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A class of fascinating optoelectronic materials: Triarylboron compounds

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Triarylboron compounds are significant optoelectronic materials due to their excellent emissive and electron-transport properties, and could be applied in organic light-emitting diodes as emissive and/or electron-transport layers. Triarylboron compounds have vacant p_π orbital and have received increasing interest as fluoride ion and cyanide ion sensors utilizing specific Lewis acid-base interaction. This review summarizes their structural characteristics, optical properties and applications in chemosensors for anions and optoelectronic devices developed in recent years and discusses the problems and prospects.

OLEDs, optical properties, sensors, structure-property relationships, triarylboron compounds

1 Introduction

Triarylboron compounds have emerged as a significant class of optoelectronic materials because of their intriguing electronic and optical properties [1–5]. Triarylboron compounds (Figure 1) are isoelectronic and isostructural with a positively charged carbocation. With its vacant p_π orbital, the boron center is inherently electron deficient and often acts as a strong π-electron acceptor, which may lead to significant delocalization when conjugated with an adjacent organic π-system [1] and is responsible for some excellent properties, such as the formation of charge-transfer states when accompanied by electron donors and highly efficient emission in both solution and solid states. These properties have permitted their potential uses for various photonic and optoelectronic applications, such as luminescent sensors for anions [6–10], emitters and charge-transport materials in organic light-emitting devices (OLEDs) [11–15], and two-photon excited emitters [16, 17].

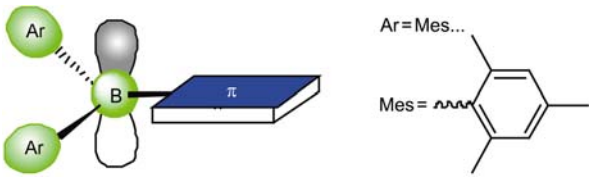


Figure 1 Structure of triarylboron compounds.

The application of triarylboron compounds as anion sensors utilizes the specific Lewis acid-base interaction between the boron center as Lewis acid and anions as Lewis base. The complexation of the boron π-electron systems with anions would interrupt the π-conjugation extended through the boron center, causing the variation in photophysical properties. Bulky *ortho*-substituted aryls, such as mesityl (2,4,6-trimethylphenyl, Mes in Figure 1), are often employed to protect the boron center from nucleophilic attack because of the electrophilicity of triarylboron. Such bulky *ortho*-substituted aryls could also render the Lewis

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acidic p_π orbital on the boron center inaccessible to all but the smallest anions such as fluoride and cyanide. Hence, highly sensitive and selective detection for fluoride and cyanide could be realized. In addition, the application of triarylboron compounds in OLEDs is very promising due to their excellent emission and charge-transport properties.

In this paper, the photophysical properties and structure-property relationships of triarylboron compounds are summarized and their applications in luminescent sensors for anions and OLEDs are reviewed.

2 Basic properties of triarylboron compounds

2.1 Structural characteristics of triarylboron compounds

Triarylboron compounds have interesting optical and electronic properties. However, they are often unstable due to the electrophilicity of triarylboron. One common strategy for the enhancement of their kinetic stability could be achieved by steric hindrance of the p orbital using bulky substituents. In particular, the mesityl group is often selected as the bulky substituent. It has been demonstrated that two mesityl groups were sufficient to provide an unusual degree of stability [18]. Therefore, the compounds containing dimesitylboryl ($BMes_2$) groups are significant triarylboron compounds.

The typical design of mesitylboryl-functionalized chromophores is according to the following two structural principles: (1) $BMes_2$ substituents as electron acceptors are placed either at one terminal position of the molecular long axis in push-pull systems or at both terminals (Figure 2(a)), which could extend the π-system; (2) $BMes_2$ substituents are introduced at the lateral positions of the π-conjugated framework, leading to novel emissive properties (Figure 2(b)) [3].

2.2 Photophysical and excited state properties of triarylboron compounds

Williams *et al*. [18] had demonstrated that triarylboron compounds with donor-π-acceptor structures have high quantum yields than those only with acceptors because of the promotion of donor-acceptor charge-transfer upon excitation with light. For instance, in cyclohexane, the quantum yields of **1** and **2** (Figure 3) with donor-π-acceptor structures were 0.88 and 0.42, respectively, whereas **3** (Figure 3) only with acceptors showed very low quantum yield of 0.016. The different quantum yields of **1** and **2** revealed that the electron-donating ability of the donor could influence the photophysical properties of triarylboron compounds. Therefore, the triarylboron compounds with donor-π-acceptor structures have been a class of promising optoelectronic materials.

Not only the donor but also the π-linker could influence the photophysical properties of triarylboranes [16, 17]. Stilbene- and styrylthiophene-based donor-π-acceptor type compounds with the $BMes_2$ group as the acceptor (**4–11** in Figure 4) were prepared to investigate the influence of the π-linker.

Compounds **4–11** exhibited strong two-photon-excited fluorescence (TPEF) in a wide spectral range from blue (466 nm) to green (564 nm). The styrylthiophene backbone was found to be less effective than the stilbene π-system in enhancing the efficiency of TPEF because the heavy sulfur atom in thiophene may enhance intersystem crossing or other non-radiation processes to quench fluorescence. However, the replacement of the strong donor dialkylamino with the moderate donor diarylamino results in a significantly increased quantum yield, which may be attributed to the larger delocalization of lone pair electrons and, therefore, a

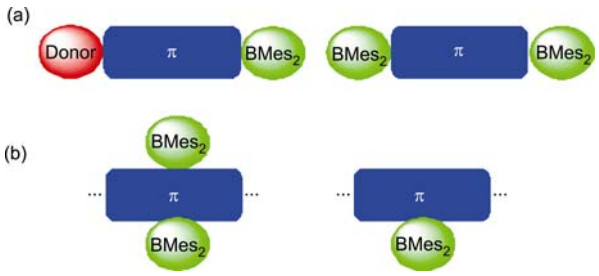


Figure 2 Schematic presentations of π-conjugated systems containing the $BMes_2$ group (a) at the terminal positions, and (b) at the lateral positions.

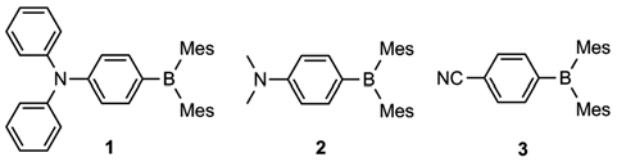


Figure 3 Structures of some triarylboron compounds.

