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Four-coordinate organoboron compounds for organic light-emitting diodes (OLEDs)

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Four-coordinate organoboron compounds with rigid  $\pi$ -conjugated structures are intensely luminescent and have high carrier mobility which enables them to be applied in optoelectronics including organic light-emitting diodes (OLEDs), organic field-effect transistors, as well as photoresponsive, sensory and imaging materials. Various chelate ligands and boron moieties have been explored to construct proper electronic structures and suitable molecular arrangements, which play important roles on the photophysical and electronic properties of the four coordinate boron compounds. These efforts have produced a number of fascinating molecules, some of which have exhibited high performance as light emitting materials. In this article, we provide an overview of the progress in the molecular construction of four-coordinate organoboron compounds with an emphasis on their applications in OLEDs.

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## 1. Introduction

Four-coordinate organoboron compounds are promising light emitting materials owing to their intense luminescence and high carrier mobility. The structures of the boron-bridged molecules are  $\pi$ -conjugated and can easily be modified for desirable properties. Much effort has been made to address the molecular design of four-coordinate boron compounds some of which have fascinating structures and have been widely used in optoelectronics including organic light-emitting diodes (OLEDs),<sup>1,2</sup> organic field-effect transistors,<sup>3</sup> photoresponsive materials,<sup>4-14</sup> sensory<sup>15-21</sup> and imaging materials.<sup>22</sup> In the construction of four-coordinate organoboron compounds, chelate ligands with rich  $\pi$ -electrons are coordinated with boron moieties with vacant p-orbitals, to allow intramolecular electron delocalization and the formation of rigid  $\pi$ -conjugated skeletons. Such ring-fused structures (Chart 1) not only constrain the  $\pi$ -conjugated framework to intensify the emission but also affect the electronic state by lowering the lowest unoccupied molecular orbital (LUMO) level to enhance the electron affinity.



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**Chart 1** Four-coordinate organoboron compounds with rigid molecular structures.

The type of the ligands and the nature of the substituted groups on either the ligands or the boron centers have a great influence on the photophysical and electronic properties of the compounds due to the  $\pi \to \pi^*$  electronic transitions of the chelate or chargetransfer transitions from the substituted groups to the chelate in the exciting process. In the past decade, the method of coordination to boron moieties of many kinds of ligands, such as 8-hydroxyquinolinate, 2-pyridylphenolate and their substituted derivatives has been investigated and the fluorescence of the resulting organoboron compounds cover a wide spectral range from deep blue to near-infrared with high efficiency. Some of the organoboron compounds have been proven to perform well in OLEDs either as emitting materials or electron-transporting materials.

In this review, we focus on the molecular design and properties of four-coordinate organoboron compounds as well as their performance in OLEDs. Other interesting four-coordinate organoboron compounds, which have electroluminescent properties have not been examined, will not be discussed here.<sup>23–40</sup> The compounds presented herein are divided into different systems according to the ligand type, and the modifications in each system such as the introduction of substituted groups and their substituted positions will be discussed. We wanted to gain a fundamental insight into the design strategy of four-coordinate organoboron compounds for their applications in OLEDs. Moreover, the common relationship between the molecular structures of the boron compounds and their photoelectronic properties will be revealed.

# 2. Basic concept for OLEDs

The commonly accepted notion of an OLED is a thin organic film device exploiting charge-recombination electroluminescence. The electroluminescence phenomenon was first observed from the anthracene crystal in 1963<sup>41</sup> and revolutionized into multilayer low-driving-voltage devices by C. W. Tang in 1987.<sup>42</sup> Since then, great efforts have been devoted to the exploration of high performance EL materials and the development of the mechanism and technology for the fabrication of the devices.<sup>43–49</sup> This is inspired by OLEDs' considerable industrial perspectives to develop light-weight, low-cost and large-area display devices or light sources on flexible substrates. Nowadays, high performance display panels based on OLEDs are already commercial available on cell phones, digital cameras, and TV sets. Despite this success, there is a strong demand to significantly improve the performance and durability of blue, green, red, and white OLEDs for displays and lighting applications.

Classical OLEDs with simple sandwich-like device architectures are shown in Chart 2, where electrons are injected from a cathode (usually a metal with a low work function like Mg, Al, Ca) and transported in the electron-transport layer (ETL), and at the same time, holes are injected from an anode (usually a transparent layer of indium-tin-oxide (ITO)) and transported in the hole-transport layer (HTL) under an applied electric field. The carriers approach one another in the emitting layer (EML) of the device and their radiative decay produces EL light. There



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Chart 2 Typical device configuration of OLEDs.

are several important figures that characterize the performance of OLEDs, such as turn-on voltage, brightness, energy conversion efficiency (luminous efficiency and power efficiency), quantum EL efficiency and illumination quality (EL spectra and CIE coordinates). According to the EL mechanisms, several principles for the selection of materials and the construction of the device are crucial to optimize the performance of the OLED, which are (i) the injection and transport of charge carriers and (ii) the charge recombination. For part (i), the energy levels of each of the functional layers need to be appropriate for facilitating injection of the opposite-sign charge carriers and at the same time, electrons and holes should be transported in the relative ETL and HTL effectively with balanced mobilities. Among the available charge transporting materials, high-performance electron-transporting materials are relatively rare compared with the hole-transporting materials, and thus, it is necessary to explore effective electron-transporting materials with low LUMO energy levels and high electron mobility. In other cases, the hole buffer layer or hole blocking layer is introduced into the device to balance the opposite charge carriers and constrain the recombination zone within the emitting layer. For part (ii), the quality of the emitting layer plays a key role for effective charge recombination. This requires that the emitting materials should have high luminous efficiency with desired emission peak, good thermal and chemical stability under thermal evaporation and applied bias voltage. The nature of the luminescent materials including the film-forming property, the molecular structure, the arrangement of the molecule in the film and the transporting ability of the charge carriers has a great influence on the recombination procedure, so proper emitting materials and device architectures are required to make sure that the recombination occurs in the desired zone and maximizes the proportion of radiative transition.

# 3. Four-coordinate boron compounds for OLEDs

Among the photoelectronic applications of four-coordinate boron compounds, the most widely and successfully practised one is OLED. Since the four-coordinate boron compounds are proved to be with good chemical and thermal stability, high fluorescence efficiency and high carrier mobility, many types of four-coordinate boron compounds with different ligands have been investigated and their photoelectronic properties strongly depend on the nature of the ligands. Here, according to the chelate ligands, we mainly classify the four-coordinate boron compounds so far reported for OLEDs into four parts, including hydroxyquinolinate boron derivatives, pyridylphenolate boron derivatives, N-heterocycle-phenolate boron derivatives and N-heterocycle–N-heterocycle boron derivatives. Molecule design strategy and the relative photoelectronic properties will be discussed in detail for each part.

### 3.1 Hydroxyquinolinate boron derivatives

8-Hydroxyquinolinate (q) boron compounds were firstly developed by Wang and co-workers in 2000 to overcome the



shortcomings of the excellent light emitting material Alq<sub>3</sub> from its blue shifted emissions and high long-term stability in the device.<sup>51,52</sup> Boron moieties are coordinated with the ligands to form N,O-B chelated five-membered rings. Typically, the boron center displays a typical tetrahedral geometry and the fivemembered chelate ring is coplanar with the corresponding quinoline ring in each molecule. Another two groups are attached to the boron center providing the remaining electrons to satisfy the boron octet.<sup>52</sup> Wang and co-workers reported a group of 8-hydroxyquinolinate boron compounds with the general formula of  $BR_2q$  (1-4; Scheme 1), where R = ethyl, phenyl, 1-naphthyl, and 2-naphthyl.<sup>50,51</sup> These compounds emitted a greenish blue color at 490-500 nm under UV irradiation, and the melting points of  $BPh_2q$ ,  $B(1-naph)_2q$ , and  $B(2-naph)_2q$  $(>200 \ ^{\circ}C)$  were much higher than BEt<sub>2</sub>q (45  $\ ^{\circ}C)$  for the high rigidity of aromatic substitutes on boron atoms. Thus, BPh<sub>2</sub>q, B(1-naph)<sub>2</sub>q, and B(2-naph)<sub>2</sub>q were investigated in OLEDs as emitters and electron-transporting layers. Though the devices were not efficient due to the influence of exciplex emission at the interface of NPB (N,N'-di-1-naphthyl-N,N'-diphenylbenzidine) or TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'diamine) and the boron compounds, these boron compounds were found to be good electron-transporting materials in EL devices. On the basis of this work, molecule design based on 8-hydroxyquinolinate ligand has been carried out. Anderson and co-workers studied the influence of substituted positions on the absorption and emission (photoluminescence and electroluminescence) characteristics of 8-hydroxyquinolinate boron compounds in solution and in the solid state. They observed that a methyl at the 4-position induced the largest blue shift of the emission, while a methyl at the 5-position induced the largest red shift of the emission in solution. The device of 5-substituted compound showed particularly bright and uniform emission reaching a luminance of 4000 cd m<sup>-2</sup>.53

