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Synthesis, Structures, and Luminescent Properties of Aluminum Complexes with Chelating Anilido-Imine Ligands

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

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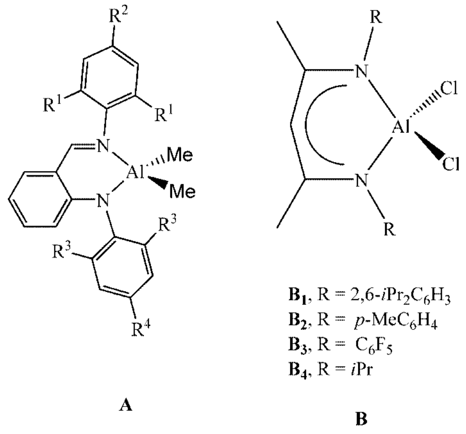
The syntheses of a number of four-coordinate aluminum complexes, *ortho*-$C_6H_4(NAr')(CH{=}NAr'')AlCl_2$ [Ar′ = Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**2a**); Ar′ = 2,6-iPr$_2$C$_6$H$_3$, Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**2b**); Ar′ = Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**2c**); Ar′ = p-MeC$_6$H$_4$, Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**2d**)], are described. Complexes **2a**–**2d** were synthesized from the reaction of $AlCl_3$ with lithium salt of the corresponding ligand at room temperature. All complexes were characterized by ^1H and ^{13}C NMR spectroscopy and molecular structures of complexes **2a**, **2b**, and **2d** were determined by X-ray crystallography. Luminescent properties of complexes **2a**–**2d** in both solution and the solid state were studied.

Introduction

Luminescent metal complexes have attracted increasing attention because of their potential application in areas of chemistry, medicine, and material science.[1] Many luminescent complexes of main group and transition metals, such as Al^{III},[2] Zn^{II},[3] Pt^{II},[4] Ir^{III},[5] and Re^{I},[6] have been designed and synthesized in recent years. Particularly, chelated aluminum complexes have attracted much attention because of their low cost, and good luminescent and electron-transporting properties. As the well-known tris(8-hydroxyquinolinyl)aluminum (Alq$_3$) was found to be a good emitter, and a highly efficient electron-transporting material and host material in organic electroluminescence devices,[7–9] a large number of its derivatives with modified 8-hydroxyquinoline ligands have been investigated.[1b,2,10] Aluminum complexes with nitrogen-containing ligands have also been reported,[11] while the luminescent properties of coordinative unsaturated aluminum complexes have not been extensively explored, probably because of their instability to air and moisture.[12,13] We have recently focused our attention on the synthesis of aluminum complexes of this type. As a continuation of our studies on the luminescent alkylaluminum complexes with chelating anilido-imine ligands (Scheme 1 A),[14d] herein we report the syntheses, characterization, and fluorescent properties of a number of aluminum dichloride complexes with anilido-imine ligands, *ortho*-$C_6H_4(NAr')(CH{=}NAr'')AlCl_2$ [Ar′ = Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**2a**); Ar′ = 2,6-iPr$_2$C$_6$H$_3$, Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**2b**); Ar′ = Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**2c**); Ar′ = p-MeC$_6$H$_4$, Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**2d**)].



Scheme 1.

Results and Discussion

Ligand Synthesis

Free ligands, *ortho*-$C_6H_4(NHAr')(CH{=}NAr'')$ [Ar′ = Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**1a**); Ar′ = 2,6-iPr$_2$C$_6$H$_3$, Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**1b**); Ar′ = Ar′′ = 2,6-Me$_2$C$_6$H$_3$ (**1c**); Ar′ = p-MeC$_6$H$_4$, Ar′′ = 2,6-iPr$_2$C$_6$H$_3$ (**1d**)], were synthesized by a literature procedure.[15] Of these free ligands, compounds **1a**, **1c**, and **1d** are known, while **1b** is a new compound. The new ligand **1b** was prepared by the reaction of *ortho*-$C_6H_4F(CH{=}NC_6H_3Me_2\text{-}2,6)$ with LiN(H)Ar (Ar = 2,6-iPr$_2$C$_6$H$_3$) (Scheme 2) in good yield (72% isolated yields). The reaction was carried out in THF and the crude product

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[a] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 10 Qianwei Road, Changchun 130012, People's Republic of China
Fax: +86-431-5193421
E-mail: ymu@mail.jlu.edu.cn

