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Boron Complexes with Chelating Anilido-Imine Ligands: Synthesis, Structures and Luminescent Properties

Yi Ren,[a] Xiaoming Liu,[a] Wei Gao,[a] Hong Xia,[a] Ling Ye,[a] and Ying Mu*[a]

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Three new boron complexes with anilido-imine ligands, *ortho*-$C_6H_4(NAr^1)(CH{=}NAr^2)BF_2$ [Ar^1 = 2,6-$Et_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**3a**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**3b**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = 2,6-$Me_2C_6H_3$ (**3c**)] were synthesized by the reaction of $BF_3(OEt_2)$ with the lithium salt of the corresponding ligands. All complexes were characterized by ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopy, elemental analyses and mass spectrometry. The molecular structures of complexes **3a**–**3c** were determined by X-ray crystallography. DSC analysis of **3a**–**3c** demonstrates their good thermal stability. Luminescent properties of the ligands and the complexes **3a**–**3c** in solution and the solid state were studied.

Introduction

Luminescent tricoordinate and tetracoordinate boron complexes, due to their high thermal stability, adequate electron transport and excellent luminescent properties, have recently attracted a great deal of attention in the field of organic light-emitting devices (OLEDs) application.[1] Marder et al.[2] and Cornu et al.[3] focus their works on the three-coordinate organoboron compounds and π-conjugated systems incorporating closo-dodecaborate clusters, respectively, and study their optical properties. Wang and co-workers have explored some devices made from BR_2q [R = Et, Ph, 2-naphthyl, q = 8-hydroxyquinolato][4] and boron complexes with modified 8-hydroxyquinoline ligands,[5] which not only are promising emitters, but also were found to possess excellent electron transport properties. Y. Wang's group has reported some boron complexes with phenol-pyridyl ligands and investigated their applications in OLEDs.[6] Meanwhile, many boron complexes with N,N-chelate ligands were reported.[7] Some of these complexes provide excellent luminescent properties, and cover almost the entire visible region when changing substituents on the ligands.[7a–7f] Recently, some luminescent complexes with Schiff-base ligands were synthesized and showed potential applications in organic optoelectronics.[8] However, luminescent boron complexes with Schiff-base ligands are rather rare. We recently reported a new class of aluminum complexes with Schiff base type chelating anilido-imine ligands showing good luminescent properties.[9] However, the aluminum complexes are usually vulnerable, to some extent, to air and moisture.[10] In contrast, the boron complexes are generally chemically and thermally stable, and thus more promising for practical applications.[7b,11] We have therefore synthesized a number of new boron complexes with anilido-imine ligands: *ortho*-$C_6H_4(NAr^1)(CH{=}NAr^2)BF_2$ [Ar^1 = 2,6-$Et_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**3a**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**3b**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = 2,6-$Me_2C_6H_3$ (**3c**)]. Herein, we report the syntheses, characterizations, and fluorescent properties of these complexes.

Results and Discussion

Synthesis of Ligands

Anilido-imine ligands *ortho*-$C_6H_4(NHAr^1)(CH{=}NAr^2)$ [Ar^1 = 2,6-$Et_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**2a**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = *p*-MeC_6H_4 (**2b**); Ar^1 = 2,6-*i*$Pr_2C_6H_3$, Ar^2 = 2,6-$Me_2C_6H_3$ (**2c**)] were synthesized in good yields by the reaction of *ortho*-$C_6H_4F(CH{=}NAr^2)$ (**1**) with corresponding $LiN(H)Ar^1$ (Scheme 1) according to the literature procedure.[9,12] Among the ligands, **2a** and **2b** are new compounds while **2c** has been reported previously.[9] The reaction was carried out in THF and the crude products were purified by crystallization from methanol. Compounds **2a** and **2b** were characterized by ^1H and ^{13}C NMR spectroscopy along with elemental analyses. The ^1H NMR spectra of both compounds exhibit resonances around δ 8.59 ppm for the CH protons in –CH=N– group, with the corresponding ^{13}C NMR resonances occurring about δ = 162.4 ppm. The NH resonances appear at characteristically low field (δ = 10.65, 10.60 ppm). The infrared absorption bands of the imine C=N stretching occur at 1615 and 1624 cm^{-1}. These data are similar to the corresponding values of **2c**.[9]

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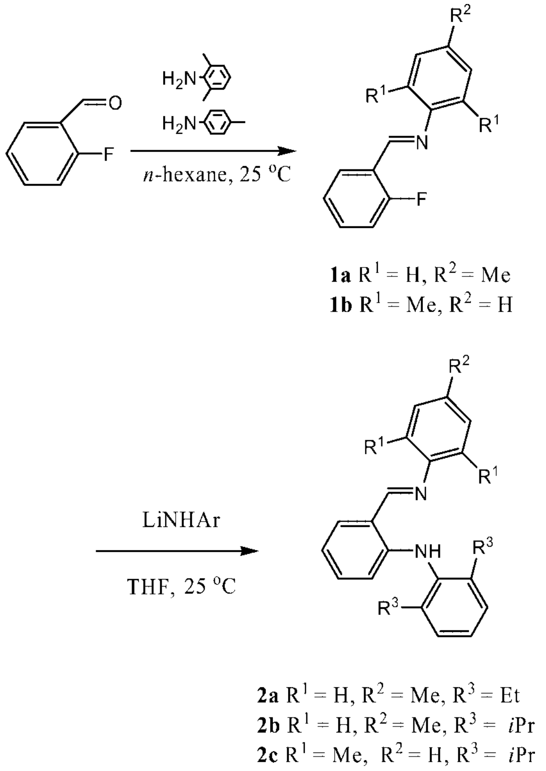
[a] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China
Fax: +86-431-85193421
E-mail: ymu@mail.jlu.edu.cn



