1.34 Chemical Sensors: Main Group Compounds for Anion Detection

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1.34.1 Introduction

Anions play important roles in a wide variety of chemical and biological processes. For example, chloride ion, which is an ubiquitous ion in our body fluid, is indispensable to the control of our vital functions including acid/base balance, neural transmission, and cell membrane permeability. The other anions also have the characteristic chemical and biological functions, and the development of their efficient detection methods has been desired for a long time. Anion-sensing molecules have been developed by utilizing the interaction between a target anion and organic compounds, organometallic compounds, or metal complexes. The efficient anion sensors require the following properties: (1) They are available even at low concentrations such as parts per million (ppm) and parts per billion (ppb). (2) Their sensing ability is not prevented by other contaminating anions. (3) They show readily detectable responses such as change of optical and/or electronic properties. For a long time, it has been difficult, however, to develop a sensor for anions such as fluoride and cyanide ions with high bioactivity. Although it has been known that compounds containing boron, silicon, phosphorus, and tin often have high Lewis acidity and high affinity to Lewis bases such as fluoride and cyanide ions, use of such main group compounds as an anion sensor has been limited. In 1990s, fluoride ion sensor utilizing a combination of trapping of an anion with a main group element and change of optical and electronic property was developed by introduction of Lewis acidic main group element to π-conjugated molecules and has been recognized as a useful method for fluoride ion sensing. Sensing of phosphate ions having important functions in vital phenomenon, agriculture, and environmental sciences was also achieved by utilizing selective complexation with Lewis acidic main group metal ions such as a zinc ion.

This article is restricted to molecular anion sensors based on main group organometallic compounds as anion-binding sites and/or reporters that exhibit optical or electrochemical responses to the anion-detection events. The major part of this article focuses on the recent progress in the detection of fluoride or cyanide ion utilizing molecular sensors based on functionalized triarylboranes. Optical sensing of other bioactive anions such as phosphate ions is also included in this article.

1.34.2 Fluoride Sensing

Fluorine-containing compounds exhibit characteristic biological activity, and their environmental degradation produces

fluoride ion. For example, sarin (*O*-isopropyl methylphosphonofluoridate) and its analogous phosphonofluoridate esters are well-known strong nerve agents and easily hydrolyzed to afford aqueous fluoride ion. The detection of the released fluoride ion gives evidence for the presence of such highly toxic compounds. Meanwhile, the fluoride ion itself also has important effects on our health. In some countries including the United States, water fluoridation, the controlled addition of fluoride ion into tap water, is carried out to reduce the incidence of tooth decay. On the other hand, excessive uptake of fluoride ion invokes fluorosis of tooth and bones, and thus fluoride ion concentration in the environment should be checked carefully. These examples indicate the importance of the fluoride ion sensing with high sensitivity, accuracy, and usability. For the detection of the fluoride ion in the environment or biological systems, Lewis acids containing a main group element, such as boranes, silanes, and stannanes, are potential structural motifs because of the strong Lewis acid–base interactions between these Lewis acids and fluoride ion. In addition, these Lewis acids can recognize fluoride ion selectively in the presence of other contaminating anions. Therefore, the fluoride ion receptors based on these main group elements will exhibit high sensitivity and accuracy. In this chapter, the recent development of the fluoride ion sensors by taking advantage of boron- or silicon-based Lewis acids is described.

1.34.2.1   Boron Compounds

1.34.2.1.1   *Triarylboranes*

Triarylboranes have a vacant p orbital at the boron atom and the π-conjugation extended over the whole molecule through the vacant p orbital gives rise to their characteristic lowest unoccupied molecular orbital (LUMO). Upon addition of fluoride ion to a triarylborane, the boron atom is coordinated by the fluoride ion and the coordination number of the boron atom is changed from 3 to 4. In the tetracoordinated state of the boron, the extension of the conjugation on the LUMO is changed due to the lack of the vacant p orbital. The change of LUMO involves changes in the light absorption and fluorescence behaviors. That is, triarylboranes can receive fluoride ion as an input and their π-conjugated systems report the event in the form of the changes of light absorption and fluorescence. If the triaryborane shows absorption and/or fluorescence in the visible region of the wavelength, the change can also be observed with the naked eye.

However, the fluoride-sensing ability of ordinary triarylboranes (e.g., Mes_3B) is not high enough for practical applications. Although triarylboranes generally form strong complexes with fluoride ion in aprotic solvents, especially in tetrahydrofuran (THF), the complexation reactions are often hampered in aqueous media that are common in the biological conditions. In aqueous solvents, fluoride ion is strongly trapped in hydrogen-bonded networks of water molecules, preventing the coordination of the fluoride ion to triarylboranes. Recent progress in the molecular design of the triarylborane-based fluoride ion receptors has made it possible to detect fluoride ion even in pure water.

Another current topic in the field of triarylborane-based fluoride ion sensors is the progress in the reporting of the fluoride complexation. The complexation events were often outputted by the decrease in the ultraviolet (UV)-vis absorption or fluorescence emission, but such turn-off type sensing is not ideal, considering the sensitivity. Recently, triarylborane-based anion sensors that exhibit more sensitive output responses, including fluorescence turn-on response and phosphorescence change, have been achieved.

1.34.2.1.1.1   *Without cationic group and metal complex moiety*

Fluoride ion affinity of triarylboranes is strongly affected by the electronic and steric effects of the aryl substituents. Introduction of electron-withdrawing and/or small aryl groups on the boron sites is thought to improve the fluoride ion complexation constants.
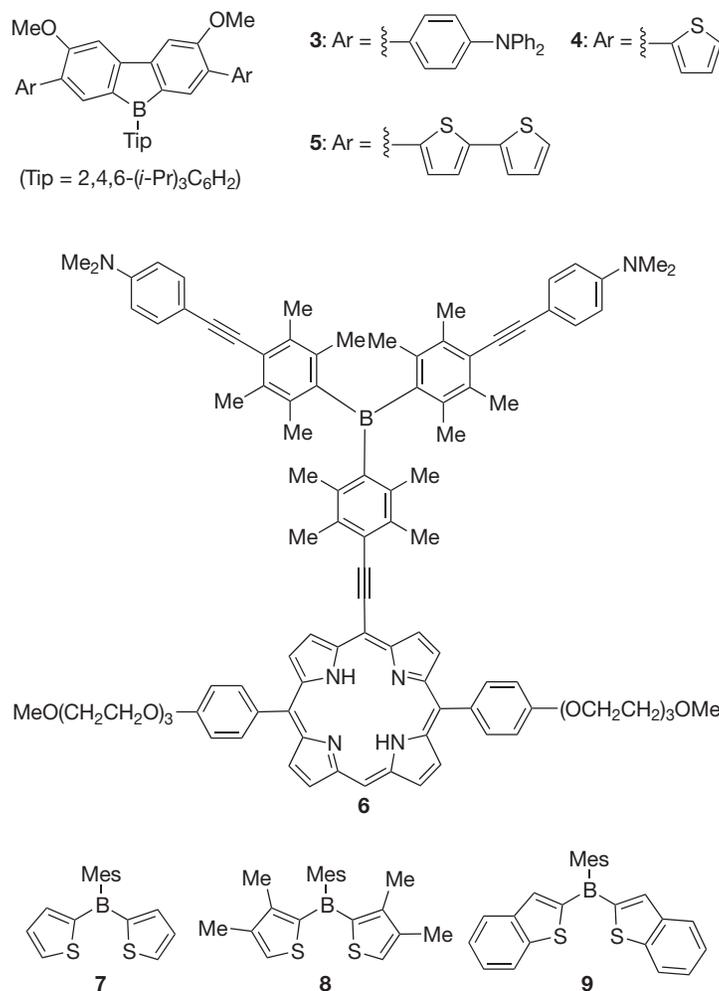
Yamaguchi and Tamao et al. reported that anthrylboranes **1** and **2** show change of absorption spectra in the solution upon fluoride ion complexation based on the disconnection of the π-conjugated system on the boron atom.[1] Complexation of **1**, showing orange color in THF (λ_{max} 470 nm), with a fluoride ion affords blue shift of absorption maxima (λ_{max} 406 nm) with color quenching. The association constant (K_a) of **1** toward a fluoride ion was reported to be $2.8(3) \times 10^5$ M^{-1} in THF. In absorption spectra, tetrakis(triarylborane) **2** shows multistep changes due to sequential coordination of fluoride ions.

1   **2**
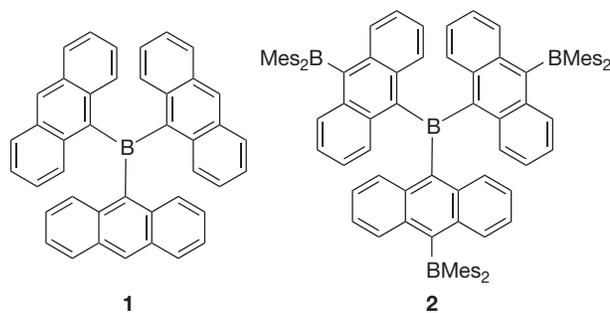
From the viewpoint of the more sensitive sensing, a system providing output signals in both before and after complexation is favorable rather than turn-off sensing, as the ratiometric measurement providing high sensitivity can be applied. Dibenzoboroles **3**–**5** show orange and blue fluorescence in THF solution under UV irradiation before and after fluoride complexation, respectively (Table 1).[2] The difference in the response behavior toward fluoride ion between dibenzoboroles

Table 1   Wavelengths of fluorescence maxima (λ_{em}), fluorescence quantum yields (Φ_F), and binding constants (K_a) of **3**–**5** in THF

Compounds	λ_{em}/nm (Φ_F) without fluoride	λ_{em}/nm (Φ_F) with fluoride	K_a/M^{-1}
3	561 (0.030)	419 (0.92)	$3.5(4) \times 10^5$
4	550 (0.041)	417 (0.86)	$1.1(5) \times 10^6$
5	576 (0.022)	478 (0.42)	$1.4(3) \times 10^6$

3: Ar = —⟨ ⟩—NPh₂   **4**: Ar = —thiophene

5: Ar = —bithiophene

(Tip = 2,4,6-(*i*-Pr)₃C₆H₂)

6

7   **8**   **9**

10 (R = Ph)
**11** (R = Me)

3–5 and simple triarylboranes such as **1** is attributed to the fact that the dibenzoboroles have a π-conjugation extended over the whole molecule through a normal C–C bond in the tetra-coordinate state of the boron atom, while simple triarylboranes do not.

