

Luminescence and electroluminescence of Al(III), B(III), Be(II) and Zn(II) complexes with nitrogen donors

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Abstract

Blue luminescent complexes of aluminum(III), boron(III), beryllium(II) and zinc(II) using ligands that contain only nitrogen donor atoms are presented. The ligands in these complexes are based on di-2-pyridylamine and 7-azaindole. Complexes containing derivatives of 7-

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azaindole and di-2-pyridylamine are described. Electroluminescent properties for some of the promising compounds are also discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Luminescent organic and organometallic compounds have attracted much attention recently because of their potential applications in organic-light-emitting-devices (OLEDs). OLEDs are based on electroluminescence and belong to the general research area of electroluminescent displays. A recent review article by Chen and Shi gives a very nice, up-to-date account on the development and chemical aspect of metal chelate compounds in electroluminescent displays [1]. Chen and Shi's article focused on compounds that use chelate ligands containing both oxygen and nitrogen donor atoms. The driving force in investigating chelate compounds with oxygen and nitrogen as donor atoms is mostly due to the earlier discovery of Alq_3 , $q = 8\text{-hydroxyquinolinato}$, which is a bright and stable emitter in OLEDs [2]. Since the publication of Chen and Shi's article, a few new electroluminescent chelate compounds using oxygen and nitrogen as donor atoms have been reported (Fig. 1): $\text{Al}(\text{POP})_3$, a blue emitter [3], $\text{POP} = 2\text{-(5-phenyl-1,3,4-oxadiazol-yl)phenonate}$; $\text{Li}(\text{PBO})$, a blue emitter [4], $\text{PBO} = 2\text{-(2-hydroxyphenyl)benzoxazolato}$; and $\text{Be}(\text{POP})_2$ and $\text{Be}(\text{NOP})_2$, blue emitters [5], $\text{NOP} = 2\text{-(5-naphthyl-1,3,4-oxadiazol-yl)phenonate}$. Because of the extensive coverage on electroluminescent chelate

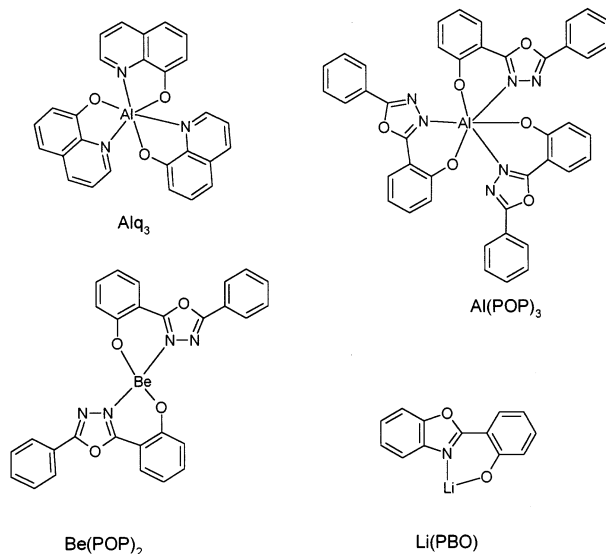


Fig. 1. Structures of $\text{Al}(\text{POP})_3$, $\text{Li}(\text{PBO})$, and $\text{Be}(\text{POP})_2$.

compounds with oxygen and nitrogen donor atoms, this review will focus on complexes that have chelate or bridging nitrogen donor atoms and will, thus, complement the previous review.

There are two classes of luminescent compounds employed in OLEDs: fluorescent and phosphorescent compounds. Using phosphorescent compounds in OLEDs was not initiated until recently [6]. As a result, examples of phosphorescent compounds in OLEDs are still scarce and will not be covered herein.

It has been well established that compounds that can be used in OLEDs must be: (a) photoluminescent with a high quantum yield; (b) chemically and thermally stable; (c) sublimable so that gas-phase deposition techniques may be employed. Using these criteria, our group initiated the search for good luminescent, especially blue luminescent compounds with nitrogen donor atoms a few years ago. This article gives an overview of our investigation on luminescent compounds and their applications in electroluminescent displays. Related work by other research groups will be discussed as well.

2. Di-2-pyridylamine and derivatives

The free ligand, di-2-pyridylamine (dpaH), has no emission band in the visible region. Although some Zn(II) complexes of dpaH have been reported to have a near UV emission band [7], they are in general very weak. We discovered that the removal of the proton from dpaH shifts the emission energy to blue and significantly enhances the emission intensity. The dpa anion is, however, very unstable toward air and moisture. The formation of a complex of dpa with a metal ion can improve its stability without losing its bright luminescence. Several Al(III) complexes of dpa have been synthesized and characterized by our group [8]. The simplest member is $\text{Al}(\text{CH}_3)_2(\text{dpa})$ (**1**) (Fig. 2) with a zwitter-ion structure and is highly air-sensitive due to the two methyl ligands. The attachment of a second aluminum center to the amido nitrogen site in **1** yielded compound **2**, $\text{Al}_2(\text{CH}_3)_5(\text{dpa})$, (Fig. 2) which is also highly air-sensitive. Both compounds have a sharp emission band at 475 nm and 445 nm, respectively. The introduction of an oxo ligand in the dpa complex has been found to enhance the stability of the complex. For example, the tetranuclear complex, $\text{Al}_4(\mu_3\text{-O})_2(\text{CH}_3)_6(\text{dpa})_2$, (**3**), (Fig. 2) obtained from the reaction of $\text{Al}(\text{CH}_3)_3$ with dpaH in the presence of moisture, is stable for a few hours in the solid state under air. Compound **3** has a sharp emission band at 450 nm with a photoluminescent quantum efficiency of 0.37, relative to that of 9,10-diphenylanthracene. However, compound **3** does not have sufficient volatility for vacuum deposition. Therefore, OLEDs based on aluminum(III) dpa compounds have not been fabricated. The dpa ligands in **1–3** display a chelate and a bridging bonding modes. The Al(III) ion is four-coordinate in **1** and **2** and four- and five-coordinate in **3**.

