

Blue Luminescent Three-Coordinate Organoboron Compounds with a 2,2'-Dipyridylamino Functional Group

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Received November 13, 2002

Two new three-coordinate organoboron compounds tris[*p*-(2,2'-dipyridylamino) phenylduryl]borane (**1**) and tris[*p*-(2,2'-dipyridylamino)biphenylduryl]borane (**2**) have been synthesized in good yields by using Pd-catalyzed Suzuki–Miyaura coupling reactions between tri(*p*-iododuryl)borane and the corresponding boronic acid. Both compounds display bright blue luminescence when irradiated by UV light. The emission band of both compounds is highly solvent-dependent, indicating the presence of a highly polarized excited state. These new boron compounds are stable under air in solution and the solid state, and are capable of binding to metal ions such as Zn(II) via the 2,2'-dipyridylamino chelating sites. The crystal structures of **1** and **2** have been determined.

Introduction

Three-coordinate luminescent organoboron compounds are an important class of molecules because of their potential applications in advanced materials. The availability of one empty p_{π} orbital on the boron center makes three-coordinate boron compounds highly susceptible to the addition by Lewis bases, resulting in their relatively poor stability. Bulky substituents are often necessary to improve the stability of three-coordinate organoboron compounds.^{1–3} On the other hand, the empty p_{π} orbital of the boron center facilitates highly polarized electronic transitions where the boron center acts as an electron acceptor. These highly polarized transitions have been demonstrated to be responsible for solvatochromism, frequently observed for three-coordinate organoboron compounds.^{2,3} It has also been demonstrated by Marder and others that highly polarized transitions of three-coordinate boron compounds facilitate their use as frequency-doubling materials in nonlinear optics.^{3,4} Recently, three-coordinate organoboron compounds that have intense and highly polarized emission have found use as fluorescent sensors for the detection of a certain type of anions (Lewis bases) via the interaction of the Lewis base with the empty p orbital of the boron atom,⁵ and as well as electron transport materials and emitters

in organic-light-emitting devices.⁶ Despite the impressive recent achievements, stable and highly emissive three-coordinate organoboron compounds are still scarce. In view of the important potential applications of three-coordinate emissive organoboron compounds and their relative scarcity, we explored the syntheses of new three-coordinate boron compounds that have extensive π conjugation and the 2,2'-dipyridylamino functional group. The inclusion of the 2,2'-dipyridylamino group is based on our recent finding that this group is an efficient chromophore, capable of emitting light in the near-UV or the blue region,⁷ when attached to a carbon atom, or a metal ion such as Al(III) or Zn(II). Furthermore, the chelate functionality of the 2,2'-dipyridylamino group provides new capability for the boron compounds to bind to or interact with metal ions.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Solvents for synthesis were freshly distilled over appropriate drying reagents. All experiments were carried out under a dry nitrogen

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atmosphere following standard Schlenk techniques. TLC was carried out on SiO₂. Flash chromatography was carried out on silica (silica gel 60, 70–230 mesh). ¹H and ¹³C spectra were recorded on a Bruker Avance 300 spectrometer. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model 2 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. *p*-(2,2'-Dipyridylamino)bromobenzene and *p*-(2,2'-dipyridylamino)bromobiphenyl were based on a modified literature method.⁸ Dibromodurene and tri(*p*-iododuryl)borane were prepared according to the literature procedures.^{2,9,10}