Wang and co-workers have shown that attachment of benzothienyl or naphthyl groups in the 5-position of the quinolate ligand (5–6; Scheme 2) led to a red-shift in the emission, but the poor photoluminescent efficiency of these compounds made them unsuitable for OLEDs. At the same time, they introduced 2-benzothienyl ligands to boron centers instead of phenyl groups on boron centers (7), which did not change the emission energy significantly. The EL property of 2-benzothienyl-boron compound 7 as both emitter and ETL was investigated, determined with a high turn-on voltage at 10 V and a maximum brightness of 1050 cd m<sup>-2</sup>. This type of compound has the tendency to form an exciplex with the NPB hole transport layer



and their performance in EL is not as satisfactory as that of the  $\mathrm{Alq_3}.^{54}$ 

Jäkle's group made a further modification on 5-position to investigate the relationship between the electronic properties of the substituents and the photophysical properties of the compounds (Scheme 3). They placed electron-withdrawing and electron-donating groups in the 5-position and found that the emission spectra of the derivatives with  $NO_2$  (8), Bpin (9), and  $C_6F_5$  (10) groups were blue-shifted relative to the parent compound 11, while the electron-donating groups  $C_6H_4$ -NMe<sub>2</sub> (12) and  $C_6H_4OMe$  (13) led to a strongly red-shifted emission. This correlated to the electronic effect and extended  $\pi$ -conjugation of the substitutes that influenced the energy levels of the molecules. Among the organoboron quinolates, significantly higher quantum efficiencies were observed for compounds with electron-withdrawing substituents rather than those with electron-donating substituents with the exception of the NO<sub>2</sub> group, which could be due to the charge-transfer character of the lowest energy absorption bands for the NO<sub>2</sub> derivatives and

this is a common phenomenon in most four-coordinate organoboron systems. Notably, the new pinacolborane-substituted organoboron quinolate **9** showed a high quantum efficiency of 39% with blue emission at 485 nm, which makes it a good candidate as a blue emitting material in OLEDs. Additionally, it was demonstrated that direct reaction of methyl protected hydroxyquinoline derivatives with bromoboranes, Ar<sub>2</sub>BBr, could be applied advantageously to synthesize a series of new organoboron quinolate derivatives.<sup>55</sup>

Jäkle's work uses an effective route to systematically tune the emission color of organoboron quinolates from blue to red, and so provides a conventional guide to choose the substituents and their functional position for four-coordinate organoboron molecules. Moreover, Slugovc and co-workers further introduced extended  $\pi$  systems including phenyl (14), biphenyl (15), and 9,9-dihexylfluorenyl (16) in the 5- and 7-positions of the quinolate ligand in Ph2Bq, and the relative products exhibited a significant bathochromic shift of the emission with quantum yields of 22-30% in solution (Scheme 4). Light emitting devices based on compounds 14, 15, and 16 gave bright vellow to orange EL with attractive turn on voltages and brightness, at the same time, no exciplex emission was evident for this group of compounds, which might be attributed to the influence of energy level and molecule packing mode with the additional substitution at 7-position.<sup>56</sup> Besides the compounds with a single boron center, Wang's group also developed polyboron chelate compounds to investigate the molecule packing structures and the intermolecular interactions, which have a significant impact on the thermal stability and the HOMO and LUMO energy levels.<sup>57</sup> Moreover, luminescent organoboron quinolate polymers were synthesized with bright luminenscence.58,59



Scheme 3 Molecular structures of boron compounds 8–13.

Scheme 4 Molecular structures of boron compounds 14–16.

Wang and co-workers have undertaken a lot of research in this area and more details can be found in her forum article.<sup>60</sup>

#### 3.2 Pyridylphenolate boron derivatives

Compared with the 8-hydroxyquinolinate ligand, the pyridylphenolate ligand is less conjugated which can blue-shift the emission region. Wang and coworkers have already proved that phenol-pyridyl beryllium complexes are effective blue-emitting materials as well as host materials in OLEDs, but the toxicity of the beryllium element limits broad applications of these materials.<sup>61-64</sup> Since boron is an element adjacent to beryllium in the periodic table of elements, it has a similar atomic radii and coordinating ability. Thus, pyridylphenolate boron compounds have been investigated for their mode of action as efficient and stable blue emitters.

**3.2.1 1,6-Bis(2-hydroxyphenyl)pyridine boron compounds.** 1,6-Bis(2-hydroxyphenyl)pyridine is tridentate ligand, and boron moieties including  $BR_3$  (R = F, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>) and  $BR(OH)_2$  (R = aromatic groups) coordinate with the ligand by forming O–B, N–B and O–B bonds synchronously. The boron centers are four-coordinate and adopt a typical tetrahedral geometry, resulting in the formation of two twisted six-membered rings after coordination. The ligand is slightly distorted from planarity, and the substituent on the boron atom is greatly distorted from the ligand plane due to the geometry of boron.

We first synthesized 1,6-bis(2-hydroxyphenyl)pyridine boron molecule with a F attached on the boron atom (17) and demonstrated that it exhibited a strong blue emission at *ca.* 445 nm (Scheme 5). The molecules exhibited intermolecular  $\pi$ - $\pi$  interactions, leading to columnar aromatic stacks. This is beneficial in terms of charge mobility. Light emitting devices based on 17 using TPD as HTL exhibited electroluminescence at 550 nm

Scheme 5 Molecular structures of boron compounds 17-22.

from exciplex, while PVK used as HTL instead of TPD, formed little exciplex and the EL spectrum was located at 450 nm.<sup>65,66</sup> This suggests that the organic–solid interface could determine the EL properties of organic light emitting devices. Device performances of **17** are not so effective and the B(OCH<sub>3</sub>) and B(OC<sub>2</sub>H<sub>5</sub>) analogues behave similarly to **17** in OLEDs.<sup>67</sup>

Based on the diphenol-pyridine ligand, further research was performed by attaching aromatic groups to the boron center. Compounds 18-21 were synthesized by refluxing 1,6-bis(2-hydroxyphenyl)pyridine and its methyl derivatives with naphthylboronic acid and 2-methoxylphenylboronic acid in THF. Intermolecular  $\pi$ - $\pi$  interactions could also be observed in the molecular packing structure and the distance between the adjacent molecules varied from 3.3 Å to 3.4 Å due to the steric hindrance of the substituted groups on the boron centers. This guaranteed effective chargetransfer pathways in the solid state. The emission spectra of the four compounds were in the blue region (450-480 nm) both in solution and in the solid state with medium quantum efficiency (0.14-0.30). Compounds with electron-donating methyl groups on the para-position of oxygen atoms red shifted the emission spectra, and substitution with conformationally mobile methoxy relatively decreased the quantum efficiency due to the energy loss via nonradiative decay caused by thermal motion. These compounds were investigated as light emitting materials as well as electron-transporting materials in OLEDs while NPB was used as the hole transporting material (Table 1). As observed for compound 17, the formation of exciplexes was unavoidable, and interestingly the devices exhibited white emission under applied bias (Fig. 1). The broad spectrum of white emission arose from the combined blue emission of boron compound and orange emission of the exciplex. The performance of triple-layer devices with Alq<sub>3</sub> as additional ETL was better than those of the double-layer because of the enhanced electron transport and efficient radiative carrier recombination. In order to eliminate the formation of the exciplex, a second hole-transporting layer of CBP (N,N-dicarbazolyl-4,4-biphenyl) was inserted between NPB and boron compounds. Devices with bright blue emissions were obtained and the exciplexes disappeared. This was attributed to the proper