Triarylborane **6** also shows color change and ratiometric fluorescence response upon complexation with fluoride ion.[3] The solution and fluorescence colors of **6** in THF without fluoride ion are purple and red, respectively. These colors change to green (solution color) and bluish color (fluorescence) upon complexation with fluoride ion. The mechanism of the color change upon complexation is based on the energy transfer between two chromophores, a triarylborane center, and a porphyrin moiety. The Dexter-type energy transfer from the excited aryl borane moiety to the porphyrin moiety occurs before complexation and only emission of the porphyrin moiety can be observed. In contrast, complexation of the boron center with a fluoride ion blocks this energy transfer, resulting in independent emission from the aryl borane and porphyrin moieties.

Kawashima et al. reported that dithienylboranes **7–9** exhibit higher fluoride ion complexation constants than those of neutral and monodentate borane-based anion receptors.[4] Their association constants (K_a) in MeCN were too large to be estimated correctly ($K_a > 10^8$ M^{-1}), while in CH₂Cl₂ the association constants of **7**, **8**, and **9** were determined as 2.3×10^6, 4.4×10^5, and 6.2×10^7 M^{-1}, respectively. The electron-withdrawing thiophene rings enhance the Lewis acidity of the boron centers. The smallness of the thiophene rings compared to benzene rings may also improve the fluoride ion affinity because of the decrease in the steric repulsion in the tetracoordinated fluoroborates.

Triarylborane–orthocarborane hybrids **10** and **11** have exceptionally high fluoride ion association constants among neutral triarylboranes.[5] The fluoride complexation was accomplished in an aqueous media, THF–H₂O (9:1, v/v), with the association constants of 5.0×10^3 M^{-1} (**10**) and 7.7×10^3 M^{-1} (**11**), respectively. The improved Lewis acidity of **10** and **11** is attributed to the strong σ-withdrawing effect of the orthocarborane cages.
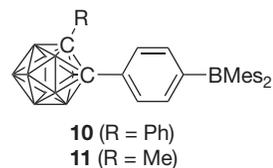
Synergetic interactions of several triarylborane units through π-conjugated frameworks lower the LUMO energy levels and thus enhance the Lewis acidity of the boron

sites. Kawashima et al. reported the optoelectronic properties and fluoride-sensing ability of 9,10-dibora-9,10-dihydroanthracene **12**.[6] Triarylborane **12** binds fluoride ion strongly in THF ($K_a = 2(1) \times 10^8$ M^{-1}). Formation of the corresponding fluoroborate $[12\bullet F]^-$ is accompanied by blue shifts of the absorption and emission bands. Further addition of fluoride ion decreases the absorption and emission intensities, indicating the formation of difluoroborate $[12\bullet F_2]^{2-}$.

12
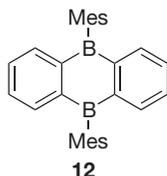
The same group also developed ladder-type conjugated molecules bearing triarylborane units and electron-donating elements (N or S) **13–16**.[7] Although their fluoride ion affinity is only moderate and comparable to that of Mes$_3$B, they exhibit stepwise changes in the UV–vis absorption and the fluorescence color as a function of the number of the captured fluoride ions (from 0 to 2 for **14** and from 0 to 3 for **16**). The UV–vis absorption and fluorescence color shifts are attributed to the change in the type of intramolecular charge transfer (ICT) upon the complex formation.

A dibenzoazaborine bearing two Mes$_2$B groups **17** captures up to two fluoride or cyanide ions in THF in a step-by-step manner.[8] The electronic interactions between the three triarylborane units increase the anion affinity, as revealed by the values of K_a, which exceed the limit value for the direct determination by the standard titration techniques. The complexation of the first fluoride or cyanide ion resulted in the red shift of the fluorescence maximum because of the ICT between the borate moiety and the free triarylborane units (Table 2).

Similar fluorescence red shift upon fluoride ion complexation is observed in oligofluorene **18**[9] and pyrene **19**,[10] bearing two Mes$_2$B groups at their periphery. Upon addition of one equivalent of fluoride ion, the fluorescence maxima of these
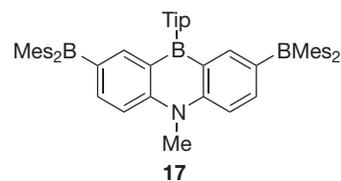

17

Table 2 The first and second complexation constants of **17** to fluoride and cyanide ions in THF

|	K_a^1/M^{-1}	K_a^2/M^{-1}
F$^-$	$>10^8$	$>10^8$
CN$^-$	$>10^8$	$7(1) \times 10^5$

compounds are bathochromically shifted, owing to the ICT between the fluoroborate moieties and the free Mes$_2$B sites.

Compared to the classical fluorescence turn-off sensors, fluorescence turn-on response to a fluoride ion is superior in terms of the sensitivity and the easiness for naked-eye detection. Wang et al. developed a fluorescence turn-on sensor **20** for the detection of fluoride in CH$_2$Cl$_2$.[11] In the free host state, the fluorescence from the triarylamine is quenched by a photo-induced electron transfer (PET) from the amine to the triarylborane. The coordination of a fluoride ion to the triarylborane unit inhibits the PET process and intensifies the fluorescence emission. The K_a value is equal to 4.0×10^4 M^{-1}, which is comparable to those of the ordinary triarylboranes under similar conditions. A fluorescence turn-on type response to fluoride ion was also observed in a V-shaped triarylborane–triarylamine dyad **21**, bearing a diarylsilylene spacer.[12]

1.34.2.1.1.2 Chelating structures

Bidentate and chelating Lewis acids show strong and selective complexation ability toward specific Lewis bases. These bidentate anion receptors exhibit exceptionally high affinity toward fluoride ion, owing to the chelation effects. This section focuses

13

14

15

16

18 ($R^1 = n\text{-}C_8H_{17}$, $R^2 = \text{-}C_6H_4\text{-}p\text{-}(n\text{-}C_8H_{17})$)

19

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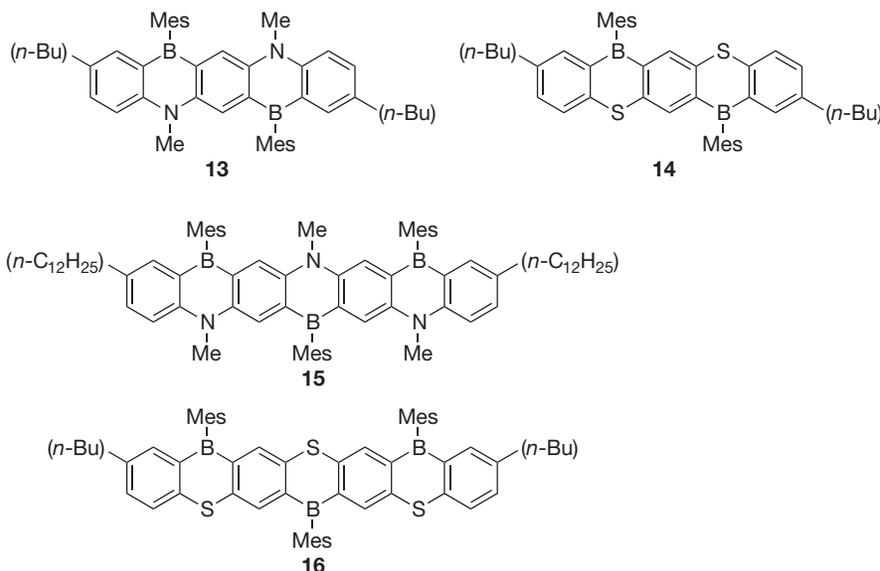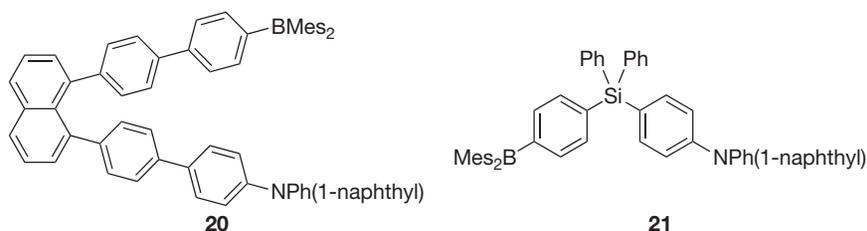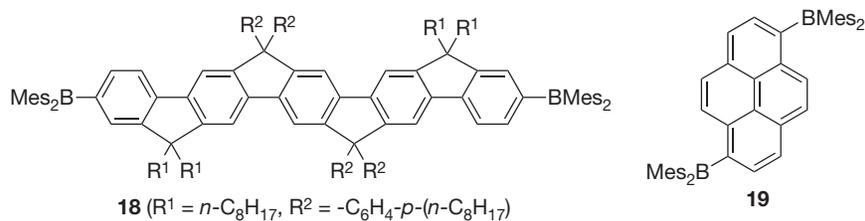
on neutral chelating anion receptors bearing at least one borane unit. Cationic and/or organometallic anion sensors are described later.

Bidentate boron compound **22** bearing two triarylborane moieties, reported by Gabbaï, shows an extremely high binding constant ($> 5 \times 10^9$ M^{-1} in THF) with fluoride ion.[13] Chelation of a fluoride ion with two boron centers was confirmed by the X-ray crystallographic analysis. The strong complexation ability of **22** by such a chelating effect prevents decomplexation of the fluoride complex upon addition of water.

