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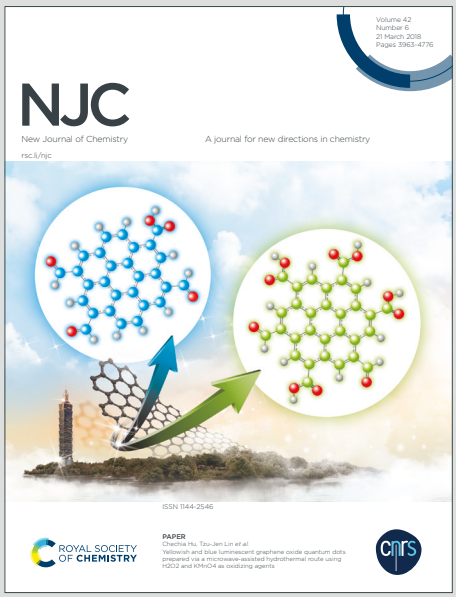

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ARTICLE

Synthesis of pyramidal tetraarylborate pentads

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In the present study, we designed tetrahedral tetraarylborate pentads which were synthesized by a typical click reaction, copper-catalyzed azide-alkyne cyclization. The synthesis of the borate pentads was confirmed by FT-IR and NMR spectroscopies, and NMR measurements indicated a rapid exchange of bound and unbound counter cations. The obtained borate pentads exhibited a representative behavior of weak electrolytes, thus decrease of their concentration caused rapid increase of their molar conductivity, especially at the limit of dilution. Additionally, the observed association constant did not correspond to the theoretical association constant, probably because of the multivalent ionic dissociation dependent on the dielectric constant of the media.

Introduction

Ionic compounds generally experience the ionic dissociation to provide a cation and an anion in water or highly polar organic solvents such as alcohols, amides, and nitriles. By attaching bulky and lipophilic groups on the ionic species, the ionic dissociation can take place even in low polar or non-polar organic solvents. For anions, such lipophilic species have been regarded as "weakly-coordinating anions" (WCAs).[1] WCAs having bulky and lipophilic substituents have been explored toward various applications including stabilization of active cationic species in organic reactions[2–5] and single crystals,[6–8] mediator of electrochemical reactions,[9–11] providing high solubility to ionic compounds in organic solvents.[12–15] We have also reported the usage of WCAs for polyelectrolytes,[16] polyelectrolyte gels,[17,18] polyelectrolyte brushes,[19] conjugated microporous polymers,[20] polymer blends,[21] and micelles,[22] which exhibited which work in non-polar organic solvents or liquid crystals.[23] The ionic dissociation in the solution can be anticipated from the relationship between the dielectric constant of the solvent and the ionic radii of the ionic species by using Bjerrum's theory,[24] and it plays a key role for constructing functional materials different from neutral organic compounds.

Because of the ease of chemical modification, tetraarylborate derivatives frequently appear as WCAs. To enhance the dissociability of WCAs in non-polar organic solvents, Mullen and Floudas have reported the attachment of bulkier substituents on a tetraethynylarylborate by Diels–Alder reactions with tetraphenylcyclopentadienones.[25–28] The dendritic encapsulation of tetraarylborates resulted in the ionic dissociation in low polar solvent such as THF,[25] and photoswitchable conductivity.[27] In this study, we designed rigid tetrahedralborate pentads realized by Sonogashira-Hagihara cross coupling reaction, and investigated their ionic dissociation.

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Electronic Supplementary Information (ESI) available: ^{1}H, ^{13}C spectra, FT-IR spectra, HRMS spectra, and DOSY NMR spectra. See DOI: 10.1039/x0xx00000x