To further improve the stability of dpa complexes, we carried out the modification on dpa: one of the pyridyl rings is replaced by a pentafluorophenyl group, yielding the new ligand pfpdH. Because the pentafluorophenyl group is highly

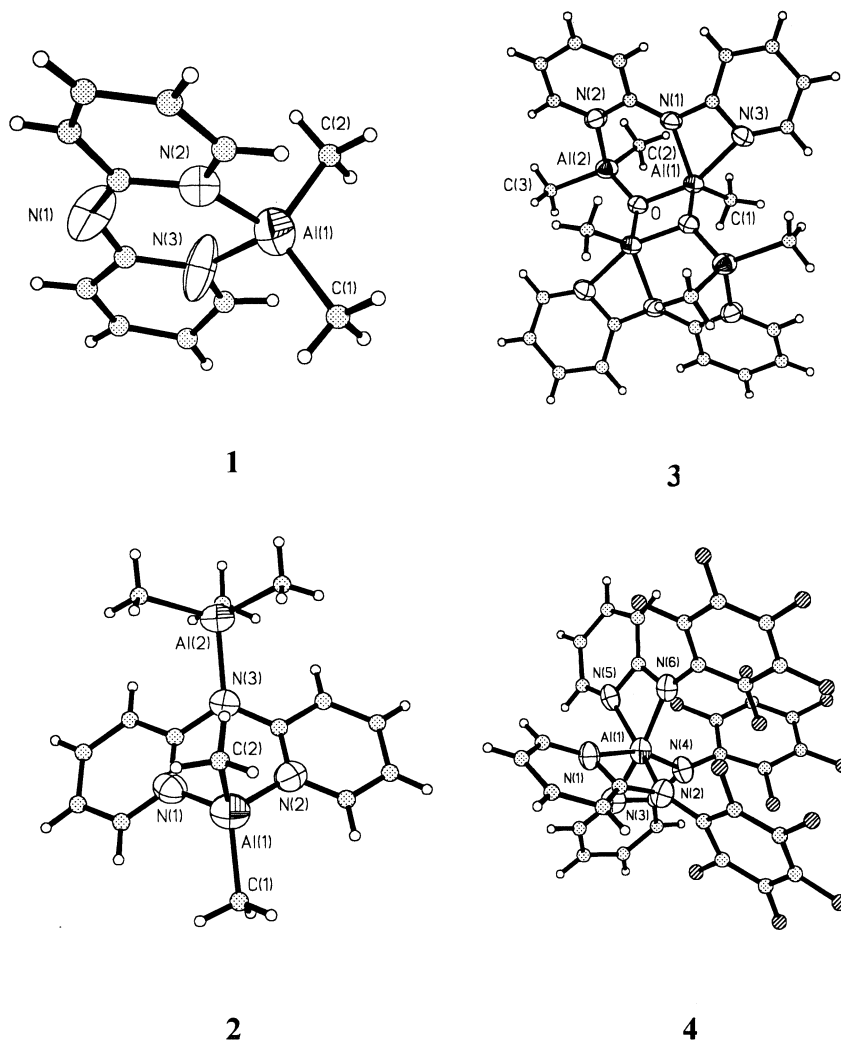


Fig. 2. Structures of 1–4.

electron-withdrawing, it could stabilize the negative charge on the amido nitrogen atom, thus enhancing the overall stability of the complex, we believe. Indeed, the new aluminum complex, $\text{Al}(\text{pfpa})_3$ (**4**), (Fig. 2) obtained from the reaction of $\text{Al}(\text{CH}_3)_3$ with pfpaH in a 1:3 ratio [8], is fairly stable in the solid state under air. Compound **4** is six-coordinate with a *fac* structure in the solid state while in solution **4** is fluxional and the *mer* isomer appears to be dominant, based on a solution NMR spectroscopic study. The emission band of **4** is at 409 nm (Fig. 3), a significant blue shift in comparison to that of *dpa* complexes, attributable to the electron-withdrawing pentafluorophenyl group. Compound **4** has a high melting

point ($> 280^{\circ}\text{C}$), but cannot be sublimed under our laboratory conditions (0.10 mmHg, 240°C). Therefore, electroluminescent properties of **4** have not been investigated.

The second type of modification we carried out on the dpaH ligand is the replacement of the proton by an aromatic group. The rationale is that by increasing the degree of conjugation, we can, perhaps, shift the emission energy of the neutral ligand from UV to blue. 2,2'2''-tripyridylamine (2,2',2''-tpa) and 2,2',3''-tripyridylamine (2,2',3''-tpa) (Scheme 1) have been synthesized [9]. Unfortunately, no significant emission energy shift, in comparison to that of dpaH, was observed in solution. Single-crystal X-ray diffraction analyses revealed that 2,2'2''-tpa and 2,2',3''-tpa have a propeller-like structure due to steric interactions between the pyridyl rings, thus preventing an extended conjugation. Nonetheless, Zn(II) complexes of 2,2',2''-tpa and 2,2',3''-tpa were synthesized and found to emit in the blue region [9]. The Zn(II) ion has a tetrahedral geometry in **5**, a *cis*-, octahedral geometry in **6**, and a *trans* octahedral geometry in **7** (Fig. 4). In the solid state, compounds **5** and **6** have a broad emission band at ca. 400 nm while **7** has a broad emission band at ca. 470 nm. In solution, $\text{ZnCl}_2(2,2',2''\text{-tpa})$ (**5**), $\text{Zn}(\text{O}_2\text{CCF}_3)_2(2,2',2''\text{-tpa})_2$ (**6**), and $\text{Zn}(\text{O}_2\text{CCF}_3)_2(2,2',3''\text{-tpa})_4$ (**7**) have a broad emission band at $\lambda_{\text{max}} = 422\text{--}432$ nm (Fig. 5) with a quantum yield of 0.054, 0.22 and 0.10, respectively. NMR studies established that compounds **5** and **6** are highly dynamic in solution, due to an exchange process between coordinate and non-coordinate 2-pyridyl groups, and *cis*–*trans* isomerization in the case of **6**. The dramatic change of emission bands from solution to the solid state by **5**–**7** has not yet been understood. Compounds **5**–**7** have not been studied for electroluminescent applications because they are either very weak emitters or have a melting point that is too low for OLED fabrication.

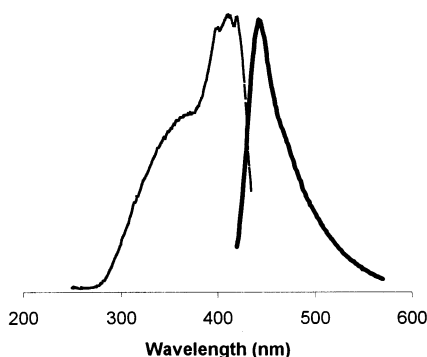
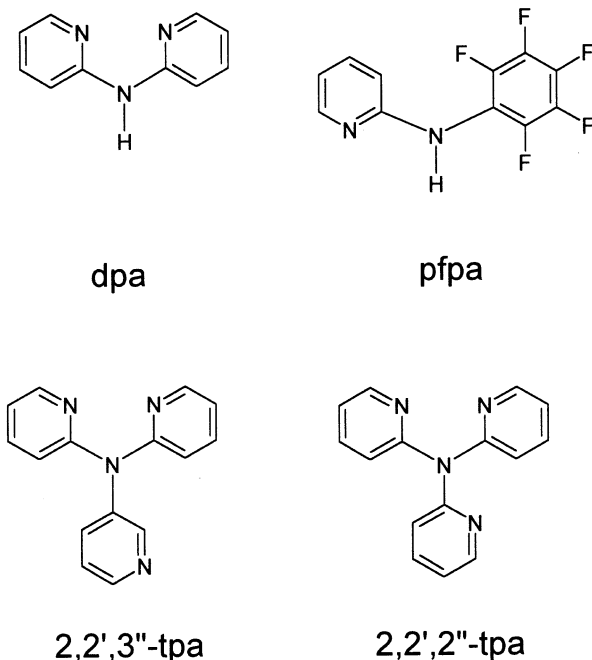


Fig. 3. The excitation and emission spectra of $\text{Al}(\text{pfpa})_3$ in the solid state.