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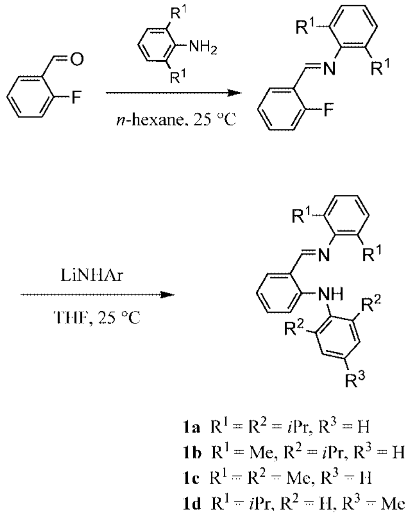
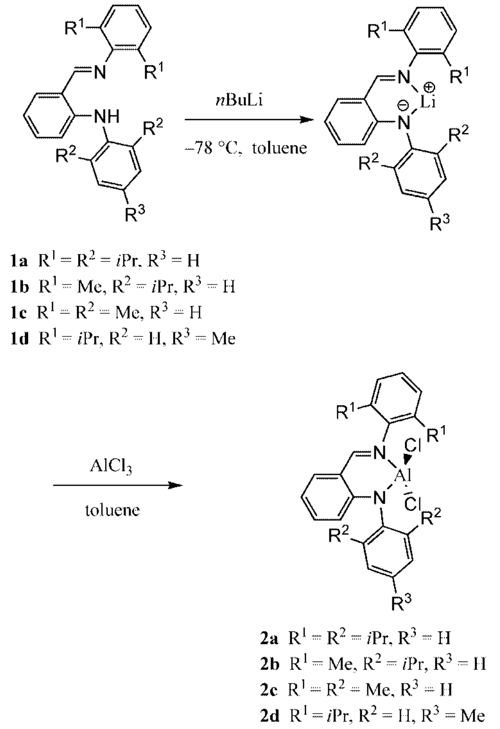
was purified by crystallization from methanol. Compound **1b** was characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analysis. The ^{1}H NMR spectrum of **1b** exhibits resonance at δ = 8.39 ppm for the imino CH proton, with the corresponding ^{13}C NMR resonance at δ = 166.25 ppm. The NH resonance appears at characteristically low field (δ = 10.5 ppm). The infrared absorption band of the imine C=N stretch occurs in the region 1617 cm^{-1}. Those data are similar to the corresponding values of **1a**, **1c**, and **1d**.[14d]



Scheme 2. Synthetic procedure of ligands **1a**–**1d**.

Complex Synthesis

The aluminum dichloride complexes **2a**–**2d** were synthesized in reasonable yields (68–75%) by reaction of $AlCl_3$ with the lithium salt of the corresponding ligand that was generated in situ by treating the free ligand with *n*BuLi in hexanes at –78 °C (Scheme 3). All complexes are well soluble in toluene, dichloromethane, diethyl ether, and THF, but sparingly soluble in saturated hydrocarbon solvents. Complexes **2a**–**2d** were all characterized by elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, and satisfactory analytic results were obtained for all compounds. In the ^{1}H NMR spectra of these complexes, the resonances for the imino CH protons (δ = 7.32–7.90 ppm) shift about 1 ppm towards high field compared to the corresponding signals of the free ligands. However, the resonances (δ = 173.5–174.5 ppm) for the imino CH carbons in the ^{13}C NMR spectra shift to low field in comparison with the corresponding ones of the free ligands and the dialkylaluminum complexes.[14d] The N–H signals of the free ligands disappear in the ^{1}H NMR spectra of complexes **2a**–**2d**, which is indicative of formation of an Al–N bond in these compounds. The two methyl groups of the isopropyl units in complexes **2a**, **2b**, and **2d** are inequivalent, as the coordination of the anilido-imine ligands to the aluminum center causes rotation about the N–aryl bond to become slow on the NMR timescale.[16] In addition, ^{1}H and ^{13}C NMR spectra reveal that these complexes all have C_s-symmetric structures in solution. All complexes are more stable than the corresponding alkylaluminum complexes in solution; they have pretty good thermal stability and can be heated in boiling toluene for several hours without obvious decomposition.