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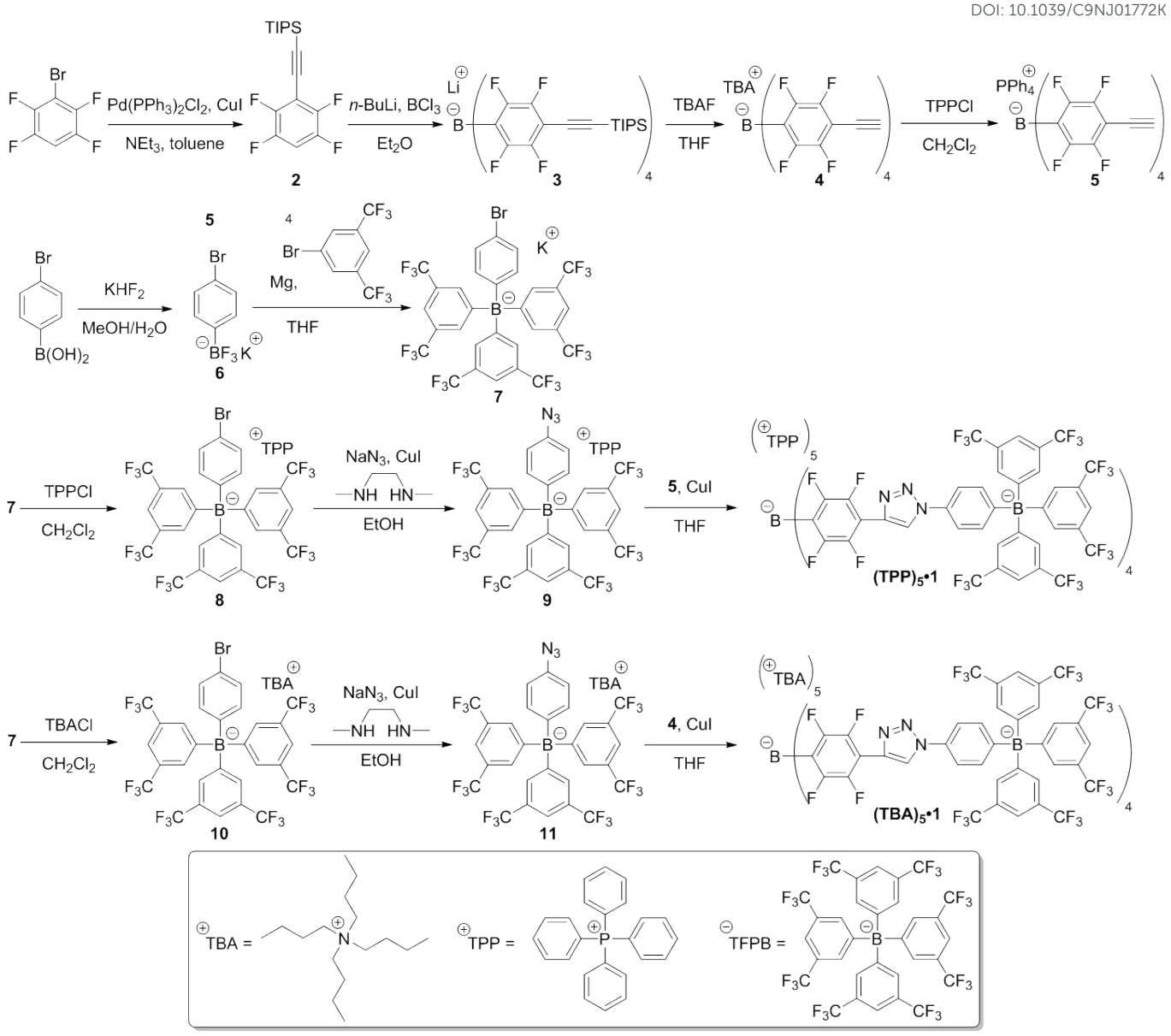

Figure 1. Synthetic route for borate pentads **(TPP)$_5$·1** and **(TBA)$_5$·1**.

Experimental Section

Materials and Measurements

All reagents were obtained from a commercial source (Wako Chemicals and Tokyo Chemical Industry) and used without further purification. The ^{1}H (300 MHz and 500 MHz) NMR measurements were performed with a JEOL JNM-AL300 and a Bruker Biospin AVANCE DRX500, respectively, using 0.05% tetramethylsilane as the internal standard at room temperature. Conductometry was performed with a TOA DKK CM-30G conductivity meter.