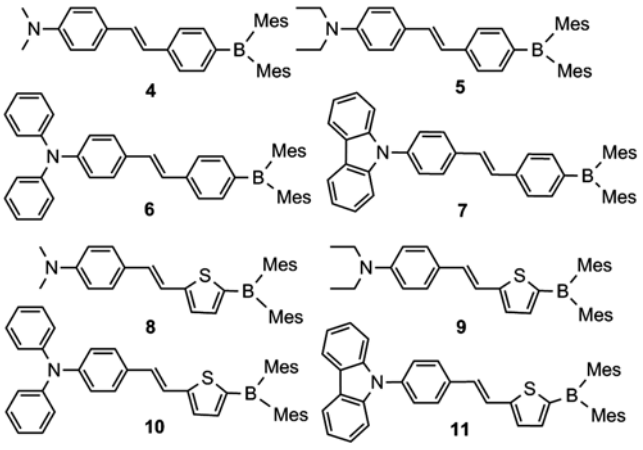


Figure 4 Stilbene- and styrylthiophene-based donor-π-acceptor type triarylboron compounds.

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larger molecular stabilization effect for the excited state of the aromatic arylamino groups.

All the above triarylboron compounds were based on the π-skeleton with $BMes_2$ substituents at the terminal position. Yamaguchi *et al*. [19] introduced $BMes_2$ groups at the lateral positions of π-conjugated framework and synthesized a class of novel boron-based π-electron compounds (**12–15** in Figure 5). In both solution and solid states, intriguing intense fluorescence properties were found for these compounds. For example, **12** exhibits a very intense emission at 536 nm with a quantum yield of 0.99 in cyclohexane and an emission at 562 nm retaining a high quantum yield of 0.90 in the spin-coated film. This was because the sterically bulky skeleton could prevent the intermolecular interaction and consequently the nonradiative energy migration through the Dexter mechanism. According to this design principle, they also prepared compounds **16–20** (Figure 5) based on 3-boryl-2,2′-bithiophene-based π-conjugated materials as a new highly emissive system. The employment of the bithiophene as an electron-donating π skeleton allowed them to achieve not only intense solid-state emission, but also full-color emission covering a wide range from blue (477 nm) to deep red (660 nm) through modifying the donors [20]. These studies provided a new design principle for triarylboron compounds.

Conjugated triarylboron polymers, due to their high delocalization through the empty p-orbital of the boron atom, are new π-conjugated polymers and have attracted much attention in recent years. Yamaguchi *et al*. [21] incorporated diborylphenylene into the poly(aryleneethynylene)-type systems and synthesized polymers **21–25** (Figure 6). All these polymers showed an intense emission not only in solution but also in the solid state. Polymer **21** exhibits an intense bluish-green emission at 487 nm with a high quantum yield of 0.85 in benzene and retains a high quantum yield of 0.62 even in the thin film, suggesting the utility of the incorporation of diborylphenylene skeleton into poly(aryleneethynylene) systems for preventing interactions between the conjugated backbones. Lambert *et al*. [22]

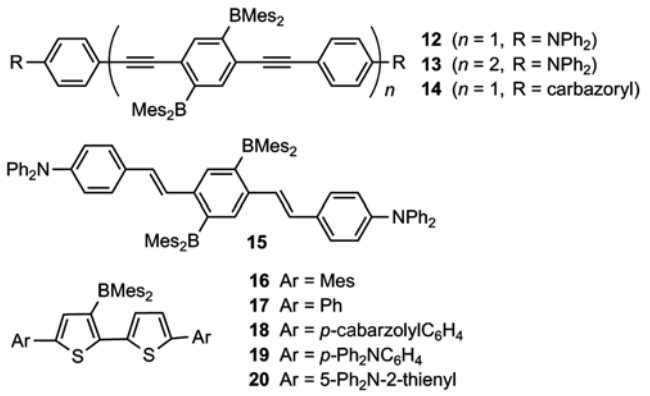


Figure 5 Triarylboron compounds with the $BMes_2$ group at the lateral position.

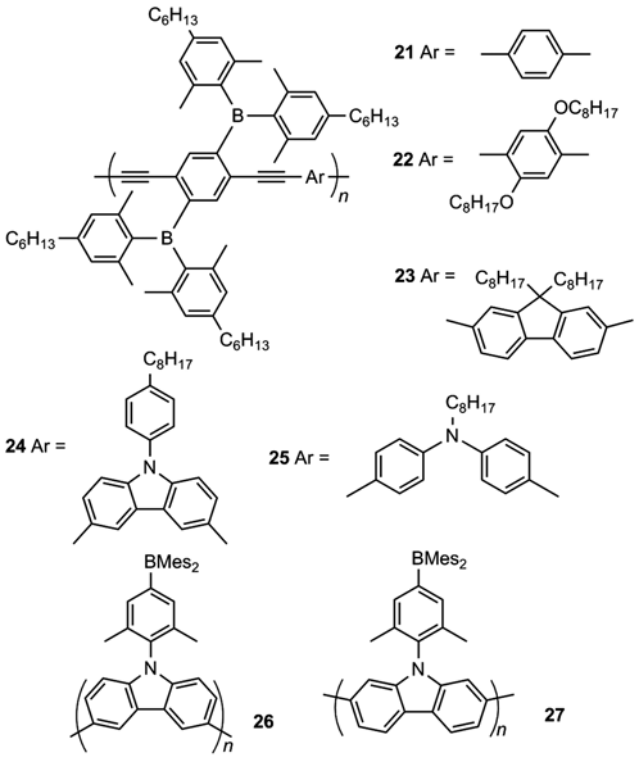


Figure 6 Polymers containing the boryl group.

demonstrated that the link position of polycarbazoles containing $BMes_2$ group has an influence on their absorption and emission properties. The introduction of triarylborane acceptor in polymer **26** (Figure 6) has a strong impact on the optical properties of this 3,6-linked carbazole main chain polymer and results in an enhanced fluorescence quantum yield due to a low-lying fluorescent charge-transfer state, while the same acceptor substituent does not influence the optical properties of 2,7-linked polycarbazole (polymer **27** in Figure 6). This is assigned to the effective conjugation along the polymer backbone for polymer **26**, which results in a polymer state being lower in energy than an intramolecular charge transfer state involving the boron and nitrogen centers. Polymer **26** is a blue emitter with Commission International d'Eclairagee (CIE) coordinates of (0.17, 0.21) and a reasonably high quantum yield in both solution and solid states, indicating the possible application in OLEDs.