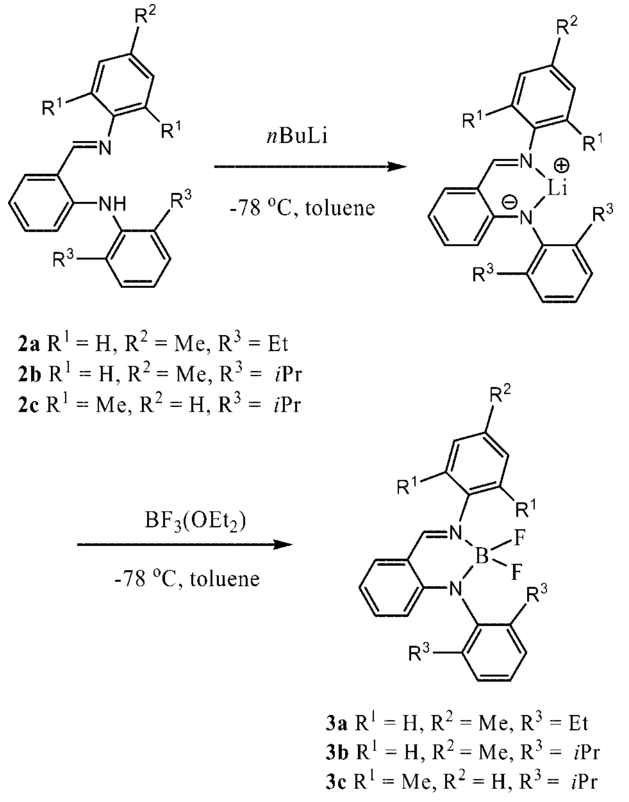
1a $R^1 = H$, $R^2 = Me$
1b $R^1 = Me$, $R^2 = H$

2a $R^1 = H$, $R^2 = Me$, $R^3 = Et$
2b $R^1 = H$, $R^2 = Me$, $R^3 = i\text{Pr}$
2c $R^1 = Me$, $R^2 = H$, $R^3 = i\text{Pr}$

Scheme 1. Synthetic procedure of ligand **2a**–**2c**.

Synthesis of Complexes

The boron difluoride complexes **3a**–**3c** were synthesized in reasonable yields (71–78%) by the reaction of $BF_3(OEt_2)$ with the lithium salt of corresponding ligand that was generated in situ by treating the free ligand with *n*BuLi in toluene at –78 °C (Scheme 2). These complexes are well soluble in dichloromethane, diethyl ether, toluene and THF, but less soluble in saturated hydrocarbons. All complexes **3a**–**3c** were characterized by elemental analyses, ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectroscopy, and satisfactory analytic results were obtained. In the ^{1}H NMR spectra of **3a**–**3c**, the resonances for the imino CH protons are at δ = 8.37, 8.37 and 8.12 ppm, respectively. While the resonances (δ = 159.9–163.9 ppm) for the imino C-atoms in the ^{13}C NMR spectra shift to high field in comparison with the corresponding signals of the free ligands and the dichloride aluminum complexes.[13] The N–H signals of the free ligands disappear in the ^{1}H NMR spectra of the complexes **3a**–**3c**, which is indicative of the formation of B–N bond in these complexes. The two methyl groups of the isopropyl units in complexes **3b** and **3c** are inequivalent, since the coordination of the anilido-imine ligands to the boron center causes rotation about the N–aryl bond to become slow on the NMR time scale.[14] In addition, in the ^{1}H and ^{13}C NMR spectra of these complexes **3a**–**3c**, the resonances for 2,6-substituents of the aromatic ring at the amido nitrogen are equal, which indicates these complexes all have Cs-symmetric structures in solution. In ^{11}B NMR spectra, complexes **3a**–**3c** exhibit triplet at δ 4.534, 4.527 and 4.335 ppm respectively, due to coupling with two equivalent fluorine atoms. These resonances of complexes **3a**–**3c** are in lower field compared to those of 2,4-diethyl-4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene (δ_B = 3.8)[15a] and *p*-Tol_2nacnacBF_2 (δ_B 2.0),[15b] while in substantially higher field in comparison with that of tricoordinate boron complex $[(\text{Tolylnacnac})BMe]^+[MeB(C_6F_5)_3]^-$ (δ_B = 37.1).[15b] The narrow linewidth of ^{11}B NMR spectra for all complexes is consistent with tetrahedral boron. Complexes **3a**–**3c** are air- and moisture-stable in solution and solid state. Differential scanning calorimetry (DSC) analysis of complexes **3a**–**3c** shows that complexes **3a**–**3c** melt at 159.8, 176.8 and 221.5 °C, respectively. These data are close to the melting points of similar tetra-coordinated boron complexes, 2-(4′-methylquinolinyl)-2-phenolato)BPh_2 (210 °C),[16a] and 1,6-bis(2-hydroxyphenyl)pyridylboron–2-methoxybenzene (227 °C).[16b] DSC analysis of **3a**–**3c** also exhibits their high thermal stability since they can be heated to 250 °C without decomposition. They also have good thermal stability in solution and can be heated in boiling toluene or ethanol for several hours without obvious decomposition.



