

# Blue-Luminescent/Electroluminescent Zn(II) Compounds of 7-Azaindole and *N*-(2-Pyridyl)-7-azaindole: Zn(7-azaindole)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>, Zn(NPA)(CH<sub>3</sub>COO)<sub>2</sub>, and Zn(NPA)((*S*)-(+)-CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)COO)<sub>2</sub> (NPA = *N*-(2-Pyridyl)-7-azaindole)

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A new 7-azaindole zinc(II) compound, Zn(7-azaindole)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> (**1**), a new ligand *N*-(2-pyridyl)-7-azaindole (NPA), and two NPA zinc(II) complexes, Zn(NPA)(CH<sub>3</sub>COO)<sub>2</sub> (**2**) and Zn(NPA)((*S*)-(+)-CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)-COO)<sub>2</sub> (**3**), have been synthesized and structurally characterized. Compound **1** has a tetrahedral geometry, whereas compounds **2** and **3** have irregular six-coordinate geometry. The NPA ligand in compounds **2** and **3** functions as a bidentate chelate to the zinc center. Compound **1** has a blue luminescence in the solution and the solid state. Compounds **2** and **3** emit a blue color in the solid state. In solution, compounds **2** and **3** are fluxional, as established by <sup>1</sup>H NMR experiments. Compound **1** is thermally stable, whereas compounds **2** and **3** undergo decomposition when heated in the solid state. A blue electroluminescent device using compound **1** as the emitting layer has been fabricated. Crystal data: NPA, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.993(5) Å, *b* = 8.456(3) Å, *c* = 16.886(5) Å, β = 104.666(12)°, *V* = 1932.9(11) Å<sup>3</sup>; **1**, triclinic, *P* $\bar{1}$ , *a* = 9.5114(18) Å, *b* = 10.460(7) Å, *c* = 11.002(3) Å, α = 117.18(3)°, β = 103.287(18)°, γ = 90.94(2)°, *V* = 938.3(7) Å<sup>3</sup>; **2**, monoclinic, *C*2/*c*, *a* = 13.234(6) Å, *b* = 9.373(3) Å, *c* = 13.956(7) Å, β = 113.24(3)°, *V* = 1590.7(12) Å<sup>3</sup>; **3**, monoclinic, *P*2<sub>1</sub>, *a* = 11.047(7) Å, *b* = 15.343(9) Å, *c* = 13.785(8) Å, β = 100.123(9)°, *V* = 2300(2) Å<sup>3</sup>.

## Introduction

Since Tang and Van Slyke reported<sup>1</sup> the first double-layer green organic electroluminescent (EL) device using Alq<sub>3</sub> (q = 8-hydroxyquinolyl) in 1987, there have been intense research activities in organic EL devices.<sup>2–6</sup> The prerequisite for a compound to be useful in EL devices is that it must be photoluminescent and stable. Consequently, there has been an increasing interest in luminescent compounds.<sup>7–14</sup> We have

demonstrated that the 7-azaindole anion (7-azaindoyl) forms various bright-blue-luminescent complexes upon reaction with Al(III) or B(III).<sup>15–18</sup> In general, 7-azaindoyl aluminum complexes are not stable enough for EL applications because the Al<sup>δ+</sup>–N<sup>δ-</sup> (indole) bond is readily broken upon reaction with water from air. Recently, we have synthesized several organoboron compounds<sup>18</sup> by using 7-azaindole. The 7-azaindoyl boron compounds are much more stable because of the increased covalency of B–N bonds in comparison to that of the corresponding Al–N bonds. Blue EL devices<sup>18b</sup> by using 7-azaindoyl boron compounds as the emitting layer have been fabricated. These devices do not, however, have a long-term stability. Although the cause of it has not been understood yet, we believe the poor stability of the EL device is likely to be associated with the negatively charged 7-azaindoyl ligand in the boron compounds.

Recently Che and co-workers<sup>19</sup> reported a Zn(II) compound, Zn<sub>4</sub>O(7-azaindoyl)<sub>6</sub>, which emits a blue color with an emission maximum at 433 nm in the solid state. Negatively charged 7-azaindoyl ligands are known to cause the complexes to have

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a poor stability toward oxidation (chemically or electrochemically) and moisture, thus limiting their applications in EL devices.<sup>15–18</sup> If blue luminescence can be achieved by using the neutral 7-azaindole as the ligand, the complex would be more chemically and electrochemically stable, thus more suitable in EL applications than the 7-azaindolyl complexes. We have observed in our earlier investigation that the neutral 7-azaindole and its aluminum or boron complexes usually have no emission in the visible region, and the removal of the proton from 7-azaindole is often necessary to shift the emission energy to blue. Recently, however, we have found that the neutral 7-azaindole ligand reacts readily with Zn(OAc)<sub>2</sub> to form a bright blue-luminescent compound Zn(7-azaindole)<sub>2</sub>(OAc)<sub>2</sub>, which is described herein.

In addition to the new 7-azaindole zinc compound, we have also carried out the modification of the 7-azaindole ligand to improve the stability of the complexes.<sup>20</sup> One of the modifications that we carried out is to replace the proton on the indole nitrogen with a 2-pyridyl group, resulting in the new ligand *N*-(2-pyridyl)-7-azaindole (NPA). Unlike 7-azaindole or 7-azaindolyl ligands that can only bind to a metal center as either a bridging ligand or a monodentate terminal ligand, the NPA ligand is capable of chelating to a metal center. In addition, the NPA ligand is neutral and may be able to form stable metal complexes. The syntheses, structures, and luminescent properties of NPA and its zinc complexes are presented herein.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere. Reagent-grade solvents were used without further purification. All starting materials were purchased from Aldrich Chemical Co. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on Bruker Advance 300 MHz and AM 400 MHz NMR spectrometers in CDCl<sub>3</sub> for the NPA ligand and compound **1** and in CD<sub>3</sub>OD for **2** and **3** (compounds **2** and **3** have a poor solubility in CDCl<sub>3</sub>). Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. Melting points were measured on a Fisher-Johns melting point apparatus. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model C-60 spectrometer. The solution's fluorescent spectra were measured by using 0.01 M solutions. Optical rotation measurements were carried out on an Autopol I automatic polarimeter by using toluene as the solvent. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 analyzer.