22
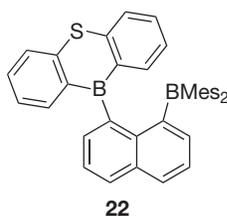
Yamamoto and Kawachi reported that boron–silicon bidentate Lewis acids **23** and **24** have higher fluoride ion affinity than monodentate triarylborane PhBMes$_2$. Although the fluorosilane moieties in **23** and **24** are clearly involved in the binding of a fluoride ion, their effects on the improvement in the fluoride ion affinity are moderate.[14]

23 (R = Me)
24 (R = Ph)
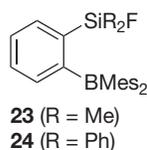
Boron–tin bidentate Lewis acids **25** and **26** bearing a ferrocene-1,2-diyl linker were synthesized by Jäkle et al.[15] The addition of potassium fluoride (KF) and 18-crown-6 in THF to **25** and **26** results not only in the complexation of fluoride ion on the borane sites but also in the substitution of the chloro groups on the boron and tin with fluoride. One of the captured fluoride ions is located in the middle of the two Lewis acidic sites, revealing the chelation effect of the boron–tin bidentate Lewis acids. In addition, the fluoride complexation leads to

cathodic shifts of the oxidation potentials of the ferrocene unit, which can be utilized for electrochemical sensing of fluoride ion.

A boron–boron bidentate Lewis acid based on a ferrocene-1,2-diyl backbone (**27**) captures fluoride ion in THF or cyanide ion in THF or CDCl$_3$.[16] The cyanide affinity of **27** ($K_a = 3.7(6) \times 10^4$ M^{-1} in THF) is lower than that of FcBMes$_2$ ($K_a = 8(2) \times 10^4$ M^{-1} in CH$_2$Cl$_2$), indicating that the second BMes$_2$ group destabilizes the borates due to an increase in the steric repulsion. The coordinated fluoride ion is located between the two boron sites, whereas the cyanide ion is coordinated to only one boron site. Triarylborane **27** shows higher selectivity to cyanide ion than fluoride ion, but the reason for this anion selectivity is unclear.

25 (R = Cl)
26 (R = Ph)

27
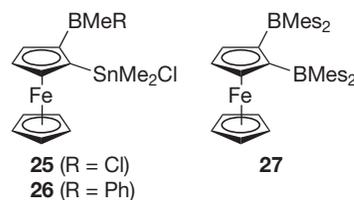
Hydrogen-bond donors are also utilized as fluoride ion recognition sites because fluoride ion is one of the strongest hydrogen-bond acceptors. A triarylborane–trifluoroacetamide dyad **28** binds fluoride ion in a chelation fashion using the amide proton.[17] The affinity constant of **28** toward fluoride ion in THF is larger than 10^7 M^{-1}, that is, the limiting value for the direct determination of the affinity constant. Fluoride ion complexation incorporating the hydrogen bond is also found in triarylborane–ammonium hybrid receptors as described later.

28
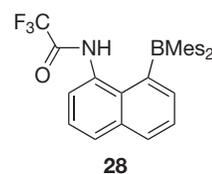
1.34.2.1.1.3   With cationic group(s)

Combination of triarylboranes with cationic groups is beneficial for the improvement of the anion-sensing ability. Cationic

29

30 (Ch = S)
31 (Ch = Se)

32 (Ar = Mes, R¹ = Ph, R² = Bn)
33 (Ar = Tip, R¹ = R² = Me)
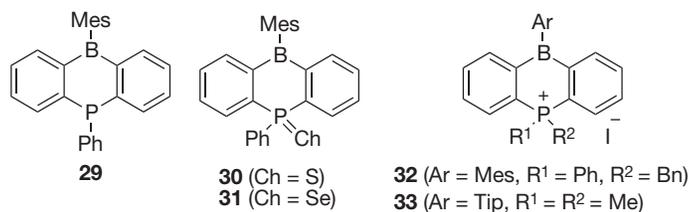
groups are strongly electron withdrawing and enhance the Lewis acidity of the triarylborane moieties. In addition, electrostatic attractive force between the cationic groups and the resulting borate moiety thermodynamically stabilizes the borane–anion complexes. Furthermore, due to the ionic nature, the cationic triarylboranes are more hydrophilic than the neutral compounds and expected to be applied to the anion sensing in water. These advantages facilitate the development of the anion sensors based on cationic triarylboranes.

The Lewis acidity of the boron atom in dibenzophosphaborin **29** is increased by the *P*-functionalization.[18] Phosphane chalcogenides **30** and **31** exhibit relatively high fluoride ion affinity, owing to the electron-withdrawing effects of the pentavalent phosphorus atoms. The phosphonium salt **32** is an exceptionally strong borane-based Lewis acid and captures even bromide ion to afford the corresponding zwitter ion at low temperatures in CH_2Cl_2. Under a biphasic condition (CH_2Cl_2–H_2O), cationic dibenzophosphaborin **33** captures fluoride ion in pure water to afford the corresponding zwitter ion.[19] Low water solubility and the lack of the fluorescence activity of **33** hamper its application to the anion sensing in pure water.

Diphosphoniodibenzoazaborine **34** shows fluorescence turn-off response to fluoride ion in DMSO–H_2O mixture (3:1, v/v) buffered with HEPES and NaOH (pH 7.0).[20] The association constant for fluoride ion is estimated to be $1.9(3) \times 10^2$ M^{-1}. The ammonium analog **35** does not react with fluoride ion under the same conditions, probably because of its higher hydrophilicity that destabilizes the fluoroborate in aqueous media.


34 (FG = PMePh₂⁺)
35 (FG = NMe₃⁺)
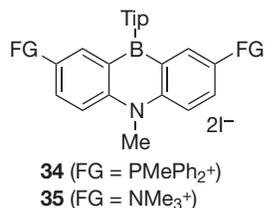
Gabbaï et al. reported that triarylborane–phosphonium hybrid **36** binds fluoride ion efficiently in H_2O–MeOH mixtures (9:1, v/v).[21] The K_a value of this reaction is $8.4(5) \times 10^2$ M^{-1}. In the same solvent, the fluoride ion affinity of a series of analogous cationic triarylboranes **37**, **38**, and **39** increases in this order ($K_a = 2.5(2) \times 10^3$ M^{-1} for **37**, $4.0(3) \times 10^3$ M^{-1} for **38**, and $1.1(1) \times 10^4$ M^{-1} for **39**), indicating that the bulkier and more hydrophobic triarylboranes show higher fluoride ion affinity. Especially, triarylborane **39** bearing a triphenylphosphonio group exhibits a UV–vis absorption change in the presence of ppm-order concentration of fluoride

ion in pure water.[22] Triarylborane–phosphonium hybrid **40**, an ortho-substituted isomer of **36**, exhibits much higher fluoride ion affinity in MeOH ($K_a > 10^6$ M^{-1} for **40**, $K_a = 4.1(5) \times 10^2$ M^{-1} for **36**).[23] The proximity of the two Lewis acidic sites in **40** allows the chelation to a fluoride ion, which enhances the fluoride ion affinity. In pure water, **40** is easily hydrolyzed, which hampers the further application to the anion sensing in aqueous media. Its application to the recognition of azide ion under a biphasic condition is described later.

36 (R = Me)
37 (R = Et)
38 (R = *n*-Pr)
39 (R = Ph)

40
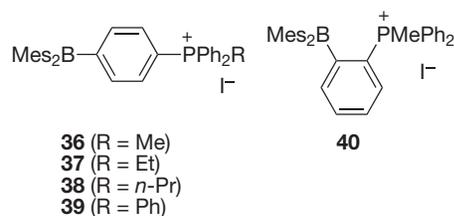
Similar to the phosphonium groups, chalcogenium groups are useful to improve the fluoride ion affinity of triarylborane-based receptors. Triarylborane–tellurium mixed Lewis acid **41** shows high fluoride ion affinity in MeOH ($K_a = 7.5 \times 10^2$ M^{-1}), while its sulfur-analog **42** does not react with fluoride ion in MeOH even in the presence of 1000 equivalents of fluoride ion.[24] The improved fluoride ion affinity of **41** originates from a donor–acceptor interaction between the bound fluoride ion and the σ^*(Te–Ph) orbital.

Ammonium groups also act as sensing sites of fluoride ion. Triarylborane–ammonium hybrid Lewis acid **43** reacts with fluoride ion under a biphasic condition, CDCl₃–H_2O mixtures.[25] The fluoroborate is stabilized by intramolecular hydrogen bond between one of the α-hydrogen atoms of the ammonio group and the bound fluoride ion.

41 (Ch = Te)
42 (Ch = S)

43
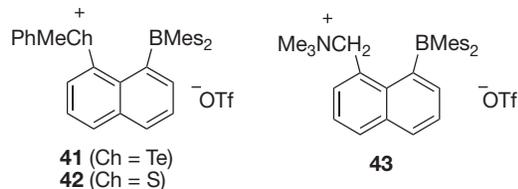
Triarylborane–ammonio group hybrid molecules **44** and **45** bearing a ferrocene-1,2-diyl or a ferrocene-1,1′-diyl spacer, respectively, bind fluoride and cyanide ions in CH_2Cl_2.[26] The substitution position of the ammonio group is critical for the anion affinity. The association constants of **44** to fluoride or cyanide ion are much larger than those of its isomer **45** (Table 3). In the case of **44**, the σ-electron-withdrawing effect of the ammonio group to the boron site may be more effective than that in **45**.