2a $R^1 = H$, $R^2 = Me$, $R^3 = Et$
2b $R^1 = H$, $R^2 = Me$, $R^3 = i\text{Pr}$
2c $R^1 = Me$, $R^2 = H$, $R^3 = i\text{Pr}$

3a $R^1 = H$, $R^2 = Me$, $R^3 = Et$
3b $R^1 = H$, $R^2 = Me$, $R^3 = i\text{Pr}$
3c $R^1 = Me$, $R^2 = H$, $R^3 = i\text{Pr}$

Scheme 2. Synthetic procedure of complexes **3a**–**3c**.

Crystal Structures

Molecular structures of the complexes **3a**–**3c** were determined by X-ray crystallographic analysis. The crystals of complexes **3a**–**3c** suitable for crystal structure analysis were obtained from *n*-hexane at 5 °C. The ORTEP drawings of molecular structures of **3a**, **3b** and **3c** are shown in Figures 1, 2, and 3, respectively. Selected bond lengths and angles for these complexes are given in Table 1. The X-ray analysis reveals that complexes **3a**–**3c** are four-coordinate and adopt a distorted tetrahedral geometry at the boron center. Complex **3a** belongs to the monoclinic space group *P*21/*n*, **3b**,**3c** to the triclinic space group *P*-1. In these complexes, the anilido-imine ligands chelate to the boron center to form the six-membered chelating rings that are nearly planar with the boron atom lying 0.0594 Å, 0.3127 Å, and 0.3020 Å out of the plane, respectively. The imino C=N bonds in these complexes retain their double bond character, being 1.307(2) Å, 1.302(2) Å, and 1.306(3) Å for **3a**, **3b**, and **3c**, respectively. The B–N (amido) distances (1.510(3) Å for **3a**, 1.521(3) Å for **3b**, 1.531(3) Å for **3c**) are shorter than the B–N (imine) distances (1.564(3) Å for **3a**, 1.580(2) Å for **3b**, 1.581(3) Å for **3c**) which is consistent with the fact that the B–N (amido) bond is a covalent bond while the B–N (imine) bond is a coordination bond. The B–N (imine) distances are larger than those values (1.550(3) Å and 1.553(3) Å] previously reported for *p*-Tol$_2$nacnacBF$_2$,[15b] while the B–N (amido) distances are shorter than the values (1.740(4) Å] of 2,6-(NMe$_2$)$_2$C$_6$H$_3$BCl(Ph).[15c] The average B–F bond lengths of 1.382(9) Å in those boron complexes are close to those values of 2,2-difluoro-1,3,4,6-tetramethyl-3-aza-1-azonia-2-bora-4,6-cyclohexadiene (1.403(2) Å][17a] and 4,4-difluoro-1,3,5,7,9-pentamethyl-3a,4a-diaza-4-bora-*s*-indacene (1.394(3) Å].[17b,17c] The F–B–F bond angles (107.5(2)° for **3a**, 108.86(18)° for **3b**, 108.5(2)° for **3c**) of those complexes are similar, which are slightly larger than 107.1(2)° for 2,2-difluoro-1,3,4,6-tetramethyl-3-aza-1-azonia-2-bora-4,6-cyclohexadiene,[17a] but smaller than the ideal tetrahedral angles (109.49°). The dihedral angles between the six-membered chelating ring and the aromatic ring at the amido nitrogen are 87.00° for **3a**, 83.65° for **3b**, and 82.00° for **3c**, while the dihedral angles between the six-membered chelating ring and the aromatic ring at the imine nitrogen are 51.40°, 55.17° and 80.60° for **3a**, **3b** and **3c**, respectively.

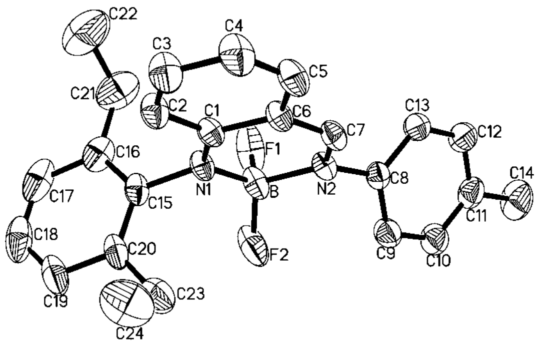


Figure 1. Molecular structure of complex **3a** (thermal ellipsoids are drawn at the 30% probability level).