**Synthesis of NPA.** 7-Azaindole (20 mmol, 2.364 g), 2-bromopyridine (20 mmol, 3.160 g), potassium carbonate (15 mmol, 2.073 g), and cupric sulfate (0.40 mmol, 0.100 g) were added to a flask. The mixture was heated at 200 °C for 4 h under N<sub>2</sub>. After cooling to ambient temperature, the residue was dissolved in 400 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic layer was separated, dried with sodium sulfate, and concentrated by vacuum. Then 10 mL of hexanes was added to the oily residue, and the solution was kept refrigerated. Colorless crystals of NPA were obtained in 64% yield with a mp of 58 °C. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 298 K): 8.90 (d, <sup>3</sup>J = 8.3 Hz, 1H, 7-azain), 8.47 (d, <sup>3</sup>J = 4.0 Hz, 1H, Py), 8.38 (d, <sup>3</sup>J = 4.8 Hz, 1H, Py), 8.35 (d, <sup>3</sup>J = 3.9 Hz, 1H, 7-azain), 7.93 (d, <sup>3</sup>J = 7.7, 1H, 7-azain), 7.85 (t, <sup>3</sup>J = 8.7 Hz, 1H, Py), 7.16–7.01 (m, 2H, 7-azain and Py), 6.62 (d, <sup>3</sup>J = 3.9 Hz, 1H, 7-azain). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>, 298 K): 150.74 (py), 148.16 (Py), 147.47 (7-azain), 143.00 (7-azain), 138.35 (Py), 128.97 (7-azain), 126.36 (7-azain), 123.25 (7-azain), 120.25 (Py), 117.09 (Py), 115.67 (7-azain), 102.52 (7-azain). Elem anal. Calcd for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>: C, 73.82; H, 4.65; N, 21.53. Found: C, 73.49; H, 4.43; N, 21.70.

**Synthesis of Zn(7-azaindole)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> (1).** 7-Azaindole (1 mmol, 0.118 g) was dissolved in 10 mL of ethanol. Zinc acetate (0.5 mmol, 0.0915 g) was added to the above stirred solution. The solution was stirred for 2 h and had a strong blue luminescence under UV light.

The solution was then concentrated by vacuum. After the solution was allowed to stand for a few days, colorless crystals of compound **1** formed in 86% yield with a mp of 100 °C. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 298 K): 8.29 (d, <sup>3</sup>J = 4.8 Hz, 2H, 7-azain), 8.17 (d, <sup>3</sup>J = 8.1 Hz, 2H, 7-azain), 7.47 (d, <sup>3</sup>J = 2.7 Hz, 2H, 7-azain), 7.16 (dd, <sup>3</sup>J = 7.8, 4.8 Hz, 2H, 7-azain), 6.60 (d, <sup>3</sup>J = 2.7 Hz, 2H, 7-azain), 2.13 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>, 298 K): 180.07 (CO), 146.91 (7-azain), 141.57 (7-azain), 132.27 (7-azain), 126.97 (7-azain), 123.08 (7-azain), 115.64 (7-azain), 101.25 (7-azain), 23.22 (CH<sub>3</sub>). Elem anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>Zn: C, 51.51; H, 4.32; N, 13.35. Found: C, 51.31; H, 4.34; N, 13.31.

**Synthesis of Zn(NPA)(CH<sub>3</sub>COO)<sub>2</sub> (2).** *N*-(2-Pyridine)-7-azaindole (1 mmol, 0.195 g) was dissolved in 15 mL of ethanol. Zinc acetate (1 mmol, 0.186 g) was added to the above stirred solution. The blue luminescence of the solution became stronger compared to that of the free ligand solution after being stirred for 2 h. The solution was stirred for another 2 h and then concentrated by vacuum. After the solution was allowed to stand for a few days, colorless crystals of compound **2** formed in 66% yield with a mp of 178 °C. <sup>1</sup>H NMR (δ, CD<sub>3</sub>OD, 298 K): 8.57 (d, <sup>3</sup>J = 4.5 Hz, 1H, 7-azain), 8.44 (d, <sup>3</sup>J = 5.0 Hz, 1H, py), 8.22–8.06 (m, 3H, 7-azain, py), 8.05 (t, <sup>3</sup>J = 5.4 Hz, 1H, py), 7.37–7.32 (m, 2H, 7-azain, py), 6.80 (d, <sup>3</sup>J = 4.2 Hz, 1H, 7-azain), 1.87 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (δ, CD<sub>3</sub>OD, 298 K): 182.10 (CO), 152.81 (py), 149.74 (py), 147.55 (7-azain), 144.93 (7-azain), 143.18 (py), 133.98 (py), 128.73 (7-azain), 126.54 (7-azain), 122.60 (7-azain), 119.98 (py), 116.91 (7-azain), 106.41 (7-azain), 21.92 (CH<sub>3</sub>). Elem anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>Zn: C, 50.75; H, 3.99; N, 11.10. Found: C, 50.77; H, 3.94; N, 11.13.