Scheme 1.

3. 7-Azaindole

Free 7-azaindole has no emission in the visible region in solution and has a very weak emission band at λ ca. 400 nm in the solid state. In contrast, the anion of 7-azaindole, after the removal of the indole proton, exhibits a bright blue emission in solution and the solid state. The 7-azaindole anion (7-aza) is however unstable toward air and moisture. One way to stabilize the 7-aza anion is to bind it to a central metal ion. Our initial study focused on using the aluminum(III) ion as a stabilizing center for 7-aza. Aluminum complexes of 7-aza can be obtained readily by the reaction of $\text{Al}(\text{CH}_3)_3$ with 7-azaH. Depending on the stoichiometry and the reaction conditions, a variety of 7-aza aluminum complexes have been obtained by our group.

3.1. Dinuclear aluminum 7-azaindole complexes

From the reaction of $\text{Al}(\text{CH}_3)_3$ with 7-azaH in a 1:1 ratio, $\text{Al}_2(\text{CH}_3)_4(7\text{-aza})_2$ (**8**) (Fig. 4), was obtained while the reaction of $\text{Al}(\text{CH}_3)_3$ with 7-azaH in a 1:2 ratio yielded $\text{Al}_2(\text{CH}_3)_2(7\text{-aza})_4$ (**9**) (Fig. 6) in high yield [10]. The 7-aza ligands in **8** and **9** function as bridging ligands. Compound **9** exhibits a complex disordering of the 7-aza ligands in the solid state. Solution and solid state ^{27}Al -NMR studies estab-

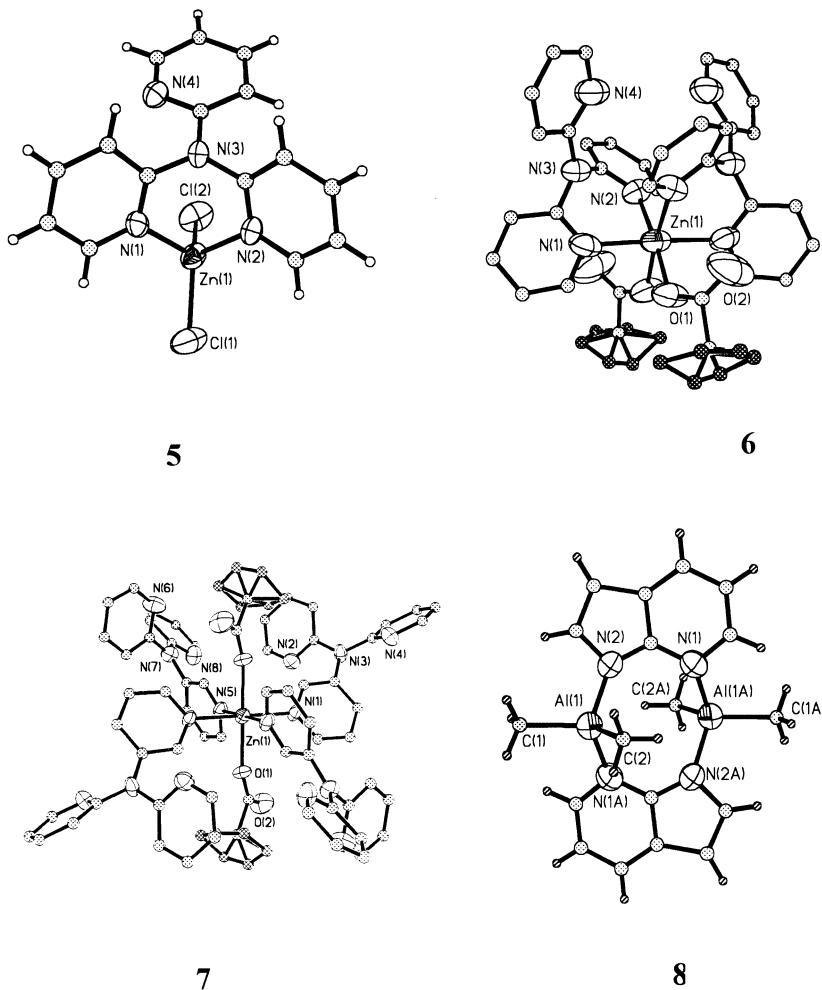


Fig. 4. Structures of 5–8.

lished that the observed disordering of **9** is caused by the co-existence of isomers **9a** and **9b** in a 1:1 ratio in the solid state [11] Table 1. The NMR data for compound **9** are given in Table 2.

Compounds **8** and **9** are bright blue emitters in solution and the solid state with $\lambda_{\text{max}} = 430$ and 442 nm, respectively. The photoluminescent efficiency of these two compounds in solution are ca. 40%, relatively to that of 9,10-diphenylanthracene. Ab Initio molecular orbital calculations indicated that the emission is from a $\pi^* \rightarrow \pi$ transition of the 7-aza ligand and the role of the aluminum ions is simply to stabilize the ligand without changing the band gap significantly (Fig. 7).

Compounds **8** and **9** have high melting points (ca. 300°C), but they are not stable enough for electroluminescent applications. We attempted to improve the stability

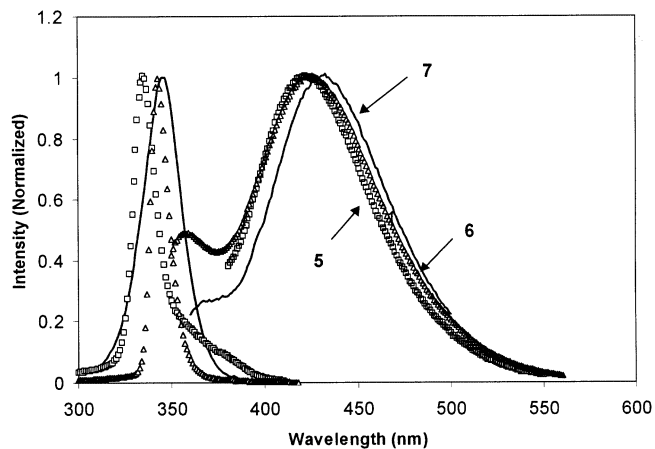


Fig. 5. Excitation and emission spectra of **5–7** in THF.