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

Crystal Structure

The molecular structures of the complexes **2a**, **2b**, and **2d** were determined by X-ray crystallographic analysis. Crystals of all three complexes suitable for X-ray crystal structure determination were grown from *n*-hexane at room temperature. The ORTEP drawings of molecular structures of **2a**, **2b**, and **2d** are shown in Figure 1 (top), Figure 2, and Figure 3, respectively. Selected bond lengths and angles for these complexes are given in Table 1. The X-ray analysis reveals that all three complexes adopt a distorted tetrahedral geometry with the metal center chelated by the bidentate ligand through the imine and amido nitrogen atoms. The N–Al–N bite angle in **2b** [99.27 (6)°] is larger than those in **2a** [97.59 (8)°] and **2d** [97.82 (8)°], but similar to the one in the related β-diketiminato aluminum complex [Scheme 1; $\mathbf{B_1}$ 99.36 (4)°, $\mathbf{B_2}$ 99.41(12)°],[17a,17b] which contains a similar six-membered C_3N_2Al metallacycle. In these three complexes, the six-membered chelating rings are nearly planar with the aluminum atom lying 0.5017, 0.0963, and 0.3065 Å out of the plane, respectively. The imino C=N bonds in these complexes retain their double bond character, being 1.303(2), 1.303(2), and 1.310(3) Å for **2a**, **2b**, and **2d**, respectively. The Al–N (amido) distances [1.8327(19) Å for **2a**, 1.8397(14) Å for **2b**, 1.826(2) Å for **2d**] are much shorter than the Al–N (imine) distances [1.894(2) Å for **2a**, 1.8927(15) for **2b**, 1.8937(19) Å for **2d**] because the anionic amido nitrogen can also π-donate to the aluminum, whereas the neutral imine nitrogen does not have an available lone pair for π-donation. The Al–N (imine) distances (1.893 Å average) are shorter than the values (1.953 Å average) previously reported for *ortho*-$C_6H_4(NAr')(CH=NAr')AlMe_2$[14d] because of the more electrophilic aluminum center in the dichloro aluminum compounds, but larger than the one [1.850(2) Å] in (TTP)$AlCl_2$.[17b] The Cl–Al–Cl angles (109.40° average) in **2a** and **2d** are close to the ideal tetrahedral angle of 109.47°, and they are similar to that of the reported diketiminatolaluminum complex (Scheme 1; B).[17] In addition, X-ray diffraction analysis reveals that intermolecular π–π interaction appears in the solid state of complex **2a** (Figure 1, bottom). One phenyl ring in the ligand of **2a** stacks together with the corresponding one in an adjacent molecule by the π–π interaction with a distance of 3.6 Å.[18]

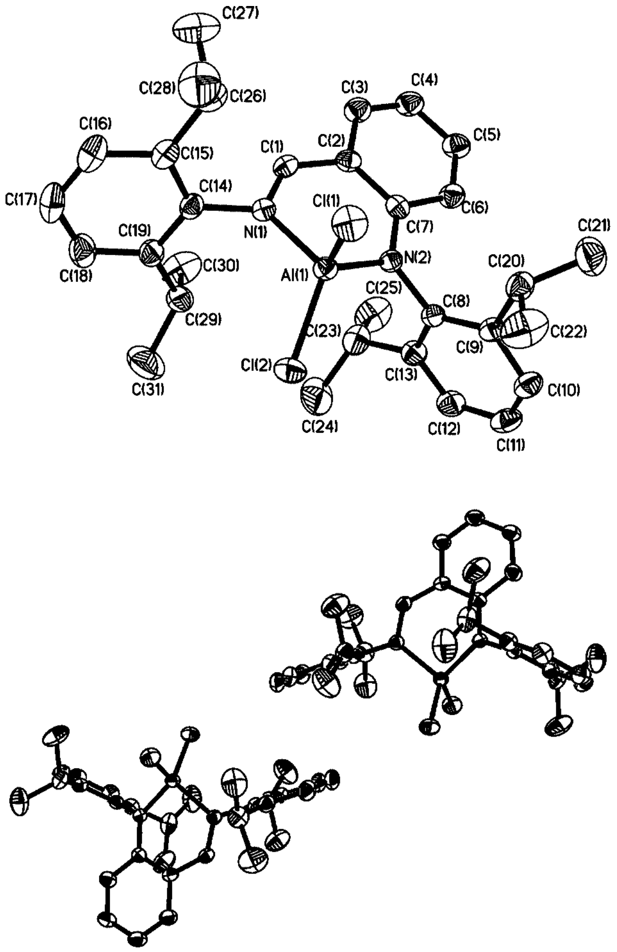


Figure 1. Top: Molecular structure of complex **2a**; bottom: Crystal packing diagram between two adjacent molecules of **2a** showing the existence of a π–π stacking interaction in the solid state. (Thermal ellipsoids are drawn at the 30% probability level.).

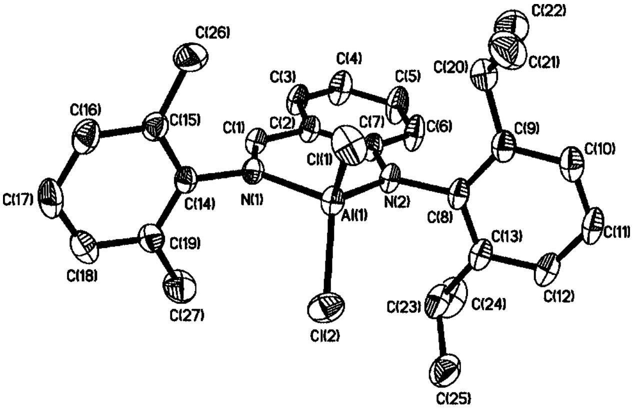


Figure 2. Molecular structure of complex **2b** (thermal ellipsoids are drawn at the 30% probability level).