**Synthesis of Zn(NPA)((*S*)-(+)-CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)COO)<sub>2</sub> (3).** ZnO (1 mmol, 0.0814 g) and (*S*)-(+)-2-methylbutyric acid (2 mmol, 0.2043 g) were added to 10 mL of toluene. A clear solution was obtained after the mixture was stirred for 4 h. Then NPA (1 mmol, 0.195 g) was added to the above solution. The solution was concentrated by vacuum after being stirred for another 4 h, and then 2 mL of hexanes was added to the solution. Colorless crystals of compound **3** formed in 81% yield with a mp of 121 °C. <sup>1</sup>H NMR (δ, CD<sub>3</sub>OD, 298 K): 8.62 (d, <sup>3</sup>J = 5.0 Hz, 1H, 7-azain), 8.47 (dd, <sup>3</sup>J = 5.0, 1.0 Hz, 1H, py), 8.18–8.13 (m, 2H, 7-azain, py), 8.03–7.99 (m, 2H, 7-azain, py), 7.37–7.29 (m, 2H, 7-azain, py), 6.75 (d, <sup>3</sup>J = 4.4 Hz, 1H, 7-azain), 2.43–2.33 (m, 2H, CH), 1.75–1.25 (m, 4H, CH<sub>2</sub>), 1.14 (d, <sup>3</sup>J = 6.9 Hz, 6H, CH<sub>3</sub>), 0.90 (t, <sup>3</sup>J = 7.4 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (δ, CD<sub>3</sub>OD, 298 K): 187.19 (CO), 152.25 (py), 149.65 (py), 147.34 (7-azain), 144.74 (7-azain), 143.01 (py), 134.06 (py), 128.28 (7-azain), 126.55 (7-azain), 122.22 (7-azain), 119.62 (py), 116.15 (7-azain), 106.62 (7-azain), 43.32 (CH), 28.48 (CH<sub>2</sub>), 17.87 (CH<sub>3</sub>), 12.17 (CH<sub>3</sub>). Elem anal. Calcd for C<sub>22</sub>H<sub>27</sub>N<sub>3</sub>O<sub>4</sub>Zn·H<sub>2</sub>O: C, 54.72; H, 6.05; N, 8.70. Found: C, 54.55; H, 5.68; N, 8.52.

**Fabrication of the EL Device.** The EL device using Zn(7-azaindole)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> as the emitting layer was fabricated on an indium–tin–oxide (ITO) substrate, which was cleaned by an ultraviolet ozone cleaner immediately before use. Organic layers, LiF, and a metal cathode composed of Al were deposited on the substrate by conventional vapor vacuum deposition. Prior to the deposition, all of the organic materials were purified via a train-sublimation method. *N,N'*-Di-1-naphthyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPD) was employed as the hole-transport layer and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was employed as the electron-transport layer in the device. A LiF layer was deposited between the PBD layer and the aluminum layer to facilitate the electron transport (the LiF LUMO energy level is between that of PBD and that of the work function of the aluminum electrode). The active device area is 1.0 × 5.0 mm<sup>2</sup>. The device structure is ITO/NPD, (40 nm)/compound **1**, (9 nm)/PBD, (15 nm)/LiF, and (1.5 nm)/Al. The current–voltage characteristic was measured using a Keithley 238 current–voltage unit. The EL spectrum and the luminance for the device were measured by using a Photo Research 650 spectra colorimeter.

**X-ray Crystallographic Analysis.** All crystals were obtained either from solutions of CH<sub>2</sub>Cl<sub>2</sub>/hexanes or toluene/hexanes or from a concentrated ethanol solution. All crystals were mounted on glass fibers. The data of NPA, **1**, and **2** were collected on a Siemens P4 single-crystal X-ray diffractometer with graphite-monochromated Mo Kα

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**Table 1.** Crystallographic Data

compound	NPA	1	2	3
formula	C <sub>12</sub> H <sub>9</sub> N <sub>3</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Zn	C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> Zn	C <sub>22</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> Zn
fw	195.2	419.7	378.7	462.8
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> , Å	13.993(5)	9.5114(18)	13.234(6)	11.047(7)
<i>b</i> , Å	8.456(3)	10.460(7)	9.373(3)	15.343(9)
<i>c</i> , Å	16.886(5)	11.002(3)	13.956(7)	13.785(8)
α, deg	90	117.18(3)	90	90
β, deg	104.666(12)	103.287(18)	113.24(3)	100.123(9)
γ, deg	90	90.94(2)	90	90
<i>V</i> , Å <sup>3</sup>	1932.9(11)	938.3(7)	1590.7(12)	2300(2)
<i>Z</i>	8	2	4	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.342	1.486	1.581	1.310
<i>T</i> , °C	23	23	23	23
μ, cm <sup>-1</sup>	0.84	13.40	15.70	10.98
2θ (max), deg	50	45	45	46.8
reflms measured	3537	2492	1092	8310
reflms used	3389	2325	1041	5409
parameters	343	246	123	519
final <i>R</i> ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0656 <i>wR</i> <sub>2</sub> <sup>b</sup> = 0.1059	<i>R</i> <sub>1</sub> = 0.0643 <i>wR</i> <sub>2</sub> = 0.1519	<i>R</i> <sub>1</sub> = 0.0828 <i>wR</i> <sub>2</sub> = 0.2116	<i>R</i> <sub>1</sub> = 0.0549 <i>wR</i> <sub>2</sub> = 0.1127
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.1760 <i>wR</i> <sub>2</sub> = 0.1466	<i>R</i> <sub>1</sub> = 0.0934 <i>wR</i> <sub>2</sub> = 0.1690	<i>R</i> <sub>1</sub> = 0.1037 <i>wR</i> <sub>2</sub> = 0.2333	<i>R</i> <sub>1</sub> = 0.1816 <i>wR</i> <sub>2</sub> = 0.1574
goodness of fit on <i>F</i> <sup>2</sup>	1.06	1.09	1.06	0.939

<sup>a</sup> *R*<sub>1</sub> = Σ|*F*<sub>o</sub>| - |*F*<sub>c</sub>|/Σ|*F*<sub>o</sub>|. <sup>b</sup> *wR*<sub>2</sub> = {Σ*w*[(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>. <sup>c</sup> *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.075*P*)<sup>2</sup>], where *P* = [Max(*F*<sub>o</sub><sup>2</sup>, 0) + 2*F*<sub>c</sub><sup>2</sup>]/3.