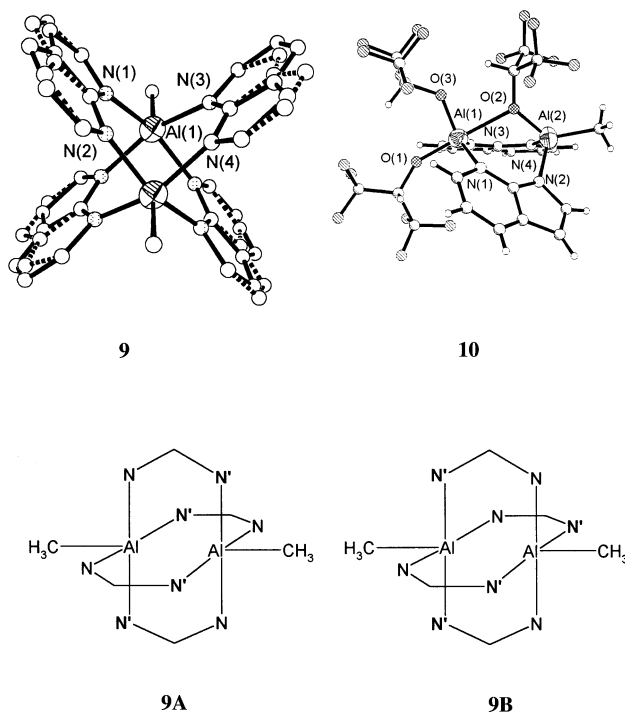


Fig. 6. Structures of **9** and **10**.

of these complexes by replacing the methyl groups with alkoxo ligands, an example of which is $\text{Al}_2(\mu\text{-OCH}(\text{CF}_3)_2)(\text{CH}_3)(7\text{-aza})_2(\text{OCH}(\text{CF}_3)_2)_2$ (**10**) (Fig. 6). Again the 7-aza ligands in **10** function as bridging ligands [10]. One of the hexafluoroiso-

Table 1
Photoluminescent excitation and emission data

Compound	Excitation, λ_{max} (nm)	Emission, λ_{max} (nm)
1	400	475
2	410	445
3	405	450
4	385	409
5	340	422
6	330	426
7	345	432
8	390	430
9	397	442
10	375	430
11	379	430
12	365	420
13	345	445
14	350	448
15	360	430
16	357	419
17	390	450
18	360	435
19	398	450
20	380	443
21	360	431
22	424	488
23	418	525
24	410	490
25	410	476

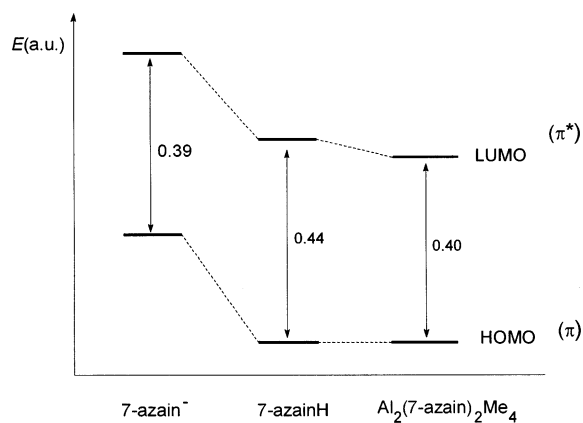


Fig. 7. The relative HOMO and LUMO levels of 7-azaH, 7-aza, and $\text{Al}_2(\text{CH}_3)_4(7\text{-aza})_2$, obtained from an ab initio molecular orbital calculation.

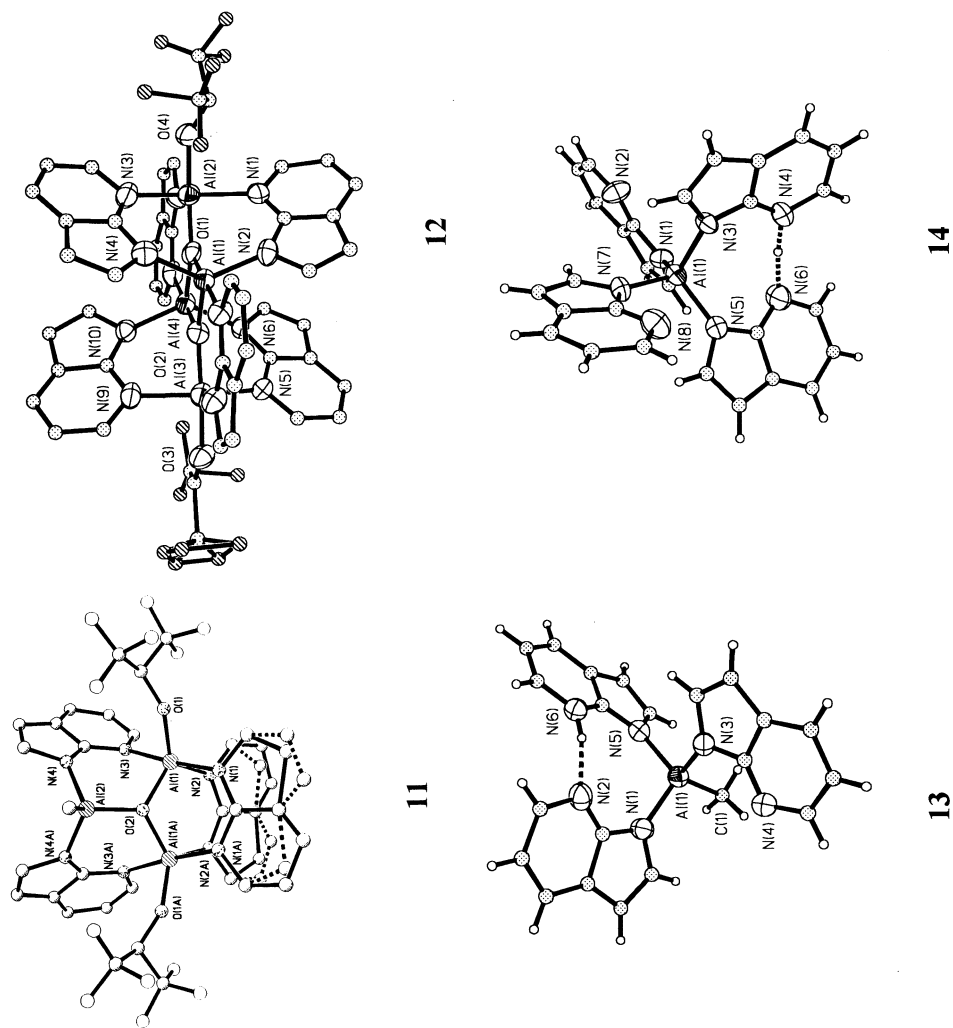
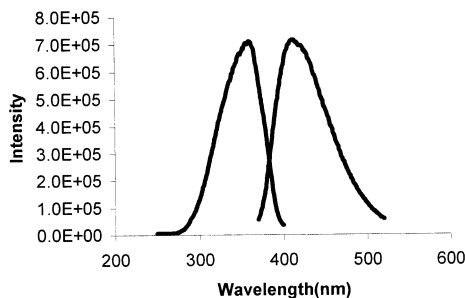


Fig. 8. Structures of 11–14.