Table 3 The association constants of **44** and **45** (in M^{-1}) to fluoride and cyanide ion in CH$_2$Cl$_2$

	F$^-$	CN$^-$
44	$6(2) \times 10^9$	$6(2) \times 10^9$
45	$9(3) \times 10^5$	$6(2) \times 10^5$

44   **45**
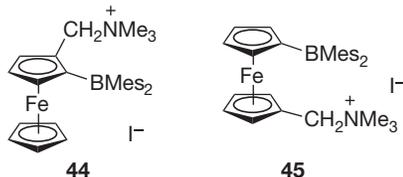
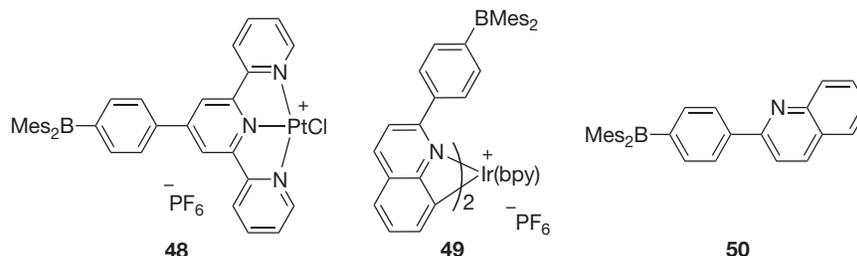### 1.34.2.1.1.4 With metal complex or an organometallic moiety

Combination of triarylboranes with metal complexes or organometallic substituents has advantages in the improvement of the anion-sensing abilities. (1) Transition metal ions are inherently electron withdrawing and enhance the Lewis acidity of the boron centers. (2) Metal complexes have characteristic optical and electronic properties useful for the reporting signals of the anion complexation events, such as light absorption and fluorescence in the long wavelength region, reversible redox processes, and phosphorescence emission.

1.34.2.1.1.4.1 Absorption and fluorescence color changes as output responses

A Pt(II)–bipyridine complex bearing two Mes$_2$B groups (**46**) binds up to two fluoride ions in CH$_2$Cl$_2$ with large association constants ($K_{a1} > 10^9$ M^{-1}, $K_{a2} \sim 10^6$ M^{-1}).[27] The Pt(II) ion inductively withdraws electron density from the bipyridine ligand and enhances the fluoride ion affinity. Pt complex **46** can react with fluoride ion even in more competing solvents, such as THF–EtOH and N,N-dimethylformamide (DMF) H$_2$O mixtures. Pt(II) complex **47** bearing Ph$_2$N and Mes$_2$B groups shows fluorescence-color change (orange to blue) and an increase in the fluorescence intensity upon addition of fluoride ion because of the switching of the emissive state from the N→B charge transfer to the π–π* transition. In CH$_2$Cl$_2$, the association constant is equal to 7.0×10^5 M^{-1}.

46 (R = BMes$_2$)
**47** (R = NPh$_2$)
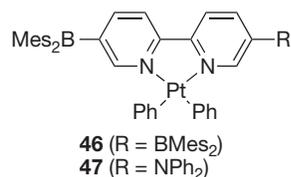
1.34.2.1.1.4.2 Phosphorescence changes as output responses

The introduction of phosphorescent heavy metal complexes (e.g., phosphors based on Pt(II), Ir(III), and Hg(II) complexes) into triarylboranes enables the detection of anions with the change of the phosphorescence emissions. Hybrids **48**[28] and **49**[29] of a Mes$_2$B group and a Pt(II)-terpyridine complex or a cyclometallated Ir(III) complex show phosphorescence turn-off type responses to the addition of fluoride ion. The first and second association constants of **49** in CH$_3$CN are estimated to be 1.29×10^6 and 4.27×10^5 M^{-1}, respectively. These values are larger than that of free ligand **50** (4.70×10^4 M^{-1}), indicating that the electron-withdrawing Ir(III) center enhances the Lewis acidity of the boron sites.

Hybrid **51** of a BMes$_2$ group with a cyclometallated Ir(III) complex shows phosphorescence color change upon addition of fluoride ion.[30] The formation of the corresponding difluoroborate is accompanied by a red shift of the phosphorescence emission. The association constant of fluoride ion per a Mes$_2$B unit is equal to $9.2(3) \times 10^4$ M^{-1}. The poly(methyl methacrylate) film containing **51** also shows phosphorescence color change in response to aqueous fluoride ion.


51
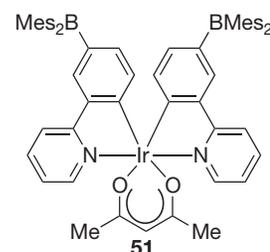
Pt(II) complex **52**[31] bearing a Mes$_2$B-substituted chelating ligand exhibits phosphorescence color change response to the addition of fluoride ion. Compound **52** shows oxygen-sensitive yellow phosphorescence due to the metal to ligand charge transfer (MLCT) state in CH$_2$Cl$_2$. Upon addition of fluoride ion, the emission color changes from yellow to green because of switching from the MLCT to ligand-centered emission.


52
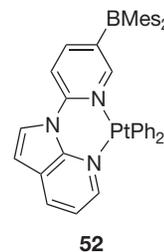
Wang et al. reported that **53**, a triarylborane–Pt(II) dyad linked by a diarylsilylene spacer, shows phosphorescence turn-on response to the reaction with fluoride ion in CH$_2$Cl$_2$.[32] The

48   **49**   **50**

phosphorescence of **53** is quenched by the PET from the Pt(II) complex to the Mes$_2$B group. The coordination of fluoride ion to the boron site inhibits the PET process and intensifies the phosphorescence emission.


53
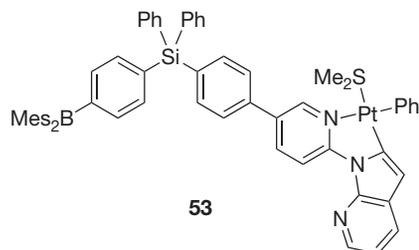
Triarylboranes **54**–**57** bearing an organomercury(II) moiety as a chelating Lewis acid site were also reported by Gabbaï.[33] Triarylborane **54** forms a fluoride complex with a large binding constant ($k > 10^8$ M^{-1} in THF and $2.3(2) \times 10^4$ M^{-1} in 90:10 (v/v) THF/water mixture) and shows a phosphorescence color change upon complexation. The frozen THF solution of **54** and its fluoride complex emit yellow and white phosphorescence, respectively. Introduction of an ammonio group into the 2,6-dimethylphenyl group attached to the mercury of the B–Hg bidentate motif enhances the fluoride ion affinity. In a THF–H$_2$O mixture (9:1, v/v), the fluoride ion binding constants of neutral Lewis acid **55** and cation **56** are equal to $1.3(1) \times 10^2$ and $6.2(2) \times 10^4$ M^{-1}, respectively, revealing the positive effect of the ammonio group on the fluoride affinity. The phosphorescence activities of **55** and **56** are not reported.

54   **55** (R = NMe$_2$)
              56 (R = $^+$NMe$_3^-$OTf)
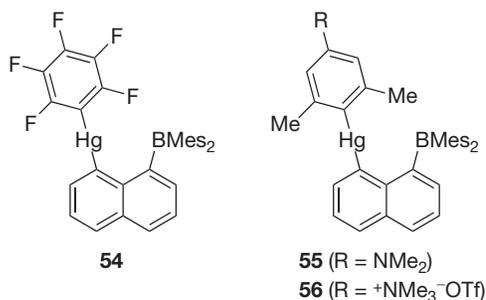
1.34.2.1.1.4.3   Redox behavior switching as an output response Combination of a triarylborane and redox-active organometallics makes it possible to utilize the change of the redox behavior of the organometallic units as the reporter signals of the fluoride complexation. Considering the redox stability, synthetic accessibility, and chemical stability of the compounds, ferrocenes and Ru(II) complexes are mainly used as the organometallic units for redox-based reporters.

Ru(II)–borane hybrid anion sensor **57** reacts with fluoride and cyanide ions in a CHCl$_3$/DMF mixture (9:1, v/v), and the association constants are equal to $1.1(1) \times 10^4$ and $3(1) \times 10^6$ M^{-1}, respectively.[34] Although the association constants of **57** are larger than those of free ligand **58** (K_a(F$^-$) = $7.5(5) \times 10^2$ M^{-1}, K_a(CN$^-$) = $4(2) \times 10^5$ M^{-1}), the effect of the Ru(II) complex on the anion affinity is rather small compared to that of the phosphonium groups: phosphonium–triarylborane hybrid **36** binds fluoride ion more tightly (in CHCl$_3$, K_a(F$^-$) = $6.5(5) \times 10^6$ M^{-1}). The cationic charge of the Ru(II) center is dispersed over the three ligands, and hence the inductive

influence on the boron site is much weaker than the phosphonium group. The Ru(II)/Ru(III) oxidation potential of **57** is shifted upon addition of fluoride or cyanide ion in DMF, enabling the anion detection with electrochemical methods.


57   **58**
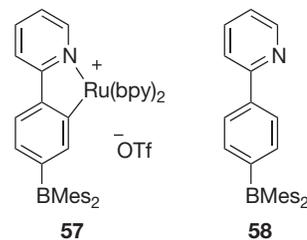
1.34.2.1.2   Boronic acids

Boronic acids (RB(OH)$_2$) react with fluoride ion to afford the corresponding trifluoroborates [RBF$_3$]$^-$. This ligand exchange reaction is specific to fluoride ion and silent for other simple anions, such as cyanide ion, and thus boronic acids are potential fluoride-selective receptors.

Yoon et al. reported that boronic acid–fluorescein hybrid **59** exhibits a fluorescence turn-on response to fluoride ion in MeCN–MeOH (9:1, v/v).[35] The fluorescence emission of **59** is quenched by the PET from the amino group to the fluorescein moiety. The addition of fluoride ion transforms **59** into the corresponding trifluoroborate **60**, in which an intramolecular hydrogen bond involving the amino group eliminates the PET process and intensifies the fluorescence emission. The apparent association constant for fluoride ion is 9.2×10^{10} M^{-3} in a MeCN–MeOH mixture (9:1, v/v).