Triisopropylsilylethynyl-2,3,5,6-tetrafluorobenzene (2).[26]

In a 100 mL round bottom flask, 2,3,5,6-tetrafluoro-bromobenzene (2.0 g, 8.7 mmol), triphenyl phosphine (0.23 g, 0.87 mmol), CuI (0.17 g, 0.87 mmol), $Pd(PPh_3)_2Cl_2$ (0.31g, 0.44 mmol) were dissolved in triethylamine (15 mL) and toluene (15 mL), and the mixture was heated to 80 ºC. Then, triisopropyl acetylene (2.4 g, 13 mmol) was added dropwise, and the mixture was stirred for 24 h at 80 ºC. After cooling to room temperature, the mixture was washed with 1M NH_4Cl aq. for 3 times, distilled water for 3 times, and the organic layer was dried over $MgSO_4$, followed by removal of the solvent. The residue was purified by silica gel column chromatography

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(hexane) to obtain compound **2** (2.2 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.18 (21H, *t*, -Si(C_3H_7)$_3$), 7.03 (1H, *m*, ArH).

Lithium tetrakis(2,3,5,6-tetrafluoro-(4-(triisopropylsilyl)ethynyl)phenyl)borate (3).

In a 50 mL two necked flask, compound **2** (2.2 g, 6.8 mmol) was dissolved in diethylether (9.0 mL), and cooled to -78 ºC. Then 1 M n-butyllithium hexane solution (4.1 mL, 6.6 mmol) was added dropwise, and stirred for 1 h at -78 ºC. To the mixture was added 1 M boron trichloride heptane solution (1.7 mL, 1.7 mmol), and the mixture was warmed to room temperature and stirred for additional 24 h. The mixture was filtered and the solvent was evaporated. The residue was purified by reprecipitation to obtain compound **3** (0.93 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.07 (21H, *m*, -Si(C_3H_7)$_3$).

Tetrabutylammonium tetrakis(2,3,5,6-tetrafluoro-(4-(triisopropylsilyl)ethynyl)phenyl)borate (4).

In a 100 mL round bottom flask, compound **3** (0.90 g, 0.68 mmol) was dissolved in THF (15 mL), and 0.5 M TBAF THF solution was added dropwise at room temperature, followed by stirring for 24 h at room temperature. The mixture was filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (dichloromethane) to obtain compound **4** (271 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (12H, *m*, -N(CH_2)$_3$CH_3), 1.32 (8H, *m*, -N(CH_2)$_2$CH_2CH$_3$), 1.54 (8H, *m*, -NCH$_2$CH_2C$_2$H$_5$), 2.96 (8H, *m*, -NCH_2CH$_2$C$_2$H$_5$), 3.45 (4H, s, -C*H* (acetylene)).

Tetraphenylphosphonium tetrakis(2,3,5,6-tetrafluoro-(4-(triisopropylsilyl)ethynyl)phenyl)borate (5).

In a 100 mL round bottom flask, compound **4** (130 mg, 0.13 mmol) was dissolved in dichloromethane (1 mL), and dichloromethane solution (1 mL) of tetraphenylphosphonium chloride (103 mg, 0.27 mmol) was added dropwise to the solution. The mixture was stirred for 12 h at room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (dichloromethane) to obtain compound **5** (53 mg, 37 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 3.41 (4H, *s*, -C*H* (acetylene)), 7.56-7.60 (8H, *m*, *o-H* in phosphonium), 7.67-7.71 (8H, *ddd*, *J* = 15.9 Hz, 15.9 Hz, 3.3 Hz, *m-H* in phosphonium), 7.85 (4H, *m*, *p-H* in phosphonium).

Potassium 4-bromophenyl trifluoroborate (6).

In a 100 mL Teflon beaker, 4-bromophenyl boronic acid (8.0 g, 40 mmol) was dissolved in methanol (15 mL). In another 100 mL Teflon beaker, potassium hydrogenfluoride was dissolved in distilled water, and the solution was added dropwise to the first methanol solution. After 2 h stirring at room temperature, saturated $Ca(OH)_2$ aq. was added to the reaction mixture, and methanol was removed under reduced pressure. After filtration, the obtained solid was dissolved in a small amount of acetone, and it was reprecipitated from diethyl ether to obtain compound **6** (8.9 g, 85%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.28 (4H, *m*, -C_6H_4-).