Fig. 9. The excitation and emission spectra of **12** in the solid state.Table 2
NMR data for compound **9**

	Site	δ_{iso} (ppm)	χ (MHz)	η
Solid	1	55	6.5	0.75
	2	56	6.5	0.20
Solution		80		

propanolato ligands acts as a bridging ligand while the remaining two as terminal ligands. The luminescent properties of **10** are similar to those of **8** and **9**, but it has a low melting point and hydrolyzes rapidly when exposed to air.

3.2. Trinuclear and tetranuclear aluminum 7-azaindole complexes

In search of stable 7-aza aluminum complexes, we attempted to introduce oxo ligands into the complex. A trinuclear compound $\text{Al}_3(\mu_3\text{-O})(\text{CH}_3)(7\text{-aza})_4(\text{OCH}(\text{CF}_3)_2)_2$ (**11**) (Fig. 8) and a tetranuclear compound $\text{Al}_4(\mu_3\text{-O})_2(7\text{-aza})_6(\text{OCH}(\text{CF}_3)_2)_2$ (**12**) (Fig. 8) have been obtained [10]. In **11** one oxo ligand is bound to three Al(III) ions while in **12**, there are two triply bridging oxo ligands. Compounds **11** and **12** have a bright blue emission (Fig. 9) similar to those of **8–10** (Table 1), but are remarkably stable toward air, attributable to the presence of oxo ligands. The attempts to use compounds **11** and **12** in electroluminescent devices were unsuccessful due to their poor volatility.

3.3. Mononuclear aluminum 7-azaindole complexes

Due to the geometry of the 7-aza ligand, it has the tendency to function as a bridging ligand, leading to the formation of dinuclear and polynuclear complexes. Mononuclear 7-aza aluminum complexes can be obtained readily if 7-azaindole ligands are used in excess in the reaction with $\text{Al}(\text{CH}_3)_3$. For example, by using

excess 7-azaindole, we have obtained two mononuclear complexes [12] $\text{Al}(\text{7-aza})_2(\text{7-azaH})(\text{CH}_3)$ (**13**) and $\text{Al}(\text{7-aza})_3(\text{7-azaH})$ (**14**) (Fig. 8). The 7-aza ligands in these two complexes are terminal ligands and bound to the aluminum by the indole nitrogen atom in the solid state. There is an intramolecular hydrogen bond between the 7-aza and 7-azaH ligands. In the presence of excess 7-azaindole and hexafluoroisopropanol, a mononuclear compound $\text{Al}(\text{7-aza})(\text{7-azaH})(\text{OCH}(\text{CF}_3)_2)_2$ (**15**) (Fig. 10) was obtained [12]. The 7-aza and 7-azaH ligands in **15** have a similar bonding mode as those in **13** and **14**. In solution, these mononuclear compounds are highly fluxional, most likely caused by the interconversion of indole-bound and

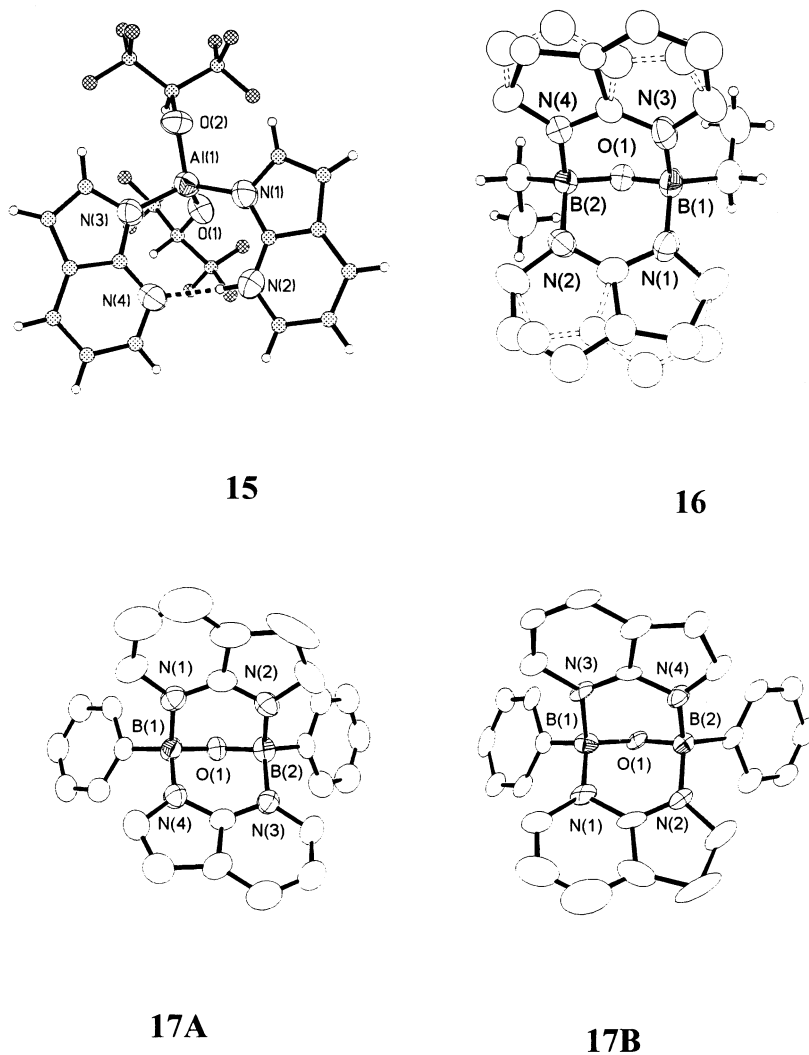


Fig. 10. Structures of **15**–**17**.