59   **60**
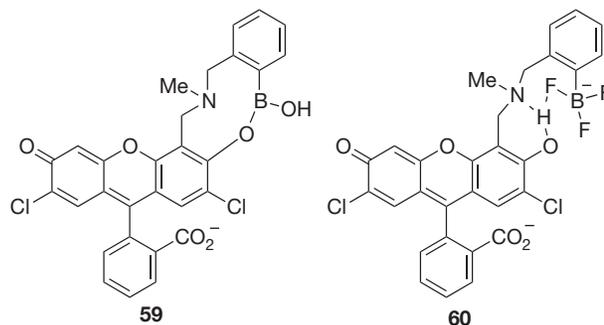
Boronic acids **61**–**64** containing an electron donor or acceptor moiety show optical responses toward fluoride ion based on ICT process.[36] A tricoordinated dihydroxyboryl group, which is an electron-withdrawing group, is changed to an electron-donating tetracoordinated trifluoroborate ion by the reaction with fluoride ion. The reaction of boronic acid **61** with three equivalents of fluoride ion (stability constant, $K = 2.9 \times 10^3$ M^{-3}) results in the red shift of fluorescence maximum due to enhancement of ICT property. Conversely, boronic acids **62**–**64** show a blue shift of fluorescence upon complexation due to loss of ICT property by change of the acceptor group into a donor group. Oxazole-bridged donor–acceptor molecule **64** showed a large blue shift from 554 nm to 490 nm and an increase in fluorescence quantum yield from 0.17 to close to unity upon complexation.

Hybrid molecules **65**–**67** of a boronic acid and an imidazolium fluorophore react with fluoride ion in MeCN to exhibit
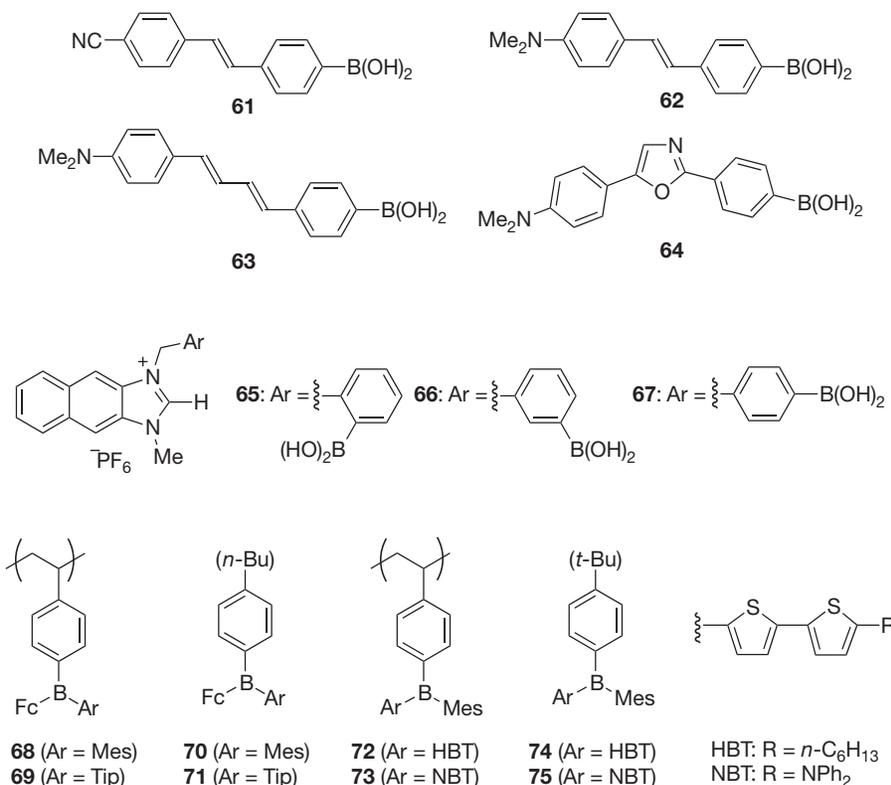
blue shifts of the fluorescence maxima. Among these probes, ortho-substituted derivative **65** shows much stronger fluoride affinity compared to **66** and **67**, judging from the stability constants of the corresponding trifluoroborates (**65**: $5.1(2) \times 10^5$ M^{-1}, **66**: $6.7(2) \times 10^3$ M^{-1}, **67**: $5.7(2) \times 10^3$ M^{-1}).[37] Ortho-substituted derivative **65** also reacts with fluoride ion in a MeCN–HEPES mixture (95:5, v/v), whereas the other two probes show only slight fluorescence change under these conditions.

1.34.2.1.3 Polymers

From the viewpoint of application, polymer-type anion sensors are superior to the small-molecular sensors because of the easy recovery and reuse of the sensors. From such a background, Jäkle et al. synthesized functionalized polystyrenes bearing pendant triarylborane units by taking advantage of tandem transmetallation reactions (see **Chapter 1.27**). Ferrocenyl derivatives **68** and **69** react with fluoride ion in THF, showing a decrease in the UV–vis absorption bands. Their association constants per a triarylborane unit (**68**: $K_a = 2.9 \times 10^4$ M^{-1}, **69**: $K_a = 2.7 \times 10^4$ M^{-1}) are much smaller than those of the corresponding model monomers **70** and **71** (**70**: $K_a = 4.7 \times 10^6$ M^{-1}, **71**: $K_a = 3.4 \times 10^6$ M^{-1}), probably due to the steric and electronic interactions between the tetrahedral fluoroborate units in the same polymer chain.[38] Jäkle et al. also reported the fluoride- and cyanide-sensing abilities of polymers **72** and **73** bearing bithienylborane pendant groups.[39] Their fluoride complexation constants per a borane unit in THF are equal to 8×10^6 (**72**) and 8×10^6 M^{-1} (**73**), which are much smaller than those of the model monomers **74** (3×10^7 M^{-1}) and **75** (4×10^7 M^{-1}) under the same conditions. This is likely due to the steric and electronic interactions

between the fluoroborate units. Polymers **72** and **73** also react with cyanide ion in THF. The addition of fluoride or cyanide ion to the THF solutions of these polymers results in the blue shift of the fluorescence maxima, indicating that these polymers can be used for fluorescence color change sensing of the anions.

π-Conjugated polymers bearing triarylborane moieties in their main chains have been also developed for polymer-based anion sensors. Dibenzoborole–fluorene random copolymer **76** exhibits fluorescence turn-off response to fluoride and cyanide ions in THF.[40] The fluorescence quenching of **76** is much more sensitive to iodide ion than fluoride and cyanide ions, indicating that dynamic quenching by iodide ion hampers the fluoride- or cyanide-selective detection.
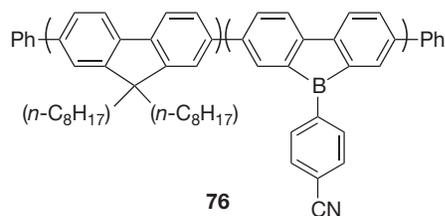

1.34.2.2 Silicon Compounds

Yamaguchi and Tamao et al. reported that trianthrylfluorosilane **77** shows a turn-on type fluorescence response against fluoride ion.[41] The binding constant of **77** and fluoride ion in THF is $2.8(2) \times 10^4$ M^{-1}. Upon complexation of **77** with fluoride ion in THF solution, a blue shift of fluorescence maxima (from 416 nm to 396 nm) and a drastic increase in fluorescence quantum yield (0.033 to 0.64) occur, which can be recognized by the naked eye. This spectral change is explained

77   **78**   9-Ant:
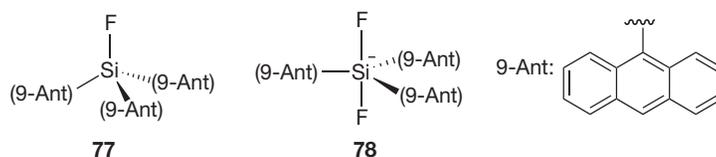
by the structural modification of **77** from tetrahedral tetracoordinated silane to trigonal bipyramidal pentacoordinated silicate **78**, invoking change in the through-space interaction among the anthryl groups.

Gabbaï et al. reported fluorosilane–sulfonium hybrid Lewis acid **79** has high affinity toward fluoride ion.[42] The binding constant of **79** and fluoride ion in $CHCl_3$ is equal to $7(1) \times 10^6 \, M^{-1}$, which is comparable to the value reported for triarylborane–phosphonium hybrid receptor **36** $(6.5(5) \times 10^6 \, M^{-1})$ under the same condition. The reference neutral silane **80** hardly reacts with fluoride ion under the same condition $(K_a = 8(1) \, M^{-1})$, revealing the importance of the cationic, bidentate Lewis acid structure.

79   **80**
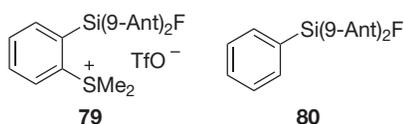
Silyl-protected benzothiazole **81** reacts with aqueous fluoride ion to give fluorescence color-change response.[43] Probe **81** exhibited violet fluorescence in hexadecyltrimethylammonium bromide micelles dispersed in water. Fluoride ion cleaves the silyl ether moiety in **81** to afford the yellow-fluorescent derivative **82**. This reaction is highly efficient, and even ppb-order concentration of fluoride ion can be detected. Probe **81** is easily recovered by sequential treatment of **82** with sodium and $Ph_2(t\text{-}Bu)SiCl$.

81 (R = Si(t-Bu)Ph$_2$)
82 (R = H)
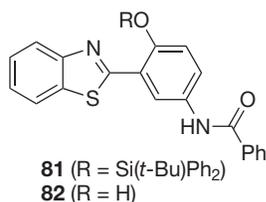
### 1.34.3 Cyanide Sensing

1.34.3.1 Boron Compounds

1.34.3.1.1 Triarylboranes

The detection of aqueous cyanide ion has recently become possible with triarylborane receptors in combination with onium groups (ER_n^+, E: main group elements). Similar to the aqueous fluoride detection, the cationic groups enhance the Lewis acidity of the borane sites and stabilize the cyanoborates electrostatically, enabling the complexation of aqueous cyanide ion efficiently.

Cationic dibenzothiaborin **83** strongly binds cyanide ion both in THF and in $MeNO_2$–H_2O biphasic system.[44] In THF, the association constants of **83** with fluoride and cyanide ions exceed $10^7 \, M^{-1}$, while under the biphasic condition **83** reacts with only the cyanide ion. Cationic triarylborane **83** has not

been used for the detection of cyanide ion in pure water due to the slow decomposition in water.