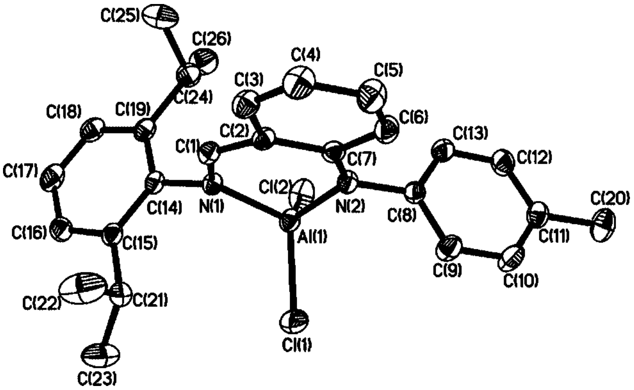


Figure 3. Molecular structure of complex **2d** (thermal ellipsoids are drawn at the 30% probability level).

Fluorescent Properties

Table 2 summarizes the UV/Vis and fluorescent properties of compounds **1a**–**1d** and **2a**–**2d** determined in both solution and the solid state. In solution, the free ligands **1a**–**1d** have a weak emission band at λ_{max} = 419, 420, 423, and 430 nm, respectively. When these ligands were bound to an aluminum center, strong green luminescence was observed. The observed luminescence of the complexes could be attributed to a π*–π transition of their chelated anilido-imine conjugated ligands. As shown in Figure 4, in contrast to the free ligands, each of complexes **2a**–**2d** in solution gives a broad emission band (bandwidth at half-height = 70–90 nm) with λ_{max} = 512, 510, 505, and 554 nm, respectively. The emission energies of these complexes are significantly red-shifted in comparison with the free ligands. The role of the aluminum atom in the luminescence of **2a**–**2d** should be twofold, as pointed out in the literature for coordination complexes.[19] First, the formation of covalent bonds between the Al and N atoms by the donation of lone pairs of the N atom to the Al atom changes the emission energy, owing to the lowering of the energy gap between π* and π. Second, after coordination with the Al atom, the ligand becomes more rigid, which can reduce the loss of energy by vibrational motions and increase the emission efficiency. The emission maxima of complexes **2a**–**2c** in solution are

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

Complex **2a**			
Al(1)–N(1)	1.894(2)	N(1)–Al(1)–Cl(2)	114.54(7)
Al(1)–N(2)	1.8327(19)	N(2)–Al(1)–Cl(1)	115.53(7)
Al(1)–Cl(2)	2.0978(10)	N(1)–Al(1)–Cl(1)	106.18(7)
Al(1)–Cl(1)	2.1190(11)	Cl(2)–Al(1)–Cl(1)	109.46(4)
N(1)–C(1)	1.303(3)	C(1)–N(1)–Al(1)	119.83(16)
N(2)–C(7)	1.370(3)	C(14)–N(1)–Al(1)	123.33(15)
N(1)–Al(1)–N(2)	97.59(8)	C(7)–N(2)–Al(1)	122.40(15)
N(2)–Al(1)–Cl(2)	113.02(7)	C(8)–N(2)–Al(1)	120.78(14)
Complex **2b**			
Al(1)–N(1)	1.8927(15)	N(1)–Al(1)–Cl(1)	109.36(5)
Al(1)–N(2)	1.8397(14)	N(2)–Al(1)–Cl(2)	116.17(6)
Al(1)–Cl(1)	2.1154(8)	N(1)–Al(1)–Cl(2)	110.40(5)
Al(1)–Cl(2)	2.1182(9)	Cl(1)–Al(1)–Cl(2)	107.00(4)
N(1)–C(1)	1.303(2)	C(1)–N(1)–Al(1)	121.47(11)
N(2)–C(7)	1.372(2)	C(14)–N(1)–Al(1)	122.05(10)
N(2)–Al(1)–N(1)	99.27(6)	C(7)–N(2)–Al(1)	125.07(11)
N(2)–Al(1)–Cl(1)	114.36(6)	C(8)–N(2)–Al(1)	117.04(11)
Complex **2d**			
Al(1)–N(1)	1.8937(19)	N(1)–Al(1)–Cl(2)	110.46(7)
Al(1)–N(2)	1.826(2)	N(2)–Al(1)–Cl(1)	110.55(7)
Al(1)–Cl(2)	2.1064(12)	N(1)–Al(1)–Cl(1)	113.73(7)
Al(1)–Cl(1)	2.1146(10)	Cl(2)–Al(1)–Cl(1)	109.34(5)
N(1)–C(1)	1.310(3)	C(1)–N(1)–Al(1)	120.93(15)
N(2)–C(7)	1.367(3)	C(14)–N(1)–Al(1)	123.09(13)
N(2)–Al(1)–N(1)	97.82(8)	C(7)–N(2)–Al(1)	126.00(15)
N(2)–Al(1)–Cl(2)	114.65(8)	C(8)–N(2)–Al(1)	114.41(13)