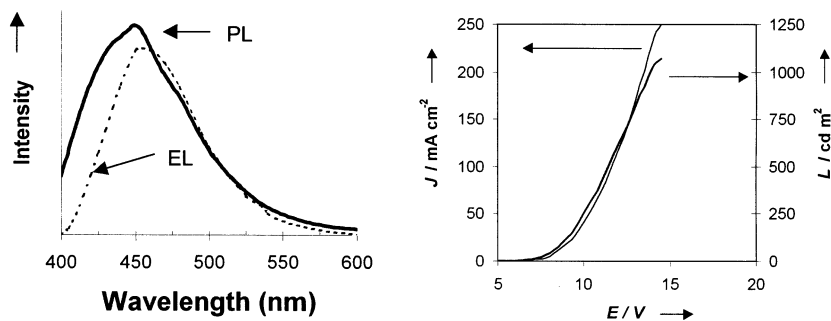


Fig. 11. Left: PL (solid line) and EL (dashed line) of **17A**. Right: current density, voltage and luminance characteristics of the **17A** EL device.

pyridyl-bound 7-aza ligands. The emission peaks of the mononuclear 7-aza complexes are considerably broader than those of dinuclear and polynuclear compounds, but are in the same energy region (Table 1). Compounds **13–15** are fairly stable. Their electroluminescent properties have not yet been studied.

3.4. Dinuclear boron 7-azaindole complexes

The instability of aluminum 7-aza complexes originates mostly from the ionic character of Al–C and Al–N bonds. B–C and B–N bonds, on the other hand, are fairly covalent, hence much more stable than Al–C and Al–N bonds. Although we obtained a number of mononuclear 7-aza boron compounds by the reaction of BR_3 with 7-azaindole [13], none of them show promising luminescent properties and thermal stability that are suitable for electroluminescent devices. However, two dinuclear boron compounds synthesized by our group, $\text{B}_2(\text{O})(7\text{-aza})_2(\text{C}_2\text{H}_5)_2$ (**16**) and $\text{B}_2(\text{O})(7\text{-aza})_2\text{Ph}_2$ (**17**) (Fig. 10) display very promising stability and luminescent properties [14,15]. **16** and **17** are analogs with similar structures. However, for compound **16**, only isomer **A** was observed [14] while for compound **17**, both isomer **A** and **B** (Fig. 10) were observed in solution and the solid state [15], of which **A** is thermally much more stable than **B**. Interestingly, no interconversion between **A** and **B** was observed in solution. Compounds **16** and **17** display a bright blue emission at 450 and 430 nm, respectively. In solution the photoluminescent yields of **16** and **17** are greater than 40%, compared with that of 9,10-diphenylanthracene. The emission lifetime for **16** and **17** was determined to be ca. 10–30 ns. Compounds **16** and **17A** are stable and have a melting point close to 300°C and can be sublimed readily, making them ideal emitters for electroluminescent devices. By using NPB (*N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine) as the hole transport material, Alq_3 as the electron transporting layer, and either **16** or **17A** as the emitter, bright blue electroluminescent devices were achieved [15]. The electroluminescent data for **17A** are shown in Fig. 11. The EL devices of **16** and **17A** do not have a long-term stability, the cause of which has not been fully understood.

3.5. Zinc 7-azaindole complexes

The first Zn(II) complex of 7-azaindole, $\text{Zn}_4(\text{O})(7\text{-aza})_6$, was reported by Che and coworkers [16]. Recently it has been demonstrated that the $\text{Zn}_4(\text{O})(7\text{-aza})_6$ compound can produce blue electroluminescence [17]. We have synthesized recently a mononuclear Zn(II) complex [18], $\text{Zn}(\text{O}_2\text{CCH}_3)_2(7\text{-azaH})_2$ (**18**) (Fig. 12), which exhibits a bright blue emission in solution and the solid state. Results from preliminary investigation indicated that compound **18** is capable of producing a blue light in electroluminescent devices.

4. 7-Azaindole derivatives

4.1. Aluminum complexes of 2-phenyl-7-azaindole and 2-methyl-7-azaindole

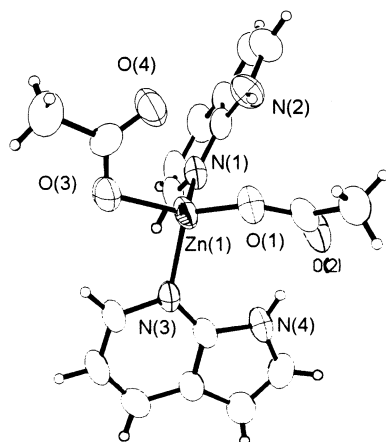
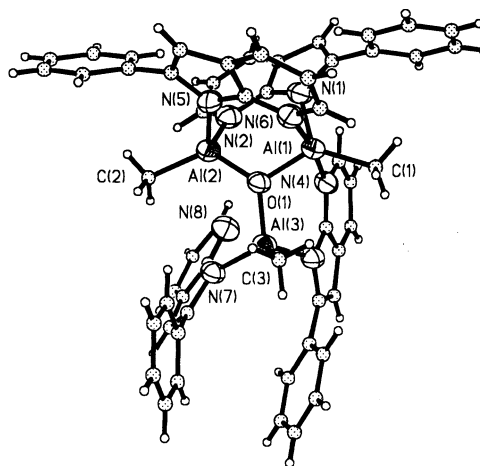
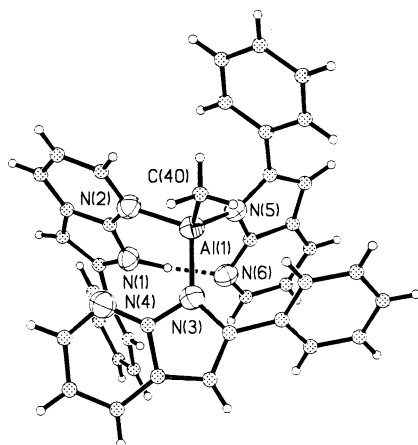
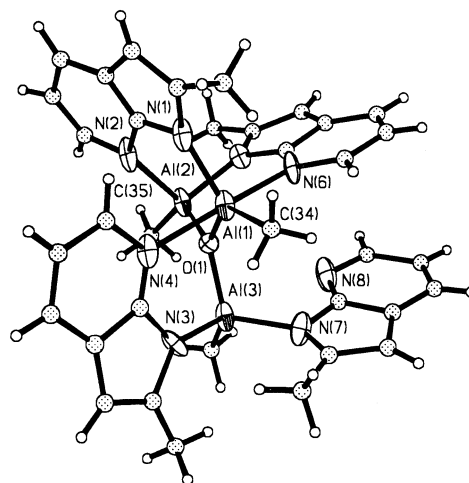
Two derivatives of 7-azaindole, 2-phenyl-7-azaindole (2-Ph-7-azaH) and 2-methyl-7-azaindole (2-Me-7-azaH) were synthesized by our group in order to examine the effect of substituents of the 7-azaindole on the structure and luminescence of the aluminum complexes. The reaction of excess 2-Ph-7-azaH (Scheme 2) with $\text{Al}(\text{CH}_3)_3$ yielded a mononuclear compound $\text{Al}(\text{CH}_3)(2\text{-Ph-7-aza})_2(2\text{-Ph-7-azaH})$ (**19**) (Fig. 12), which has the same formula as that of **13**. However, unlike **13** where all 7-aza and 7-azaH ligands are bound to the aluminum by the indole nitrogen site, the 2-Ph-7-azaH ligand in **19** is bound to the Al(III) ion by the pyridyl nitrogen atom in the solid state [19]. Steric factors may be responsible for the structural difference of **13** and **19**. Although compound **19** has a blue emission band at ca. 450 nm, it is very weak, compared with that of **13**.