Table 1         Performance of OLEDs for compounds 18–21 <sup>a</sup>						
Device	Emitter	$V_{\rm on}{}^b/V$	$L_{\rm max}^{\ \ c}/{\rm cd}\ {\rm m}^{-2}$	$\eta_{\rm c}^{\ d}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm p}{}^e/{\rm lm}~{\rm w}^{-1}$	$\operatorname{CIE}/(x, y)$
A-18	18	3.0	1016	1.68	0.68	(0.30, 0.37)
A-19	19	3.2	792	1.47	0.59	(0.28, 0.39)
A-20	20	3.8	813	1.35	0.53	(0.26, 0.36)
A-21	21	4.7	648	1.27	0.52	(0.22, 0.33)
B-18	18	4.1	1852	2.39	1.17	(0.26, 0.38)
B-19	19	4.7	1323	1.71	0.79	(0.27, 0.44)
B-20	20	3.5	1537	2.01	0.95	(0.27, 0.37)
B-21	21	4.5	1271	1.62	0.7	(0.20, 0.33)
C-18	18	4.8	1171	1.55	0.87	(0.17, 0.19)
C-19	19	5.7	527	0.82	0.43	(0.21, 0.27)
C-20	20	5.5	494	1.01	0.57	(0.18, 0.19)
C-21	21	65	445	0.71	0.31	$(0.19 \ 0.29)$

<sup>*a*</sup> Device A: ITO/NPB (50 nm)/18–21 (50 nm)/LiF (1 nm)/Al (200 nm); device B: ITO/NPB (50 nm)/18–21 (40 nm)/Alq<sub>3</sub> (10 nm)/LiF (1 nm)/Al (200 nm); device C: ITO/NPB (40 nm)/CBP (10 nm)/18–21 (40 nm)/Alq<sub>3</sub> (10 nm)/LiF (1 nm)/Al (200 nm). <sup>*b*</sup> Turn-on voltage. <sup>*c*</sup> Maximum brightness. <sup>*d*</sup> Maximum current efficiency. <sup>*e*</sup> Maximum power efficiency.



Fig. 1 Example of white OLEDs fabricated using boron compound 18.

HOMO energy level of CBP which was favorable for hole injection into the emitting layer to give an EL response dominated by emission of boron compounds in the blue region. Of these pyridylphenolate boron compounds, **18** without methyl or methoxy substituent exhibited the best performance with a maximum luminance of 1852 cd m<sup>-2</sup>, a maximum current efficiency of 2.39 cd A<sup>-1</sup> for a white emitting device and relatively 1171 cd m<sup>-2</sup>, 1.55 cd A<sup>-1</sup> for a blue emitting device.<sup>68</sup>

Since 1,6-bis(2-hydroxyphenyl)pyridine boron molecules have been demonstrated to be good electron-transporting materials in the double-layer devices, efforts have been taken to improve the performance of the boron compounds with balanced hole and electron mobility and a novel multifunctional 1,6-bis(2-hydroxyphenyl)pyridine boron bis(4-n-butyl-phenyl)phenyleneamine compound (22) was developed, in which a triphenylamine group with superior hole mobility could provide the hole-transporting channel for the molecules. The PL emission band located around 550 nm and the HOMO and LUMO energy levels were calculated to be -5.3 eV and -2.9 eV which were comparable to the HOMO level of NPB and the LUMO level of Alq<sub>3</sub>, respectively. The single-layer light emitting device based on 22 showed outstanding properties with an EL emission peak at 552 nm and a maximum efficiency of 5.2 cd  $A^{-1}$  (3.6 lm  $W^{-1}$ ), a maximum brightness of 2654 cd m<sup>-2</sup>, which was close to the triple-layer device based on 22 as the emitting layer (Table 2). This indicates that by integrating hole-transporting, electron-transporting, and emitting components into one single molecule, the material is endowed with bipolar transport character and thus offers good recombination sites for hole and electron charge carriers. Double-layer devices with the structures of NPB/22 and 22/ Alq<sub>3</sub> exhibited relatively poor performance when compared with the single-layer device due to the charge recombination sites.69

In summary, 1,6-bis(2-hydroxyphenyl)pyridine boron compounds are promising blue-emitting materials and substitution on the *para*-position of oxygen or on the ligand attached to the

 Table 2
 Performance of OLEDs of compound 22<sup>a</sup>

Device	$\lambda_{\rm EL}/nm$	$V_{\rm on}/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm c}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm p}/{\rm lm~w^{-1}}$
A	552	3.8	2654	5.2	3.6
В	548	3.8	800	1.5	0.85
С	520	5.0	730	1.1	0.5
D	538	4.7	2773	6.8	4.3

<sup>*a*</sup> Device A: ITO/22(100 nm)/LiF(1 nm)/Al(200 nm); device B: ITO/ NPB(50 nm)/22(50 nm)/LiF(1 nm)/Al(200 nm); device C: ITO/22(50 nm)/ Alq<sub>3</sub>(50 nm)/LiF(1 nm)/Al(200 nm); device D: ITO/NPB(50 nm)/22(40 nm)/ Alq<sub>3</sub>(10 nm)/LiF(1 nm)/Al(200 nm).

boron atom may tune their fluorescence effectively.<sup>67–74</sup> In the light-emitting device, exciplexes can form from NPB and boron compounds, and can be prevented by inserting a second proper hole-transporting material. The introduction of flexible substituents would decrease the device performance empirically. The mobility of hole and electron can be balanced by optimizing the molecular properties which makes them good candidates for the fabrication of single-layer devices.

**3.2.2** 2,5-Bis(2-pyridyl)-1,4-hydroquinone boron compounds. Deriving from phenol–pyridyl beryllium complexes, 2-(2-pyridyl)phenol boron compounds have been synthesized with the formation of N, O–B chelated six-membered rings. Since the  $\pi$  system is a three-ring-fused ladder, we extend the planar skeleton to a five-ring-fused ladder by expanding the ligand symmetrically. After boron coordination, diboron containing ladder type molecules with five-ring-fused  $\pi$ -conjugated skeletons have been constructed, which have obviously red shifted emission and other fascinating photoelectric properties.

Zhang and coworkers synthesized compounds **23–26** with 2,5-bis(2-pyridyl)-1,4-hydroquinone and its methyl substituted derivatives as ligands (Scheme 6). Rigid phenyl groups on boron centers obtained compounds with good thermal stability compared to flexible ethyl chains. Different from the



Scheme 6 Molecular structures of boron compounds 23–27



Fig. 2 Photographic images of thin films under UV irradiation and PL spectra of 23–27.

1,6-bis(2-hydroxyphenyl)pyridine boron compounds, bulky phenyl groups attached to boron centers prevented efficient  $\pi$ -stacking in the aggregated state to avoid fluorescence quenching in solids. The emission maxima of the compounds in the solid state located in the range of 562-587 nm with moderate quantum efficiencies (Fig. 2). The LUMO energy level became lower with the extended  $\pi$ -system which resulted in compounds of high electron affinity. In the devices, exciplexes were not observed from the interface of NPB and 23 (or 24) and orange light-emitting devices were first fabricated for boron compounds. Double-layer devices of 23 and 24 gave good performance with brightness above 8100 cd  $m^{-2}$ , demonstrating the high electron mobility of these boron compounds (Table 3). Triple-layer devices of 24 with  $Alq_3$  as an additional electron-transporting layer displayed the best EL performance with brightness of 9754 cd m<sup>-2</sup> and current efficiency of 4.04 cd A<sup>-1.75</sup> Comparing with the extended five-ring-fused structures, 2-(2-pyridyl)phenol boron compound (27) with the feature of three-ring-fused structures showed high PL efficiency but poor EL performance as a light-emitting material. Youngkyu Do and co-workers demonstrated that it is an appropriate hole-blocking

