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Synthesis of reactive [Al(Et)(q′)₂] (q′ = 2-methyl-8-quinolinolato) serving as a precursor of light emitting aluminum complexes: Reactivity, optical properties, and fluxional behavior of the aluminum complexes

Takayuki Iijima, Takakazu Yamamoto *

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Abstract

Reaction of AlEt₃ with 2-methyl-8-quinolinol gave ethylbis(2-methyl-8-quinolinolato)aluminum complex [Al(Et)(q′)₂] **1**. The complex **1** provided photoluminescent Al complexes by reactions with phenols, carboxylic acid, and H_2O. The α-CH_2 hydrogens in the Et group of **1** was diastereotropic as revealed by ¹H NMR spectroscopy because of the presence of a chiral center at Al. The chirality at Al was dynamically lost at elevated temperature in $CDCl_2CDCl_2$ and DMSO-d_6, as indicated by temperature dependent ¹H NMR spectroscopy. This dynamic or fluxional behavior of **1** is explained by rotation of the 2-methyl-8-quinolinolato ligand. The kinetic parameters of the dynamic process were estimated at $\Delta H^{\ddagger} = 135$ kJ mol⁻¹ and $\Delta S^{\ddagger} = 159$ J K⁻¹ mol⁻¹ in $CDCl_2CDCl_2$ and at $\Delta H^{\ddagger} = 124$ kJ mol⁻¹ and $\Delta S^{\ddagger} = 151$ J K⁻¹ mol⁻¹ in DMSO-d_6, respectively, at 350 K. Structures of some of the obtained Al complexes were confirmed by single-crystal X-ray crystallography. These Al complexes showed photoluminescence peaks at 492–507 nm in $CHCl_3$ with quantum yields of 7–23%.
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1. Introduction

Tris(8-quinolinolato)aluminum ([Alq₃]; q = 8-quinolinolato) is one of the most widely used metal complexes for organic light emitting diodes (OLEDs), and a large number of papers have been published about chemical and physical properties of [Alq₃] and its related compounds [1–8]. For example, modifications of the 8-quinolinolato ligand to improve the OLED performance of the Al complex have been carried out [4,5]. An Al complex with a 2-methyl-8-quinolinolato (q′) ligand was found to be an excellent hole blocking material [6].
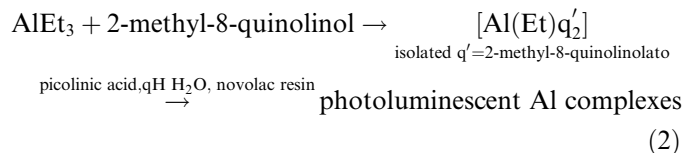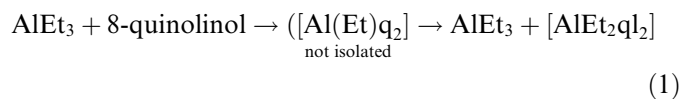
Recently, an aluminum complex having a reactive OH group, [Al(OH)(q′)₂], has also been reported [7], and such a complex is expected to serve as a good starting material for various light-emitting aluminum complexes.

[Al(Et)q₂]-type complexes having a reactive Al–Et bond are also expected as a promising starting material for the aluminum complexes. However, a 1:2 reaction of [AlEt₃] with 8-quinolinol, qH, did not give the expected [Al(Et)q₂]. The reaction afforded a mixture of tetraethylbis[μ-(8-quinolinolato-κN1,κO8:κO8)]dialuminum (**2**) (hereafter abbreviated as [Al(Et)₂q]₂) and Alq₃, and the results suggested a strong tendency for the formed [Al(Et)q₂] to disproportionate to [Alq₃] and [Al(Et)₂q]₂ because of high stability of [Alq₃].