4-Bromophenyl-tris[3,5-bis(trifluoromethyl)phenyl]borate (7).

In a 100 mL three necked flask, Mg flake (430 mg) was heated for 10 min, and stirred with dry THF (15 mL) and 1,2-dibromoethane (150 µL). Then, 3,5-bis(trifluoromethyl)bromobenzene (4.0 g, 13.7 mmol) was added to the mixture, and stirred for 30 min at room temperature. In another 100 mL two necked flask, compound **6** (1.0 g, 3.8 mmol) was dissolved in THF (20 mL), and the prepared Grignard reagent was added dropwise to the solution, followed by stirring for 17 h at room temperature. Then, K_2CO_3 aq. (50 mL) was added, and the organic layer was washed by distilled water for 3 times. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure to obtain crude compound **7** as a yellow oil, which was used for further reaction without purification.

Tetraphenylphosphonium 4-bromophenyl-tris[3,5-bis(trifluoromethyl)phenyl]borate (8).

In 200 mL round bottom flask, compound **7** (6.5 g, 7.7 mmol) was dissolved in dichloromethane (20 mL). To the solution, tetraphenyl phosphonium chloride (2.9 g, 7.7 mmol) in dichloromethane (20 mL) was added dropwise, and the mixture was stirred for 12 h at room temperature. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (acetone/hexane = 1/1) and recrystallization from ethanol to obtain compound **8** (5.9 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.06 (2H, *m*, *o-H* in bromo-C_6H_4-), 7.16 (2H, *m*, *m-H* in bromo-C_6H_4-), 7.46 (3H, *s*, *p-H* in B-Ar(CF_3)$_2$), 7.51-7.55 (8H, *m*, *o-H* in P-Ar), 7.63-7.67 (8H, *m*, *m-H* in P-Ar), 7.75 (6H, s, *o-H* in B-Ar(CF_3)$_2$), 7.81-7.82 (4H, *m*, *p-H* in P-Ar).

Tetraphenylphosphonium 4-azidophenyl-tris[3,5-bis(trifluoromethyl)phenyl]borate (9).

In a 20 mL two necked flask, compound **8** (1.6 g, 1.4 mmol), NaN_3 (91 mg, 1.4 mmol), sodium $_L$-ascorbate (10 mg, 50 µmol), CuI (20 mg, 0.11 mmol), *N*,*N*'-dimethylethylenediamine (13 mg, 0.15 mmol) was dissolved in ethanol (6 mL), and stirred for 12 h at 100 ºC. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (chloroform), followed by recrystallization from ethanol to obtain compound **9** (0.59 g, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.78 (2H, *m*, *m-H* in azide-C_6H_4-), 7.19 (2H, *m*, *o-H* in azide-C_6H_4-), 7.46 (3H, *s*, *p-H* in B-Ar(CF_3)$_2$), 7.51-7.55 (8H, *m*, *o-H* in P-Ar), 7.63-7.67 (8H, *ddd*, *J* = 15.6 Hz, 15.6 Hz, 3.5 Hz, *m-H* in P-Ar), 7.75 (6H, *s*, *o-H* in B-Ar(CF_3)$_2$), 7.81-7.82 (4H, *ddd*, *J* = 15.1 Hz, 15.0 Hz, 2.0 Hz, *p-H* in P-Ar). FT-IR (ATR-IR, cm^{-1}) 2121 (ν_{N3}).

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$(TPP)_5$· 1.

In a 10 mL ampule tube, compounds **5** (70 mg, 67 µmol) and **9** (590 mg, 0.54 mmol) and CuI (2.1 mg, 11 µmol) were dissolved in THF (9 mL), and degassed by freeze-thaw cycle. The reaction mixture was heated at 80 ºC for 7 days. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (acetone/hexane = 1/1) to obtain (**$TPP)_5$·1** (70 mg, 19%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.34 (8H, *m*, *m-H* in triazole-C_6H_4-), 7.37 (8H, *m*, *o-H* in triazole-C_6H_4-), 7.46-7.49 (40H, *m*, *o-H* in P-Ar), 7.50 (12H, *s*, *p-H* in B-Ar$(CF_3)_2$), 7.57-7.61 (40H, *ddd*, *J* = 15.9 Hz, 15.9 Hz, 3.7 Hz, *m-H* in P-Ar), 7.72-7.75 (20H, *ddd*, *J* = 15.0 Hz, 15.0 Hz, 2.0 Hz, *p-H* in P-Ar), 7.79 (24H, *s*, *o-H* in B-Ar$(CF_3)_2$), 7.98 (4H, *s*, triazole). HRMS(ESI) Calcd. for $C_{224}H_{116}B_5F_{88}N_{12}P_3$ $[M+H-2TPP]^{2+}$: *m/z* 2396.8899 Found: *m/z* 2396.8914.