Preparation of Tri[*p*-(2,2'-dipyridylamino)phenylduryl]borane (tdapb, 1). To a THF (30 mL) solution of *p*-(2,2'-dipyridylamino)bromobenzene (3.05 g, 9.36 mmol) was added a hexane solution of *n*-BuLi (1.6 M, 6.0 mL, 9.6 mmol) at –78 °C. After being stirred for 1 h at this temperature, the cold mixture was cannulated into a solution of B(OMe)₃ (1.6 mL, 19.7 mmol) in tetrahydrofuran (20 mL) at –78 °C. After the mixture was stirred for another 1 h at –78 °C, it was warmed to ambient temperature and stirred overnight. The solution was partitioned between saturated aqueous NH₄Cl (100 mL) and ethyl acetate (100 mL). The aqueous layer was extracted further with dichloromethane (2 × 50 mL) and the combined organic layers were dried over MgSO₄. The product was purified by flash chromatography (2.5% MeOH in CH₂Cl₂) to provide the boronic acid in 66% yield. A mixture of tri(iododuryl)borane (0.545 g, 0.69 mmol), Pd(PPh₃)₄ (0.07 g, 0.056 mmol), and toluene (60 mL) was stirred for 10 min. The above boronic acid (1.2 g, 4.12 mmol) in 20 mL of EtOH and NaOH (0.8 g) in 20 mL of H₂O were subsequently added. The mixture was stirred and refluxed for 36 h and allowed to cool to room temperature. The water layer was separated and extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried over MgSO₄, and the solvents were evaporated under reduced pressure. Purification of the crude product by column chromatography (THF/hexane, 1/1) afforded tdapb as a colorless solid in 51% yield. Mp: 176–178 °C. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.38 (dd, *J* = 4.8, 1.2, 6H), 7.60 (ddd, *J* = 8.1, 7.2, 1.8, 6H), 7.26 (d, *J* = 8.4, 6H), 7.16 (d, *J* = 8.4, 6H), 7.05 (d, *J* = 8.4, 6H), 6.96 (ddd, *J* = 7.2, 5.1, 0.6, 6H), 2.11 (s, 18H), 1.95 (s, 18H). ¹³C NMR in CD₃Cl (δ, ppm, 25 °C): 158.63, 149.29, 148.84, 143.32, 142.80, 140.91, 137.92, 136.08, 131.64, 131.19, 127.05, 118.44, 117.37, 20.58, 18.49. Anal. Calcd for C₇₈H₇₂N₉B·1.5CH₂Cl₂·hexane: C, 75.52; H, 6.55; N, 9.27. Found: C, 75.11; H, 6.44; N, 9.24.

Preparation of Tri[*p*-(2,2'-dipyridylamino)biphenylduryl]borane (tdabb, 2). This compound was obtained by the same procedure as above. From *p*-(2,2'-dipyridylamino)bromobiphenyl (1.72 g, 4.28 mmol), *p*-(2,2'-dipyridylamino)biphenylboronic acid was obtained in 86% yield. From the reaction of tri(*p*-iododuryl)borane (0.50 g, 0.63 mmol), Pd(PPh₃)₄ (0.06 g, 0.052 mmol), *p*-(2,2'-dipyridylamino)biphenylboronic acid (1.32 g, 6.60 mmol), and NaOH (0.8 g), tdabb was obtained as colorless crystals in 57% yield. Mp: 232–234 °C. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.40 (m, 6H), 7.67 (m, 18H), 7.33 (d, *J* = 8.4, 6H), 7.25 (d, *J* = 7.8, 6H), 7.10 (d, *J* = 8.4, 6H), 6.98 (m, 6H), 2.16 (s, 18H), 1.96 (s, 18H). ¹³C NMR in CDCl₃ (δ, ppm, 25 °C): 149.07, 146.91, 143.39, 140.20, 139.00, 136.46, 133.56, 131.96, 130.73, 128.88, 128.05, 127.37, 119.07, 117.72, 108.40, 106.57, 106.15, 20.85, 18.59. Anal. Calcd for C₉₆H₈₄N₉·0.5CH₂Cl₂: C, 81.81; H, 6.00; N, 8.90. Found: C, 81.79; H, 6.27; N, 8.65.

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TABLE 1. Crystal Data for 1 and 2

	1	2
formula	C ₇₈ H ₇₂ N ₉ B/ 2CH ₂ Cl ₂ /C ₆ H ₁₄	C ₉₆ H ₈₄ N ₉ B/ 2.7CH ₂ Cl ₂ /0.67H ₂ O
fw	1402.28	1614.06
space group	R-3c	R-3
<i>a</i> /Å	17.258(2)	23.221(4)
<i>b</i> /Å	17.258(2)	23.221(4)
<i>c</i> /Å	45.381(7)	28.923(6)
α /deg	90	90
β /deg	90	90
γ /deg	120	120
<i>V</i> /Å ³	11705(3)	13506(4)
<i>Z</i>	6	6
<i>D</i> _c /g cm ⁻³	1.194	1.192
μ /cm ⁻¹	2.02	2.25
<i>2</i> θ _{max} /deg	56.68	56.62
no. of reflns measured	26892	32960
no. of reflns used	3208	7303
no. of parameters	180	330
final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> ₁ ^a	0.0720	0.0873
<i>wR</i> ₂ ^b	0.1866	0.2144
<i>R</i> (all data)		
<i>R</i> ₁ ^a	0.1459	0.3702
<i>wR</i> ₂ ^b	0.2388	0.3047
goodness of fit on <i>F</i> ²	0.932	0.717