Table 3	Performance of OLEDs of compounds 23, 24 and 27 <sup>a</sup>						
Device	Emitter	$\lambda_{\rm EL}/{\rm nm}$	$V_{\rm on}/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm c}/{\rm cd}~{\rm A}^{-1}$		
A-23	23	588	2.6	8156	2.03		
A-24	24	500	3.2	8505	2.56		
A-27	27	485	14.0	9	0.07		
B-23	23	588	2.4	8438	2.18		
B-24	24	580	2.5	9754	4.04		
B-27	27	484	10.0	264	0.69		

<sup>*a*</sup> Device A: ITO/NPB (40 nm)/23, 24 or 27 (70 nm)/LiF (0.5 nm)/Al (200 nm); device B: ITO/NPB (40 nm)/23, 24 or 27 (60 nm)/Alq<sub>3</sub> (10 nm)/LiF (0.5 nm)/Al (200 nm).

material for phosphorescent OLEDs due to its proper energy level and band gap. $^{76}$ 

From this system one can conclude that the extension of a  $\pi$ -conjugated skeleton will red shift the emission on a large scale and enhance the electron affinity of the compounds. At the same time, introducing bulky aromatic substituents on boron can maintain the fluorescence efficiency in the solid state and ensure compounds with good thermal stability. All of the above functionalization obviously enhances the EL performance of the constructed boron compounds.

### 3.3 N-heterocycle-phenolate boron derivatives

Since C—N double-bonds in N-heteroaromatic rings are effective in coordinating with boron moieties, five-membered N-heteroaromatic rings containing C—N double-bond such as thiazole, oxazole, imidazole *etc.* are explored as ligands. Based on these ligands, four-coordinate organoboron compounds with new structures and plentiful properties for light-emitting and charge-transport have been found compared with hydroxyquinolinate boron derivatives and pyridylphenolate boron derivatives.

**3.3.1 Thiazolothiazole-phenolate boron compounds.** Yamaguchi and co-workers designed (3-boryl-2-thienyl)-2-thiazole **28** as a key building unit and explored a new route to coordinate boron moieties with the thienylthiazole ligand by lithiation of the ligand and subsequent treatment with Mes<sub>2</sub>BF (Scheme 7). The resultant C,N–B chelated five-membered ring linked the thiazole and thiophene parts together and effectively fixed the  $\pi$ -conjugated framework in a planar fashion. On the basis of the regioselective functionalization of **28**, a series of regioisomeric dimers **29–31** were also prepared. These compounds were proven to be potential electron-transporting materials from their low LUMO energy levels and relatively high electron mobility measured for **29**.<sup>77</sup>

Zhang and coworkers expanded the single thienylthiazole unit into a thiazolothiazole-phenylene skeleton with double



Scheme 7 Molecular structures of boron compounds 28–31.



coordinate sites, and BPh<sub>3</sub> or Mes<sub>2</sub>BF was coordinated with the ligand using the same method as Yamaguchi's (Scheme 8). Diboron bridged six-ring-fused skeletons were obtained in a planar mode, and electron-withdrawing/donating groups were introduced into the skeleton to modify the fluorescence of the molecules (32-35). These compounds were thermally stable and emitted in the blue and green regions. 34-35 gave obviously red shifted spectra compared with 32-33, indicating that functionalization on the boron center was more effective to tune the photophysical properties of this type of boron-containing ladder fluorophores compared with the modification of the ladder skeleton. The large steric hindrance of bulky aryl substitutents at boron centers effectively kept the fluorescent unit apart thus enable the compounds to be highly emissive in the solid state. Low LUMO energy levels were due to the extension of the  $\pi$ -conjugated structure and the coordination of boron atoms.78

Considering the attractive ladder-type structures of this type of molecule and their favourable properties for OLEDs, Zhang and coworkers further developed thiazolothiazole-phenolate derivatives as ligands and aryl substituted boron moieties were coordinated with the ligands directly by a one step reaction. The N, O-B chelated six-membered rings were formed in a chair conformation, and the bond lengths in the rings were similar to those of organoboron quinolates. Modifications were performed on the six-ring-fused skeleton by introducing electron-withdrawing/ donating groups in different positions. The resultant compounds 36-39 possessed rigid planar structures with good thermal stability, and showed intense green or yellow fluorescence both in solution and solid state because the bulky phenyl groups attached to boron centers prevented efficient  $\pi$ -stacking in the aggregated state. The substituents on the main skeletons exhibited different influences on the photophysical properties of the compounds, in which electron-donating groups substituted on the para position of the oxygen atoms could significantly red shift the fluorescence while no obvious change in emission was found when substitution was



performed on the *meta* position oxygen. Compound **36** exhibited relatively high quantum yield both in solution and in the solid state, which was probably due to the absence of fluorine or methoxyl substituents on the ladder, which increased the molecular rigidity and weakened the intermolecular interactions (Fig. 3).

Light emitting devices based on 36 and 37 as either lightemitting materials or light-emitting and electron-transporting materials showed high performance with green emission (Table 4). These could reach a maximum brightness of 15620 cd  $m^{-2}$ , current efficiency of 7.2 cd A<sup>-1</sup> and luminous efficiency of 3.2 lm  $W^{-1}$  for 36 and relatively 10340 cd m<sup>-2</sup>, 6.3 cd A<sup>-1</sup> and 2.1 lm  $W^{-1}$  for 37 as light-emitting materials. When the boron compounds were used as both light-emitting and electron-transporting layers in the devices, notable improvement was found in respect of lower turn-on voltage, higher brightness and luminous efficiency, where the relevant values were 3.5 V, 16 930 cd m<sup>-2</sup>,  $5.1 \text{ lm W}^{-1}$  for **36** and 2.5 V, 18 060 cd m<sup>-2</sup>, 4.5  $\text{Im W}^{-1}$  for 37. This comparison clearly suggested that this type of boron complex was an efficient emitter with excellent electron-transporting character, which could be further demonstrated by low LUMO energy levels and high electron mobilites  $(3.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ for } 36 \text{ and } 8.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ for } 37$ measured by means of TOF method) originating from the extended  $\pi$ -conjugated structures. Notably, exciplexes could also be observed in the interface of NPB and boron complexes, and finally we used BA (1,2-diphenyl-1H-phenanthro[9,10-d]imidazole)

Table 4	Performance of OLEDs of compounds 36 and 37 <sup>a</sup>					
Device	Emitter	$\lambda_{\rm EL}/nm$	$V_{\rm on}/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm c}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm p}/{\rm lm~w^{-1}}$
A-36	36	516	5.5	15620	7.2	3.2
A-37	37	532	6.5	10340	6.3	2.1
B-36	36	516	3.5	16930	6.4	5.1
B-37	37	532	2.5	18060	5.4	4.5

<sup>*a*</sup> Device A: ITO/NPB (15 nm)/BA (30 nm)/**36** or **37** (40 nm)/Alq<sub>3</sub> (15 nm)/ LiF (0.5 nm)/Al (200 nm); device B: ITO/NPB (15 nm)/BA (30 nm)/**36** or **37** (55 nm)/LiF (0.5 nm)/Al (200 nm).





as an additional hole buffer layer to hinder the formation of exciplexes. $^{79}$ 

New synthesis concept and novel thiazolothiazole predominant ligands were explored to construct diboron bridged  $\pi$ -conjugated skeletons, and these compounds proved to be good light-emitting and electron-transporting materials for OLEDs based on their outstanding device performance compared with reported boron contained compounds.