Tetrabutylammonium 4-bromophenyl-tris[3,5-bis(trifluoromethyl)phenyl]borate (10).

In a 200 mL, compound **7** (1.8 g, 2.2 mmol) was dissolved in dichloromethane (10 mL), and dichloromethane solution (10 mL) of tetrabutylammonium chloride (0.70 g, 2.5 mmol) was added dropwise, followed by stirring for 12 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (acetone/hexane = 1/1) to obtain compound **10** (1.5 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.92 (12H, *m*, -$N(CH_2)_3CH_3$), 1.28 (8H, *m*, -$N(CH_2)_2CH_2CH_3$), 1.48 (8H, *m*, -$NCH_2CH_2C_2H_5$), 2.90 (8H, *t*, *J* = 8.3 Hz, -$NCH_2CH_2C_2H_5$), 7.01-7.24 (4H, *m*, -C_4H_4-), 7.50 (3H, *s*, *p-H* in B-Ar$(CF_3)_2$), 7.71 (6H, *s*, *o-H* in B-Ar$(CF_3)_2$).

Tetrabutylammonium 4-azidophenyl-tris[3,5-bis(trifluoromethyl)phenyl]borate (11).

In a 10 mL two necked flask, compound **10** (304 mg, 0.29 mmol), NaN_3 (38 mg, 0.58 mmol), sodium $_L$-ascorbate (2.87 mg, 15 µmol), CuI (5.5 mg, 29 µmol), *N*,*N*'-dimethylethylenediamine (3.8 mg, 43 µmol) was dissolved in EtOH/H_2O (7/3, 0.58 mL), and stirred for 12 h at 100 ºC. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (acetone/chloroform = 1/4). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.85 (12H, *m*, -$N(CH_2)_3CH_3$), 1.28 (8H, *m*, -$N(CH_2)_2CH_2CH_3$), 1.48 (8H, *m*, -$NCH_2CH_2C_2H_5$), 2.90 (8H, *t*, *J* = 8.3 Hz, -$NCH_2CH_2C_2H_5$), 7.01-7.24 (4H, *m*, -C_4H_4-), 7.50 (3H, *s*, *p-H* in B-Ar$(CF_3)_2$), 7.71 (6H, *s*, *o-H* in B-Ar$(CF_3)_2$). FT-IR (ATR-IR, cm^{-1}) 2117 (ν_{N3}).

$(TBA)_5$· 1.

In a 1 mL ampule, compounds **4** (5 mg, 5.3 µmol) and **11** (39 mg, 32 µmol) were dissolved in THF (0.40 mL), and degassed by freeze-thaw cycle. The reaction mixture was heated at 80 ºC for 3 days. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (acetone/hexane = 2/1) to obtain **$(TBA)_5$·1** (15 mg, 57%).^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (60H, *m*, -$N(CH_2)_3CH_3$), 1.26-1.54 (80H, *m*, -$NCH_2(CH_2)_2CH_3$), 3.14 (40H, *t*, *J* = 8.3 Hz, -$NCH_2CH_2C_2H_5$), 7.23 (8H, *m*, *m-H* in triazole-C_6H_4-), 7.37 (8H, *m*, *o-H* in triazole-C_6H_4-), 7.50 (3H, *s*, *p-H* in B-Ar$(CF_3)_2$), 7.71 (6H, *s*, *o-H* in B-Ar$(CF_3)_2$), 8.21 (4H, *s*, triazole).