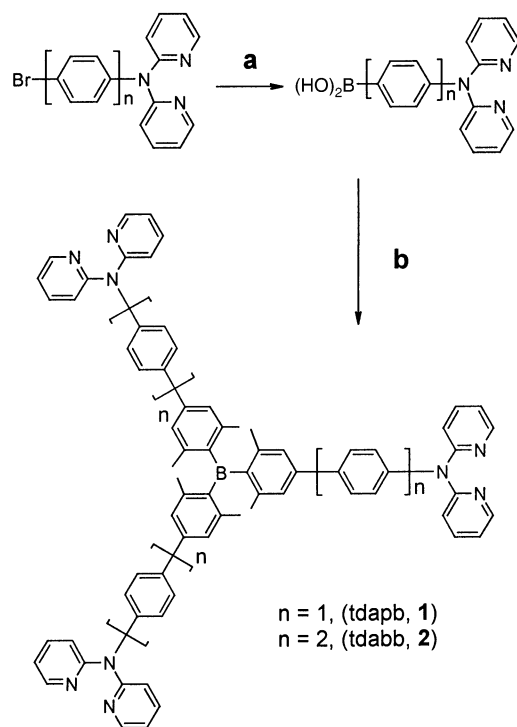
$$^a R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|. \quad ^b wR_2 = \{\sum[w(F_o^2 - F_c^2)]/\sum(wF_o^2)\}.$$

Preparation of (ZnCl₂)₃(tdapb) (3). To a solution of tdapb (0.0436 g, 0.038 mmol) in a minimum amount of CH₂Cl₂ was layered a THF solution of anhydrous ZnCl₂ (0.23 mL, 0.5 M, 0.144 mmol). After the solution was allowed to stand for a few days, a colorless solid of (ZnCl₂)₃(tdapb) was obtained in 50% yield. Mp: 260–262 °C. ¹H NMR in CD₃OD (δ, ppm, 25 °C): 8.58 (m, 6H), 7.89 (m, 6H), 7.74 (d, *J* = 8.1, 6H), 7.49 (d, *J* = 8.1, 6H), 7.35 (m, 6H), 7.14 (d, *J* = 9.0, 6H), 2.19 (s, 18H), 2.00 (s, 18H). Calcd. for C₇₈H₇₂BCl₆N₉Zn₃: C, 60.27; H, 4.64; N, 8.11. Found: C, 60.03; H, 4.57; N, 7.78.

X-ray Crystallographic Analysis. Single crystals of 1 and 2 were obtained from a solution of CH₂Cl₂/hexanes or THF/hexane (reagent grade solvents without further purification). Data were collected on a Bruker P4 single-crystal X-ray diffractometer with a CCD-1000 detector and graphite-monochromated Mo K α radiation, operating at 50 kV and 30 mA at 25 °C. The data collection *2* θ ranges are 4.50–56.6° for 1 and 4.28–56.6° for 2. No significant decay was observed. Data were processed on a PC with use of a Bruker SHELXTL software package¹¹ (version 5.10) and are corrected for Lorentz and polarization effects. Compounds 1 and 2 crystallize in the rhombohedral space groups *R* $\bar{3}c$ and *R* $\bar{3}$, respectively. All structures were solved by direct methods. Disordered solvent molecules were located in both structures. For compound 1, 2 CH₂Cl₂ and 1 hexane per molecule of 1 were found and the disordering of these solvent molecules was partially modeled. For 2, 2.7 CH₂Cl₂ and 0.67 H₂O per molecule of 2 were located. Due to the fact that these solvent molecules (water is from the solvents used in the crystallization) sit on symmetry elements, they are badly disordered and could not be modeled accurately. The partial occupancy factors are based on the best refinement results. The relatively poor refinement results of 2 can be attributed to the partially refined solvent molecules. All non-hydrogen atoms except those of disordered solvent molecules were refined anisotropically. All hydrogen atoms except those bound to the solvent molecules were calculated and their contributions to the structural factor calculation were included. Crystal data for 1 and 2 are summarized in Table 1.