**Table 2.** Selected Bond Lengths [Å] and Angles [deg] for NPA and Compounds 1–3

NPA		compound 1		compound 2		compound 3	
N(1)–C(7)	1.339(4)	Zn(1)–O(1)	1.930(5)	Zn(1)–N(1)	2.074(7)	Zn(1)–N(3)	2.01(2)
N(1)–C(1)	1.348(5)	Zn(1)–O(3)	1.963(5)	Zn(1)–O(1)	2.079(8)	Zn(1)–O(2)	2.09(2)
N(2)–C(6)	1.409(5)	Zn(1)–N(1)	2.037(6)	Zn(1)–O(2)	2.288(8)	Zn(1)–O(4)	2.107(15)
N(2)–C(8)	1.412(4)	Zn(1)–N(3)	2.059(6)			Zn(1)–N(1)	2.164(19)
N(3)–C(8)	1.334(5)					Zn(1)–O(1)	2.258(16)
N(3)–C(12)	1.340(5)					Zn(1)–O(3)	2.259(17)
C(7)–N(1)–C(1)	113.6(4)	O(1)–Zn(1)–O(3)	113.8(2)	N(1)–Zn(1)–N(1A)	89.8(4)	N(3)–Zn(1)–O(2)	95.4(8)
N(1)–C(1)–C(2)	125.1(4)	O(1)–Zn(1)–N(1)	115.7(2)	N(1)–Zn(1)–O(1)	105.6(3)	N(3)–Zn(1)–O(4)	95.4(7)
C(6)–N(2)–C(8)	123.5(4)	O(3)–Zn(1)–N(1)	110.4(2)	N(1A)–Zn(1)–O(1)	99.1(3)	O(2)–Zn(1)–O(4)	106.5(7)
C(3)–C(2)–C(1)	119.6(5)	O(1)–Zn(1)–N(3)	112.8(2)	O(1)–Zn(1)–O(1A)	145.0(4)	N(3)–Zn(1)–N(1)	87.1(8)
C(2)–C(3)–C(4)	118.2(4)	O(3)–Zn(1)–N(3)	97.6(2)	N(1)–Zn(1)–O(2A)	157.7(3)	O(2)–Zn(1)–N(1)	146.9(7)
C(8)–N(3)–C(12)	116.8(4)	N(1)–Zn(1)–N(3)	104.8(2)	N(1A)–Zn(1)–O(2A)	195.7(3)	O(4)–Zn(1)–N(1)	106.0(8)
C(3)–C(4)–C(7)	117.1(4)			O(1)–Zn(1)–O(2A)	94.9(3)	N(3)–Zn(1)–O(1)	111.0(8)
C(3)–C(4)–C(5)	136.7(4)			O(1)–Zn(1)–O(2)	58.7(3)	O(2)–Zn(1)–O(1)	56.2(6)
C(7)–C(4)–C(5)	106.2(4)			N(1)–Zn(1)–O(2)	95.7(3)	O(4)–Zn(1)–O(1)	148.8(7)
C(6)–C(5)–C(4)	108.4(4)			O(2A)–Zn(1)–O(2)	87.3(5)	N(1)–Zn(1)–O(1)	92.1(7)
C(5)–C(6)–N(2)	110.4(4)					N(3)–Zn(1)–O(3)	152.6(7)
						O(2)–Zn(1)–O(3)	99.1(8)
						O(4)–Zn(1)–O(3)	58.2(6)
						N(1)–Zn(1)–O(3)	93.1(8)
						O(1)–Zn(1)–O(3)	96.4(7)

radiation, whereas the data of **3** were collected on Siemens Smart CCD 1000 diffractometer, operating at 50 kV and 35 mA at 23 °C. The data for NPA and compounds **1–3** were collected over 2θ at 3–50, 3–45, 3–45, and 3–47°, respectively. Three standard reflections were measured every 197 reflections. No significant decay was observed for all samples during the data collection. Data were processed on a Pentium III PC using the Siemens SHELXTL software package (version 5.1) and corrected for Lorentz and polarization effects. Empirical absorption corrections were applied to all crystals. Neutral-atom scattering factors were taken from Cromer and Waber.<sup>21</sup> The crystals of NPA, **2**, and **3** belong to the monoclinic space groups *P*2<sub>1</sub>/*c*, *C*2/*c*, and *P*2<sub>1</sub>, respectively, while the crystal of **1** belongs to the triclinic space group *P*1. All structures were solved by direct methods. The NPA ligand in compound **2** is disordered over two sites related by a *C*<sub>2</sub> rotation with 50% occupancy for each site, and the disorder has been modeled and refined successfully. There are two independent molecules in the asymmetric units of NPA and **3**. One of the isobutyl groups in each independent molecule of **3** is disordered. Attempts to model the disordering in **3** were not completely successful. The quality

of the crystal of **3** is poor, which contributes further to the poor quality of the structure. All non-hydrogen atoms in NPA and **1–3** were refined anisotropically, except some of the atoms on the disordered isobutyl groups in **3**. The positions of all hydrogen atoms in **1–3** except those on disordered atoms were calculated, and their contributions in structural factor calculations were included. All hydrogen atoms in NPA were located directly from difference Fourier maps and refined successfully. The crystallographic data for compounds NPA and **1–3** are given in Table 1.

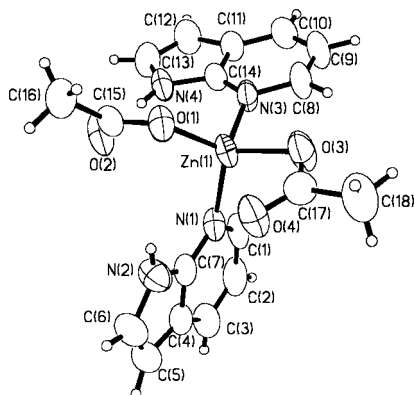
## Results and Discussion

**Synthesis and Crystal Structure of 1.** Compound **1** was obtained from the reaction of 7-azaindole and Zn(CH<sub>3</sub>COO)<sub>2</sub> in a 2:1 ratio. Compound **1** is air-stable and sublimable. The structure of compound **1** has been determined by single-crystal X-ray diffraction analysis. Important bond lengths and angles are listed in Table 2.