Results and discussion

The tetrahedral phosphonium borate pentad **$(TPP)_5$·1** and ammonium borate pentad **$(TBA)_5$·1** were synthesized as shown in Figure 1. The 2,3,5,6-tetrafluoro-bromobenzene and triisopropyl (TIPS) acetylene was reacted via Sonogashira-Hagihara cross coupling reaction under the presence of Pd(II) reagent to obtain an ethynylbenzene derivative (**2**). The aromatic proton was then lithiated by n-butyllithium, followed by mixing with boron trichloride, to obtain a tetra(4-ethynylphenyl)borate derivative (**3**).[26] The TIPS protecting group was removed by fluoride ion, simultaneously the counter ion was changed to tetrabutylammonium (TBA) (**4**). For the derivative with tetraphenylphosphonium (TPP) counter ion (**5**), the TBA counter ion was additionally exchanged to TPP under the presence of TPP chloride. The borate for peripheral moiety (**7**) was synthesized from 4-bromophenyl boronic acid via conversion to fluoroborate (**6**) and triple Grignard reaction with 3,5-bis(trifluoromethyl)bromobenzene. The counter ion was then exchanged to TPP (**8**) and TBA (**10**), followed by substitution of bromide group to azide to obtain **9** and **11**, respectively. These azide derivatives were conducted to copper-catalyzed azide-alkyne cyclization (CuAAC) with tetraalkynylphenyl borate **5** or **4**, depending on the counter ion, to obtain **$(TPP)_5$· 1** and **$(TBA)_5$· 1**, respectively.

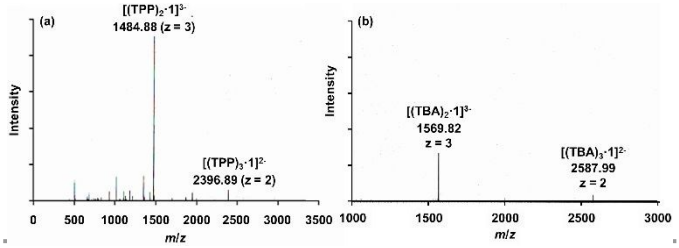

Figure 2. ESI-MS spectra of **$(TPP)_5$·1** and **$(TBA)_5$·1**.

The synthesis of **$(TPP)_5$·1** and **$(TBA)_5$·1** was mainly confirmed by ^{1}H NMR spectroscopy (Experimental section and Figure S1). In FT-IR spectroscopy, the peaks around 2120 cm^{-1} assignable to azide stretching band of compounds **9** and **11** were completely disappeared after the CuAAC reaction (Figure S2). ESI MS showed the presence of trivalent (**$[(TPP)_2)\ 1]^{3-}$** and **$[(TBA)_2{\cdot}1]^{3-}$**) and divalent anions (**$[(TPP)_3)\ 1]^{2-}$** and **$[(TBA)_3{\cdot}1]^{2-}$**) as shown in Figure 2 (see also Figure S3). The diffusion constants of **TPP^+** and **1^{5-}** were determined as 0.32 and 0.28 mm^2/ks, respectively, by DOSY NMR (Figure S4), indicating the rapid exchange of bound and unbound counter anions. Such rapid exchange of counter anions was also suggested by ^{1}H NMR spectra at low temperature, in which the signal kept the same shape even at –55 °C, as that at 10 °C.

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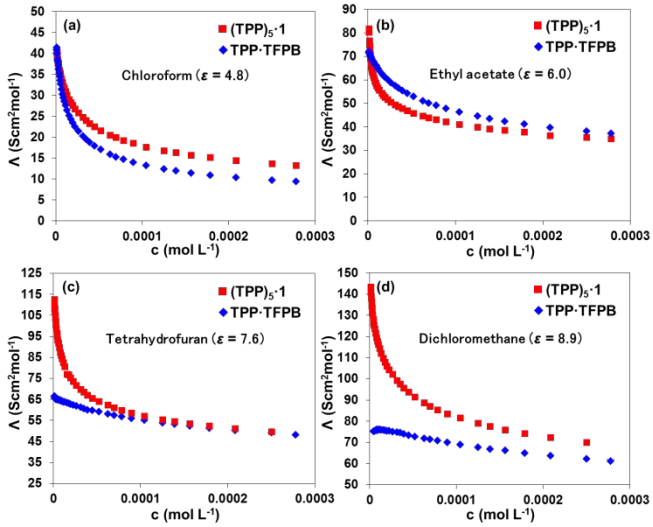

Figure 3. Conductivity of **$(TPP)_5$·1** and **TPP·TFPB** in (a) chloroform (ε = 4.8), (b) ethyl acetate (ε = 6.0), (c) tetrahydrofuran (ε = 7.6), and (d) dichloromethane (ε = 8.9).