Quantum Yield Measurements. Fluorescent quantum yields of the complexes were determined relative to 9,10-

(11) SHELXTL NT Crystal Structure Analysis Package, Version 5.10; Bruker Axis, Analytical X-ray System: Madison, WI, 1999.

SCHEME 1^{a,b}

^a Reagents and conditions: (i) *n*-BuLi, THF, $-78\text{ }^{\circ}\text{C}$; (ii) $\text{B}(\text{OMe})_3$; (iii) NH_4Cl . ^b Tri(iododuryl)borane, $\text{Pd}(\text{PPh}_3)_4$, NaOH, toluene.

diphenylanthracene in THF at 298 K ($\Phi_r = 0.90$). The absorbance of all the samples and the standard at the excitation wavelength were approximately 0.092–0.109. The quantum yields were calculated by using previously reported procedures.¹²

Results and Discussion

The syntheses of the new boron compounds tris[*p*-(2,2'-dipyridylamino)phenylduryl]borane (tdapb, **1**) and tris[*p*-(2,2'-dipyridylamino)biphenylduryl]borane (tdabb, **2**) were achieved in good yields by Pd-catalyzed Suzuki–Miyaura cross-couplings¹⁰ of tri(iododuryl)borane with the corresponding boronic acid. The tri(*p*-iododuryl)borane compound was synthesized by following the procedure reported recently by Yamaguchi et al., who have shown that the bulky duryl groups provide chemical stability to the boron center.² Dibromodurene, one of the starting materials for the synthesis of tris(*p*-iododuryl)borane, was synthesized based on a literature procedure.⁹ The starting materials *p*-(2,2'-dipyridylamino)bromobenzene and *p*-(2,2'-dipyridylamino)bromo-4,4'-biphenyl were obtained by following the Ullmann condensation methods as described previously.⁸ The intermediates *p*-(2,2'-dipyridylamino)phenylboronic acid and *p*-(2,2'-dipyridylamino)-4,4'-biphenylboronic acid were obtained by the reaction¹⁰ of $\text{B}(\text{OCH}_3)_3$ with *p*-(2,2'-dipyridylamino)phenyllithium and *p*-(2,2'-dipyridylamino)-4,4'-biphenyllithium, respectively. The synthetic procedures for **1** and **2** are summarized in Scheme 1.

Compounds **1** and **2** are fully characterized by NMR, elemental, and single-crystal X-ray diffraction analyses.

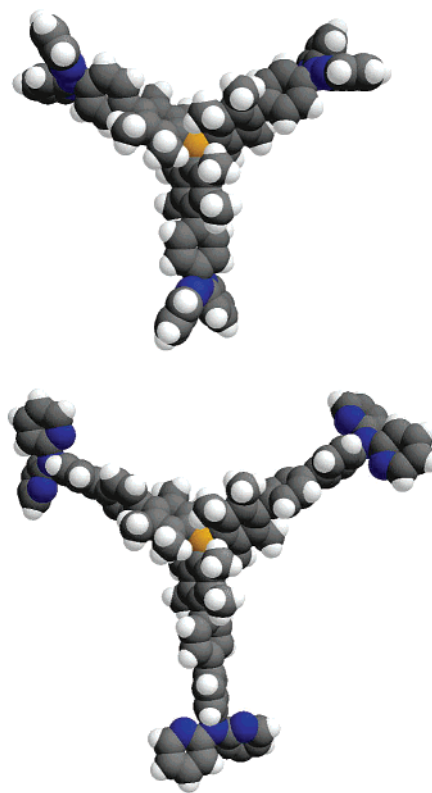


FIGURE 1. Crystal structures of **1** (top, $\text{B}-\text{C} = 1.603(3)\text{ \AA}$) and **2** (bottom, $\text{B}-\text{C} = 1.586(5)\text{ \AA}$) shown as space-filling diagrams.