By searching appropriate ligands to suppress such a disproportionation reaction, we have found that 2-methyl-8-

* Corresponding author. Tel.: +81 45 924 5220; fax: +81 45 924 5976.
E-mail address: tyamamot@res.titech.ac.jp (T. Yamamoto).

quinolinol, q′H, is an excellent compound to give the expected [Al(Et)q$_2$] type complex.

$$AlEt_3 + \text{8-quinolinol} \rightarrow (\underset{\text{not isolated}}{[Al(Et)q_2]} \rightarrow AlEt_3 + [AlEt_2ql_2]$$

(1)

$$AlEt_3 + \text{2-methyl-8-quinolinol} \rightarrow \underset{\text{isolated q}'=\text{2-methyl-8-quinolinolato}}{[Al(Et)q_2']}$$

$$\overset{\text{picolinic acid,qH H}_2\text{O, novolac resin}}{\rightarrow} \text{photoluminescent Al complexes}$$

(2)

From the Al complex **1**, photoluminescent Al compounds have been obtained as expressed in Eq. (2). We have observed interesting ^{1}H NMR-peak-averaging phenomena of **1** for the CH$_2$ group in the Et group bonded to a chiral Al center. Herein we report results of studies about the [Al(Et)(q′)$_2$] complex **1** and photoluminescent Al complexes derived from the complex **1**. Parts of the results, including synthesis of **1** [8] and fluxional behavior of **1** in a solvent (DMSO-d_6) [9], have been reported in communication forms.

2. Results and discussion

2.1. Preparation of the starting complex 1

The reaction of AlEt$_3$ with 2-methyl-8-quinolinol, q′H, in a 1:2 molar ratio selectively gave [Al(Et)(q′)$_2$] (**1**) in 97% yield as expressed in Eq. (3) [8].

$$AlEt_3 + 2 \quad \overset{\text{toluene}}{\longrightarrow} \quad [Al(Et)(q')_2]$$

1

(3)
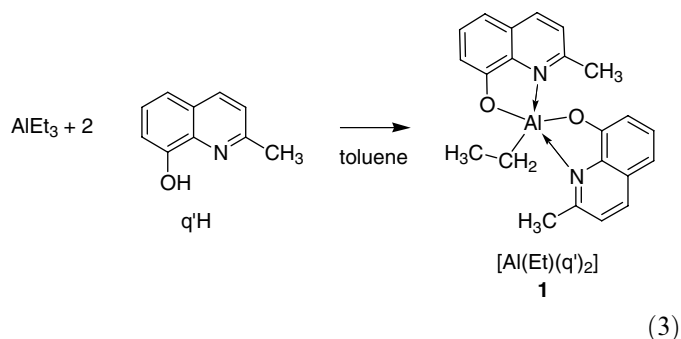
As described above, a similar 1:2 reaction of AlEt$_3$ with 8-quinolinol, qH, gave Alq$_3$ and q-ligand-bridged binuclear complex [Al(Et)$_2$q]$_2$ (**2**). Synthesis and molecular structure of the binuclear complex **2** have been reported [8]. The complex **1** was characterized by elemental analysis and NMR spectroscopy, however, crystals of **1** suited for X-ray crystallography could not be obtained. It was reported that an [Al(Me)(N–O)$_2$] type complex had a square pyramidal structure with an axial Me ligand and two N–O chelating ligands in an *N,N*-trans configuration [10]. Complex **1** may have a similar square pyramidal structure, and a blocking effect of the Me group in the q′ ligand seems to prevent attack by other compounds (e.g., by partially dissociated q′ ligand in other Al complexes) and stabilize **1**.