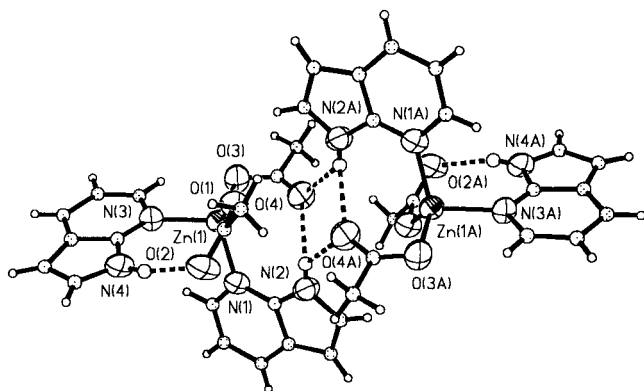
As shown in Figure 1, the two 7-azaindole ligands are coordinated to the Zn(II) center as terminal ligands through the pyridyl nitrogen atom. Previously, we have observed that the

(21) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.





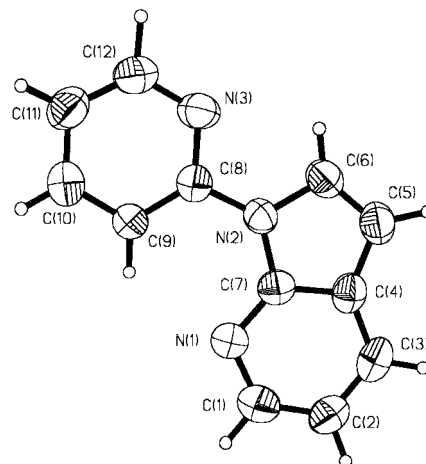
**Figure 1.** Diagram showing the structure of compound **1** with 50% thermal ellipsoids and labeling schemes.



**Figure 2.** Diagram showing the hydrogen-bonded dimer of **1**.

neutral 7-azaindole ligand can also bind to a metal center as a monodentate terminal ligand through the indole nitrogen atom (where the proton is shifted from the indole nitrogen atom to the pyridyl nitrogen atom).<sup>16,17</sup> The two acetate groups are bound to the Zn(II) center as monodentate terminal ligands through one of the oxygen atoms. The noncoordinated oxygen atoms O(2) and O(4) are at 3.054 and 2.678 Å from the Zn(II) center, respectively. Therefore, the Zn(II) ion in compound **1** has a tetrahedral geometry, typical of zinc(II) compounds. The O(3)–Zn(1)–N(3) angle of 97.6(2)° is much less than a typical tetrahedral bond angle (109°). Compound **1** is therefore a somewhat distorted tetrahedron. The Zn–N and Zn–O bond lengths are similar to those reported previously.<sup>22</sup>

An interesting feature is that the noncoordinated O(2) and O(4) atoms form hydrogen bonds with the indole proton. The O(2) atom forms an intramolecular hydrogen bond with the hydrogen atom on N(4), as evidenced by the N(4)⋯O(2) distance of 2.763 Å. In contrast, the O(4) atom forms an intramolecular hydrogen bond with the hydrogen atom on N(2) and an intermolecular hydrogen bond with the hydrogen atom on N(2A) as well, as indicated by the N(2)⋯O(4) distance of 3.038 Å and the N(2A)⋯O(4) distance of 3.961 Å. The dimer structure, linked by hydrogen bonds between N(2), N(2A), and O(4), is shown in Figure 2. In the solid state, there is a  $\pi$ – $\pi$



**Figure 3.** Diagram showing the structure of NPA with 50% thermal ellipsoids and labeling schemes.

stacking between the 7-azaindole groups, with the shortest atomic separation distance being 3.660 Å.

**Syntheses and Crystal Structures of NPA, **2**, and **3**.** As mentioned above, the deprotonated 7-azaindole in complexes are not stable because the indole nitrogen atom is negatively charged. We therefore carried out the synthesis of the modified 7-azaindole ligand, NPA. The synthesis of NPA was carried out by using Ullmann condensation methods<sup>23</sup> where copper(II) and K<sub>2</sub>CO<sub>3</sub> are used as catalysts.

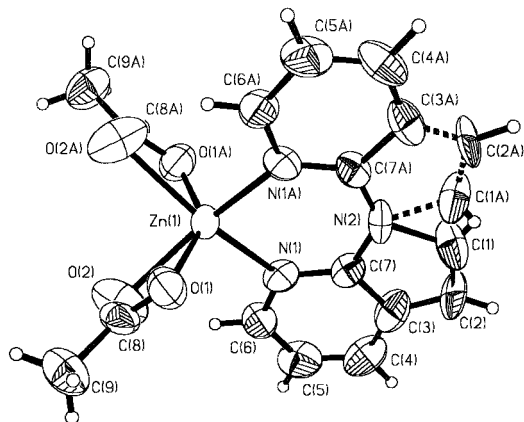
The structure of NPA was examined by a single-crystal X-ray diffraction analysis. There are two independent molecules in the asymmetric unit, one of which is shown in Figure 3. The pyridyl ring is nearly coplanar with the 7-azaindole portion. (The dihedral angle between the pyridyl ring and the 7-azaindole portion is 6.7° and 11.2° for the two independent NPA molecules, respectively.) X-ray data established unequivocally that the NPA molecule has a trans geometry; that is, the pyridyl N(3) atom is on the opposite side of the 7-azaindole nitrogen atom N(1). It is likely that the trans geometry minimizes the steric interaction between C–H groups of the pyridyl (C(9)) and the 7-azaindole (C(6)). (If C(9) and C(6) were on the same side (i.e., having a cis geometry), the separation distance between the two hydrogen atoms would be 1.84 and 1.93 Å for the two independent molecules, respectively, much less than the sum of van der Waals radii for two hydrogen atoms,<sup>24</sup> 2.40 Å.) There is extensive stacking between NPA molecules in the crystal lattice. The shortest intermolecular separation distance between two neighboring NPA molecules is 3.537(3) Å.

The NPA zinc(II) complex **2** was obtained from the reaction of Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> with NPA in a 1:1 ratio, whereas compound **3** was obtained from the reaction of NPA with Zn((S)-(+)-CH<sub>3</sub>-CH<sub>2</sub>CH(CH<sub>3</sub>)COO)<sub>2</sub> (obtained from the reaction of ZnO with (S)-(+)-CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)COOH) in a 1:1 ratio. One apparent advantage of forming complexes **2** and **3** is that the complexes have a much higher melting point (178 °C for **2** and 121 °C for **3**) than that of the free NPA (58 °C), a phenomenon common for coordination compounds.<sup>16–22</sup> The structures of compounds **2** and **3** have been determined by single-crystal X-ray diffraction analyses. Important bond length and angles are listed in Table 2.