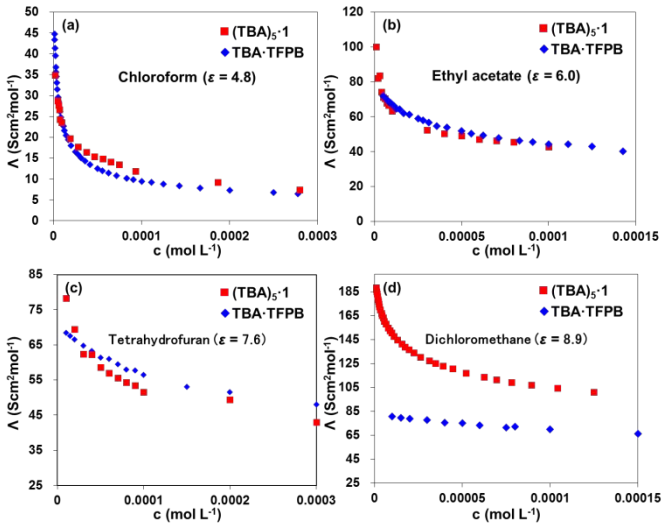

Figure 4. Conductivity of **$(TBA)_5$·1** and **TBA·TFPB** in (a) chloroform (ε = 4.8), (b) ethyl acetate (ε = 6.0), (c) tetrahydrofuran (ε = 7.6), and (d) dichloromethane (ε = 8.9).

Table 1. Summary of conductometry of **$(TPP)_5$·1**, **TPP·TFPB**, **$(TBA)_5$·1**, and **TBA·TFPB**.

Compounds	Solvents[a]	ε[b]	K_a (L·mol^{-1})	Λ_0 (S·cm^2/mol)
$(TPP)_5$·1	$CHCl_3$	4.8	3.4×10^4	40.65
	EtOAc	6.0	1.2×10^5	89.29
	THF	7.6	5.9×10^4	116.28
	DCM	8.9	6.4×10^4	151.52
TPP·TFPB	$CHCl_3$	4.8	5.2×10^4	39.37
	EtOAc	6.0	9.4×10^3	71.94
	THF	7.6	2.4×10^3	65.78
	DCM	8.9	1.3×10^3	74.07
$(TBA)_5$·1	$CHCl_3$	4.8	5.1×10^4	32.89
	EtOAc	6.0	7.9×10^3	101.01
	THF	7.6	8.5×10^4	79.37
	DCM	8.9	5.4×10^4	196.08
TBA·TFPB	$CHCl_3$	4.8	7.1×10^5	68.3
	EtOAc	6.0	2.5×10^4	80.2
	THF	7.6	5.3×10^3	73.5
	DCM	8.9	4.6×10^3	92.2

[a]$CHCl_3$ = Chloroform, EtOAc = Ethyl acetate, THF = Tetrahydrofuran, DCM = Dichloromethane. [b]Dielectric constant.

To reveal the ionic dissociation of the borate pentads **$(TPP)_5$·1** and **$(TBA)_5$·1**, conductometry was carried out in various organic solvents, as shown in Figures 3 and 4. **TPP·TFPB** and **TBA·TFPB** were employed as the reference organic electrolytes. All the measured compounds showed a typical behaviour for a weak electrolyte, thus the molar conductivity increased with decreasing the concentration. The association constant (K_a) and limit molar conductivity (Λ_0) was determined by using Arrhenius–Ostwald equation:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Lambda K_A}{\Lambda_0^2}$$

where c is concentration and Λ is molar conductivity.