close to each other, while the emission maximum of **2d** is red-shifted about 40 nm compared to other complexes. This result could be attributed to the differences in the number and size of the *ortho*-substituents on the rotatable aryl rings of their ligands, which might affect the conjugated extent of these complexes.[14a–14d] In addition, the lower basicity and lower electron density of the anilide may also be responsible for the emission red shift in **2d**.[14e] The quantum yields of these compounds are low in solution. Complexes **2a**–**2d** all emit bright fluorescence in the solid state when irradiated by exciting light. The emission spectra of complexes **2a**–**2d** in the solid state are shown in Figure 5. Complexes **2b**, **2c**, and **2d** each have a relatively narrow band (bandwidth at half-height: 60–70 nm) in the solid state with $\lambda_{\max}$ = 497, 498, and 544 nm, respectively. The emission

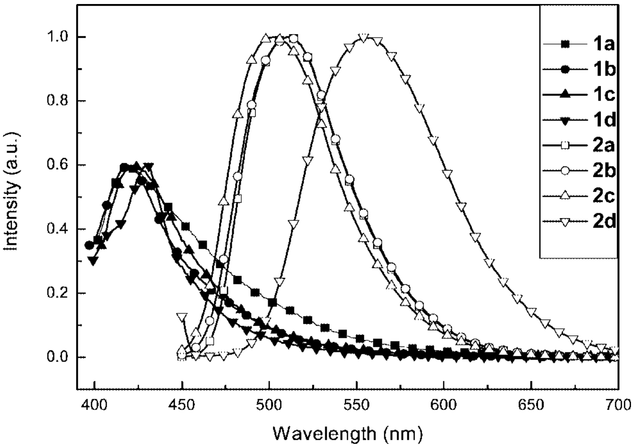


Figure 4. Emission spectra of ligands **1a**–**1d** and complexes **2a**–**2d** in *n*-hexane.

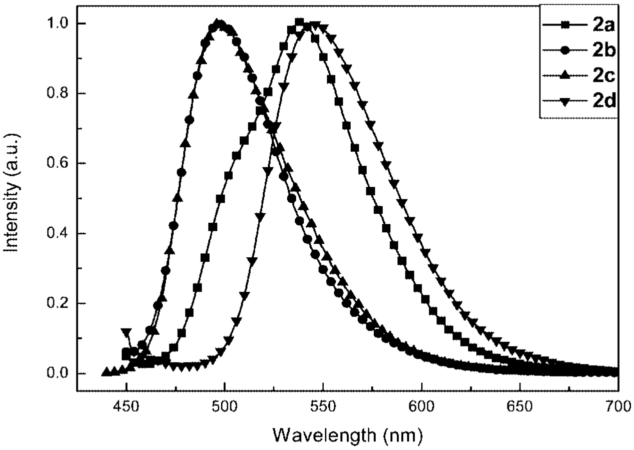


Figure 5. Emission spectra of complexes **2a**–**2d** in the solid state.

Table 2. Photoluminescent data for ligands **1a**–**1d** and complexes **2a**–**2d**.

Compound	ε [M^{-1}·cm^{-1}]	λ_{abs} [nm]	λ_{em} [nm]	Quantum yields [Φ][a]	Conditions
1a	9011	370	419	0.036	hexane, 298 K
			431		solid, 298 K
1b	11265	371	420	0.029	hexane, 298 K
			432		solid, 298 K
1c	13214	373	423	0.023	hexane, 298 K
			432		solid, 298 K
1d	10745	382	430	0.009	hexane, 298 K
			462		solid, 298 K
2a	12645	437	512	0.093	hexane, 298 K
			540		solid, 298 K
2b	12495	436	510	0.098	hexane, 298 K
			497		solid, 298 K
2c	11932	436	505	0.085	hexane, 298 K
			498		solid, 298 K
2d	10876	447	554	0.066	hexane, 298 K
			544		solid, 298 K

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

maxima of these complexes in the solid state are blue shifted compared to their corresponding emission maxima in solution, which probably resulted from the reduced conjugated extent of the three complexes, as the free rotation of the aryl rings in these complexes is blocked in the solid state. The emission maximum of complex **2a** ($\lambda_{\max}$ = 540 nm) in the solid state is red shifted compared to its corresponding emission maximum in solution, which is normal considering that red shifting of the emission maximum can be observed for most fluorescent compounds in the solid state, probably because of π–π stacking of aromatic rings in the molecules (see Figure 1, bottom). This result also implies that the rotation of 2,6-*i*Pr$_2$Ph groups about the N–aryl bond in complex **2a** is slow in solution, which is consistent with the ^{1}H NMR experimental result.