(22) (a) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 5, Chapter 56.1. (b) Auf der Heyde, T. P. E. *Acta Crystallogr.* **1984**, B40, 582. (c) Kerr, M. C.; Preston, H. S.; Ammon, H. L.; Huheey, J. E.; Stewart, J. M. *J. Coord. Chem.* **1981**, 11, 111. (d) Smith, H. W. *Acta Crystallogr.* **1975**, B31, 2701. (e) Yang, W.; Schmider, H.; Wu, Q.; Zhang, Y.; Wang, S. *Inorg. Chem.* **2000**, 39, 2397.

(23) (a) Goodbrand, H. B.; Hu, N. X. *J. Org. Chem.* **1999**, 64, 670. (b) Lindley, J. *Tetrahedron* **1984**, 40, 1433. (c) Fanta, P. E. *Synthesis* **1974**, 1.

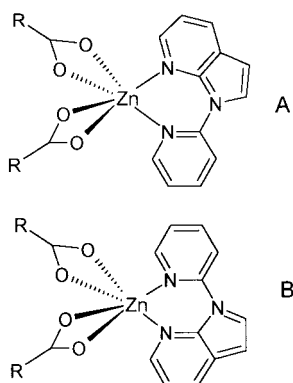
(24) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1989.



**Figure 4.** Diagram showing the structure of compound **2** with 50% thermal ellipsoids and labeling schemes.

As shown in Figure 4, compound **2** has a crystallographically imposed  $C_2$  rotation axis, on which Zn(1) and N(2) atoms are situated. As a consequence of the  $C_2$  symmetry, the NPA ligand is disordered over the two sites related by a  $C_2$  rotation with 50% occupancy for each site. Despite the disorder, the crystal data show clearly that, in contrast to the structure of the free NPA ligand, the pyridyl nitrogen atom N(1) (or N(1A)) and the 7-azaindole nitrogen atom N(1A) (or N(1)) in compound **2** are on the same side and are chelated to the Zn(II) center. The NPA ligand in **2** is nearly planar with a dihedral angle of  $7.3^\circ$  between the pyridyl and the 7-azaindole plane. The C(7A)–N(2)–C(7) angle,  $131.8^\circ$ , in **2** is, however, slightly bigger than the corresponding ones of the free ligand ( $123.5$ – $129.6^\circ$ ). The chelate effect is apparently responsible for the flipping of the pyridyl ring of the NPA ligand in **2**. Unlike compound **1** where the acetate groups are terminal ligands, the two acetate groups in compound **2** chelate to the Zn(II) center, with the Zn(1)–O bond lengths ranging from 2.079(8) to 2.288(8) Å. Therefore, compound **2** is six-coordinate with an irregular geometry. The Zn–O bond lengths in **2** are significantly longer than those in **1**, attributable to the increased number of coordination atoms in **2**. There is  $\pi$ – $\pi$  stacking between the six-membered rings (pyridyl or the six-membered ring of 7-azaindole), with the shortest separation distance being 3.729 Å in the crystal lattice of **2**.

The introduction of the optically pure (*S*)-(+)- $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}^-$  group in compound **3** was intended to overcome the disorder problem of the NPA ligand. Assuming that the disorder in **2** was caused by the coexistence of two types of structures A and B that differ only in the orientation of the NPA



**Figure 5.** Diagram showing the structure of compound **3** with 50% thermal ellipsoids and labeling schemes.

introduction of a chiral center in the carboxylate ligand in **3** would lead A and B to be diastereomers, and thus they would be unlikely to have an equal probability of existence.<sup>25</sup> The disorder observed in **2** is therefore less likely to occur. Indeed, compound **3** crystallizes in the chiral space group  $P2_1$  without the disorder of the NPA ligand. The molecular optical rotation of compound **3** is  $19.1^\circ/\text{mol}$ , similar to that ( $19.0^\circ$ ) of (*S*)-(+)- $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$ .

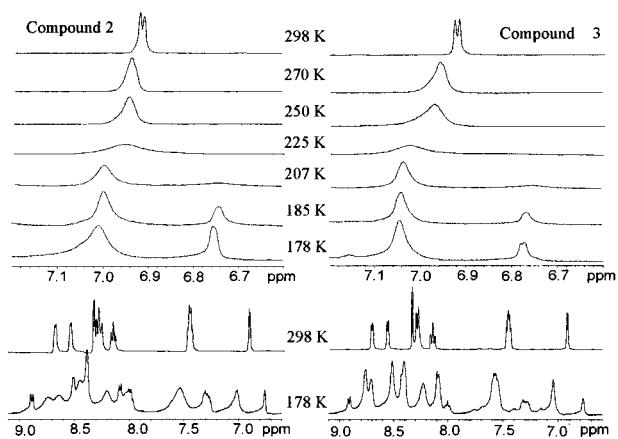
There are two independent molecules of **3** in the asymmetric unit. The structure of one of the independent molecules of **3** is shown in Figure 5. Despite the poor quality of the crystal, the X-ray diffraction data established clearly that the NPA ligand chelates to the Zn(II) center in the same manner as that observed in **2** and that the two carboxylate groups are bound to the Zn(II) center as chelate ligands with Zn–O bond lengths similar to those in **2**. One of the butyl groups in **3** is disordered. The dihedral angle between the pyridyl and the 7-azaindole plane is  $13.8$  and  $17.9^\circ$  for the two independent molecules, respectively. The separation distance between the two hydrogen atoms on C(4) and C(6) is 2.02 Å, much smaller than the sum of van der Waals radii, 2.40 Å. Therefore, some steric interactions between these two hydrogen atoms are likely to be present.

There is  $\pi$ – $\pi$  stacking between the NPA ligands in the lattice of compound **3**, with atomic separation distances ranging from 3.648 to 3.773 Å. However, unlike compound **2** where the stacking only involves six-membered rings, the stacking in **3** is between two 7-azaindole units where the five-membered ring (indole) is situated directly above the six-membered ring of the 7-azaindole and vice versa.