The conventional organic electrolytes **TPP·TFPB** and **TBA·TFPB** showed the decrease of K_a, i.e., the acceleration of ionic dissociation, with increase of the dielectric constant (ε). However, both of the borate pentads did not show such decrease of K_a, whereas the increases of Λ_0 with increase of ε for the borate pentads **$(TPP)_5$·1** and **$(TBA)_5$·1** were twice as large as those for **$(TPP)_5$·1** and **$(TBA)_5$·1**.

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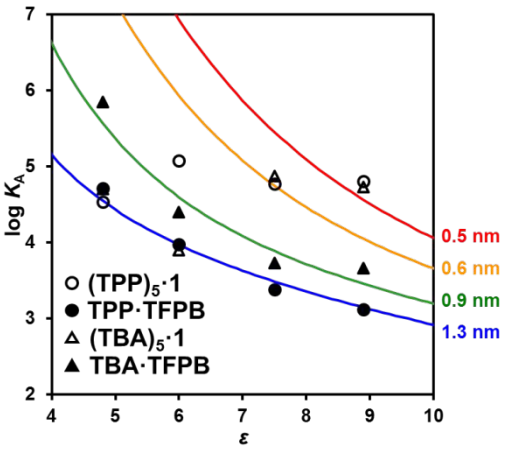

Figure 5. Plots of observed association constant (K_a) (derived using Arrhenius–Ostwald equation) of **(TPP)$_5$·1**, **TPP·TFPB**, **(TBA)$_5$·1**, and **TBA·TFPB**, vs dielectric constant (ε). The lines represent calculated K_a of an electrolyte with a specific sum of ionic radii (0.5, 0.6, 0.9, and 1.3 nm) vs dielectric constant (ε) derived using Bjerrum's theory.

The uniform decrease of K_a for the conventional organic electrolytes **TPP·TFPB** and **TBA·TFPB** with increase of ε consistent with the prediction derived from Bjerrum's theory. The observed K_a for **TPP·TFPB** and **TBA·TFPB** well agreed with the theoretical curve for electrolytes with 1.3 nm and 0.9 nm, the sum of the ionic radii which are roughly estimated by molecular modelling, respectively, as shown in Figure 5. On another front, K_as for the borate pentads **(TPP)$_5$·1** and **(TBA)$_5$·1** were not consistent with the theoretical curves. For an example, K_a for **(TPP)$_5$·1** in dichloromethane (6.4×10^4 L·mol^{-1}) is clearly higher than the predicted K_a curve which is consistent with the observed K_a for **(TPP)$_5$·1** in chloroform (3.4×10^4 L·mol^{-1}). This mismatch comes from the assumption of the monovalent electrolytes for Arrhenius–Ostwald equation. In other words, multivalent ionic dissociation of the borate pentads would take place with increase of ε, which is probably responsible for the mismatch of the observed K_as and the predicted K_as derived from Bjerrum's theory.

Conclusions

As a summary of this study, we synthesized tetrahedral borate pentads by using a typical azide alkyne click reaction. The obtained borate pentads exhibited a rapid exchange of counter cations, revealed by NMR spectroscopies. From the conductometry, the borate pentads behaved as a typical weak electrolyte, thus the molar conductivity rapidly increased at around the limit of dilution, which was similar with that for the reference organic electrolytes. However, the association constants for the obtained borate pentads were not consistent with those predicted by using Bjerrum's theory, probably due to the variation of valence with the change of dielectric constant of the media.

Conflicts of interest

The authors declare no conflicts of interests.

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Graphical Abstract for Table of Contents (TOC)

Synthesis of pyramidal tetraarylborate pentads

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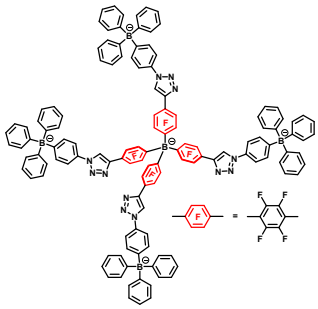

Tetrahedral tetraarylborate pentads were synthesized by a typical click reaction, copper-catalyzed azide-alkyne cyclization, which exhibited interesting ionic dissociation in low polar organic solvents.