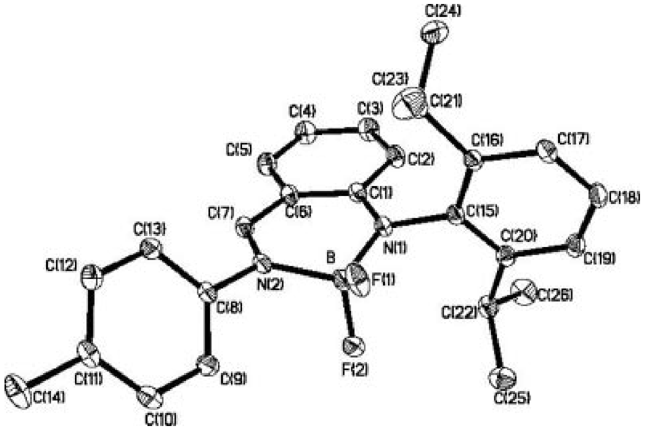


Figure 2. Molecular structure of complex **3b** (thermal ellipsoids are drawn at the 30% probability level).

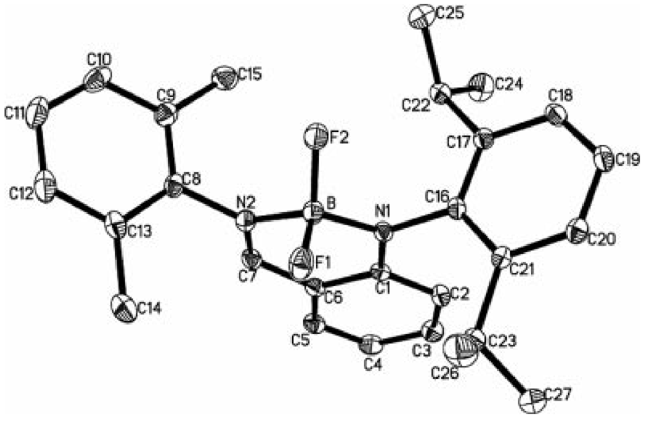


Figure 3. Molecular structure of complex **3c** (thermal ellipsoids are drawn at the 30% probability level).

Table 1. Selected bond lengths [Å] and angles [°].

Complex **3a**			
N(1)–B	1.510(3)	C(1)–N(1)–B	124.97(16)
N(2)–B	1.564(3)	F(2)–B–N(2)	110.3(2)
F(1)–B	1.387(3)	C(15)–N(1)–B	116.93(15)
F(2)–B	1.368(3)	C(7)–N(2)–B	121.67(18)
N(1)–C(1)	1.364(2)	C(8)–N(2)–B	118.67(16)
N(2)–C(7)	1.307(2)	F(1)–B–F(2)	107.5(2)
N(1)–B–N(2)	110.15(17)	F(1)–B–N(1)	112.0(2)
F(1)–B–N(2)	105.88(18)	F(2)–B–N(1)	110.95(19)
Complex **3b**			
N(1)–B	1.521(3)	C(1)–N(1)–B	123.68(15)
N(2)–B	1.580(2)	F(2)–B–N(2)	106.75(17)
F(1)–B	1.367(3)	C(15)–N(1)–B	117.34(14)
F(2)–B	1.395(3)	C(7)–N(2)–B	120.86(16)
N(1)–C(1)	1.358(2)	C(8)–N(2)–B	119.83(14)
N(2)–C(7)	1.302(2)	F(1)–B–F(2)	108.86(18)
N(1)–B–N(2)	108.00(15)	F(1)–B–N(1)	112.08(17)
F(1)–B–N(2)	108.81(17)	F(2)–B–N(1)	112.15(17)
Complex **3c**			
B–F(2)	1.384(3)	F(1)–B–N(1)	111.85(19)
B–F(1)	1.389(3)	F(2)–B–N(2)	109.70(18)
B–N(1)	1.531(3)	F(1)–B–N(2)	107.93(18)
B–N(2)	1.581(3)	N(1)–B–N(2)	107.28(18)
C(1)–N(1)	1.365(3)	C(1)–N(1)–B	123.69(18)
C(7)–N(2)	1.306(3)	C(16)–N(1)–B	117.35(16)
F(2)–B–F(1)	108.5(2)	C(7)–N(2)–B	122.19(18)
F(2)–B–N(1)	111.53(19)	C(8)–N(2)–B	119.59(17)