3 Triarylboron compounds as chemosensors for anions

3.1 Fluoride ion sensors based on triarylboron compounds

Chemosensors are one of the most effective methods in detecting ions [23, 24]. Fluoride anion (F^-), the smallest anion, plays an essential role in a broad range of biological, medi-

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cal, and chemical processes and in applications such as dental care, treatment of osteoporosis, fluorination of water supplies, and even chemical and nuclear warfare agents [25–27]. As a result, its recognition and detection are of growing interest. Recently, specific Lewis acid-base interactions, such as the strong affinity of a boron atom toward F^-, have been adopted as an efficient approach for fluoride detection due to the high sensitivity and selectivity [28, 29]. Some triarylboron compounds with a donor-π-acceptor chemical structure [1], in which the $BMes_2$ group was adopted as the electron acceptor, were reported to be highly selective colorimetric chemosensors. In the presence of F^-, the strong B-F interaction could interrupt the extended π conjugation of these organoboron derivatives, thereby causing an evident change in the photophysical properties.

3.1.1 Fluorescent fluoride sensors based on organic triarylboron compounds

3.1.1.1 Fluoride detection in organic media U-shaped and V-shaped triarylboron compounds, due to their unusual photophysical properties of the donor-π-accepter molecules and the various potential applications of switchable dual emission (through-space charge transfer and π-π* transition) systems, have attracted much attention. Wang *et al*. [29] prepared two U-shaped branched organoboron compounds **28** and **29** (Figure 7). Both of them displayed distinct fluorescent responses to F^-. The addition of F^- to a solution of **28** quenched the emission due to the occupation of the empty p_π orbital of boron by F^-. Thus, **28** can be described as a "turn-off" sensor for F^- (see Figure 7). The response of **29** to F^- is in sharp contrast to that of **28**. Instead of fluorescence quenching, the addition of F^- changed the color of **29** from green to blue and the emission intensity was significantly enhanced due to the charge-transfer emission between the N donor and the B acceptor as well as π*-π emission localized on the N donor, thus producing a sensitive and selective "turn-on" fluorescent sensor for F^- (see Figure 7).

Under the new design strategy, they prepared three V-shaped branched organoboron compounds (**30–32** in Figure 8) [30]. The emission color of these compounds changed evidently after addition of F^-, which was attributed to the dual fluorescent emission. Liu *et al*. [31] prepared a novel V-shaped branched triarylboron compound **33** (Figure 8) containing a phenylamino group as a π-electron donor, fluorene groups as π-bridges and $BMes_2$ groups as electron acceptors and investigated its F^- recognition properties. **33** was able to recognize F^- in high sensitivity. The association constants of **33** with F^- were determined as $K_1 = 3.5 \times 10^5$ M^{-1} and $K_2 = 1.1 \times 10^5$ M^{-1}, indicating that **33** could recognize F^- with high sensitivity.

In addition to the U-shaped and V-shaped triarylboron compounds, Mullen *et al*. [28] prepared two $BMes_2$ substituted ladder-type pentaphenylenes (**34** and **35** in Figure 9) and studied their sensing properties. **34** acts as a colorimetric and fluorescent chemosensor with high sensitivity and

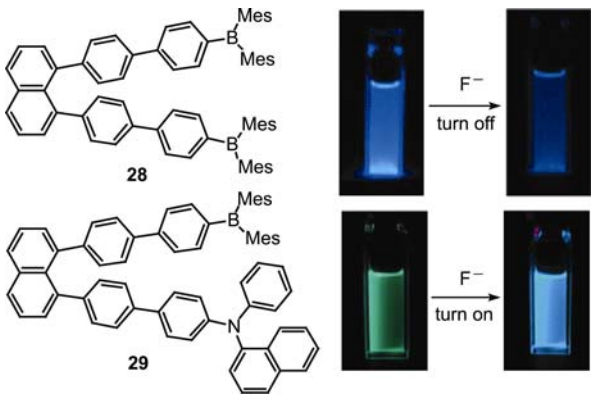


Figure 7 U-shaped triarylboron compounds as "turn on" and "turn off" fluoride sensors (Adapted from ref. [29]).

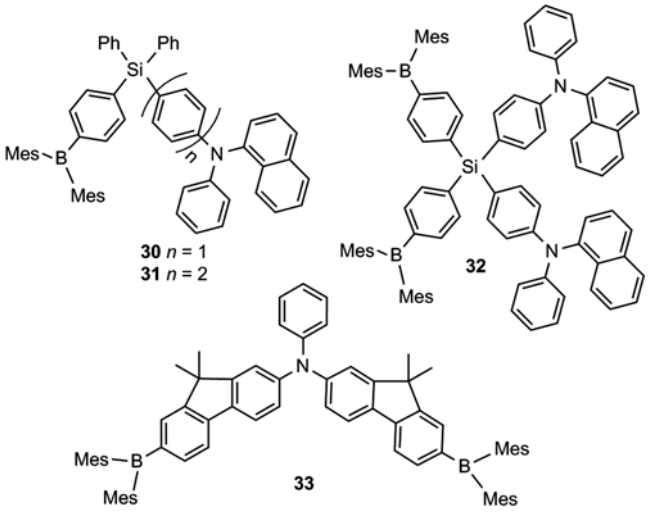


Figure 8 V-shaped triarylboron compounds as fluoride sensors.

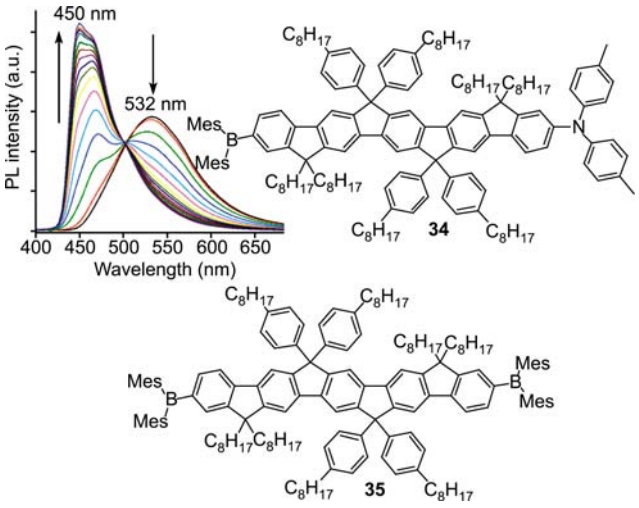


Figure 9 Ladder-type pentaphenylenes **34** and **35** and PL spectra of compound **34** upon addition of F^- (adapted from ref. [28]).

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selectivity for F^- over other halogen ions. With the stepwise addition of F^-, the charger-transfer emission band at 532 nm is turned off and a new blue emission band at 450 nm is turned on (see Figure 9), due to the inhibition of the charge transfer from the N center to the B center, even though the distance between B and N centers is as long as 22 Å. A charger-transfer emission was observed for **35** with two $BMes_2$ groups, which can be used as F^- sensory material utilizing the switched "on" and "off" of charger-transfer emission. This is the first report about intramolecular charger-transfer emission between the two B centers.