**Fluxional Behavior of 2 and 3 in Solution.** Compounds **2** and **3** have been found to be dynamic in solution (in  $\text{CDCl}_3$  or  $\text{CD}_3\text{OD}$ ), as established by variable-temperature  $^1\text{H}$  NMR experiments. At ambient temperature, one set of chemical shifts due to the NPA ligand are present in the  $^1\text{H}$  NMR spectra of **2** and **3**, consistent with the crystal structures. As the temperature decreases, all peaks become broad. At 180 K, two sets of well-resolved chemical shifts due to the NPA ligands are observed for both compounds (Figure 6), one of which is identical to that of the free NPA ligand. (The chemical shifts of alkyl groups in **2** and **3** became very broad and not well resolved at 180 K.) Therefore, we believe that compounds **2** and **3** are dynamic in solution, which is likely to be caused by an exchange between a coordinated NPA ligand and a noncoordinated NPA ligand (dissociated from the complex) as shown by eq 1. The ratio of

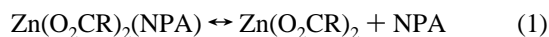
ligand, the absence of a chiral center in **2** makes A and B identical isomers with an equal probability of existence. The

(25) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; part A.



**Figure 6.** Variable-temperature  $^1\text{H}$  NMR spectra of compounds **2** and **3** in  $\text{CD}_3\text{OD}$ . Bottom: the entire aromatic region at 178 and 298 K. Top: the change of the peak at the far right of the aromatic region from 178 to 298 K.

the coordinated and noncoordinated NPA ligands at 180 K is  $\sim 2:1$  for **2** and  $\sim 3:1$  for **3**, based on the NMR data.

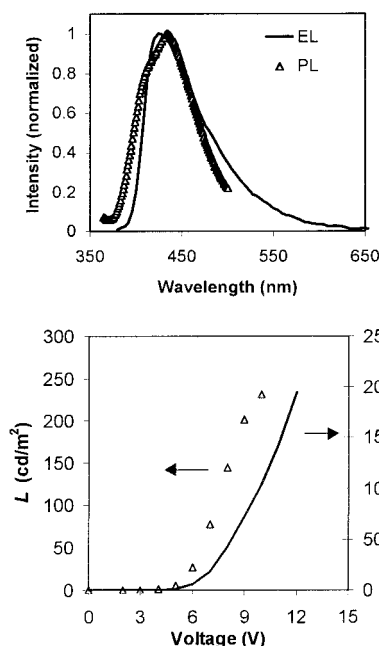


To further understand the process shown in (1), we examined the  $^1\text{H}$  NMR spectra of **2** and **3** in the presence of the free NPA ligand. The mixture of NPA with **2** or **3** shows only one set of NPA chemical shifts at ambient temperature, which is shifted toward the chemical shifts of the free NPA ligand, as the amount of NPA added to the solution increases. This supports further that the dynamic behavior of **2** and **3** is caused by an exchange between coordinated and noncoordinated NPA ligands. The activation energy for the exchange process was calculated<sup>26</sup> to be  $32.8 \text{ kJ mol}^{-1}$  for **2** and  $44.3 \text{ kJ mol}^{-1}$  for **3**.

The fluxional behavior of **2** and **3** leads us to believe that the NPA ligand is a fairly poor chelate ligand. The driving force for the dynamic process shown in (1) is likely to be the steric interactions between the two adjacent protons of 7-azaindole and pyridyl (e.g., C(4)-H and C(6)-H in **3**), which favors the trans geometry of the NPA ligand more than the cis chelate geometry. However, other factors such as the chelate ring constraint may also contribute to the poor stability of the NPA complexes. Further study is required to have a good understanding of the dynamic behavior of **2** and **3**.

Variable-temperature  $^1\text{H}$  NMR studies were also carried out for compound **1** in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ . Only one set of chemical shifts of 7-azaindole were observed, which are distinctly different from those of free 7-azaindole and do not change in the temperature range of 180–298 K, indicating that compound **1** is not dynamic in solution.

**Thermal Properties.** Compound **1** can be sublimed readily under vacuum, whereas attempts to sublime compounds **2** and **3** lead to the decomposition of the complex. Therefore, we examined the thermal stability of compounds **2** and **3** by thermogravimetric analyses. Compound **2** undergoes a clear two-stage weight loss at temperatures above  $170 \text{ }^\circ\text{C}$ , whereas compound **3** starts losing weight continuously at  $\sim 140 \text{ }^\circ\text{C}$ . The first stage of weight loss in **2** appears because of the loss of the NPA ligand on the basis of TGA data, which was also confirmed by trapping the free NPA ligand formed during the attempted sublimation of compounds **2** and **3**. The poor thermal stability



**Figure 7.** Top: EL and PL spectra of **1**. Bottom:  $L$ - $V$ - $J$  plots of the EL device.

of **2** and **3**, again attributable to the fact that the NPA ligand is a poor chelate ligand, precludes their applications in EL devices. In contrast, compound **1** is a bright and stable emitter, and thus it is potentially useful in EL devices.

**Luminescent and EL Properties of 1.** Free 7-azaindole ligands have no emission in the visible region. In contrast to the free 7-azaindole, compound **1** has a strong blue luminescence with an emission maximum at 434 nm in the solid state. Because  $\text{Zn}(\text{CH}_3\text{COO})_2$  has no luminescence, the observed blue luminescence is attributed to the coordinated 7-azaindole. Compound **1** is the first example of blue-luminescent complexes with only neutral 7-azaindole ligands. Our previously reported blue-luminescent 7-azaindole Al(III) and B(III) compounds all contain 7-azaindole anions.<sup>15–18</sup> The importance of the neutral 7-azaindole in compound **1** is that it improves the stability of the complex, in comparison to complexes containing 7-azaindole anions. Solution emission and excitation spectra of compound **1** were also measured. Compound **1** in a toluene solution has a broad emission band with the maximum at  $\lambda_{\text{max}} = 424 \text{ nm}$ , similar to that of the solid state, but the solution excitation spectrum of **1** is much narrower, compared to the solid-state excitation spectrum. In a toluene solution, the free 7-azaindole molecule has an emission band at  $\lambda_{\text{max}} = 357 \text{ nm}$ . The dramatic red shift of the emission energy in solution by complex **1**, relative to that of the free ligand, is clearly caused by the formation of coordination bonds between the 7-azaindole and the zinc(II) ion. Similar phenomena have been observed in tripyridylamine Zn(II) complexes.<sup>22e</sup> The luminescent quantum yield of compound **1** in solution was determined to be 0.42, relative to that of 9,10-diphenylanthracene, indicating that compound **1** is a bright-blue emitter.

