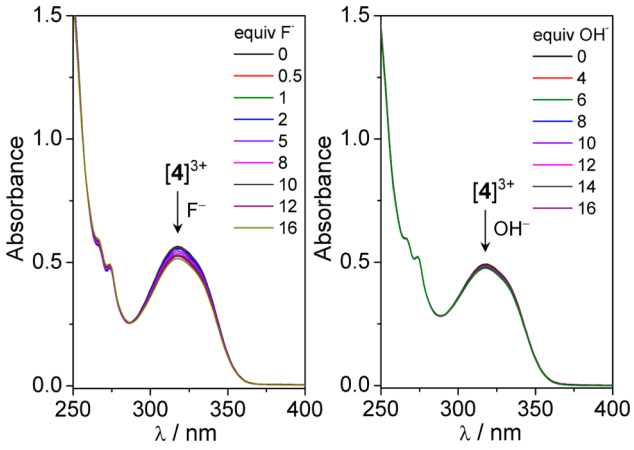

Figure 6. Spectral changes in the UV−vis absorption of a solution of [**4**]Cl_3 in buffered H_2O (3.9 × 10^{-5} M for F^- and 3.4 × 10^{-5} M for OH^-, 10 mM HEPES, pH 7) upon addition of KF (left) and NaOH (right).

CONCLUSION

We have synthesized and characterized a series of mono-, di-, and triphosphonium-substituted triarylboranes, [**2**]$^+$, [**3**]$^{2+}$, and [**4**]$^{3+}$. It was demonstrated by absorption titrations with fluoride and cyanide ions in a DMSO/H_2O (7:3 v/v) mixture that the introduction of multiple phosphonium moieties into the triarylborane significantly enhances the Lewis acidity of a boron center and has an additive effect on the Lewis acidity enhancement probably due to the increased Coulombic and

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inductive effects of phosphonium groups. The results also showed that the cyanide binding constants of the cationic boranes are greater by 2−4 orders of magnitude than those in the fluoride binding. More importantly, while fluoride hardly binds the boron center of triphosphonium borane $[\mathbf{4}]^{3+}$ in water at pH 7, $[\mathbf{4}]^{3+}$ complexes cyanide ions under the same conditions with a high binding constant of 1.7×10^7 M^{-1}. These results indicate that multiphosphonium boranes such as $[\mathbf{4}]^{3+}$ can be used as a selective sensor for cyanide in real physiological systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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