The output signals for the above sensors were all based on single-photon absorption and emission. Two-photon chemosensors, due to their intrinsic high three-dimensional resolution and the penetrating ability of the excitation light, have aroused great research interest in recent years. Liu *et al*. [32] designed two highly selective two-photon chemosensors for F^- based on compounds **6** and **10** (Figure 4). Taking compound **6** for example, the addition of F^- caused the characteristic strong absorption band of **6** at 400 nm to completely disappear, and a new band centered at 370 nm appeared. The color of **6** also changed from green to colorless (see Figure 10), with the binding constant of 2.3 (±0.3) $\times 10^5$ M^{-1}. The single-photon excited fluorescence (SPEF) emission spectra of **6** displayed apparent changes when F^- was added. However, the two-photon excited fluorescence (TPEF) spectrum of **6-F** is different from SPEF of **6-F**. No apparent TPEF signal is recorded under the excitation of femtosecond laser from 730 to 800 nm, indicating that **6-F** is not TPEF-active. Thus, these organoboron compounds are shown to be two-photon fluorescent sensors for F^- with high sensitivity and selectivity.

3.1.1.2 Fluoride detection in aqueous media All fluoride sensors discussed above realized the detection in organic solvents with the binding constants ranging from 10^5 to 10^6 M^{-1}. Owing to the high hydration enthalpy ($\Delta H° = -504$ kJ/mol) of F^-, it is problematic to realize the detection in aqueous systems [33, 34]. In order to increase the compatibility of these fluoride receptors with aqueous environments, bidentate boranes [34–36] whose F^- affinity exceeds that of their monofunctional analogs by at least three orders of magnitude, have been investigated recently. Gabbaï *et al*. [34] designed a sensor necessitating the incorporation of a chromophoric boron moiety in a bidentate Lewis acid (**36** in Figure 11). The addition of F^- to a solution of **36** causes a steady and linear decrease of the absorbance at 363 nm, which reaches the baseline after a total addition of exactly one equivalent of F^-. Further addition of F^- does not lead to additional perturbation of the spectrum, indicating the formation of a 1:1 complex with a binding constant of 5×10^9 M^{-1}, which is remarkably high and by far exceeds that measured for monofunctional borane receptors. In an extension of this research, they have investigated the synthesis of heteronuclear bidentate Lewis acids, such as **37–39** (Figure 11), which also have high fluoride affinity [34–36].

Bidentate boranes show an increased fluoride affinity but remain incompatible with aqueous solutions. Studies of several groups have demonstrated that boron based receptors that are bidentate and cationic capitalize on both Coulombic and cooperative effects leading to a further enhancement of their F^- affinity. Consequently, F^- detection in aqueous media could be realized [37–40]. In order to recognize F^- in water solution, Gabbaï *et al*. [37–40] developed a number of cationic boranes (**40–44** in Figure 12). These compounds were able to bind with F^- in organic solvent/water mixed solution with high sensitivity and selectivity. They also realized the complexation of cationic boranes (**45–48** in Figure 12) with F^- in water below the 4 ppm maximum contaminant level set by the Environmental Protection Agency (EPA) [41]. The titration experiment monitored by UV-vis spectroscopy provided information on the fluoride affinity of these molecules. The resulting titration data were fitted to a 1:1 binding isotherm with fluoride binding constants of 840 (± 50) M^{-1}, 2500 (± 200) M^{-1}, 4000 (± 300) M^{-1}, and 10500 (± 1000) M^{-1} for **45–48**, respectively. These results show that the fluoride binding constant increases with the increase of hydrophobicity of the borane. The replacement of the $PMePh_2$ moiety of **45** with a PPh_3 moiety in **48** results in an increase of the fluoride binding constant by more than 1 order of magnitude. In addition, the acidity of **48** enhances with the increase of

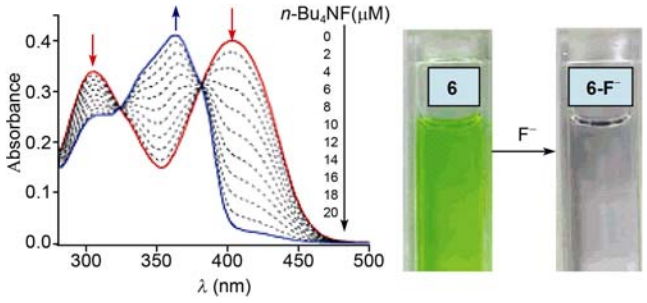


Figure 10 Changes in UV-vis absorption spectra (right) and the color change response of **6** (10 μM) at 20 °C in THF upon the addition of F^- (adapted from ref. [32]).

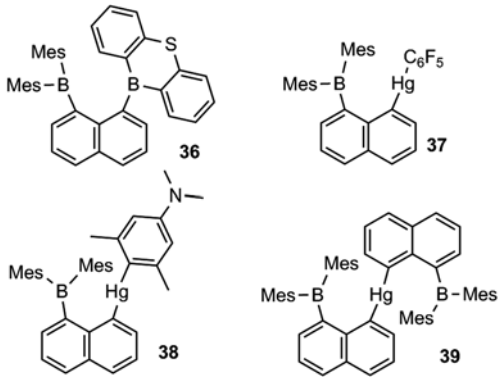


Figure 11 Structures of bidentate boranes.

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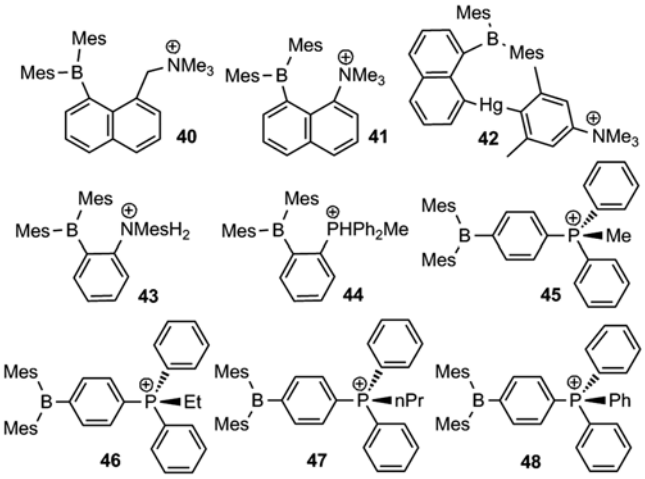


Figure 12 Structures of cationic boranes.

solution polarity and the resulting fluoride binding constant in pure water is equal to 30000 (± 5000) M^{-1}. They also measured the extent of absorbance quenching experienced by **48** in the presence of F^- in pure water. At pH 4.9, a readily detectable 63% quenching of the absorbance was observed, thereby demonstrating that **48** could be used as a chemosensor for drinking water analysis.