3.3.2 Benzothiazole(oxazole)-phenolate boron compounds. Kang and co-workers synthesized BPh2 coordinated three-ring-fused compounds using oxazolylphenolate as ligands (Scheme 9). They incorporated electron-withdrawing and donating groups [ArX (X = 4-cyano-, 2,4-difluoro-, 4-chloro-, phenyl, 4-methoxy-, and 4-dimethylaminophenyl) or NPh<sub>2</sub>](40-46) on the 4-position of the phenoxide to systematically tune the electronic structures of the boron compounds. The emission bands of 40-46 located in the blue and green region where the absorption and emission maxima of the electron-donating groups substituted compounds showed a significant red-shift compared to those with electron-withdrawing groups. Since 46 had relatively higher fluorescence efficiency among these compounds and a bipolar character that corresponded to suitable energy levels, a three-layer light-emitting device was fabricated using 46 as the emitting layer and the device displayed a maximum brightness of 2905 cd  $m^{-2}$ , a current efficiency of 1.63 cd  $A^{-1}$  and a turn-on voltage of 4.3 V.80

Based on the principle that three-ring-fused boron bridged ladders with oxazolylphenolate ligands are promising blue and green emitters in OLEDs, Zhang and coworkers further extended the three-ring-fused system into a four-ring-fused system by employing benzothiazole/oxazole phenolate as ligands (Scheme 10). Kwak and Kim reported two BF<sub>2</sub>-chelate fluorophores **47–48** based on 2-(2'-hydroxyphenyl)benzoxazole (HBO) and 2-(2'-hydroxyphenyl)benzothiazole (HBT) ligands that emitted blue fluorescence with moderate quantum yields ( $\Phi_{\rm F} = 0.20$  and 0.23) in solution.<sup>81</sup>

By employing HBO and HBT ligands, Zhang and coworkers synthesized two BPh<sub>2</sub>-chelate analogs **49** and **50** having fourring-fused core skeletons together with bulky side aryl groups and found that these boron complexes emitted very bright blue or cyan fluorescence both in solution ( $\Phi_{\rm F} = 0.55$  for **49** and 0.65 for **50**) and in the solid state ( $\Phi_{\rm F} = 0.53$  for **49** and 0.60 for **50**).<sup>82</sup> They attempted further *para*-modification by introducing amino



substituents to the fluorescent skeletons of **49** and **50** and obtained a series of strongly fluorescent materials **51–54** which together with **49** and **50** exhibited emission colors ranging from deep blue to saturated red (Fig. 4). The emission spectra gradually red shifted with an increase of donor strength from carbazole, to diphenlyamine and finally dimethylamine. Moreover, changing the bridging atom from O to S also red shifted the emission band due to the heavy atom effect. The fluorescence



Fig. 4 PL and EL properties of boron compounds 49-54.

Table 5 EL performance of devices employing boron complexes  $49{\text -}54$  as emitters  $^{\text{a}}$ 

Emitter	$\lambda_{\rm EL}/nm$	$V_{\rm on}/V$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm c}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm p}/{\rm lm~w^{-1}}$	$\operatorname{CIE}/(x, y)$
49	465	5.0	2237	4.4	2.6	(0.16, 0.19)
50	500	4.8	3639	7.8	4.4	(0.19, 0.44)
51	544	4.5	9181	3.1	1.8	(0.41, 0.55)
52	560	3.0	31 220	5.5	4.8	(0.45, 0.53)
53	612	4.5	14 010	4.5	3.1	(0.61, 0.39)
54	652	4.0	4662	0.59	0.47	(0.66, 0.34)

 $^a$  ITO/NPB (20 nm)/BA (15 nm)/1 or 2 (25 nm)/Alq<sub>3</sub> (40 nm)/LiF (0.5 nm)/Al; ITO/NPB (35 nm)/boron complexes (3, 4 and 6) (25 nm)/Alq<sub>3</sub> (40 nm)/LiF (0.5 nm)/Al; ITO/NPB (35 nm)/5 (25 nm)/TPBi (7 nm)/Bebq<sub>2</sub> (40 nm)/LiF (0.5 nm)/Al.

efficiencies of 51 and 52 in green to yellow bands were above 0.72 in solution and 0.57 in the solid state, at the same time, 53  $(\Phi_{\rm F}$  = 0.48) and 54 ( $\Phi_{\rm F}$  = 0.36) showed high solid-state quantum yields in the red to deep red spectral region. Similarly with 32–39, bulky phenyl groups on boron prevented the  $\pi$ -stacking and guaranteed the high quantum efficiency of 49-54 in the solid state. Simple OLEDs employing these boron complexes as emitters also kept the full-color tunable emission feature and showed very high EL performance (Table 5). Of particular note, is the efficiency of the device based on 50 which was 7.8 cd  $A^{-1}$  and the brightness of the device based on 52 reached a value of 31 220 cd m<sup>-2</sup>, while the non-doped red-emitting device based on 53 was comparable to that of a typical red color device which employs DCJTB as a dopant. Of these compounds, exciplexes were formed between NPB and the non-substituted 49-50 instead of amine substituted 51-54, and at the same time, the presence of amino groups in 51-54 had a favorable effect acting to enhance the HOMO levels close to that of NPB, resulting in better hole-injection or transport ability, and thereby improving luminance.

In order to evaluate the substituent position (*para* or *meta*) effect on the photophysical properties, compound 55 with diphenylamine group substituted at the *meta*-position of the bridging oxygen atoms was synthesized to compare with the *para*-substituted 53. They found 55 was green fluorescent with 35 nm red shift for emission maxima compared with non-substituted 50 while 53 was red fluorescent with the emission red shifted by 142 nm compared with 50, which demonstrated that derivation at the *para*-position was more effective in tuning the luminescent properties of HBO- and HBT-chelate boron complexes.<sup>83</sup>

For these type of boron compounds, further utilization of the substitution effect was performed by Ahn and co-workers. They chose BF<sub>3</sub> to coordinate with HBT ligands, alkylamino groups were substituted on either *meta* or *para* position of the bridging oxygen atom (56–59). *meta* Substituted boron compounds 56–58 emitted strong blue luminescence ( $\mathbb{R}' = \mathbb{CH}_3 \rightarrow \mathbb{C}_2\mathbb{H}_5 \rightarrow n$ -Hex:  $\lambda_{em} = 430 \rightarrow 434 \rightarrow 448$  nm), whereas *para* substituted 59 emitted orange luminescence ( $\lambda_{em} = 597$  nm) in solution, which indicated that the emission bands of these compounds could be tuned flexibly in a wide spectral region by changing the substituted sites. Furthermore, both the *meta* and *para* substituted boron complexes showed bright luminescence



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Scheme 11 Molecular structures of boron compounds 60 and 61.

in the solid state on account of low or small spectral overlap as well as the absence of  $\pi$ - $\pi$  stacking interactions in the solid state. The blue compound 57 was explored as a dopant in an OLED device and showed chromaticity close to an ideal deep blue with a maximum brightness of 716 cd m<sup>-2</sup> and a current efficiency of 1.7 cd A<sup>-1</sup>.<sup>84</sup>

Extended  $\pi$ -skeletons based on benzothiazole(oxazole)phenolate boron units were constructed to obtain highly bright emissive organic solids with red-shifted emissions. Zhang and co-workers chose symmetric 2,5-di(benzo[d]oxazol-2-yl)benzene-1,4-diol and its thiazole analogue as ligands, and the phenyl substituted boron atoms bridged the molecules into seven-ring-fused  $\pi$ -conjugated ladders 60–61 (Scheme 11). The extended  $\pi$ -conjugated skeletons enabled two compounds with bright red (632 nm) and deep red (670 nm) solid-state fluorescence (Fig. 5). Moreover, the bulky phenyl groups on the boron atoms kept the luminescent unit apart, which ensured that these red fluorophores had relatively highly emissivity in the solid state (fluorescence quantum yields: 0.30 for 61 and 0.41 for 60). Compound 61 with S as the bridging atom in the benzothiazole group red shifted the emission band from red to deep red compared with the O bridged compound 60,



Fig. 5 PL and EL spectra of boron compounds 60 and 61.