UV/Vis and Fluorescent Properties

Table 2 summarizes the UV/Vis and fluorescent properties of compounds **2a**–**2c** and **3a**–**3c** determined in both solution and the solid state. The free ligands **2a**–**2c** all display weak blue fluorescence with emission maxima of 448, 446 and 420 nm, respectively. UV/Vis absorptions of complexes **3a**–**3c** are displayed in Figure 4. The maximal absorptions of **3a**–**3c** (λ_{abs} = 440, 440 and 429 nm) are close to those of their aluminum analogues (λ_{abs} = 437, 436, 436, 447 nm).[13] The fluorescent spectra of complexes **3a**–**3c** are shown in Figure 5. Complexes **3a**–**3c** in solution all give a broad emission band (bandwidth at half-height: 64, 61, 69 nm) with λ_{max} = 511, 512 and 491 nm, respectively. The quantum yields of these complexes are relatively high in solution. The emission energies of these complexes are significantly red-shifted in comparison with their free ligands. As previous reported,[9,13] the observed luminescence of these complexes could be attributed to π^*–π transition of their conjugated chelating anilido-imine ligands. The role of the coordination of the ligand to the boron atom in the luminescence of **3a**–**3c** should be twofold as pointed out in literatures for coordination complexes.[18] The formation of the B–N bond via the donation of lone-pair of the N atom to the B atom lowers the energy gap between π^* and π of the ligand, and the chelating ring makes the ligand more rigid, which can reduce the loss of energy via vibrational motions and increase the emission efficiency. The emission maxima of complexes **3a** and **3b** are close to each other, while the emission maximum of **3c** is blue-shifted for about 20 nm compared to the ones of **3a** and **3b**. Such a result might be attributed to the differences in the number and size of the *ortho*-substituents on the rotatable aryl rings of their ligands that could affect the dihedral angles between the six-membered chelating ring and the aromatic ring at the imine nitrogen and thus the conjugated extent of these complexes.[5,19a,19b] In addition, the lower basicity and electron density of the anilido may also be responsible for the emission red shift in **3a** and **3b**.[19c] Compared to its aluminum analogue, [*ortho*-$C_6H_4N(C_6H_3i\mathrm{Pr}_2\text{-}2,6)(CH{=}NC_6H_3Me_2\text{-}2,6)AlCl_2$] ($\lambda_{max}$ = 510),[13] the emission maximum of complex **3c** is blue-shifted by 19 nm in hexane. The emission energies of complexes **3a**–**3c** in solution are close to or slightly higher than those of related boron compounds, 4,4-difluoro-8-(4-hydroxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (λ_{abs} = 518 nm)[20a] and 2,4-diethyl-4-fluoro-1,3,5,7,8-pentamethyl-4-phenyl-4-bora-3a,4a-diaza-*s*-indacene (λ_{abs} = 536 nm).[20b] All complexes **3a**–**3c** exhibit bright

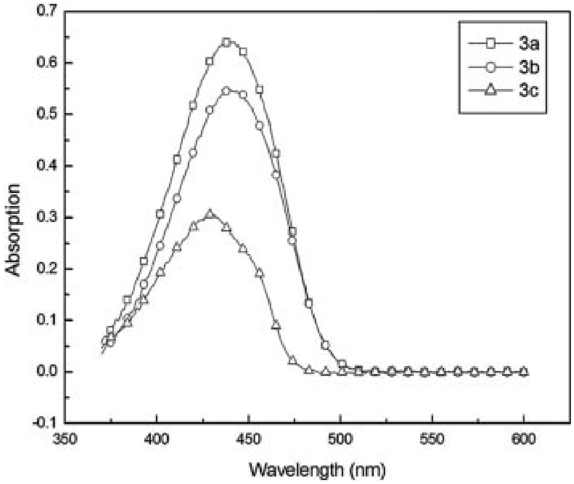


Figure 4. UV/Vis absorption of complexes **3a**–**3c** in hexane.

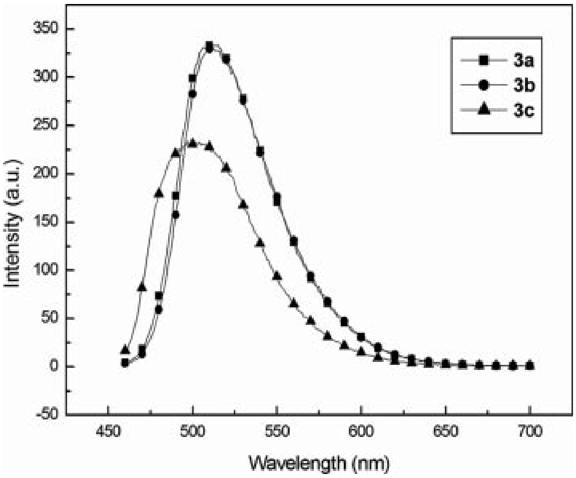


Figure 5. Emission spectra of complexes **3a**–**3c** in *n*-hexane.

Table 2. Photoluminescent data for ligands **2a**–**2c** and complexes **3a**–**3c**.

Compound	Conditions	λ_{abs} [nm]	λ_{em} [nm]	ε [M·cm^{-1}]	Quantum yields [Φ][a]
2a	hexane, 298 K	386	448	12587	0.027
	solid, 298 K		468		
2b	hexane, 298 K	386	446	10358	0.032
	solid, 298 K		461		
2c	hexane, 298 K	371	420	11265	0.029
	solid, 298 K		432		
3a	hexane, 298 K	440	511	9521	0.549
	solid, 298 K		527		
3b	hexane, 298 K	440	512	9785	0.574
	solid, 298 K		518		
3c	hexane, 298 K	429	491	9840	0.582
	solid, 298 K		519		

[a] Determined using quinine sulfate in 0.1 M sulfuric acid as a standard.

fluorescence in the solid state when irradiated with an adequate excitation wavelength. The emission spectra of these complexes in the solid state are shown in Figure 6. Complexes **3a**, **3b**, and **3c** each has a relatively narrow emission band (bandwidth at half-height: 55, 75, 74 nm) with λ_{max} = 527, 518 and 519 nm, respectively. The emission maxima of these complexes in the solid state are red-shifted compared to their corresponding emission maxima in solution. Red shifting of emission maximum can be normally observed for most fluorescent compounds in the solid state due probably to π-π staking of aromatic rings in the molecules.