3.1.2 Phosphorescent fluoride sensors based on heavy-metal complexes containing $BMes_2$ groups

The output signals of most fluoride chemosensors are limited to fluorescence signals. Compared with the fluorescence signals, phosphorescence signals have many advantages, such as emission color shifts with the changes in local environment, significant Stokes shifts for easy separation of excitation and emission, and relatively long lifetimes compared to purely organic luminophores. Especially, the long lifetime of phosphorescence could eliminate the interference of the short-lifetime background fluorescence and scattering light by using a time-resolved luminescence technology. Gabbai *et al*. [34] reported the first example of a phosphorescent F^- sensor based on a heteronuclear B/Hg bidentate Lewis acid **37** (Figure 11). The titration experiment indicated the formation of a 1:1 complex with the binding constant of more than 10^8 M^{-1}. While repeated in a 90:10 (*v*:*v*) THF/water mixture, the stability constant was as high as 2.3 (± 0.2) × 10^4 M^{-1}. However, this phosphorescent F^- sensor could only be realized at a low temperature (77 K), limiting the scope of its use. Therefore, room temperature phosphorescent anion sensors were necessary. Wang *et al*. [42] prepared one Pt(II) complex containing the $BMes_2$ group (**49** in Figure 13), which displayed bright yellow-green phosphorescence in the solid state at ambient temperature with emission wavelengths at 519 nm (τ = 10.9 μs). The addition of F^- to the solution of **49** causes a phosphorescent color switch from yellow to green, serving as a "naked-eye" indicator of F^-. ^{19}F NMR and UV-vis titration experiments also

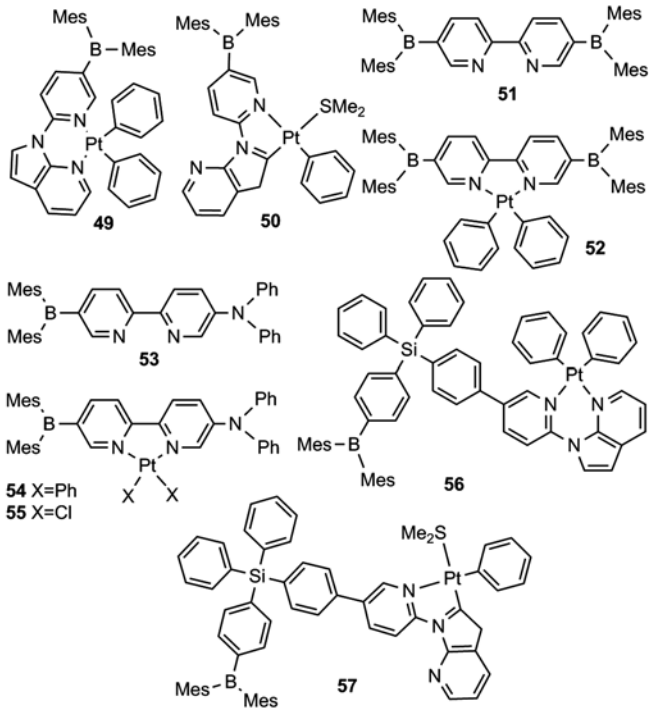


Figure 13 Fluoride sensors based on Pt(II) complexes containing the $BMes_2$ groups.

confirmed the complexation of F^- with boron atoms.

Complexes **50**, **52** and **54–57** are other examples of phosphorescent fluoride sensors based on Pt(II) complexes containing $BMes_2$ groups [8, 43, 44]. For these complexes and the corresponding ligands containing $BMes_2$ groups, the electron-accepting ability or the Lewis acidity of the boron center could be significantly enhanced by metal chelation/binding to a conjugate triarylboron ligand [8], and consequently the affinity of the boron center for F^- would be increased, leading to the development of more sensitive and versatile sensing systems. Wang *et al*. [8] synthesized **51** and its Pt(II) complex **52** (Figure 13) and examined the impact of metal chelation on Lewis acidity of **51**. Cyclic voltammetry diagrams demonstrated that the electron-accepting ability of **51** was significantly enhanced by metal chelation. The metal complex is capable of binding to F^- with a high selectivity. The addition of 1 equiv of F^- changes the color of **52** from red to orange, and further addition of 1.5 equiv of F^- changes **52** from orange to light yellow. This two-stage color change is attributable to the formation of a 1:1 adduct and a 2:1 adduct, with the F^- binding constants K_1 and K_2 of 10^9 and 10^6 M^{-1}, respectively. They also prepared conjugated triarylboryl donor-acceptor ligand **53** (Figure 13) [43] and investigated the impact of metal-chelation on intraligand charge transfer emission. **53** displays a "turn-on" fluorescent response while **51** has a "turn-off" response upon binding with fluoride ions. Complexes **54** and **55** based on ligand **53** display room temperature phosphorescence in solution that has a dramatic "turn-on" response

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toward F^- with color change from orange or red-orange to whitish blue-green, attributed to the switch of the excited state from an N-B charge transfer transition to a π-π* transition on ligand **53**. The binding constants with F^- for these two complexes were estimated to be 7.0×10^5 and 5.0×10^6 M^{-1}, respectively. The conjugated donor-acceptor Pt(II) complexes **49** and **50** also showed bright and fluoride-switchable phosphorescence at ambient temperature, but they were not dual emissive and showed solely metal-to-ligand charge-transfer-based phosphorescence. For non-conjugated donor-acceptor triarylboron–Pt(II) complexes **56** and **57** (Figure 13), they displayed ambient temperature singlet–triplet dual emission which was due to acceptor-based Mes-B charge transfer and donor-based ^{3}π-π* transitions, respectively. However, the phosphorescent efficiency of **57** was higher than that of **56** due to the formation of a more stable chelate ring [44]. The singlet-triplet dual emission in the non-conjugated system could be perturbed selectively by F^- through binding to the boron receptor site, thus providing a new strategy for the development of sensing systems based on singlet-triplet switching.