Fig. 1 exhibits ^{1}H-^{13}C COSY NMR spectrum of **1** in CDCl$_3$ at −55 °C, and Fig. 2 shows temperature dependence of the –CH$_2$CH$_3$ ^{1}H NMR signals of **1** in CDCl$_2$CDCl$_2$ and DMSO-d_6. As shown in Figs. 1 and 2,
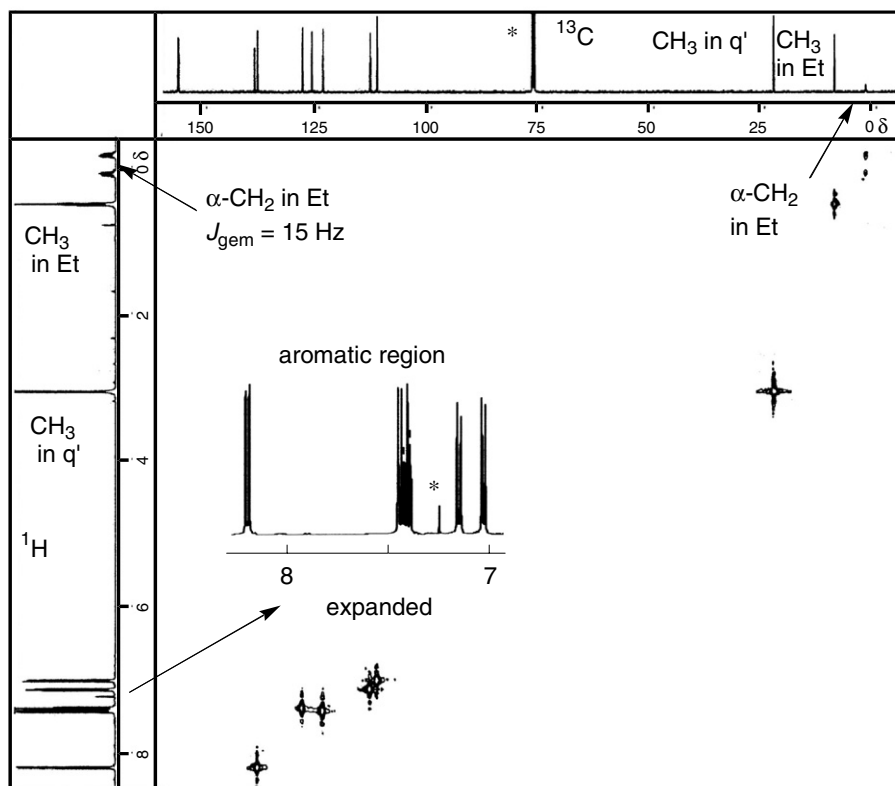

Fig. 1. ^{1}H-^{13}C COSY NMR spectrum of **1** in CDCl$_3$ at −55 °C. The peaks with the * mark are due to the solvent.
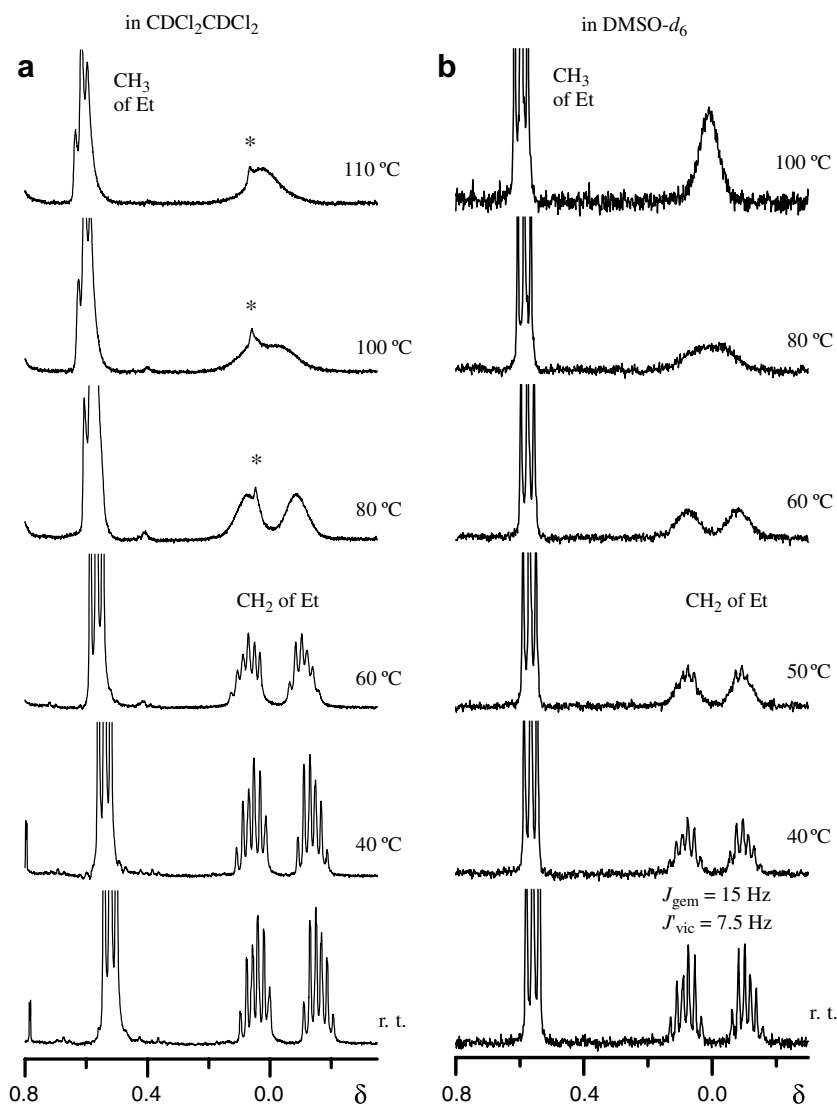
Fig. 2. Variable temperature ^{1}H NMR spectra of **1** (a) in CDCl$_2$CDCl$_2$ and (b) in DMSO-d_6. **1** seems to be partially decomposed above 80 °C in CDCl$_2$CDCl$_2$ to give additional peaks in the aromatic region and the peak with the * mark. Cooling the high temperature sample to r.t. gave essentially the same original NMR spectrum for the Al–Et signal region both in CDCl$_2$CDCl$_2$ and DMSO-d_6.