83
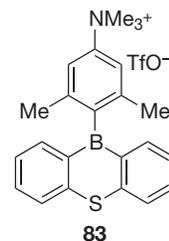
The colorimetric and fluorometric detections of cyanide ion in pure water have been demonstrated by diphosphoniodibenzoazaborine **34**. The cyanide complexation constant of **34** is equal to $5.2(5) \times 10^4 \, M^{-1}$, which is comparable to that in a DMSO–HEPES mixture (3:2, v/v) $(K_a = 1.2(4) \times 10^5 \, M^{-1})$. Under the same conditions, fluoride ion does not coordinate to **34**, showing high cyanide ion selectivity of this probe.

Borane–sulfonium bidentate Lewis acid **84** binds cyanide ion in a H_2O–MeOH mixture (3:2, v/v) strongly $(K_a > 10^8 \, M^{-1})$ and even reacts with ppb-order concentration of cyanide ion in water buffered with HEPES.[45] The sulfonium group not only electrostatically stabilizes the cyanoborate but also participates in the chelation to the cyanide ion in a side-on fashion.

84
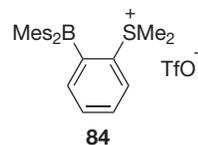
The detection of ppb-order concentration of cyanide ion in pure water has also been achieved with tricationic triarylborane **85**.[46] This probe is highly selective toward cyanide ion in pure water and does not show responses to other nucleophilic anions including fluoride ion. Its dicationic analog **86** does not react with cyanide ion, revealing that at least three ammonium groups are necessary for the aqueous cyanide detection.

85 (R^1 = R^2 = $^+NMe_3^-OTf$)
86 (R^1 = H, R^2 = $^+NMe_3^-OTf$)
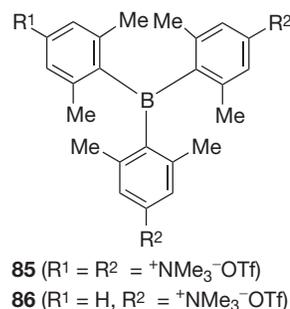
1.34.3.1.2 Boronic acids

Boronic acids bearing a cationic moiety can also detect cyanide ion. Complexation of **87–89** with aqueous cyanide ion changes

**87**: Ar = (ortho, (HO)₂B) **88**: Ar = (meta, B(OH)₂) **89**: Ar = (para, B(OH)₂)
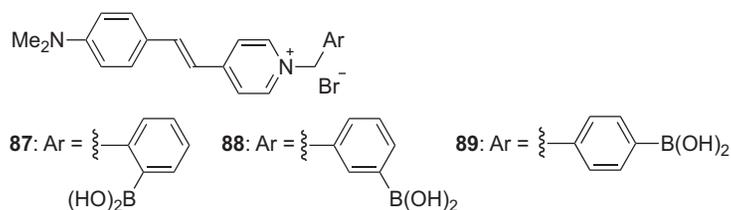
their electron-deficient $B(OH)_2$ group into electron-rich $B(CN)_3^-$ group, just like the reaction of boronic acids with fluoride ion, resulting in the blue shift of their absorption due to reducing ICT between dimethylamino group and pyridinium moiety.[47] The ortho-substituted isomer **87** shows a notable ratiometric response in its absorption spectra at 475 and 375 nm in water with increasing cyanide concentration over the range of up to 30 μM cyanide ion. In contrast, **88** and **89** show responses in a narrower range of concentration. Ratiometric responses in their fluorescence spectra at 600 and 650 nm are also available for determining concentration of the cyanide ion in water.

1.34.3.1.3 Polymers
Fluorene–borylene alternative copolymer **90** shows a two-step change of the fluorescence spectra upon addition of cyanide or fluoride ion in THF.[48] At the first stage of the anion complexation, a broad and red-shifted emission band develops, which is thought to originate from the charge-transfer excited state between the borate and borane moieties through the conjugated polymer backbone. Further addition of the anions completely quenches the fluorescence emission. A similar fluorescence change is observed in π-conjugated molecules bearing several triarylborane units (e.g., **17**, **18**, and **19**).

90
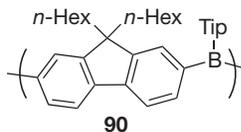
1.34.3.2 Imines

Although imines are known to effectively capture cyanide ion under acidic conditions to afford α-aminonitrile derivatives (the Strecker reaction),[49] the poor fluorescence activity of the imine derivatives hampers their application for the fluorescent cyanide sensors. Kawashima et al. reported that the introduction of a B $(C_6F_5)_2$ group to diarylazomethine derivatives (Ar—CHN—Ar′) substantially enhances the fluorescence intensity as well as the reactivity of the imine moieties toward cyanide ion because of the intramolecular B—N coordinative interactions. Boryl-substituted aldimine **91** reacts with cyanide ion in DMF to show fluorescence turn-off response, while π-extended derivative **92** exhibits fluorescence color-change response upon addition of cyanide.[50]
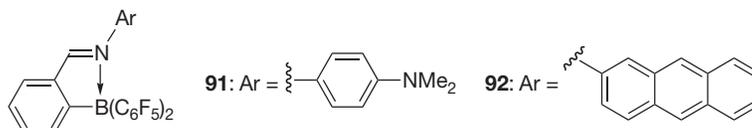
1.34.4 Control of the Selectivity in Fluoride and Cyanide Sensing

Although triarylborane-based anion sensors are generally selective toward fluoride and cyanide ions over the other environmental anions, it has been difficult to distinctively detect fluoride and cyanide by using triarylborane probes because of their similar nucleophilicity.

Gabbaï et al. have succeeded in the selective sensing of fluoride and cyanide ions in a H_2O–MeOH mixture (6:4, v/v) by a change in the substitution pattern of triarylborane–ammonium hybrid probes.[51] Para-substituted derivative **93** reacts with cyanide ion very readily in the aqueous solution $(K_a = 3.9(1) \times 10^8 \text{ M}^{-1})$ and does not respond to fluoride ion. On the other hand, its ortho-isomer **94** solely binds fluoride ion under the same conditions, but the binding is much weaker $(K_a = 9.1(5) \times 10^2 \text{ M}^{-1})$. The selectivity principle of the anions is thought to be governed by the balance of the Lewis acidity and bulkiness of the two probes. The boron site of **93** is a weaker Lewis acid and sterically less demanding, while that of **94** is more Lewis acidic and sterically crowded. Fluoride ion, the weaker Lewis base under the conditions, coordinates to the more Lewis acidic **94**, while the bulkier cyanide ion prefers less hindered **93**.

93 **94**
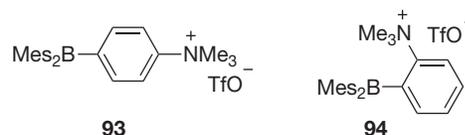
The selective recognition of fluoride and cyanide ions has also been achieved by a combination of ferrocenylborane **95**, ferrocenylboronate **96**, and tetrazolium violet (**97**).[52] The anion complexation to these ferrocenylboron derivatives enhances the electron-donating and reducing activities of the ferrocene cores, resulting in the reduction of tetrazolium violet to afford a purple formazane dye (**98**). The stronger Lewis acid **95** reacts with both fluoride and cyanide ions in MeCN–MeOH mixtures (>100:1, v/v) in the presence of tetrazolium violet to give a colorimetric response due to the formation of **98**, whereas **96**-tetrazolium violet mixtures respond only to fluoride ion. This color change is utilized for the naked-eye detection of fluoride or cyanide ion.

91: Ar = (para NMe₂) **92**: Ar = (anthracenyl)

95   **96**

97 (colorless)   Reductants ⟶   **98** (purple)
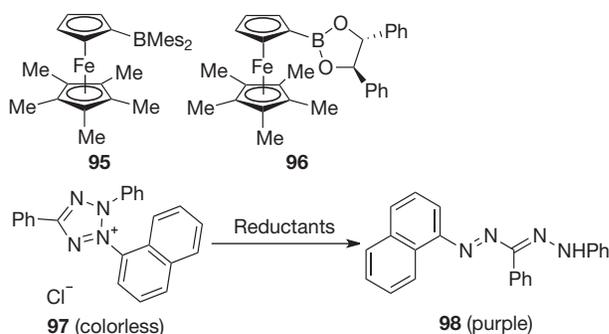
1.34.5   Miscellaneous Anion Sensing

1.34.5.1   Azide Ion

Like fluoride and cyanide ions, azide ion has a special biological and chemical reactivity. Although the detection of azide ion with main group element compounds has not been investigated widely, triarylborane-based probes with improved Lewis acidity are expected to be used for the azide recognition in the environment. Triarylborane–phosphonium bidentate Lewis acid **40** reacts with azide ion in a biphasic system, $CHCl_3$–H_2O. The azide ion coordinates to the receptor in a η^1,μ^2-fashion. In pure water, **40** strongly binds a molecule of water and does not react with azide ion.

1.34.5.2   Acetate and Chloride Ions

Silanols form strong hydrogen bonds with halide and acetate ions. *gem*-Silanediol **99** binds strongly acetate ion rather than chloride, bromide, and iodide ions (Table 4).[53] The higher affinity toward acetate ion originates from the formation of doubly hydrogen-bonded structure between **99** and acetate ion. In contrast, disiloxane-type diol **100** as well as tetraols **101** and **102** selectively form hydrogen-bonded complexes with chloride ion rather than bromide and iodide ions.[54] The chloride complexation constants of tetraols **101** and **102** are larger than those of diols **99** and **100** in CD_3CN, indicating that the four silanol groups cooperatively bind one chloride ion in the tetraol receptors. Silanols **100**–**102** react with acetate in MeCN to afford precipitates, probably because of the formation of the polymers.