Table 6 Performance of OLEDs of compounds 60 and 61<sup>a</sup>

Device	Emitter	$\lambda_{\rm EL}/nm$	$V_{\rm on}/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm p}/{\rm lm}~{\rm w}^{-1}$	$\operatorname{CIE}/(x, y)$
A	60	628	2.5	3704	0.53	(0.64, 0.36)
B	61	680	3.0	2636	0.46	(0.70, 0.30)

<sup>a</sup> Device A: ITO/NPB (35 nm)/DPVBi (2 nm)/60 (60 nm)/Bphen (3 nm)/ LiF (0.5 nm)/Al (200 nm); device B: ITO/NPB (35 nm)/TCTA (2 nm)/61 (60 nm)/Bphen (3 nm)/LiF (0.5 nm)/Al (200 nm).

probably due to the heavy atom effect which influenced the energy levels. Similar to six-ring-fused thiazolothiazole boron compounds, the seven-ring-fused ladders also possess good thermal stability and high electron-transporting ability (7.7  $\times$  $10^{-4} \mathrm{~cm^2~V^{-1}~s^{-1}}$  for 60 and 2.2  $\times$   $10^{-4} \mathrm{~cm^2~V^{-1}~s^{-1}}$  for 61 measured by TOF). OLEDs employing simultaneously 60 or 61 as non-doped emitters and electron-transporting materials exhibited bright red and near-infrared electroluminescence (Table 6). For compound 60, the device turned on at 2.5 V and reached a maximum brightness of 3704 cd m<sup>-2</sup> and a maximum power efficiency of 0.53 lm W<sup>-1</sup> with electroluminescence peaking at 628 nm (CIE coordinates X = 0.64; Y = 0.36). The relative values of compound **61** were 3.0 V, 2636 cd m<sup>-2</sup>, 0.46 lm W<sup>-1</sup> and  $\lambda_{\rm EL}$  = 680 nm (CIE coordinates X = 0.70; Y = 0.30). In this seven-ringfused system, exciplexes were found in the interface between boron compounds and NPB. DPVBi (4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl) and TCTA (Tris(4-carbazoyl-9-ylphenyl)amine) were chosen as additional hole buffer layers for 60 and 61, respectively, to ensure that the devices emitted the pure red emissions originating from the boron compounds.82

By investigating new ligands such as thiazolothiazole or benzothiazole-benzooxazole, the fluorescence of the four-coordinate boron compounds were expanded from blue and green regions to the entire visible spectral region and the charge transport abilities were improved. A new route to construct C,B-N five-membered rings to bridge the ladder skeletons was established, which enriched the varieties of four-coordinate boron compounds. To obtain boron materials with high fluorescence efficiency, good stability and high carrier mobility which are favoured properties for OLEDs, the key points for molecular design were the construction of extended  $\pi$ -conjugated skeletons and the introduction of bulky substituents on the boron centers. The fluorescence of the compounds was tuned by changing the length of the  $\pi$ -system and the substituents on the effective positions. In fabrication of the devices, the boron compounds could serve as multi-functional materials and exciplexes could be omitted by the addition of another hole buffer layer.

#### 3.4 N-heterocycle–N-heterocycle boron derivatives

Besides the N,O–B coordination mode, N,N–B is another important chelate form for four-coordinate boron compounds. Of the two N atoms, one can form a chemical bond with the B center and the other N provides a lone-pair electron to the vacant p orbital of B atom along with a formation of a coordinate bond. The N,N–B chelated five- or six-membered ring bridges the  $\pi$ -conjugated skeleton. Wang and co-workers first developed 7-azaindolyl boron compounds **62–64** and they proved to be efficient blue/green



emitters (Scheme 12).<sup>85,86</sup> Among these compounds, **62** with ethyl substituents on the two boron centers had a bright blue photoluminescence, but this was not stable enough for OLED applications. To improve the stability of the boron compound so that electroluminescence can be achieved, phenyl substituted isomers **63** and **64** were synthesized, in which **63** adopted an approximate twofold rotation symmetry and **64** adopted an approximate mirror plane symmetry. The PL spectra of both isomers were very similar with bright blue emissions at 450 nm. Compound **63** had a higher decomposition temperature compared with **64**, and thus was used to fabricate EL devices as a light-emitting layer. The device had a turn-on voltage of approximately 7 V and provided a luminance of 1024 cd m<sup>-2</sup> with an emission maximum at 450 nm.

Due to the geometry of the 7-azaindole ligand, which can only bind to the central atom as either a terminal ligand or a bridging ligand. Wang *et al.* further modified the 7-azaindole ligand into 2-(2-pyridyl)-7-azaindole and 2-(2-pyridyl)indole so that the ligands could chelate to a central atom, and so improve the stability and the performance of the EL devices (Scheme 13). First, the non-substituted 2-(2-pyridyl)indole and 2-(2-pyridyl)-7-azaindole were coordinated with BPh<sub>3</sub> and two



Scheme 13 Molecular structures of boron compounds 65-77.

novel boron compounds 65 and 66 were obtained. There was only a subtle difference in the molecular structure, the more electronegative N atom in 66 was located by the C atom in 65 as a bridging atom, but this caused the two compounds to crystallize in two different space groups, with a different melting point (compound 66 was about 40 °C higher than that of 65). The emission maxima of 65 and 66 were at 516 and 476 nm, respectively. The reason for this blue shift was the replacement of an indole CH by the more electronegative N atom which lowered the HOMO level, increasing the HOMO-LUMO gap. Compound 66 was used as an emitter in EL devices because of its fairly high melting point (291 °C). However, it could form an exciplex with NPB. With the addition of a bicarbazole layer, no exciplex was observed and the device achieved an emission maximum at 490 nm, an external efficiency of 2.34 cd A<sup>-1</sup> and a maximum brightness of about 2300 cd m<sup>-2</sup>.87

In order to examine the effect of substituent groups on the luminescence of 2-(2-pyridyl)indole boron complexes, electronwithdrawing fluoro/chloro atoms and an electron-donating methoxy group were introduced to the 5-position of indole in 65. The resulting compounds 67-69 exhibited emission maxima at 490, 487 and 532 nm in solution, respectively, indicating that the modification on the 5-position of indole in 2-(2-pyridyl)indole boron complexes could efficiently tune the luminescence of these compounds. Among the three compounds, F substituted compound 67 had the highest quantum yield (0.32) while Cl substituted 68 had a relatively lower one (0.22) due to the heavy-atom effect. Conversely, OMe substituted 69 had a low quantum yield (0.036), probably due to the thermal motion of the conformationally mobile methoxy group. 67 was employed to fabricate an EL device as both emitting layer and electron-transporting layer. The device showed a luminance of 141 cd  $m^{-2}$  and an external efficiency of 0.82 cd  $A^{-1}$  with a turn-on voltage of 11 V.88

Finally, in an effort to expand the emission zone from blue to the red region based on the same  $BPh_2(N,N)$  system, the effect of substitution and conjugation of the chelate ligand on the emission color of the boron compounds was further investigated for this system. Further modifications were performed: (1) more electron-withdrawing F atoms were introduced into different positions of the negatively charged portion of the ligand (70-73); (2) The CH was replaced by a N atom on the negatively charged ring (74); (3) The neutral portion of the chelate ligand was modified mainly by increasing the conjugation size (75–77). For these type of compounds, the HOMO levels are dominated by the negatively charged portion of the ligand and the LUMO levels are dominated by the neutral portion of the chelate ligand. On this basis, the fluorescent spectra of these compounds are different and cover the entire visible region together with the emissions of 65-69. The substitution of F gradually blue shifted the emission from 481 to 467 nm with increasing number of F atoms. On the other hand, the emission energy seemed insensitive to the position of the F atoms as shown by the similar emission bands of 70 and 71. The emission band of 74 had the shortest wavelength at 445 nm and exhibited an obvious blue shift (more than 20 nm) compared with that of 66, which indicated that the

 Table 7
 Performance of OLEDs of compounds 74 and 76<sup>4</sup>

Device	Emitter	$\lambda_{\rm EL}/nm$	$V_{\rm on}/{\rm V}$	$L_{\rm max}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm c}/{\rm cd}~{\rm A}^{-1}$
A-74	74	450, 572	11	429	1.36
B-74	74	450	10	174.5	0.70
C-74	74	452	8	412	0.83
D-76	76	632	6	38.5	0.008
E-76	76	432, 636	10	157	0.04