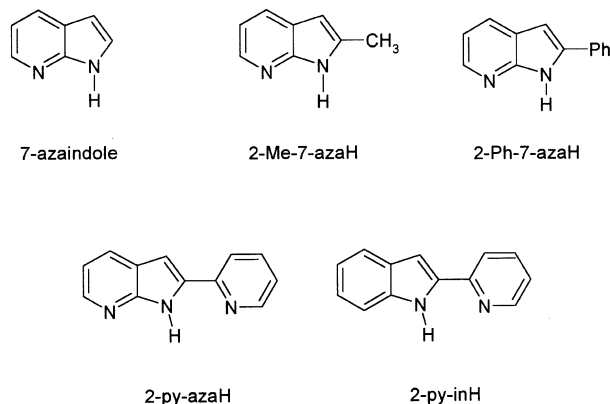
In the presence of moisture, the reaction of 2-Ph-7-azaH with $\text{Al}(\text{CH}_3)_3$ yielded a trinuclear compound $\text{Al}_3(\mu_3\text{-O})(\text{CH}_3)_3(2\text{-Ph-7-aza})_4$ (**20**) (Fig. 12), which is isoelectronic with that of **11** (except that the two alkoxo ligands in **11** were replaced by two methyl groups in **20**). However, unlike **11** that displays a symmetric structure, **20** does not have any symmetry and each Al(III) ion in **20** has a distinct chemical environment. The reaction of 2-Me-7-azaH (Scheme 2) with $\text{Al}(\text{CH}_3)_3$ under the same reaction conditions yielded an analogous compound $\text{Al}_3(\mu_3\text{-O})(\text{CH}_3)_3(2\text{-Me-7-aza})_4$ (**21**) (Fig. 12), which has a structure similar to that of **20** in the solid state [19]. The methyl or phenyl substituent at the two position of the 7-azaindole ligand clearly leads to the dramatic structural difference between that of **11** and those of **20** and **21**.

Compound **20** has a very weak blue emission while compound **21** has a bright blue emission similar to that of **11**. The weak emission intensity of **19** and **20** was attributed to the phenyl group, which perhaps causes the loss of energy via thermal vibrations.

Compounds **20** and **21** are highly dynamic in solution. At ambient temperature, all three Al(III) ions in **20** and **21** appear to have an identical chemical environment in solution in the NMR time scale. Variable-temperature 1D and low-temperature 2D EXSY ^1H -NMR experiments established that an unusual intramolecular migra-

tion of the coordinated 2-R-7-aza ligands are responsible for the fluxional behavior of **20** and **21** in solution. Compounds **19**–**21** are not stable enough for electroluminescent applications.

**18****20****19****21**Fig. 12. Structures of **18**–**21**.



Scheme 2.

4.2. Complexes of 2-(2-pyridyl)indole and 2-(2-pyridyl)-7-azaindole

The bonding mode of 7-azaindole is limited to either bridging or terminal. It is not possible to obtain stable 7-azaindole chelate complexes because of the geometry of the 7-azaindole ligand. In order to achieve the chelate bonding mode, we attached a pyridyl group at the two position of the 7-azaindole ligand, obtaining a new ligand 2-(2-pyridyl)-7-azaindole (2-py-azaH) (Scheme 2). For comparison purpose, we also synthesized 2-(2-pyridyl)indole (2-py-in). Several bright luminescent complexes with 2-py-aza or 2-py-in ligands $\text{Zn}(\text{2-py-in})_2(\text{THF})$ (**22**), $\text{BPh}_2(\text{2-py-in})$ (**23**), $\text{Be}(\text{2-py-in})_2$ (**24**) and $\text{BPh}_2(\text{2-py-aza})$ (**25**) (Fig. 13) have been obtained by either the reaction of the anionic ligand with the corresponding metal chloride or the reaction of the neutral ligand with BPh_3 [20].

Compound **22** is not stable under air while compounds **23–25** are air stable, readily sublimable, and have a melting point above 250°C. In the solid state, compounds **22–25** have an emission maximum at $\lambda = 488, 516, 490$ and 476 nm, respectively. The addition of the pyridyl group to the 7-azaindole significantly shifts the emission energy of the complex toward a longer wavelength in comparison with that of 7-azaindole complexes, attributable to the increased conjugation in 2-py-aza. The structures of compounds **23** and **25** are similar. However, there is a 40 nm difference in emission energy of **23** and **25**. The blue shift of emission energy displayed by compound **25**, in comparison to that of **23** is attributed to the presence of an extra nitrogen atom in the 2-py-aza ligand based on the results of an ab initio calculations on compounds **23** and **25**.

Electroluminescent devices of compounds **24** and **25** were fabricated by using *N,N'*-di-1-naphthyl-*N,N'*-diphenylbenzidine (NPB) as the hole transporting layer, Alq_3 ($q = 8\text{-hydroxyquinolato}$) as the electron transporting layer, and compound **24** or **25** as the light emitting layer [20]. At 20 mA cm^{-2} the EL device of **24** has an external efficiency of 1.06 cd A^{-1} while the EL device of **25** has an external efficiency of 2.34 cd A^{-1} , demonstrating that compounds **24** and **25** are efficient

and promising emitters in electroluminescent devices. The data of electroluminescence for **24** and **25** are shown in Table 3, and Figs. 14 and 15.

5. Summary

The nitrogen donor ligands, dpa and 7-azaindole, form a variety of bright blue luminescent compounds with Al(III), Zn(II) and B(III) as the coordinating centers.