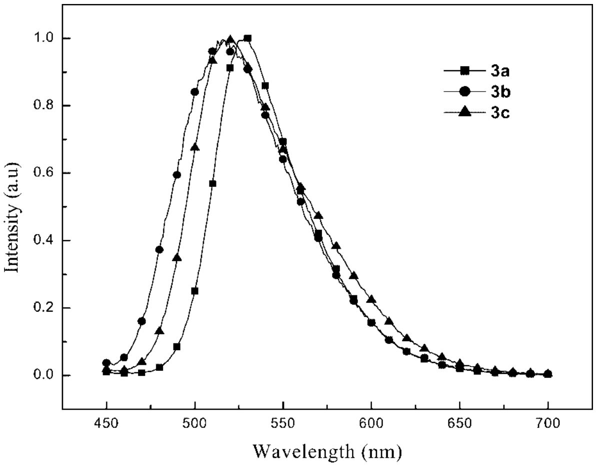


Figure 6. Emission spectra of complexes **3a**–**3c** in the solid state.

Experimental Section

General: All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene, hexane, THF, and diethyl ether were dried by reflux over sodium and benzophenone and distilled under nitrogen prior to use. C_6D_6 was dried with activated 4-Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. $CDCl_3$ was dried with CaH_2 for 48 h and vacuum-transferred to an air-free flask. $BF_3(OEt_2)$ and *n*BuLi were purchased from Aldrich and used as received. The pre-ligands and the ligands were synthesized according to literature procedures.[9,12] ^{1}H and ^{13}C NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer. ^{11}B NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer at 160 MHz with $BF_3(OEt_2)$ as external reference (positive values downfield).^{19}F NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer at 376.27 MHz with $CFCl_3$ as external reference (positive values downfield). The elemental analysis was performed with a Perkin–Elmer 2400 microanalyzer. UV/Vis absorption spectra were recorded on a PE UV-lambdazo spectrophotometer. Fluorescence measurements were carried out on a Shimadzu RF-5301PC. The melting points were determined on a Fisher–Johns melting point apparatus. Differential scanning calorimetric measurements were performed on a NETZSCH DSC204 instrument.

***ortho*-$C_6H_4NH(C_6H_3Et_2$-2,6)(CH=NC_6H_4Me-*p*) (2a):** A solution of *n*BuLi (25.29 mL, 30.35 mmol) in hexanes was added to a solution of 2,6-diethylaniline (5.0 mL, 30.35 mmol) in THF (20 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The resulting solution of LiNHAr was transferred into a solution of *ortho*-C_6H_4F(CH=NC_6H_4Me-*p*) (6.47 g, 30.35 mmol) in THF (20 mL) at 25 °C. After stirring for 24 h, the reaction was quenched with H_2O (20 mL), the mixture was extracted with *n*-hexane, and the organic phase evaporated to dryness in vacuo to give the crude product as yellow solid. Pure product (7.79 g, 75%) was obtained as yellow crystals by recrystallization from ethanol at –20 °C. $C_{24}H_{26}N_2$ (342.48): calcd. C 84.17, H 7.65, N 8.18; found C 84.12, H 7.67, N 8.21%. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ = 1.09 (t, 6 H, CH_2CH_3), 2.30 (s, 3 H, CH_3), 2.47 (q, 2 H, CH_2CH_3), 2.57 (q, 2 H, CH_2CH_3), 6.18 (d, 1 H, Ph-*H*), 6.62 (t, 1 H, Ph-*H*), 7.03–7.34 (m, 9 H, Ph-*H*), 8.59 (s, 1 H, C*H*=NAr) 10.65 (s, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 293 K): δ = 15.1 (CH_3), 21.0 (CH_2CH_3), 25.1 (CH_2CH_3), 76.8, 77.1, 77.3, 111.9, 115.5, 117.1, 120.9, 126.8, 127.0, 127.6, 129.9, 132.0, 134.6, 142.9, 149.0, 149.1, 162.4 (*C*H=NAr) ppm.

***ortho*-$C_6H_4NH(C_6H_3$*i*Pr_2-2,6)(CH=$NC_6H_3C_6H_4$Me-*p*) (2b):** A solution of *n*BuLi (22.1 mL, 26.5 mmol) in hexanes was added to a solution of 2,6-diisopropylaniline (5.0 mL, 26.5 mmol) in THF (20 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The resulting solution of LiNHAr was transferred into a solution of *ortho*-C_6H_4F(CH=NC_6H_4Me-*p*) (5.7 g, 26.5 mmol) in THF (20 mL) at 25 °C. After stirred for 24 h, the reaction was quenched with H_2O (20 mL), the mixture was extracted with *n*-hexane and the organic phase evaporated to dryness in vacuo to give the crude product as yellow solid. Pure product (7.7 g, 78%) was obtained as yellow crystals by recrystallization from ethanol at –20 °C. $C_{26}H_{30}N_2$ (370.53): calcd.C 84.28, H 8.16, N 7.56; found C 84.31, H 8.11, N 7.58%. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ = 1.07 (d, 6 H, CH($CH_3)_2$), 1.10 (d, 6 H, CH($CH_3)_2$), 2.29 (s, 3 H, CH_3), 3.09 (sept, 2 H, $CH(CH_3)_2$), 6.18 (d, 1 H, Ph-*H*), 6.61 (t, 1 H, Ph-*H*), 7.02–7.33 (m, 9 H, Ph-*H*), 8.59 (s, 1 H, C*H*=NAr), 10.60 (s, 1 H, N*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 293 K): δ = 21.1 (CH_3), 22.9 (CH($CH_3)_2$), 25.0 (CH($CH_3)_2$), 28.6 ($CH(CH_3)_2$), 76.8, 77.1, 77.3, 112.1, 115.4, 116.9, 120.9, 123.8, 127.4, 129.8, 132.0, 134.5, 135.0, 135.5, 147.6, 149.0, 149.8, 162.4 (*C*H=NAr).