Conclusion

Our research results indicate that the chelating bidentate anilido-imine conjugated ligands are well suited for synthesizing the four-coordinate aluminum complexes by a salt metathesis reaction of AlCl$_3$ with the lithium salt of corresponding ligands at room temperature. ^{1}H and ^{13}C NMR spectra reveal that these aluminum complexes have C_s-symmetric structures in solution and X-ray diffraction analysis indicates that the six-membered chelating ring in these complexes is nearly planar with the aluminum lying slightly out of the plane. These complexes produce bright fluorescence in both solution and the solid state, and the emission color in solution can be tuned by the *ortho* substituents on the rotatable aryl rings of the ligands. The four-coordinate aluminum complexes are a new class of luminescent material with potential applications in optoelectronic devices.

Experimental Section

All reactions were performed using standard Schlenk techniques in high-purity nitrogen or glovebox techniques. Toluene, *n*-hexane, THF, and diethyl ether were dried by refluxing over sodium and benzophenone and distilled under nitrogen prior to use. C$_6$D$_6$ 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. AlCl$_3$ and *n*BuLi were purchased from Aldrich and used as received. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. The elemental analysis was performed with a Perkin–Elmer 2400 analyzer. UV/Vis absorption spectra were recorded with a UV-3100 spectrophotometer. Fluorescence measurements were carried out on an RF-5301PC.

***ortho*-C$_6$H$_4$[NH(C$_6$H$_3$*i*Pr$_2$-2,6)](CH=NC$_6$H$_3$Me$_2$-2,6) (1b):** A solution of *n*BuLi (30.32 mL, 48.5 mmol) in hexanes was added to a solution of 2,6-diisopropylaniline (8.1 mL, 48.5 mmol) in THF (30 mL) at –78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting solution of LiNHAr was transferred into a solution of *ortho*-C$_6$H$_4$F(CH=NC$_6$H$_3$Me$_2$-2,6) (11.0 g, 48.5 mmol) in THF (40 mL) at 25 °C. After stirring for 2 h, the reaction was quenched with H$_2$O (25 mL), extracted with *n*-hexane, and the organic phase was evaporated to dryness in vacuo to give the crude product as a yellow solid. Pure product (13.4 g, 72 %) was obtained as yellowish-green crystals by recrystallization from ethanol at –20 °C. C$_{27}$H$_{32}$N$_2$ (384.56): calcd. C 84.33, H 8.39, N 7.28; found C 84.28, H 8.48, N 7.24. ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ = 1.15, 1.17 [d, J = 6.6 Hz, 2×6 H, CH(C*H*$_3$)$_2$], 2.21 (s, 6 H, C*H*$_3$), 3.22 [sept, J = 6.6 Hz, 2 H, C*H*(CH$_3$)$_2$], 6.30 (d, J = 8.1 Hz, 1 H, Ph-*H*), 6.71 (t, J = 6.6 Hz, 1 H, Ph-*H*), 6.98 (t, J = 7.2 Hz, 1 H, Ph-*H*), 7.09–7.38 (m, 7 H, Ph-*H*), 8.39 (s, 1 H, C*H*=NAr), 10.53 (s, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$, 293 K): δ = 18.7 (*C*H$_3$), 23.2 [CH(*C*H$_3$)$_2$], 25.0 [CH(*C*H$_3$)$_2$], 28.8 [*C*H(CH$_3$)$_2$], 112.2, 115.3, 116.5, 124.0, 127.7, 127.9, 128.3, 132.5, 134.7, 134.8, 147.7, 150.2, 151.1 (Ph), 166.2 (*C*H=NAr) ppm.