<sup>a</sup> Device A: ITO/NPB (40 nm)/74 (40 nm)/Al; device B: ITO/NPB (40 nm)/
Bicarb (20 nm)/74 (40 nm)/Al; device C: ITO/NPB (40 nm)/Bicarb
(20 nm)/74 (40 nm)/Mg: Ag (100 nm)/Ag; device D: ITO/NPB (40 nm)/
76 (40 nm)/LiF (1 nm)/Al; device E: ITO/NPB (40 nm)/Bicarb (10 nm)/76
(40 nm)/ LiF (1 nm)/Al.

aza substituent at position 3 of indolyl group could lower the HOMO energy level more effectively than the aza group at position 7, thus providing a more obvious influence on the emission spectrum. At the same time, it could be surmised that the addition of one extra electronegative nitrogen atom on the negatively charged ring was more effective than the electronwithdrawing F substituents in terms of increasing the energy gap. Different from the blue to green luminous compounds 70-75, compounds 76 and 77 exhibited bright red (611 nm) and orange (583 nm) luminescence in the solid state because increasing the size of the neutral portion of the chelate ligand extended conjugation of the chelate ligands, and thus decreased the HOMO-LUMO energy gaps. EL devices were fabricated based on 74 and 76 for their pure blue and rare red fluorescence, respectively (Table 7). Each of the two compounds was used as both an emitting layer and an electrontransporting layer. An exciplex was formed between 74 and NPB, rather than 76 and NPB, because of their relatively different HOMO energy levels. The HOMO level (-5.3 eV) of 76 was more comparable to that of NPB (-5.2 eV). With the addition of a hole-blocking layer, bicarbazole, that removed the exciplex emission and a Mg: Ag electrode, the EL device based on 74 gave a performance in which the EL spectrum was centered at 452 nm, the maximum brightness was 412 cd m<sup>-2</sup> and the current efficiency was 0.83 cd  $A^{-1}$ . For the red emitting compound 76, the bilayered device with NPB/76 gave an EL emission maximum at 632 nm but a poor performance of low luminance (38.5 cd m<sup>-2</sup>) and current efficiency (0.008 cd A<sup>-1</sup>).<sup>89</sup>

Chen and co-workers synthesized N, N–B chelated compounds **78–80** based on 2-(2-pyrrolide)pyrrolide ligands (Scheme 14). Similarly with the pyridyl-indole–azaindole boron system above, the lowest electronic excitation incorporated pyrrolide (HOMO) and pyridine-containing (LUMO) moieties. The emission maxima of **78–80** were 490, 510 and 575 nm, respectively. The elongated  $\pi$ -conjugated system in quinoline stabilized the LUMO and red shifted the emission of **79**, and the additional electron-withdrawing N atom on the quinoline would further decrease the energy gap to ensure additional red shift for the fluorescence of **80**. For OLED applications, compound **80** was chosen as the emitting material in the EL device for its most red-shifted PL emission. Doped devices in which Alq<sub>3</sub> was used as the electron-transporting and host matrix for orange emitting compound **80** exhibited yellow-orange (560 nm) to orange-red (574 nm) emission with different dopant



concentration of **80**. On the other hand, the non-doped device with **80** as the emitting layer, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as the hole blocking layer, and Alq<sub>3</sub> as the electron-transporting material was fabricated. This type of device gave a maximum brightness of 5000 cd m<sup>-2</sup> and a small FWHM (full width at half maximum) of electroluminescence that peaked at around 580 nm, chromaticity (0.55, 0.45) fell on the saturated red-orange edge.<sup>90</sup>

Chen and co-workers synthesized pyridyl–imidazole derivatives as chelate ligands, and BPh<sub>3</sub> or BF<sub>3</sub> was coordinated with the relative ligands to get N,N–B five-membered ring bridged  $\pi$ -skeletons **81–84**. Interestingly, the emission bands of **81**, **83** and **84** were concentration-dependent in DMF, which red shifted from the blue to yellow or red regions with increase in the concentration. The thin films of the three compounds possessed moderate to high PL quantum yields (0.15–0.80) and their PL spectra were similar to that of these compounds in higher concentrations in DMF solutions. EL devices based on **81** as the emitting layer showed a yellow emission with a turnon voltage of 3.5 V, a maximum luminance of 332 cd m<sup>-2</sup> and luminance efficiency of 0.02 lm W<sup>-1</sup> (Table 8). Since the

Table 8	Performance of OLEDs of c	84 <sup>a</sup>	
Device	Emitter	$\lambda_{\rm EL}{}^a/{\rm nm}$	$\operatorname{CIE}/(x, y)$
A-81	81	543	(0.45, 0.53)
B-83	83	618	(0.66, 0.32)
C-83	83	608	
D-83	83	596	(0.52, 0.48)
E-83	83	526	(0.47, 0.50)
F-84	84	400-750	(0.33, 0.37)

 $^a$  Device A: ITO/NPB (50 nm)/81 (50 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (100 nm); device B: ITO/NPB (50 nm)/83 (50 nm)/Mg: Ag (200 nm); device C: ITO/NPB (50 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (200 nm); device D: ITO/NPB (50 nm)/80% of 83 in NPB (50 nm)/Alq<sub>3</sub> (50 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (200 nm); device E: ITO/NPB (50 nm)/10% of 83 in NPB (50 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (200 nm); device F: ITO/NPB (50 nm)/Alq<sub>3</sub> (50 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (200 nm); device F: ITO/NPB (50 nm)/84 (30 nm)/Alq<sub>3</sub> (50 nm)/Mg: Ag (200 nm).



Scheme 15 Molecular structures of boron compounds 85–93.

fluorescence of this type of compound was tunable with different concentrations, both non-doped and various-concentration doped devices were fabricated based on compound **83** and the devices exhibited emission maxima from 526 to 618 nm. When compound **84** was used as the emitting layer in a classic threelayer device, an emission band covering the whole visible region from 400 to 750 nm with maximum brightness of 320 cd m<sup>-2</sup> was observed, and a perfect white light OLED (CIE = 0.33, 0.37) was obtained.<sup>91,92</sup>

Recently, Gomes and co-workers explored a new type of fourcoordinate boron compound (85-87) containing 2-(N-aryl)formiminopyrrolyl moieties (Scheme 15). The emission maxima of these compounds were located in the blue to green range, and the diboron doped compounds 86 and 87 gave red shifted fluorescence (512 nm for 86, 497 nm for 87) and higher quantum efficiencies (0.69 for 86, 0.64 for 87) compared to that of the monoboron compound 85 (451 nm, 0.34). With suitable energy levels and fluorescence efficiencies, a single-layer non-doped EL device was prepared by spin-coating in which 86 or 87 was used as both emitter and ambipolar charge transporting material which exhibited high brightness in the order of  $10^3 \mbox{ cd} \mbox{ } m^{-2}$ and efficiencies of ca. 0.3 cd A<sup>-1</sup>.93,94</sup> Moreover, pyridyl pyrazolate boron complexes 88-93 were synthesized by Chi and co-workers, in which 88-90 exhibited remarkable dual fluorescence properties due to the photoinduced electron transfer reaction.95

Chujo and co-workers prepared a low-molecular-mass organoboron aminoquinolate compound **94** and a new series of organoboron polymers **95–97** (Scheme 16) containing organoboron aminoquinolate structures in the main chain. The single molecule and polymers exhibited similar intense green photoluminescence, which could be explained by the energy transfer from the  $\pi$ -conjugated linkers in the main-chain to the



Scheme 16 Molecular structures of boron compounds 94–97.



Scheme 17 Molecular structures of boron compounds 98-108.

acetylaminoquinoline ligands on the boron centers.<sup>96</sup> Gardinier and co-workers investigated BORAZAN fluorescent dyes based on 2-(pyrazolyl)aniline chelates of diphenylboron (**98–108**; Scheme 17). The color of emission could be tuned from blue to yellow-green by increasing the electron-donating power of *para*-aniline substituent. Meanwhile, the di-pyrazolyl derivatives exhibited red-shifted emission, greater stability toward solvolysis and higher photoluminescent quantum yields compared with their monopyrazolyl counterparts presumably due to kinetic stabilization of the chromophore imparted by the second pyrazolyl ligand.<sup>97,98</sup>

Recently, Curiel and co-workers presented a novel class of double-laddered  $\pi$ -conjugated system, which combined the indolo[3,2-b]carbazole unit with the formation of four-coordinate boron complexes 109-110 (Scheme 18). The boron complexation narrowed the HOMO-LUMO energy gap effectively and this narrowing was almost exclusively due to a decrease in the LUMO energy, which approached the ambipolar materials energy range. This type of double-laddered  $\pi$ -conjugated compounds exhibited a wide absorption range relatively different from other fourcoordinate boron compounds, covering most of the visible spectrum (200-700 nm) while the emission spectra recorded for 109 and 110 displayed very weak fluorescence with respective quantum efficiencies of 6.4% and 2.8% in solution.99 However, these compounds (88-110) have not been applied in OLEDs yet, other potential applications in organic electronics have been explored according to their photophysical and electronic properties.