***ortho*-$C_6H_4N(C_6H_3Et_2$-2,6)(CH=NC_6H_4Me-*p*)BF_2 (3a):** 0.49 mL of an *n*BuLi solution (0.58 mmol) was added to the solution of the ligand **2a** *ortho*-$C_6H_4NH(C_6H_3Et_2$-2,6)(CH=NC_6H_4Me-*p*) (0.2 g, 0.58 mmol) in toluene with stirring at –78 °C. The mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension of $BF_3(OEt_2)$ (0.71 mL, 0.58 mmol) at –78 °C with stirring. The mixture was warmed to room temperature, then stirred overnight at 80 °C. The solvent was removed in vacuo. The 9 mL of hexane was added to the yellow solid residue. Insoluble material was removed by filtration through Celite. Yellow crystals (0.18 g, 78%) were obtained from *n*-hexane solution at 5 °C. $C_{24}H_{25}BF_2N_2$ (390.28): calcd. C 73.86, H 6.46, N 7.18; found C 73.89, H 6.41, N 7.14%. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ = 1.11 (t, 6 H, CH_2CH_3), 2.40 (s, 3 H, CH_3), 2.45 (q, 2 H, CH_2CH_3), 2.64 (q, 2 H, CH_2CH_3), 6.25 (d, 1 H, Ph-*H*), 6.70 (t, 1 H, Ph-*H*), 7.24–7.49 (m, 9 H, Ph-*H*), 8.37 (s, 1 H, C*H*=NAr) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 293 K): δ = 14.7 (CH_3), 21.3 (CH_2CH_3), 23.9 (CH_2CH_3), 76.8, 77.2, 77.4, 77.7, 112.9, 115.6, 116.5, 124.1, 126.6, 127.6, 130.2, 133.3, 137.6, 137.7, 138.7, 141.2, 142.9, 151.9, 159.9 (*C*H=NAr) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz, 293 K): δ = 4.534 (t, 1:2:1, *J* = 28.32 Hz) ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 293 K): δ = 49.7 (q, 1:1:1:1) pm. MS, *m*/*z*: 371 [(M – F)$^+$].

***ortho*-$C_6H_4N(C_6H_3$*i*Pr_2-2,6)(CH=$NC_6H_3C_6H_4$Me-*p*)BF_2 (3b):** An *n*BuLi solution (0.45 mL, 0.54 mmol) was added to a toluene solution (6 mL) of the ligand **2b** *ortho*-$C_6H_4NH(C_6H_3$*i*Pr_2-

2,6)($CH=NC_6H_3C_6H_4Me$-*p*) (0.2 g, 0.54 mmol) at –78 °C. The mixture was warmed to room temperature, then stirred overnight. The resulting mixture was added dropwise to a toluene suspension of $BF_3(OEt_2)$ (0.66 mL, 0.54 mmol) at –78 °C with stirring. The mixture was warmed to room temperature, then stirred overnight at 80 °C. The solvent was removed in vacuo. Then 9 mL of hexane was added to the yellow solid residue. Insoluble material was removed by filtration through Celite. Yellow crystals (0.16 g, 73%) were obtained from the *n*-hexane solution at 5 °C. $C_{26}H_{29}BF_2N_2$ (418.33): calcd. C 74.65, H 6.99, N 6.70; found C 74.66, H 6.96, N 6.67%. ^1H NMR (500 MHz, $CDCl_3$, 293 K): δ = 0.99 (d, 6 H, $CH(CH_3)_2$), 1.22 (d, 6 H, $CH(CH_3)_2$), 2.40 (s, 3 H, CH_3), 3.02 (sept, 2 H, $CH(CH_3)_2$), 6.28 (d, 1 H, Ph-*H*), 6.68 (t, 1 H, Ph-*H*), 7.22–7.50 (m, 9 H, Ph-*H*), 8.37 (s, 1 H, C*H*=NAr) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 293 K): δ = 21.3 (CH_3), 24.4 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 76.8, 77.2, 77.4, 77.7, 112.8, 116.3, 116.4, 124.2, 124.5, 128.0, 130.2, 133.3, 135.7, 137.4, 138.6 147.9, 152.3, 160.0 (*C*H=NAr) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz, 293 K): δ = 4.527 (t, 1:2:1, *J* = 27.84 Hz) ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 293 K): δ = 51.0 (q, 1:1:1:1) ppm. MS, *m*/*z*: 399.1 [$(M - F)^+$].