***ortho*-C$_6$H$_4$N(C$_6$H$_3$*i*Pr$_2$-2,6)(CH=NC$_6$H$_3$*i*Pr$_2$-2,6)AlCl$_2$ (2a):** A solution of *n*BuLi in hexanes (0.28 mL, 0.45 mmol) was added dropwise to a stirred toluene solution of *ortho*-C$_6$H$_4$NH(C$_6$H$_3$*i*Pr$_2$-2,6)(CH=NC$_6$H$_3$*i*Pr$_2$-2,6) (0.20 g, 0.45 mmol) at –78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl$_3$ (0.06 g, 0.45 mmol) at –78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at –20 °C overnight to let the product crystallize. The product was obtained as yellow-green crystals (0.18 g, 75 %). C$_{31}$H$_{39}$Al$_2$Cl$_2$N (537.54): calcd. C 69.27, H 7.31, N 5.21; found C 69.20, H 7.40, N 5.25. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ = 0.93, 1.00 [d, J = 6.9 Hz, 2×6 H, CH(C*H*$_3$)$_2$], 1.38, 1.46 [d, J = 6.9 Hz, 2×6 H, CH(C*H*$_3$)$_2$], 3.53 [sept, J = 6.9 Hz, 2×2 H, C*H*(CH$_3$)$_2$], 6.25 (t, J = 6.1 Hz, 1 H, Ph-*H*), 6.41 (d, J = 8.8 Hz, 1 H, Ph-*H*), 6.70 (t, J = 6.6 Hz, 2 H, Ph-*H*), 7.07–7.12 (m, 6 H, Ph-*H*), 7.92 (s, 1 H, *H*C=N) ppm. ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$, 293 K): δ = 22.9, 24.7, 25.4, 25.7 [4×CH(*C*H$_3$)$_2$], 28.7, 29.0 [2×*C*H(CH$_3$)$_2$], 115.1, 117.1, 119.3, 124.7, 125.2, 129.0, 136.9, 137.2, 137.6, 141.1, 143.5, 146.7, 158.0 (Ph), 173.5 (*C*H=NAr) ppm.

***ortho*-C$_6$H$_4$N(C$_6$H$_3$*i*Pr$_2$-2,6)(CH=NC$_6$H$_3$Me$_2$-2,6)AlCl$_2$ (2b):** A solution of *n*BuLi in hexanes (0.33 mL, 0.52 mmol) was added dropwise to a stirred toluene solution of *ortho*-C$_6$H$_4$NH(C$_6$H$_3$*i*Pr$_2$-2,6)(CH=NC$_6$H$_3$Me$_2$-2,6) (0.20 g, 0.52 mmol) at –78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl$_3$ (0.07 g, 0.52 mmol) at –78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at –20 °C overnight to let the product crystallize. The product was obtained as yellow-green crystals (0.18 g, 70 %). C$_{27}$H$_{31}$AlCl$_2$N$_2$ (481.44): calcd. C 67.36, H 6.49, N 5.82; found C 67.30, H 6.44, N 5.91. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ = 0.99 [d, J = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.42 [d, J = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.67 (s, 6 H, C*H*$_3$), 3.48 [sept, J = 6.6 Hz, 2 H, C*H*(CH$_3$)$_2$], 6.27 (t, J = 6.0 Hz, 1 H, Ph-*H*), 6.38 (d, J = 8.7 Hz, 1 H, Ph-*H*), 6.60 (d, J = 8.1 Hz, 1 H, Ph-*H*), 6.72 (t, J = 6.6 Hz,1 H, Ph-*H*), 6.81–7.19 (m, 6 H, Ph-*H*), 7.35 (s, 1 H, C*H*=NAr) ppm. ^{13}C{^{1}H} NMR (300 MHz, C$_6$D$_6$, 293 K): δ = 18.8 (*C*H$_3$), 24.6 [CH(*C*H$_3$)$_2$], 25.5 [CH(*C*H$_3$)$_2$], 28.6 [*C*H(CH$_3$)$_2$], 115.3, 116.7, 119.3, 125.2, 129.3, 132.7, 137.2, 137.3, 143.9, 146.7 (Ph), 173.8 (*C*H=NAr) ppm.

***ortho*-$C_6H_4N(C_6H_3Me_2$-2,6)($CH=NC_6H_3Me_2$-2,6)$AlCl_2$ (2c):** A solution of *n*BuLi in hexanes (0.38 mL, 0.61 mmol) was added dropwise to a stirred toluene solution of *ortho*-$C_6H_4NH(C_6H_3Me_2$-2,6)($CH=NC_6H_3Me_2$-2,6) (0.20 g, 0.61 mmol) at –78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of $AlCl_3$ (0.08 g, 0.61 mmol) at –78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at –20 °C overnight to let the product crystallize. The product was obtained as yellow crystals (0.18 g, 68%). $C_{23}H_{23}AlCl_2N_2$ (425.33): calcd. C 64.95, H 5.45, N 6.59; found C 64.82, H 5.56, N 6.64. ^1H NMR (300 MHz, C_6D_6, 293 K): δ = 2.27 (s, 6 H, CH_3), 2.37 (s, 6 H, CH_3), 6.33 (t, J = 6.3 Hz, 1 H, Ph-H), 6.68 (d, J = 8.5 Hz, 1 H, Ph-H), 6.76–7.04 (m, 8 H, Ph-H), 7.35 (s, 1 H, CH=NAr) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 293 K): δ = 18.9 (CH_3), 115.3, 116.5, 116.7, 127.2, 128.1, 129.2, 129.6, 132.9, 136.4, 137.5, 138.3, 139.8, 143.5, 156.5, 174.3 (CH=NAr) ppm.