Ir(III) complexes, as one of the best phosphorescent dyes [45–47], could also be used as highly selective phosphorescent chemosensors for F^-. Most recently, we introduced $BMes_2$ groups into the cyclometalated ligands and prepared cationic Ir(III) complex **58** (Figure 14) [48]. Its absorbances at 290 and 350 nm decreased gradually whereas that at 400 nm increased, corresponding to an isosbestic point at 379 nm when F^- was added to a solution of **58** (see Figure 15). It induced a change in the solution color from yellow to orange-red and phosphorescent quenching, indicating that **58** could act as an excellent on-off-type phosphorescent chemosensor for F^- and could serve as a "naked-eye" indicator of F^-. The ^{11}B NMR spectra of **58** before and after the addition of F^- have verified that **58** could form a 1:2 complex with 2 equiv of F^-, with the binding constants of 1.29×10^6 and 4.27×10^5 M^{-1}, respectively. Addition of a large excess of other anions causes slight changes, indicating that **58** displayed a high selectivity in sensing F^-. We prepared a novel cationic Ir(III) complex containing both triarylboron and carbazole moieties (**59** in Figure 14) which could also be used as a highly selective phosphorescent sensor for F^- [49]. The binding of F^- to **59** quenched the phosphorescent emission from Ir(III) complex and switched on the fluorescent emission from N^N ligand, corresponding to a visual change in the emission color from orange-red to blue, and enabling colorimetric as well as ratiometric fluoride ion sensing (see Figure 16), paving a new guideline for the further design of excellent phosphorescent ratiometric probes utilizing the switchable triplet and singlet emissions. Park *et al.* [50] designed and prepared an excellent phosphorescent F^- sensor with a high signal-to-noise ratio based on a neutral Ir(III) complex **60** (Figure 14). **60** exhibited both extremely high selectivity toward F^- with a binding constant of 9.17 $(\pm0.32)\times10^4$ M^{-1} and high-efficiency two-color phosphorescence behavior at room temperature, enabling colorimetric

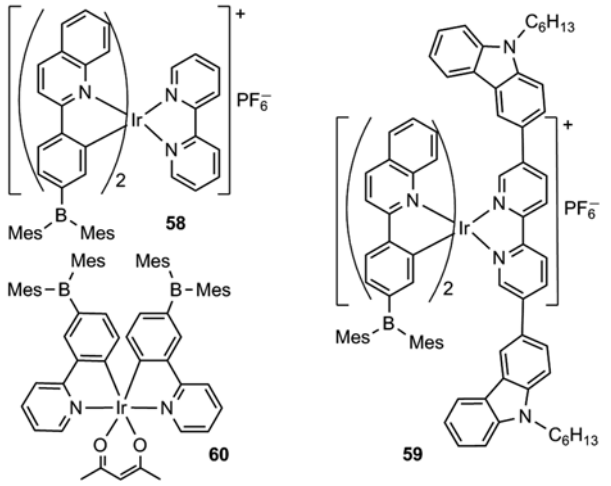


Figure 14 Highly selective phosphorescent chemosensors for fluoride based on Ir(III) complexes.

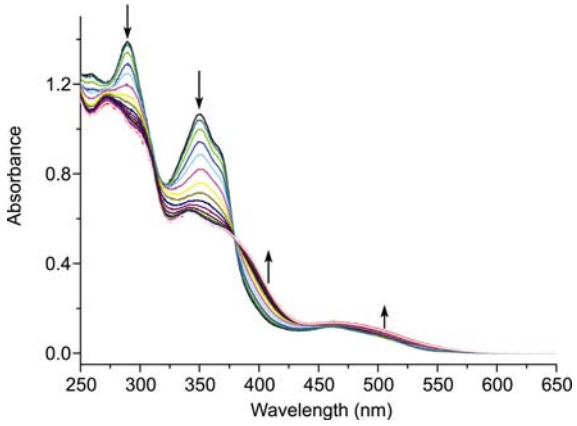


Figure 15 Change in the UV-vis absorption spectra of **58** (20 μM) in a CH_3CN solution with various amounts of F^- (adapted from ref. [48]).

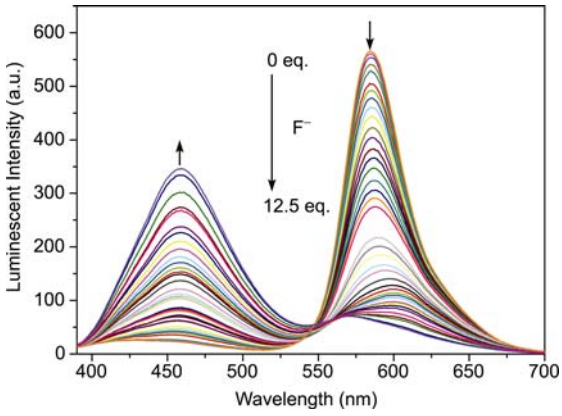


Figure 16 Change in the emission spectra of **59** (20 μM) in a CH_3CN solution with various amounts of F^- excited at 379 nm (adapted from ref. [49]).

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as well as ratiometric F^- sensing. Highly effective signal purification was demonstrated using time-gated acquisition of the phosphorescent signals to enhance the signal-to-noise ratio.

In addition to the Pt(II) and Ir(III) complexes, Yam *et al.* [51] introduced triarylboron moiety into Re(I) complexes (**61–63** in Figure 17) through an alkynyl ligand. UV-vis absorption and emission spectra were carried out to investigate the anion-binding abilities of these Re(I) complexes. Upon addition of F^- to a solution of **61**, the dramatic color changes (yellow to red) could be readily noticeable by naked eyes. The detection limit of the F^- was found to be 3.8 $(\pm 0.2) \times 10^{-6}$ M. Similar detection properties were observed in complexes **62** and **63** (Figure 17).

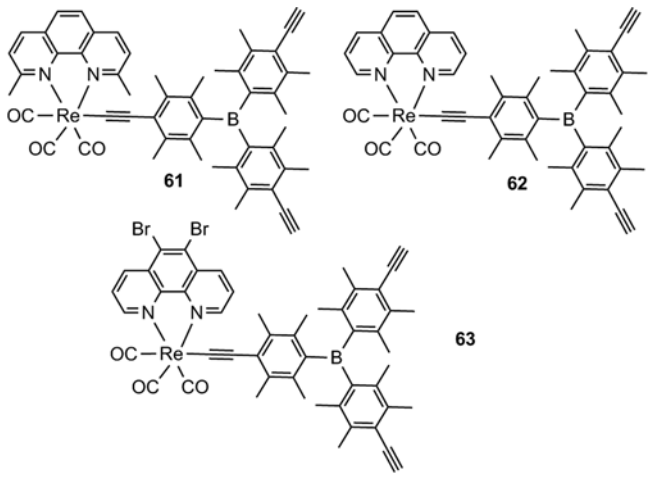


Figure 17 Highly selective phosphorescent chemosensors for fluoride based on Re(I) complexes.