***ortho*-$C_6H_4N(C_6H_3iPr_2$-2,6)($CH=NC_6H_3Me_2$-2,6)BF_2 (3c):** 0.43 mL of an *n*BuLi solution (0.52 mmol) was added to the toluene of the ligand **2c** *ortho*-$C_6H_4\{NH(C_6H_3iPr_2$-2,6)$\}$($CH=NC_6H_3Me_2$-2,6) (0.2 g, 0.52 mmol) at –78 °C. The mixture was warmed to the room temperature, then stirred until room temperature was reached. The resulting mixture was added dropwise to a toluene suspension of $BF_3(OEt_2)$ (0.64 mL, 0.52 mmol) at –78 °C with stirring. The mixture was stirred until room temperature was reached, stirring was continued overnight at 80 °C. The solvent was removed in vacuo. Then 9 mL of hexane was added to the yellow solid residue. Insoluble material was removed by filtration through Celite. Yellow crystals (0.16 g, 71%) were obtained from *n*-hexane solution at 5 °C. $C_{27}H_{31}BF_2N_2$ (432.36): calcd. C 75.01, H 7.23, N 6.48; found C 75.04, H 7.19, N 6.51%. ^1H NMR (500 MHz, $CDCl_3$, 293 K): δ = 1.01 (d, 6 H, $CH(CH_3)_2$), 1.21 (d, 6 H, $CH(CH_3)_2$), 2.34 (s, 6 H, CH_3), 3.13 (sept, 2 H, $CH(CH_3)_2$), 6.30 (d, 1 H, Ph-*H*), 6.68 (t, 1 H, Ph-*H*), 7.14–7.39 (m, 9 H, Ph-*H*), 8.12 (s, 1 H, C*H*=NAr) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 293 K): δ = 18.6 (CH_3), 24.5 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 76.8, 77.3, 77.7, 116.2, 116.4, 124.6, 128.0, 128.3, 128.8, 133.3, 134.5, 135.6, 137.5, 147.8, 152.6, 163.9 (*C*H=NAr) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz, 293 K): δ = 4.335 (t, 1:2:1, *J* = 28.48 Hz) ppm. ^{19}F NMR ($CDCl_3$, 470 MHz, 293 K): δ = 49.7 (s) ppm. MS, *m*/*z*: 413.1 [$(M - F)^+$].

PL Quantum Yield Measurements: Room-temperature luminescence quantum yields were measured at a single excitation wavelength (360 nm) referenced to quinine sulfate in sulfuric acid aqueous solution (Φ = 0.546). The quantum yields were calculated using known procedures.[21] The excitation wavelength was 440, 440, and 429 nm for complexes **3a**, **3b** and **3c**, respectively.

X-ray Structure Determinations of 3a, 3b and 3c: Single crystals of **3a**, **3b** and **3c** suitable for X-ray structural analysis were obtained from *n*-hexane. Diffraction data were collected at 293 K with a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) for **3a**, **3b** and **3c**. Details of the crystal data, data collections, and structure refinements are summarized in Table 2 and Table 3. The structures were solved by direct methods[22] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL[23] crystallographic software packages.

CCCD-619766 (for **3a**), -619767 (for **3b**), and -619768 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structural refinements details for **3a**, **3b** and **3c**.

	3a	**3b**	**3c**
Empirical formula	$C_{24}H_{25}BF_2N_2$	$C_{28}H_{29}BF_2N_2$	$C_{27}H_{31}BF_2N_2$
Formula mass	390.27	442.34	432.35
Temp. [K]	293(2)	293(2)	293(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	*P*21/*n*	$P\bar{1}$	$P\bar{1}$
a [Å]	11.225(2)	9.2815(19)	8.8684(9)
b [Å]	14.649(3)	11.852(2)	11.5381(13)
c [Å]	12.857(3)	12.451(3)	12.3418(12)
α [°]	90	111.57(3)	73.654(5)
β [°]	90.61(3)	91.95(3)	73.645(4)
γ [°]	90	110.71(3)	81.066(2)
Volume [Å^3]	2114.0(7)	1170.0(4)	1158.8(2)
Z	4	2	2
$D_{calcd.}$ [Mg cm^{-3}]	1.226	1.256	1.239
F(000)	824	468	460
θ range for data collection [°]	$2.11 \le 2\theta \le 27.48$	$3.19 \le 2\theta \le 27.47$	$1.78 \le 2\theta \le 27.48$
Limiting indices	$-14 \le h \le 0$	$-12 \le h \le 11$	$0 \le h \le 11$
	$-19 \le k \le 0$	$-14 \le k \le 15$	$-14 \le k \le 14$
	$-16 \le l \le 16$	$-16 \le l \le 16$	$-14 \le l \le 16$
Data/restraints/parameters	4840/0/263	5233/0/285	5177/0/380
Goodness-of-fit on F^2	0.773	1.041	0.951
Final *R* indices [$I > 2\sigma(I)$]	R_1[a] = 0.0485	R_1[a] = 0.0512	R_1[a] = 0.0498
	wR_2[b] = 0.1132	wR_2[b] = 0.1369	wR_2[b] = 0.1073
R indices (all data)	R_1[a] = 0.1402	R_1[a] = 0.0970,	R_1[a] = 0.1165,
	wR_2[b] = 0.1330	wR_2[b] = 0.1599	wR_2[b] = 0.1310
Largest diff. peak/hole [e·Å^{-3}]	0.210, –0.191	0.174, –0.186	0.218, –0.249

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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