1.34.5.3 HPO_4^{2-}, Pyrophosphate, and Related Phosphate Ions
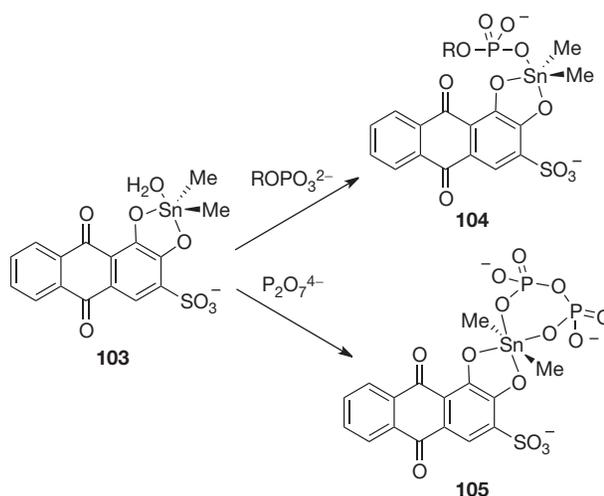
1.34.5.3.1   Tin compounds

Organotin(IV) compounds have high Lewis acidity and easily expand their coordination numbers to accommodate multidentate anions, such as phosphate and pyrophosphate (PPi), to afford penta- or hexa-coordinated hypervalent structures.

Table 4   Association constants (in M^{-1}) of the silanols **99**–**102** to anions in CD_3CN or $CDCl_3$

|	AcO^-	Cl^-	Br^-	I^-
99 ($CDCl_3$)	$5.6(7) \times 10^3$	$1.4(1) \times 10^2$	50(1)	—
99 (CD_3CN)	$2.50(5) \times 10^4$	46(6)	6.4(4)	0.7(2)
100 (CD_3CN)	—	$6.7(4) \times 10^2$	53(2)	4.3(3)
101 (CD_3CN)	—	$2.5(1) \times 10^3$	128(5)	8.6(2)
102 (CD_3CN)	—	$2.8(1) \times 10^3$	78(5)	10(2)

The complexation events are outputted by combination with appropriate signaling units.

Addition of Me_2SnCl_2 to alizarin red S (ARS) in phosphate buffer solution intensifies the fluorescence emission of the ARS, owing to the formation of organotin–fluorophore dyad **103**, which shows fluorescence turn-off response to various phosphate ions.[55] The anion affinity of **103** is in the following order: PPi (an apparent association constant, $K_{app} = 5.9(3) \times 10^4 \, M^{-1}$) > ATP ($K_{app} = 9.2(8) \times 10^2 \, M^{-1}$) > ADP > adenosine monophosphate (AMP), $MeOPO_3^{2-}$, glucose-6-phosphate, and HPO_4^{2-} ($K_{app} = 1.3(2) \times 10^2 \, M^{-1}$) >> acetate, chloride, and fluoride (no response). The binding selectivity of **103** toward PPi over ATP (affinity difference factor, $K_{app}(PPi)/K_{app}(ATP) = 64$) is higher than that reported for a dinuclear Zn(II) complex (affinity difference factor = 40).[56] The effective fluorescence quenching by PPi likely comes from the formation of nonfluorescent hexa-coordinated stannate **105**, whereas the other phosphate ions give weakly fluorescent penta-coordinated complexes **104**.

104

**103** $ROPO_3^{2-}$ ⟶

$P_2O_7^{4-}$ ⟶   **105**

1.34.5.3.2   Boron compounds

Boronic acids and their esters form Lewis acid–base complexes with the PO or P—O^- groups of phosphate ions. Macrocyclic host **106** containing boronate and crown ether motifs recognizes

99   **100**   **101**   **102** (Tx = -CMe_2CHMe_2)
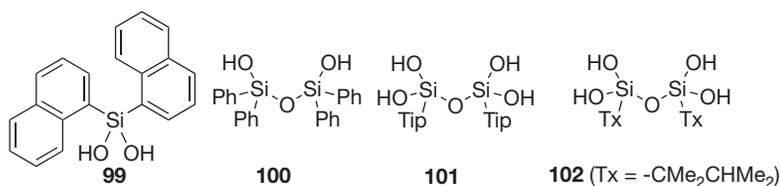
monophosphate ion in a MeCN/CHCl$_3$ mixture (9:1, v/v), resulting in the quenching of the PET from the anthracene moiety to the boronate ester and as a result the fluorescence intensity is increased.[57] The boronate ester is likely to be coordinated by the PO part of the bound monophosphate ion. Macrocyclic host **106** is highly selective to monophosphate ion (K_a/M^{-1}: 7.8×10^4 (H$_2$PO$_4^-$), 79 (HSO$_4^-$), 56 (acetate), and did not respond to chloride, bromide, and iodide).

106
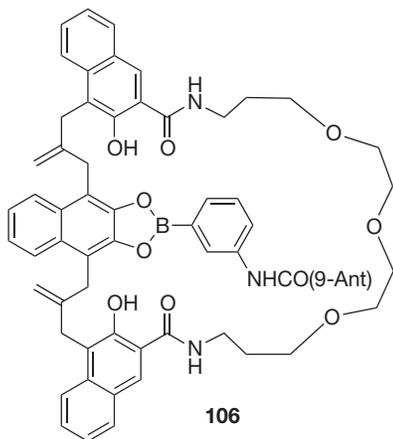
The three-component assembly **107**, which is in equilibrium with **108**, containing ARS, a boronic acid, and a Zn(II) complex, has been developed as a fluorescence turn-on probe for PPi in a MeOH–HEPES mixture (1:1, v/v).[58] The equilibrated mixture of **107** and **108** is only weakly fluorescent, probably because the nonfluorescent **108** is dominant rather than **107** under these conditions. PPi ditopically coordinates to the Zn(II) center and the boronate moiety, affording the PPi-bridged self-assembly **109** that shows intense fluorescence from ARS. The values of K_{app} for PPi, ATP, and ADP are $1.6 (4) \times 10^6$, $1.6(3) \times 10^5$, and $1.9(2) \times 10^4$ M^{-1}, respectively.
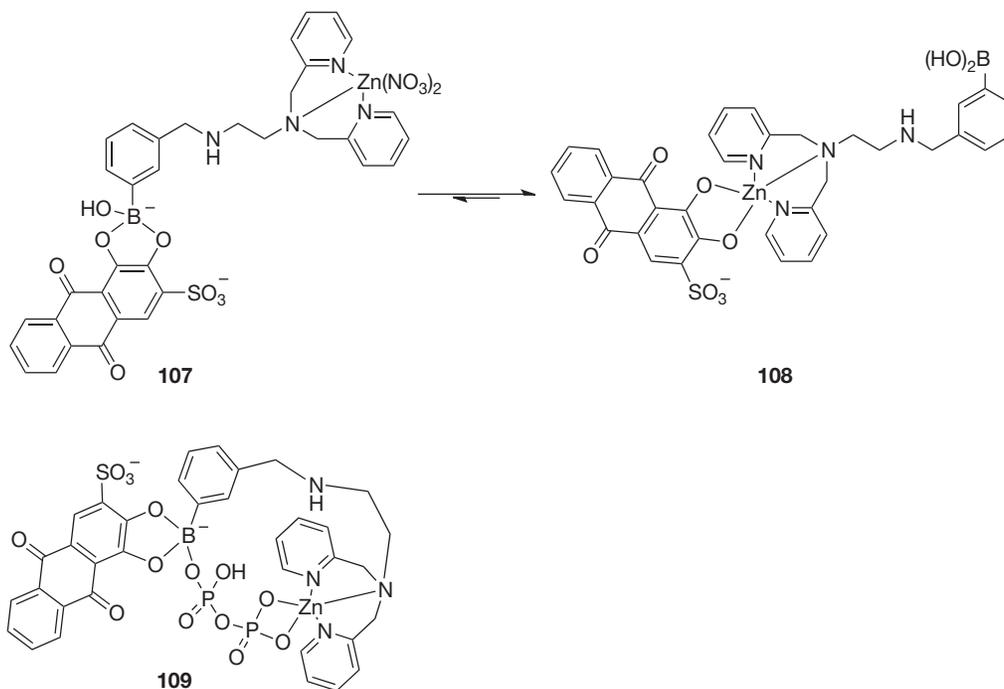
Table 5   The K_a values of **110** and **111** with the nucleotides in EtOH (in M^{-1}) estimated from the UV–vis titrations

|	AMP^{2-}	ADP^{3-}	ATP^{4-}
110	7.9×10^5	5.0×10^6	4.0×10^6
111	1.6×10^5	1.0×10^7	2.5×10^6

1.34.5.3.3   Zn(II) complexes

Zn(II) salophene complexes **110** and **111** react with nucleotides AMP^{2-}, ADP^{3-}, and ATP^{4-} to show the quenching of the fluorescence in EtOH (Table 5).[59] In contrast, inorganic phosphate ions (PO$_4^{3-}$, PPi, and P$_3$O$_{10}^{5-}$) do not affect the spectral properties of these probes, indicating that both the phosphate–Zn(II) interactions and the π–π stacking of the adenine parts with the aromatic rings of **110** and **111** are important for the complexation.

110   **111**
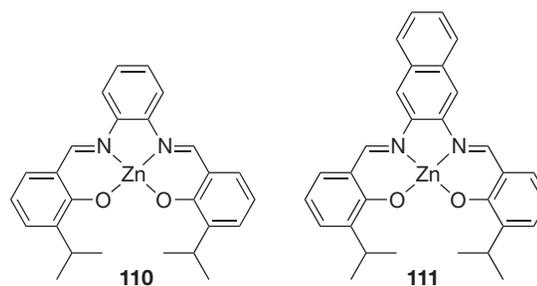
A fluorescent dinuclear Zn(II) complex **112** bearing a hydrophilic Schiff base ligand reacts with PPi, ATP, and ADP in aqueous HEPES solution to afford fluorescence turn-off responses.[60] The binding tendency is as follows: PPi ($K_{app} = 4.1 (4) \times 10^5$ M^{-1}) ≥ ATP ($K_{app} = 3.4(2) \times 10^5$ M^{-1}) > ADP ($K_{app} = 9.14(6) \times 10^3$ M^{-1}) >> monophosphates (including AMP),

**107**   **108**

109

acetate, hydrogencarbonate, halides (no response). The improved affinity toward PPi and ATP originates from the formation of two strong O—Zn bonds as well as electrostatic interactions between the highly charged anions and Zn(II) cations.