3.2 Cyanide ion sensors based on triarylboron compounds

Cyanide ion (CN^-) sensing is of interest because of its high toxicity, which binds to and deactivates the cytochrome *c* oxidase enzyme with sometimes fatal consequences, in physiological systems, as well as environmental concerns arising from both research and the widespread industrial uses of CN^- [52]. For these reasons, the development of methods that could sense this anion has become a topical objective. Some triarylboron compounds can be used as CN^- sensors utilizing the specific Lewis acid-base interaction.

Lee *et al.* [53] combined triarylboron as a donor and highly fluorescent difluoroborondipyrromethene (BODIPY) as an acceptor to construct a discrete and highly fluorescent triarylboron-based receptor that utilizes intramolecular excitation energy-transfer transitions for the selective detection of CN^-. UV-vis and photoluminescence experiments were carried out to examine the CN^- binding properties of **64** (Figure 18). Addition of CN^- to a THF solution of **64** changed the color from greenish to colorless, indicating the decomposition of BODIPY moiety. It also leads to the formation of 1:1 complex **64-CN** with a stability constant exceeding 10^7 M^{-1}. While the presence of 10 equiv of other anions such as Cl^-, Br^-, I^-, OAc^-, NO_3^-, $H_2PO_4^-$, SCN^-, HSO_4^- and ClO_4^- does not significantly affect the UV-vis absorption and emission bands of **64** in THF, indicating high selectivity for CN^-.

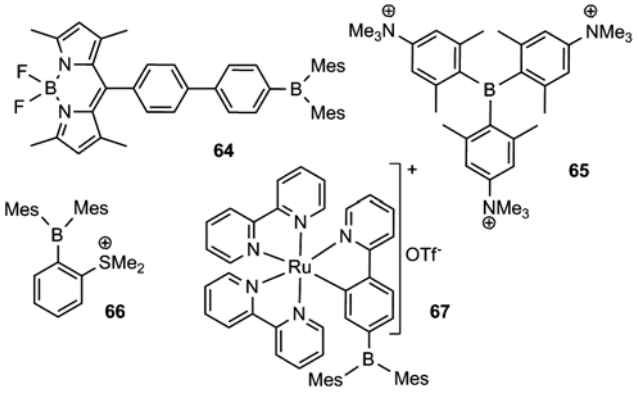


Figure 18 Cyanide ion sensors based on triarylboron compounds.

40 (Figure 12) is one type of cationic boranes which serves to enhance the Lewis acidity of boron center by Coulombic effects [37]. Owing to favorable Coulombic effects, **40** has a very high affinity for CN^- with a binding constant of 3.9 $(\pm 0.1) \times 10^8$ M^{-1} in 60:40 (*v*:*v*) H_2O/DMSO mixture (HEPES 6 mM, pH 7) and shows a negligible response in the presence of other common anions including Cl^-, Br^-, I^-, NO_3^-, OAc^-, $H_2PO_4^-$, and HSO_4^-. However, as was mentioned before, **40** could also bind with fluoride with a binding constant of 5.0 $(\pm 0.5) \times 10^6$ M^{-1} in 75:25 (*v*:*v*) THF/MeOH mixture, which is decreased by two orders of magnitude. Thus, the competition between fluoride and cyanide existed and we concluded that the competition between fluoride and cyanide could be measured by the binding constant.

More recently, one triarylboron compound **65** (Figure 18) containing multiple cationic groups which produce additive effects on the electron deficiency and Lewis acidity of the boron center was reported [54]. **65** was soluble in pure water and could not bind F^-. However, **65** could bind CN^- and converted into $\mathbf{[65\text{-}CN]^{2+}}$, which resulted in the progressive quenching of the absorbance at 307 nm with excellent selectivity. Acidification of the solution does not lead to the dissociation of $\mathbf{[65\text{-}CN]^{2+}}$, suggesting that its formation is irreversible. This is the first chemosensor for the highly toxic CN^- in pure water and the strategy of peripheral decoration with cationic groups paves a new way for increasing the anion affinity and water solubility of the boranes. Owing to the presence of low lying σ* orbitals, sulfonium ions are inherently Lewis acidic and could interact with electron-rich substrates to form donor-acceptor complexes. Gabbaï *et al.* [55] designed a CN^- receptor **66** (Figure 18) containing accessible sulfonium ions. Addition of 50 ppb of CN^- to a 4.0 μM solution of **66** in pure water re-

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sulted in a 33% quenching of the fluorescence after one hour. The presence of 0.2 ppm of CN^- almost quenched the fluorescence completely. Thus, **66** is one of the rare molecular systems competent for CN^- sensing at the sub-parts per million level in pure water.

Phosphorescent heavy-metal complexes containing $BMes_2$ groups can also be used as CN^- sensors. Gabbaï *et al.* [56] synthesized a triaryl borane **67** (Figure 18) decorated by a cationic Ru(II) complex and investigated its anion binding properties. It could bind CN^- in organic solvents to afford **67**-**CN**, which has been demonstrated by crystal structures. UV-vis titrations in 90:10 (*v*:*v*) $CHCl_3$/DMF mixture afforded the binding constant of 3.0 ($\pm$ 1.0) $\times 10^6$ M^{-1}, indicating that the cationic Ru(II) complex increases the anion affinity via Coulombic and inductive effects.

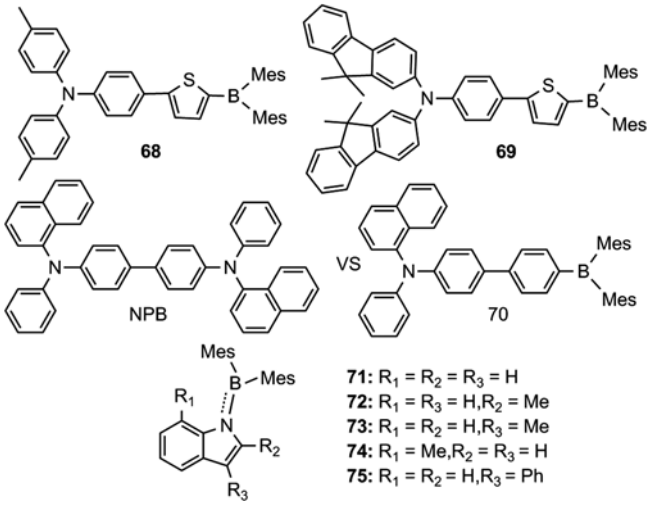


Figure 19 Several triarylboron compounds used in OLEDs.

4 The application of triarylboron compounds in OLEDs

Triarylboron compounds have become one of the most promising materials for OLEDs because they show excellent emission properties and can be used as excellent blue-emitting materials [3–5]. They have been reported as electron-transport/hole-blocking materials for OLEDs [57, 58].