The high stability, good volatility, and bright-blue luminescence displayed by **1** make it a good candidate as a blue emitter in EL devices. Therefore, attempts to fabricate EL devices using **1** as the light-emitting layer were carried out. An EL device using compound **1** as the emitting layer has been fabricated. NPD was employed as the hole-transport layer, and PBD was used as the electron-transport layer. As shown in Figure 7 (top), the EL device emits a blue light with  $\lambda_{\text{max}} = 428 \text{ nm}$ , which matches that of photoluminescence (PL) (film,  $\lambda_{\text{max}} = 434 \text{ nm}$ ),

(26) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill Book Co. (U.K.) Ltd.: London, 1987; p 103.

confirming that the light of the device originates from compound **1**. The  $L-V-J$  curves of the EL device are shown in Figure 7 (bottom). The device efficiency at 20 mA/cm<sup>2</sup> is 0.44 cd/A, and the turn-on voltage of the device is approximately 6 V. These preliminary results indicate that compound **1** is very promising in EL applications. Further investigation and optimization on EL devices using **1** as the emitting layer are in progress.

**Luminescent Properties of NPA, 2, and 3.** The NPA molecule emits a purple-blue color with an emission maximum at 416 nm in the solid state and 360 nm in a toluene solution, similar to that of 7-azaindole. The similarity of the emission energy of NPA and 7-azaindole in the toluene solution indicates that the pyridyl group has little influence on the emission energy of NPA. The red shift of the NPA emission energy from solution to solid is likely to be caused by the intermolecular  $\pi-\pi$  interactions of NPA in the solid state that effectively decrease the energy gap. The quantum yield for NPA was determined to be 0.09, relative to that of 9,10-diphenylanthracene (absolute quantum yield = 0.90), indicating that the free NPA molecule is not an efficient emitter.

In the solid state, the emission maximum of NPA in compound **2** is at 408 nm, whereas the emission maximum of NPA in **3** is at 460 nm. As mentioned above, the  $\pi-\pi$  interactions in **2** are between six-membered rings only, whereas the  $\pi-\pi$  interactions in **3** are between the entire 7-azaindole moieties. The increased intermolecular  $\pi-\pi$  interactions in **3**, compared to those in NPA and compound **2**, are likely to be responsible for the relatively low emission energy of **3** in the solid state. A similar change of emission energy from the solution to the solid state has been observed in blue-luminescent tripyridylamine Zn(II) complexes.<sup>22e</sup>

The luminescent spectra of NPA, **2**, and **3** in solution resemble each other, regardless of the solvent used (Table 3), which is attributable to the rapid exchange process in solution as confirmed by NMR experiments. In addition, the solution luminescent spectra of NPA, **2**, and **3** are highly solvent-dependent. In a solvent that does not have an acidic proton such as toluene or THF, the emission maximum of NPA, **2**, and **3** is at ~360 nm (Table 3). In a solvent that contains an acidic proton such as methanol, the emission maximum of these compounds is shifted to 385–408 nm. Hydrogen-bond formation between methanol and the NPA molecule (or dissociated NPA in the case of complexes **2** and **3**) is likely to be responsible for the shift of the emission energy. Similar emission energy red shift

**Table 3.** Luminescent Data of NPA, **2**, and **3** in Solution and the Solid State

	NPA		<b>2</b>		<b>3</b>	
	excitation $\lambda$ (nm)	emission $\lambda$ (nm)	excitation $\lambda$ (nm)	emission $\lambda$ (nm)	excitation $\lambda$ (nm)	emission $\lambda$ (nm)
methanol (0.01 M)	335	385	343	393	344	408
THF (0.01 M)	328	361	328	361	328	350
toluene (0.01 M)	329	360	329	360	329	351
solid	381	419	356	408	397	460

caused by hydrogen bonds has been well documented previously.<sup>27</sup> The emission energy of compound **1** is not solvent-dependent.

The formation of complexes appears to enhance the emission efficiency of the NPA ligand. Relative to that of 9,10-diphenylanthracene, the quantum yields for compounds **2** and **3** in solution were determined to be 0.22 and 0.16, respectively, significantly higher than that of NPA (0.09).

## Conclusion

The new NPA ligand forms novel Zn(II) complexes which are blue-luminescent in the solid state. However, the NPA ligand is a poor chelate ligand. As a consequence, the NPA zinc(II) compounds are dynamic in solution because of an exchange process between the coordinated NPA and the dissociated NPA ligand and thermally unstable in the solid state. In contrast, the new 7-azaindole zinc(II) complex **1** is a stable compound and is capable of producing a blue light in EL devices.

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

**Supporting Information Available:** Tables of crystal data, atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC000465Q

(27) (a) *Luminescence in Chemistry*; Bowen, E. J., Ed.; D. Van Nostrand Co.: London, 1968. (b) Liu, E. H.; Wang, Y.; Jin, W. K.; Shen, G. L.; Yu, R. Q. *Anal. Chim. Acta* **1999**, *383*, 299. (c) Armaroli, N.; De Cola, L.; Balzani, V.; Sauvage, J.-P.; Dietrich-Buchecker, C. O.; Kern, J.-M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 553. (d) Armaroli, N.; Balzani, V.; De Cola, L.; Hemmert, C.; Sauvage, J.-P. *New J. Chem.* **1994**, *18*, 775.