Scheme 18 Molecular structures of boron compounds 109 and 110.

N-heterocycle-N-heterocycle boron derivatives of various types are due to the abundant N-heterocycle series. When coordinated with a boron center, the two bridging N atoms in each N-heterocycle play different roles, one forms a chemical bond and the other forms a coordinate bond. In most cases, the HOMO levels are dominated by the negatively charged portion of the ligand and the LUMO levels are dominated by the neutral portion of the chelate ligand, which is the basis for molecular modification. Introduction of the substituents, replacement of C atom on the skeleton by a heteroatom and the extension/ contraction of the  $\pi$ -conjugation could all affect the electronic state of the relative energy levels and hence influence the photophysical and electronic properties of the compounds. Photoluminescence as well as electroluminescence of this type of compounds cover almost the whole visible light region and some of the compounds show good EL performance for OLEDs.

#### 3.5 Other four-coordinate boron compounds

In Section 3.3.1 we discuss that Yamaguchi and co-workers have explored a new route to coordinate boron moieties with a thienylthiazole ligand. On the basis of this synthesis route, other C,N–B chelated compounds have been explored. Thiazo-lyl-capped  $\pi$ -conjugated systems were constructed *via* a coordination/cyclization protocol with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**111–112**; Scheme 19).



Scheme 19 Molecular structures of boron compounds 111 and 112.



This kind of electronic tuning effectively enhanced the electron accepting character, giving rise to lower reduction potentials and increased thermal stability.<sup>100</sup> Furthermore, they synthesized phosphonium- and borate-bridged zwitterionic ladder stilbene and its extended analogues (**113–118**; Scheme 20) by intramolecular cyclization protocols. The zwitterionic bridges in these compounds not only fixed the molecular framework in a rigid and coplanar fashion, but also provided a highly polar electronic structure of which the phosphonium and borate functionalities served as strong electron-accepting and electron-donating moieties, respectively. Some of these compounds exhibited bright orange to red fluorescence and low LUMO energy levels<sup>101</sup> and some could be used as two-photon absorption materials.<sup>102</sup>

Wang and co-workers synthesized a series of C,N–B chelated structures with pyridyl–phenyl ligands. This type of compound was found to possess reversible photo-thermal color switching which actually is a reversible isomerization involving a tetrahedral B center and the formation/breaking of a C–C bond in the molecular structure (Scheme 21a).<sup>103,104</sup> Relative reversible photoisomerization phenomena were also found in the azobenzene



**Scheme 21** Typical chemical structures of four-coordinate boron compounds with photochromic properties.

C,N–B chelated system reported by Kawashima and co-workers (Scheme 21a). Photoirradiation induced the switch of coordination number of boron in a catecholborane and the change of the Lewis acidity toward pyridine. These compounds had potential applications in optoelectronics such as optical memory devices and molecular switches.<sup>105,106</sup> Since there were no further application of these compounds in OLEDs, we do not discuss the details here and more information can be obtained in Wang's forum article.<sup>60</sup>

Moreover, O,O-chelate boron compounds based on aromatic 1,3-diketonato ligands with the general structure of **119** proved to have intriguing optoelectronic properties especially bright fluorescence and highly tunable emission colors (Scheme 22).<sup>107–117</sup> The well-known BODIPY (boron dipyrromethene) dyes with a N,N-chelate ligand and a BF<sub>2</sub> unit, are a class of highly fluorescent molecules.<sup>118</sup> These compounds are not extensively applied in OLEDs probably due to their semiconductor characteristics, so details of these compounds are not covered in this review.

## 4. General considerations and outlook

This review covers luminescent four-coordinate organoboron compounds with an emphasis on those with applications in OLEDs. The EL performance of devices employing boron species as emitting materials relies on fluorescence efficiency as well as charge mobility of the emitters. To tune fluorescence and charge mobility of boron compounds, structural functionalization has been done on the ligands and the substituents of boron reagents. As for ligands, both the molecular rigidity and conjugation length are important for optical and electron-



Scheme 22 Molecular structures of boron compounds 119.

transporting properties of the produced boron compounds. In general, incorporating boron moieties into a rigid  $\pi$ -system can enhance not only the fluorescence quantum yield but also the electron-transporting ability of the solid materials, therefore acts to improve the EL performance of OLEDs. On the other hand, the length of  $\pi$ -conjugation is also effective in tuning the properties of boron compounds including emission color, electron mobility and thermal stability. Based on this, a wide variety of ligands have been designed and synthesized for the purpose of fabricating high performance EL devices. In contrast, the categories of substituents on boron atoms are extremely limited. Phenyl, mesityl, and fluoro are popular groups employed in most of the reported four-coordinate boron compounds reported so far.

Considering the fact that molecular rigidity and extended  $\pi$ -conjugation can effectively improve the fluorescence efficiency and carrier mobility, respectively, we propose a type of novel boron species which adopts a spiro structure by attaching all ring fused substituents on the ladder boron centers and predict them as reasonable extensions of the next generation of high-performance electroluminescent four-coordinate boron compounds because this structure endows them with very rigid molecular conformations. This three dimensional molecular structure may effectively prevent molecular aggregation in thin films. Therefore, it can be expected that these boron compounds display highly efficient luminescence in solid forms. In these types of molecules, two isolated substituents (Chart 1) on boron atoms are replaced by a ring-fused  $\pi$ -system. Large  $\pi$ -electron units may facilitate smooth charge-transporting within solid forms, which plays a crucial role in determining the performance of OLEDs. In this sense, the spiro boron compounds might show enhanced electron-injecting and transporting capability compared with previously reported boron compounds summarized here in Section 3. All the ligands summarized in this review can be used to construct these novel type boron compounds by reaction with ring-fused boron reagents such as bromodibenzoborole.

## 5. Conclusions

We have summarized several series of four-coordinate boron compounds and found that they show favoured photophysical and electronic properties for OLEDs. These compounds are flexible to design and feasible to synthesize due to the various kinds of ligands and the simple coordinate mechanism between the ligands and boron moieties. The introduction of four-coordinate boron bridges the ligand into a rigid skeleton and influences the electronic structure of the ligand, which enables many of the fascinating optoelectronic properties exhibited by these compounds. In this review, we have divided the boron compounds into several systems according to their basic ligands. In these systems, molecular modifications have been made to adjust the optoelectronic properties such as fluorescence, energy levels and carrier mobilities etc. of these boron compounds. The primary principles for molecular modification are summarized as (1) altering the  $\pi$ -conjugated length

of the system, (2) introducing functional substituents into different positions on the molecules and (3) changing the bridging atoms in the main skeletons. Basing on these means, varieties of boron compounds with full-color emissions, different energy levels and tunable carrier mobilities have been obtained by different research groups. EL devices have also been fabricated for suitable compounds. Different types of devices including doped and non-doped with single-layer to multi-layer structures have been explored to investigate the EL properties of these compounds. In these devices, most of the four-coordinate boron compounds are found to be effective light emitters with pure deep blue to saturated red fluorescence, moreover, white emission has also been obtained from the exciplexes or dual fluorescent compounds. Besides the bright electroluminescence, some of the compounds have proved to have high electron mobilities and some have balanced dipole carrier transporting abilities. High-performance OLEDs have been achieved based on the reported four-coordinate boron compounds and thus future research efforts on boron-based materials are urgently needed, not only for OLEDs, but also for other optoelectronic applications such as sensory, biological imaging materials and photoresponsive materials.

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