Yasuhiko *et al*. reported compounds **68** and **69** (Figure 19) incorporating both the triphenylamine and $BMes_2$ moieties through the π-conjugated thiophene ring, which provided both electron-donating and -accepting properties, respectively, and facilitated the formation of amorphous glasses due to their nonplanar molecular structures [58]. They fabricated two electroluminescent devices with **68** and **69** as the emitting layer and obtained bright blue-green and green emitters, respectively. The blue-green device exhibited high performance with a maximum luminance of 12500 cd/m^2, a luminous efficiency of 1.1 lm/W, and an external quantum efficiency of 0.8%. For the green device, a maximum luminance of 23700 cd/m^2, a luminous efficiency of 1.3 lm/W, and an external quantum efficiency of 1.0% were obtained. This work presents a new guideline for the molecular design of amorphous emitting materials.

NPB (Figure 19) is a good hole-transport material. In order to obtain a trifunctional molecule (blue emitter, electron-transport, and hole-transport), Wang *et al*. [11] attached part of the NPB molecule to the boron center and synthesized a novel molecule **70** (Figure 19), which is a bright blue emitter with the emission wavelength of 452 nm and a photoluminescent quantum yield of 95% in solution and 31% in the solid state. The performance of the electroluminescent device demonstrated that **70** is capable of functioning as an emitter, a hole-transport molecule, and an electron-transport molecule in EL devices, providing a new way to simplify the fabrication of the devices.

Cui *et al*. synthesized five triarylboron compounds **71–75** (Figure 19) with a B=N bond and studied the effects of the substituent on luminescence/electroluminescence [6]. A charge transfer transition between the indolyl π orbital and the boron p_π orbital was observed for all the five compounds. The substituent group on the indolyl ring was found to have a subtle impact on the electronic properties of the compounds. For instance, the methyl group at the 7-position of indole is the most effective in blocking the rotation of mesityl group around the B–C bond. A four-layer electroluminescent device where **71** was used as the emitter was fabricated which displayed a blue emission with a maximum luminance of 1037 cd/m^2 and a maximum current efficiency of 0.7 cd/A.

Carbazoles are weak π-donors which are particularly useful in generating short-wavelength absorption or emission and designing of blue light-emitting materials. For triarylboron compounds containing carbazole, they are capable of exhibiting the multifunctional properties of emission, hole transport and electron transport. Jeng *et al.* [13] synthesized compounds **76–79** (Figure 20) with carbazole-π-$BMes_2$ skeleton as bipolar blue-light-emitting materials and fabricated nondoped electroluminescent devices. These materials facilitated exciton formation and improved charge balancing in OLEDs. The device with the structure of ITO/NPB (40 nm)/**78** (20 nm)/TPBI (40 nm)/LiF (0.5 nm)/Al (100 nm) exhibits intense blue luminescence with a maximum luminance of 28300 cd/m^2, a maximum current efficiency of 10.1 cd/A and a maximum external quantum efficiency of 6.9%.

Owing to the potential impact on the lighting industry and backlight applications, white-light emission from organic compounds has aroused increasing interest. Mazzeo *et al*. [12] fabricated a bright single-layer white OLEDs by spin-coating a single emitting molecular material (**80** in Figure 20). In solution, **80** exhibits blue-green-light emission with the wavelength of 480 nm, whereas in solid-state film, an additional narrow red-shifted emission at 680 nm appears. Thus, white electroluminescence could be achieved by the

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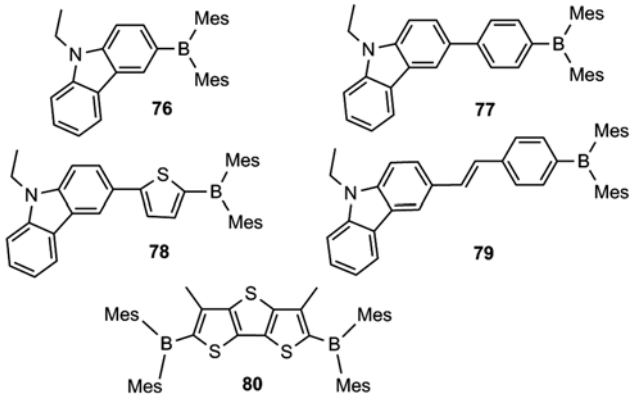


Figure 20 Carbazoles and thiophenes-containing triarylboron compounds used in OLEDs.

superposition of the intrinsic blue-green-light emission of the single molecule of **80** with a red-shifted emission that occurs solely in the solid state. The origin of the red-shifted emission peak is due to the formation of cross-like dimers between the molecules. The low-energy peak at 680 nm in electroluminescent spectrum is more intense than in PL spectrum, indicating that a more efficient population of the aggregation state occurs upon electrical injection which results in a clear white-light emission with CIE coordinates of (0.31, 0.42). A maximum luminance of 3800 cd/m^2 and external quantum efficiency of 0.35% were obtained for the fabricated device, paving the way for the fabrication of low-cost single-active-material white OLEDs.

5 Conclusions and outlooks

As a class of fascinating optoelectronic materials, many triarylboron compounds have been exploited and applied in anion sensors and OLEDs. The design and synthesis of more novel triarylboron compounds with better performances are necessary. Several problems remain to be solved.

Triarylboron compounds are among the most effective fluoride and cyanide ion sensors. Most of the reported fluoride and cyanide sensors, however, solely function in organic solvents. Few studies have been reported on fluoride sensors in pure water, especially the sensors with naked-eye detection. In terms of practical applications, fluoride and cyanide sensors with high selectivity and sensitivity in pure water will be one of the hot research fields in the future. The enhancement of Lewis acidity of triarylboron compounds via peripheral decoration paved a new way for realizing this purpose. Cationic boranes, whose Lewis acidity is increased by Coulombic effects, are one of the fluoride and cyanide sensors that could bind fluoride and cyanide ions in pure water. Fluoride and cyanide sensors with high selectivity and sensitivity based on phosphorescence signals have emerged as new materials because they could significantly improve signal-to-noise ratio through time-resolved fluorometric assay technique compared with fluorescent signals. Hence, the Lewis acidity/electron-transporting properties of triarylboranes in combination with the rich photophysical properties of phosphorescent heavy-metal complexes will lead to many new applications and avenues for research.

Highly efficient blue OLEDs are necessary for high-resolution full-color displays and solid-state lighting applications. However, blue materials were relatively less efficient than green and red emitters. As a class of promising blue luminophors, triarylboron compounds-based materials may pave an effective way for obtaining stable, pure and highly efficient blue light-emitting materials in OLEDs. Therefore, the study of triarylboron compounds would be a significant research direction in optoelectronic field.

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