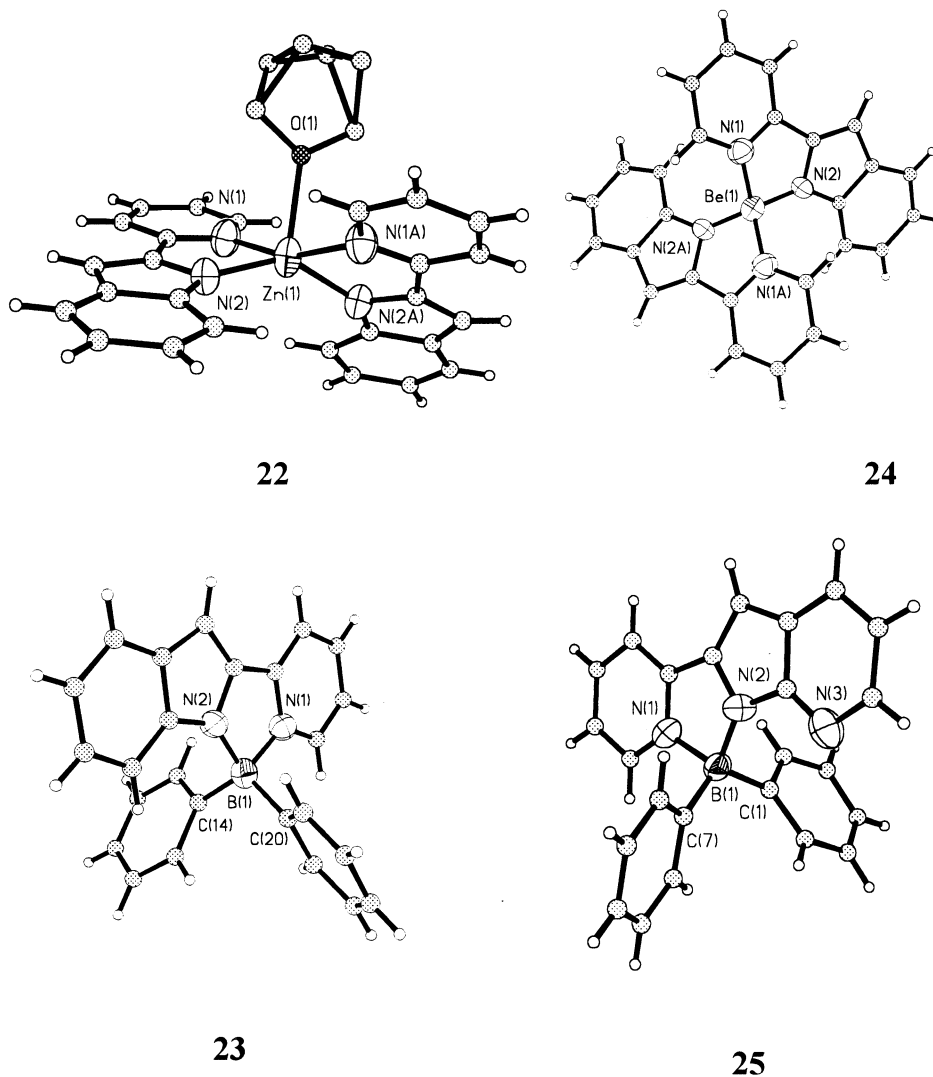


Fig. 13. Structures of **22**–**25**.

Table 3
EL device data for **24** and **25**

Device	Hole transport (thickness, nm)	Emitting layer (thickness, nm)	Electron transport (thickness, nm)	C.I.E. (x , y)	Efficiency at 20 mA cm ⁻² (cd A ⁻¹)
A	NPB (60)	Compound 24 (75)		0.306, 0.500	1.06
B	NPB (60)	Compound 25 (20)	Alq ₃ (40)	0.279, 0.463	0.57
C	NPB (60)/Bicarb (20)	Compound 25 (20)	Alq ₃ (40)	0.200, 0.325	2.34

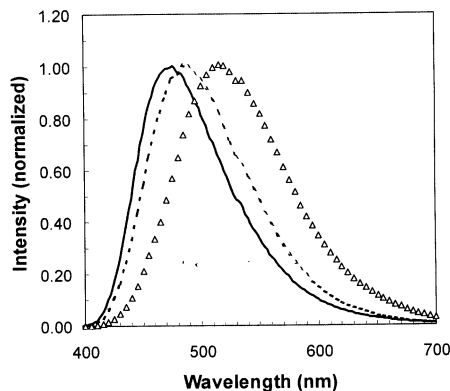


Fig. 14. PL (solid line) and EL (empty triangle, device B; dashed line, device C) of **25**.

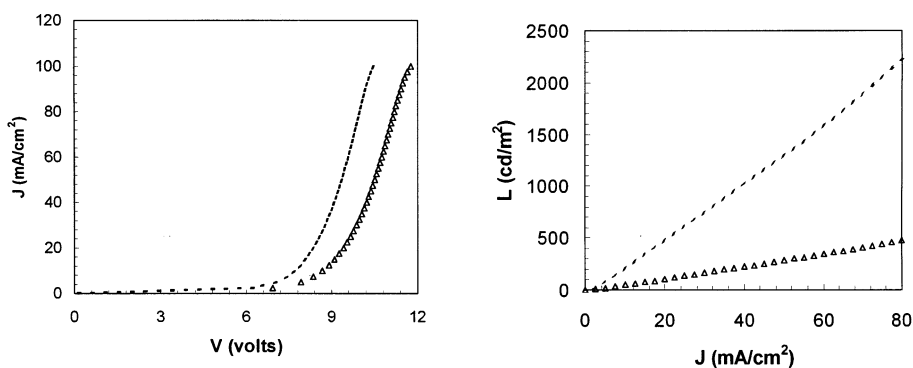


Fig. 15. Left: J – V curves (empty triangle, device B; dashed line, device C); right: L – J curve (empty triangle, device B; dashed line, device C).

The blue emission originates from a $\pi^* \rightarrow \pi$ transition of the ligand and is fluorescent in nature. The derivatives of dpa and 7-azaindole also produce blue luminescent complexes readily. The role of the central atom is to provide the stability to the ligand. The modification of the ligand often leads to the change of emission energy, emission intensity and the stability of the complex, in addition to a dramatic change of the structure and bonding. The most promising blue luminescent complexes for electroluminescent devices are boron and beryllium compounds containing 7-azaindole, 2-(2-pyridyl)-7-azaindole, and 2-(2-pyridyl)indole ligands. Unlike the corresponding Zn(II) or Al(III) compounds, which are often either chemically or thermally unstable, boron and beryllium compounds have a high chemical and thermal stability due to the high covalency of B–ligand and Be–ligand bonds. Further modification of the ligands and synthesis of new complexes could lead to the discovery of better blue emitters for OLEDs, which is being conducted in our laboratory.

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