These two compounds are stable in solution and the solid state. ^1H NMR spectra show that after several days standing under air in solution, no decomposition was observed for either compound. The bulky duryl groups are clearly responsible for the remarkable chemical stability of these two compounds, consistent with the observation made by Yamaguchi et al. in related boron compounds.² The crystals of **1** and **2** belong to the rhombohedral crystal system. As shown by Figure 1, both compounds have a propeller-like structure. The molecule of **1** has a crystallographically imposed D_3 symmetry while the molecule of **2** has a crystallographically imposed C_3 symmetry. Hence, both molecules have a chiral structure in the solid state. The crystals of both compounds are, however, achiral due to the coexistence of both enantiomers. The two enantiomers in **2** form an interlocked pair in the crystal lattice with the separation distance between the two boron centers being $6.736(6)\text{ \AA}$ (Figure 2). The aromatic rings between the amino nitrogen atom and the central boron atom are not coplanar, as evident by the dihedral angle between the duryl ring and the phenyl ring in **1** ($73.9(1)^\circ$), the dihedral angle between the duryl and the directly attached phenyl ring in **2** ($75.3(1)^\circ$), and the dihedral angle between the two phenyl rings in **2** ($37.6(1)^\circ$). The space-filling diagrams (Figure 1) for both molecules show that the boron center in both compounds is well-shielded by the *o*-methyl groups and that the free-rotation around the $\text{B}-\text{C}$ bonds is probably hindered. However, we have not been able to separate the enantiomers of these two compounds. Blount et al. reported in 1973 that the activation energies for interconversion of stereoisomers of triarylborananes with

(12) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

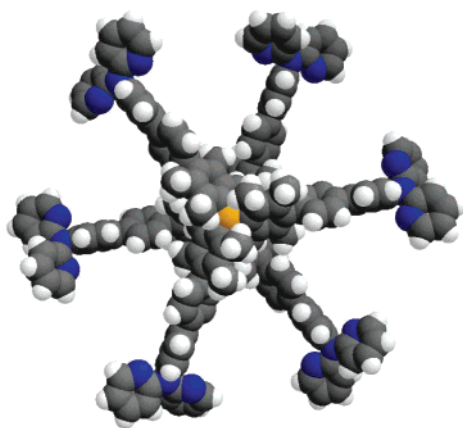


FIGURE 2. Space-filling diagram showing the interlocked pair of enantiomers in the crystal lattice of **2**.

TABLE 2. Spectroscopic Properties of 1 and 2 in THF at Ambient Temperature

compd	abs λ (nm) (ϵ , $M^{-1} \text{ cm}^{-1}$)	λ_{max} (nm)		Φ^a
		excitation	emission	
1	234 (46 794), 278 (36 829), 304 (18 043)	339	427	0.59
2	238 (164 239), 286 (163 848), 312 (181 735)	354	405	0.46

^a Measured with 9,10-diphenylanthracene as the standard at ambient temperature.

various substituents in all ortho positions are in the range of 14–16 kcal/mol, hence precluding the separation of the triarylborane stereoisomers at ambient temperature.¹³ A similar rapid enantiomer interconversion process also likely occurs in the solution of **1** and **2** at ambient temperature.

Compounds **1** and **2** are bright blue emitters in solution and the solid state when irradiated by UV light. The spectroscopic data for these two compounds in THF are summarized in Table 2. The emission spectra of **1** and **2** in the solid state at ambient temperature are similar to those of THF solutions. Compounds **1** and **2** have intense absorption bands in the UV region. The positions of these absorption bands (except the band at ~ 235 nm) are independent of solvents. Both compounds show a broad fluorescent emission band in the blue region in either THF or CH_2Cl_2 . In contrast to the absorption bands, the position of the emission band is solvent dependent. When the solvent is changed from THF or CH_2Cl_2 to DMF, the emission maximum of both compounds shifts to a longer wavelength. The shift is about 30–40 nm for **1** and 70–80 nm for **2**, as shown in Figure 3. Compounds **1** and **2** are insoluble in hydrocarbon solvents such as benzene, precluding the recording of their spectra in these solvents. Nonetheless, the trend of the solvent-dependent shift of emission energy displayed by these two compounds in CH_2Cl_2 , THF, and DMF is consistent with the behavior of three-coordinate boron compounds reported by Yamaguchi et al. and attributable to the presence of a highly polarized excited state.^{2–4} As shown in Figure 4, at 77 K, the frozen solutions of **1** and **2** in CH_2Cl_2 , THF,