112
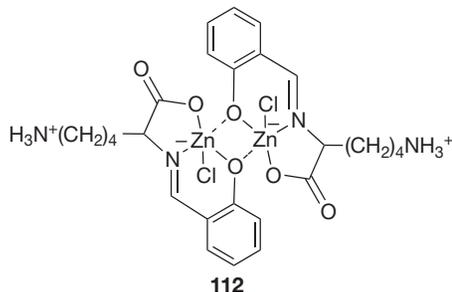
Hybrid **113** of a dinuclear Zn(II) complex and a fluorescein moiety shows fluorescence turn-on response toward PPi and nucleotides in water.[61] Free host **113** is nonfluorescent because the conjugation path of the fluorescein is destroyed by the addition of an oxygen atom that is coordinated to the two Zn(II) cations. Polyphosphate ions cleave the oxygen bridge to afford 1:1 complex **114** that contains the fully conjugated fluorescein moiety, resulting in the increase in the green fluorescence. Host **113** selectively binds polyphosphate, such as PPi $(4.0 \times 10^7 \text{ M}^{-1})$, ATP $(1.3 \times 10^6 \text{ M}^{-1})$, and ADP $(1.7 \times 10^6 \text{ M}^{-1})$, but does not respond to monophosphates (e.g., HPO_4^{2-}, AMP, and c-AMP) and nucleotide sugars, such as uracil diphosphate-galactose and adenosine diphosphate (ADP)-glucose.

Selectivity change in monophosphate versus PPi has been achieved by controlling the distance between two Zn(II) cations in a dinuclear Zn(II) motif.[62] Biphenyl-linked receptor **115** shows higher selectivity to PPi $(2.5 \times 10^4 \text{ M}^{-1})$ than monophosphate $(1.3 \times 10^3 \text{ M}^{-1})$ in HEPES buffer. In contrast, m-phenylene-linked receptor **116** shows the opposite trend (for PPi: $6.3 \times 10^2 \text{ M}^{-1}$, for monophosphate: $2.5 \times 10^4 \text{ M}^{-1}$) under the same conditions. The fluorescence responses of **115** to the phosphate ions are of interest: PPi intensifies the fluorescence, while monophosphate quenches it. This strange behavior is explained by taking into consideration that the phosphate ions change the dihedral angle of the biphenyl linker and affect the nature of the excited state.

Molecular tweezers **117** recognize polyphosphate ions, such as PPi and ATP, in MeCN–Tris HCl buffer (1:9, v/v) to show an increase in the fluorescence intensity because the polyphosphate ions bridge the two Zn(II) sites and facilitate the excimer formation of the two pyrene moieties. The association constants for PPi and ATP are $4.5(4) \times 10^6$ and $9.3(8) \times 10^4 \text{ M}^{-1}$, respectively. Monophosphate ions (e.g., AMP),


115   **116**
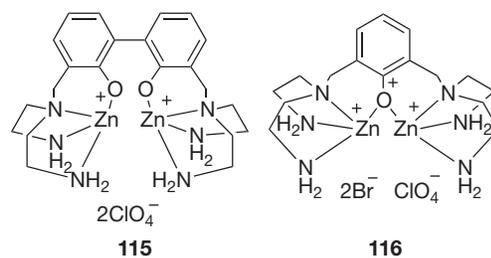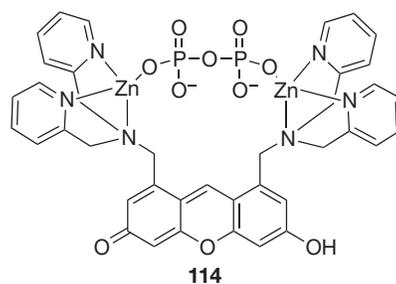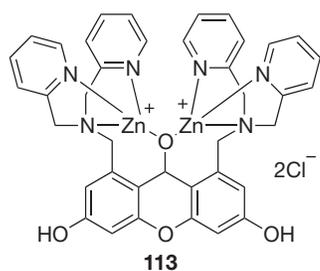
fluoride, and acetate do not react with **117**. The complexations also affect the Fe(II)/Fe(III) redox potential, which can be monitored by electrochemical methods.[63]


117
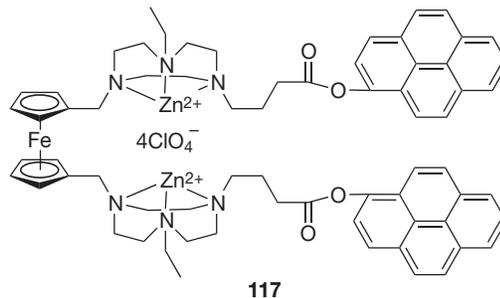
Polymeric phosphate sensors **118** and **119** have been synthesized by the hydrophobic self-assembly and photopolymerization of the corresponding diyne units.[64] These polymers are obtained as blue-colored vesicles dispersed in water. The Zn(II) sites are thought to locate on the surfaces of the double layers because of their hydrophilicity. In water, **118** and **119** react with PPi, ATP, and cyanide ion to show the color change to red and intensify the fluorescence emissions. These polymer probes show responses to ATP and PPi almost equally, whereas monophosphate ions, fluoride, and acetate do not affect the absorption and fluorescence of the probes.

1.34.6   Ion-Pair Detection

Organotin compounds bearing lariat-type crown ethers **120** and **121** form stable complexes with a specific combination of cations and anions. Recently much attention has been paid to such ion-pair receptors because of their possible use for membrane transport of the ion. Iodostannane-16-crown-5 hybrid **120** reacts with NaF in MeCN to afford the corresponding zwitterionic complex, [**120•**NaF] as an isolable, crystalline material.[65] Meanwhile, **121**, which has a 19-crown-6 moiety, selectively binds KF in MeOH to give [**121•**KF],[66] indicating

113   **114**

118   119

122   123
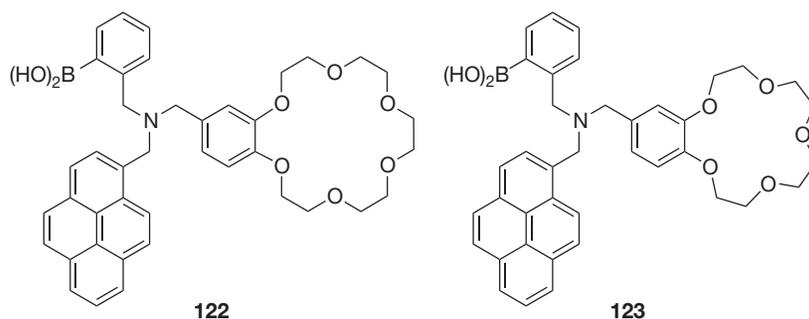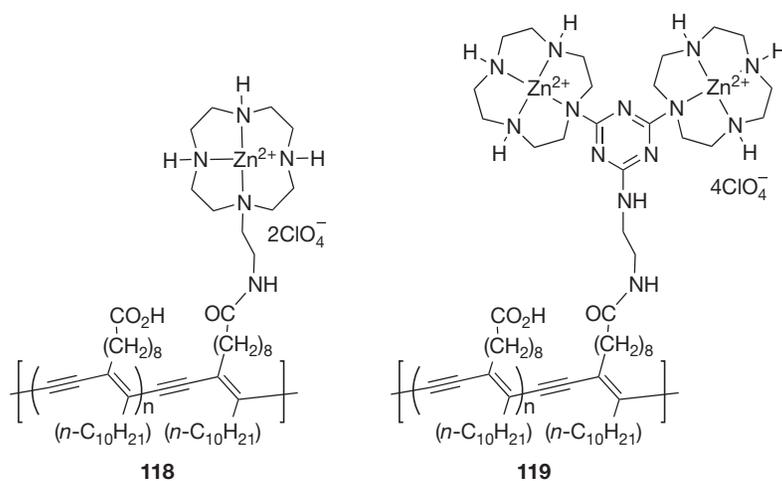
that the target ion pair can be changed by the size of the crown ether part. In both complexes, the bound fluoride ions coordinate to the two tin atoms in a μ^2-fashion. The complexation constants of these ion-pair receptors to the specific ion pairs have not been reported.

120   121
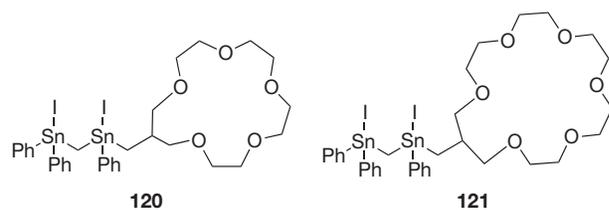
Ion-pair detection of fluoride ion with potassium ion was achieved by using boronic acid-crown ether-aminomethylpyrene hybrid molecules **122** and **123**.[67] They show a turn-on type fluorescence enhancement by addition of potassium fluoride, while no enhancement is observed with other potassium halides. Both boronic acid and crown ether moieties are critical to the enhancement fluorescence intensity upon the ion-pair recognition.

1.34.7   Conclusion

In this article, the development of molecular sensing of bioactive anions utilizing interaction between main group element Lewis acids and anions is summarized based on the papers that appeared in the last decade. The most important progress is

extremely large improvement of trapping ability by hybrids of main group element Lewis acids with cationic functional groups or chelate-type multi-interaction, demonstrating that recognition of fluoride and cyanide ions, which was possible only in organic solvents so far, can be carried out in aqueous media. In fact, the possibility of its application to life and environmental sciences is going to increase. In future, it is strongly desirable to achieve quantitative anion recognition in environmental water and a living body by increasing recognition ability against anions as well as by decreasing effects of the sensors on a living body and the environment.

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