***ortho*-$C_6H_4N(C_6H_4Me$-*p*)($CH=NC_6H_3i Pr_2$-2,6)$AlCl_2$ (2d):** A solution of *n*BuLi in hexanes (0.34 mL, 0.54 mmol) was added dropwise to a stirred toluene solution of *ortho*-$C_6H_4NH(C_6H_4Me$-*p*)-($CH=NC_6H_3iPr_2$-2,6) (0.20 g, 0.54 mmol) at –78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of $AlCl_3$ (0.08 g, 0.54 mmol) at –78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at –20 °C overnight to let the product crystallize. The product was obtained as yellow crystals (0.16 g, 71%). $C_{26}H_{29}AlCl_2N_2$ (467.41): calcd. C 66.81, H 6.25, N 5.99; found: C 66.92, H 6.11, N 5.90. ^1H NMR (300 MHz, C_6D_6, 293 K): δ = 0.89 [d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.38 [d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.03 (s, 3 H, CH_3), 3.48 [sept, J = 6.6 Hz, 2 H, $CH(CH_3)_2$], 6.31 (t, J = 6.9 Hz, 1 H, Ph-H), 6.62 (d, J = 8.8 Hz, 1 H, Ph-H), 6.72 (d, J = 8.1 Hz, 1 H, Ph-H), 6.81 (t, J = 6.6 Hz, 1 H, Ph-H), 6.94 (d, J = 8.4 Hz, 2 H, Ph-H), 7.07–7.13 (m, 2 H, Ph-H), 7.33 (d, J = 6.5 Hz, 2 H, Ph-H), 7.94 (s, 1 H, CH=NAr) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 293 K): δ = 20.8 (CH_3), 22.8 [$CH(CH_3)_2$], 26.0 [$CH(CH_3)_2$], 28.9 [$CH(CH_3)_2$], 114.7, 116.7, 117.6, 124.7, 128.5, 129.2, 131.0, 136.4, 137.0, 138.1, 140.1, 140.7, 143.8, 158.0 (Ph), 173.6 (CH=NAr) ppm.

X-ray Structure Determinations of 2a, 2b, and 2d: Single crystals of **2a**, **2b**, and **2d** 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 **2a**, **2b**, and **2d**. Details of the crystal data, data collections, and structure refinements are summarized in Table 3. The structures were solved by direct methods[20] 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 positions. All calculations were performed using the SHELXTL[21] crystallographic software packages.

CCDC-279167 (for **2a**), -279168 (for **2b**), and -279169 (for **2d**) 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 refinement details for **2a**, **2b**, and **2d**.

	2a	**2b**	**2d**
Empirical formula	$C_{31}H_{39}AlCl_2N_2$	$C_{27}H_{31}AlCl_2N_2$	$C_{26}H_{29}AlCl_2N_2$
Formula mass	537.5	481.42	467.39
Temp. [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a [Å]	17.474(4)	8.9391(18)	9.5066(19)
b [Å]	10.448(2)	26.151(5)	9.866(2)
c [Å]	17.528(4)	11.242(2)	14.837(3)
α [°]	90	90	107.24(3)
β [°]	108.65(3)	96.02(3)	103.70(3)
γ [°]	90	90	99.30(3)
V [Å^3]	3032.1(11)	2613.6(9)	1250.3(4)
Z	4	4	2
D_{calcd} [Mg·m^{-3}]	1.177	1.223	1.241
F(000)	1144	1016	492
Crystal size [mm]	0.40 × 0.28 × 0.24	0.51 × 0.32 × 0.21	0.41 × 0.28 × 0.21
θ Range for data collection (°)	1.23–27.50	3.07–27.44	1.51–27.48
Limiting indices	$-18 \le h \le 22$	$-11 \le h \le 11$	$0 \le h \le 12$
	$-13 \le k \le 13$	$-31 \le k \le 33$	$-12 \le k \le 12$
	$-17 \le l \le 22$	$-14 \le l \le 14$	$-19 \le l \le 18$
Data/restraints/parameters	6955/0/333	5941/0/413	5697/0/396
Goodness-of-fit on F^2	0.865	1.020	0.850
Final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0480	R_1[a] = 0.0404	R_1[a] = 0.0424
	wR_2[b] = 0.1098	wR_2[b] = 0.1032	R_2[b] = 0.1062
R indices (all data)	R_1[a] = 0.1159	R_1[a] = 0.0642	R_1[a] = 0.0776
	wR_2[b] = 0.1258	wR_2[b] = 0.1157	wR_2[b] = 0.1207
Largest diff. peak/hole [e·Å^{-3}]	0.344, –0.246	0.251, –0.285	0.850, –0.301

[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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