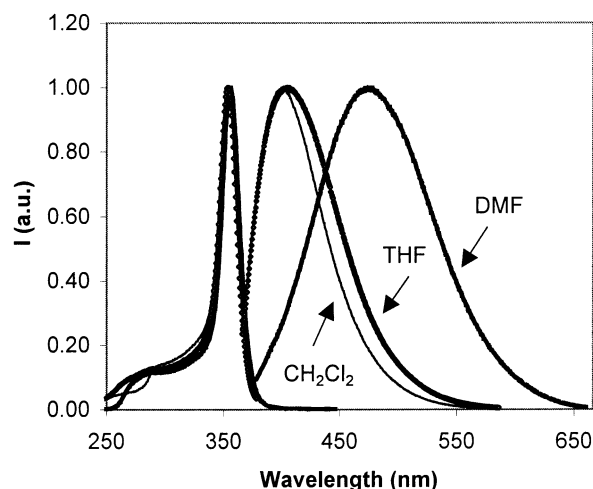
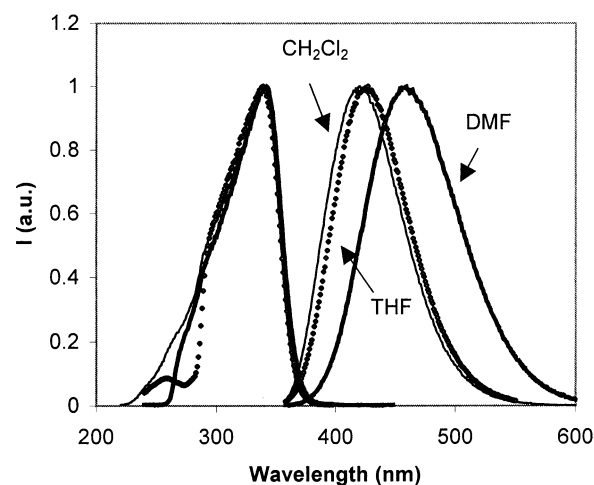


FIGURE 3. Excitation and emission spectra of **1** (top) and **2** (bottom) at ambient temperature in CH_2Cl_2 , THF, and DMF, respectively.

or DMF all display new low-energy emission bands ($\lambda = 460$ nm, $\tau = 9.1(2) \mu\text{s}$ for **1** in CH_2Cl_2 ; $\lambda = 480$ nm, $\tau = 11.0(4) \mu\text{s}$; $\lambda = 506$ nm, $\tau = 9.4(8) \mu\text{s}$ for **2** in CH_2Cl_2), in addition to the fluorescent band, which are attributed to phosphorescent transitions based on their decay lifetimes.

The ability of compounds **1** and **2** to bind or interact with a Lewis acid such as a metal ion is demonstrated by compound **3**, $(\text{ZnCl}_2)_3(\text{tdapb})$, obtained from the reaction of compound **1** with anhydrous ZnCl_2 in a 1:3 ratio (Scheme 2). Single crystals of **3** suitable for X-ray diffraction analysis could not be obtained. Compound **3** was characterized by ^1H NMR and elemental analysis. The proposed structure of **3** where the ZnCl_2 unit is chelated to the 2,2'-dipyridylamino group in a tetrahedral environment is based on the results of our earlier investigation on Zn(II) complexes of nitrogen-based starburst ligands that contain the same 2,2'-dipyridylamino functional group.⁷ Compound **3** slowly decomposes upon exposure to air, presumably caused by hydrolysis of the ZnCl_2 moiety. The Zn(II) complex **3** is also blue luminescent but the emission maximum (458 nm in THF) is shifted significantly to a longer wavelength, compared to that of **1** (427 nm in THF). Similar red-shift has been observed in previously reported Zn(II) complexes containing chelating 2,2'-dipyridylamino groups.⁷ Fluorescent

(13) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

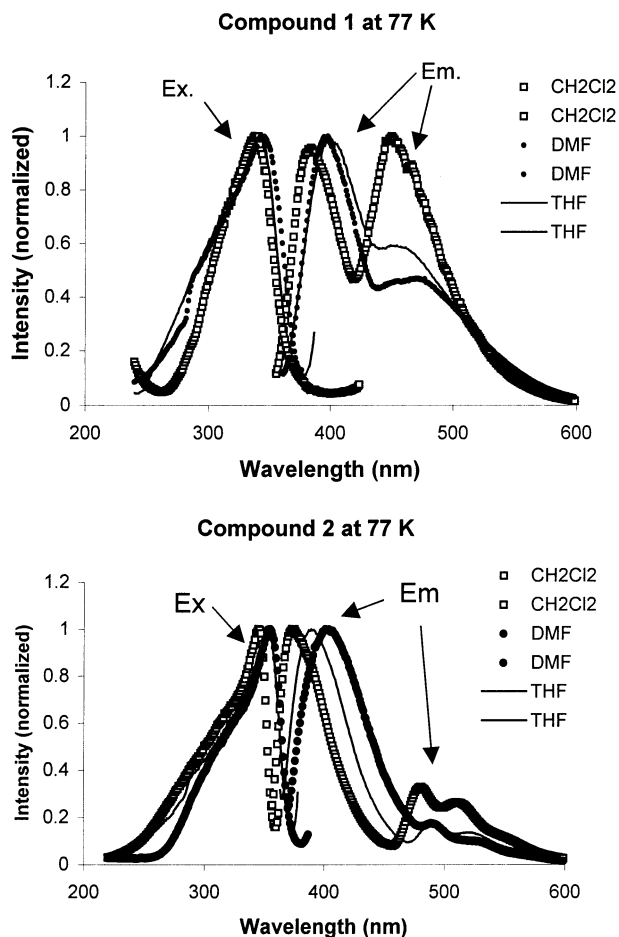
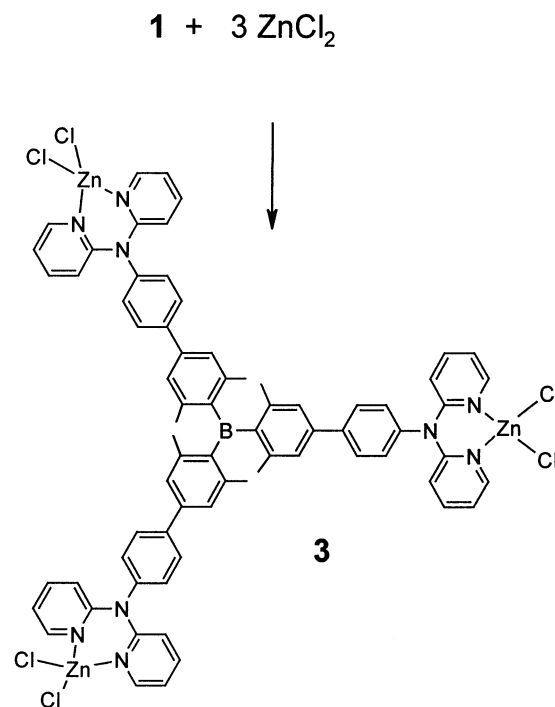


FIGURE 4. Excitation and emission spectra of **1** and **2** at 77 K in CH₂Cl₂, THF, and DMF, respectively.

titration experiments by adding Zn(II) ions to the solution of **1** at various concentrations show a slight decrease of emission intensity with the increase of Zn(II) concentration, but no red shift, which is likely caused by the presence of water molecules picked up by the anhydrous ZnCl₂ during the measurement.

In summary, two new highly emissive three-coordinate organoboron compounds have been obtained. Their remarkable chemical stability and polarized emissions make them potentially useful for applications in organic photonic/electroluminescent devices. Furthermore, the ability of these two compounds to bind to metal ions via the 2,2'-dipyridylamino functional groups renders them

SCHEME 2



new opportunities for applications such as fluorescent sensors for metal ion, metal-containing, or metal ion-modified nonlinear optical materials. The application aspects of the new boron compounds are currently being explored in our laboratory.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Note Added after ASAP Posting. There was an error in the intermediate structure of Scheme 1 in the version posted ASAP December 20, 2002. The corrected version was posted January 20, 2003.

Supporting Information Available: X-ray diffraction data for **1** and **2**, including tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen parameters, molecular diagrams showing the crystal structures of **1** and **2** with labeling schemes, and UV-vis, excitation, and emission spectra of **1** and **2** in the solid state and in frozen solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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