the α-CH$_2$ signals of the Et group appear as two sets of double quartets (e.g., at δ −0.10 and 0.08 in DMSO-d_6) with coupling constants of J_{gem}(H^{a}H^b) = 15 Hz and J'_{vic} (coupled with CH$_3$ protons) = 7.5 Hz. The spin-spin coupling between α-CH$_2$ proton and ^{27}Al was not observed, similar to the case of AlEt$_3$, presumably due to occurrence of natural decoupling of ^{27}Al; however, for several alkyl-aluminum complexes, especially for aluminate complexes, such a spin-spin coupling between ^{27}Al and α-CH proton was observed [11]. The two α-CH$_2$ signals at δ − 0.10 and δ 0.08 in DMSO-d_6 (cf. Fig. 2) give an average peak position at δ −0.01 for the α-CH$_2$ group, and following chemical shift difference, Δδ in ppm, between the α-CH$_2$ and the –CH$_3$ signals of the Et group is obtained: Δδ = δ (CH$_2$)– δ(CH$_3$) = −0.01 − (0.58) = −0.59.

For the ^{1}H NMR spectrum of the ethyl group bonded to various atoms, Narasimhan and Rogers proposed the following equation [12].

$$\chi = 0.62(\Delta\delta) + 2.07 \qquad (4)$$

where χ is the electronegativity of M in the M–C$_2$H$_5$ compounds. The χ value of 1.70 calculated for **1** is larger than those of AlEt$_3$ (χ = 1.57; Δδ = −0.8 [13]) and [Al(Et)$_2$q]$_2$ **2** (χ = 1.62; Δδ = −0.73) calculated similarly, indicating that the electronegativity or electron-withdrawing ability of the Al center is reasonably increased by replacement of the Et ligand of AlEt$_3$ with the q or q′ ligand. The α-CH$_2$ ^{13}C NMR peak was clearly observed at −55 °C as exhibited in Fig. 1, however, it became obscure at room temperature or above.

As described above, the two α-CH$_2$ hydrogens are magnetically unequivalent, and this unequivalency is considered to arise from the chiral center at Al, which makes the α-CH$_2$ hydrogens diastereotropic [14]. The chirality at Al, however, is dynamically lost at elevated temperatures as revealed by temperature dependent ^{1}H NMR spectroscopy.

2.2. Temperature dependent ^1H NMR spectroscopy of 1

Fig. 2 shows variable temperature ^1H NMR spectra of 1 in $CDCl_2CDCl_2$ and in DMSO-d_6. As shown in Fig. 2, the two α-CH_2 peaks collapse and coalesce at elevated temperatures. These NMR data indicate that the magnetic unequivalency of the two α-CH_2 protons is dynamically lost at elevated temperatures. Because a fivefold change in the concentration of the Al complex gave the same results for the temperature dependent ^1H NMR spectra, the dynamic process is considered to be an intramolecular process.

For the intramolecular dynamic process, simultaneous rotation of the two bidentate q′ ligands in 1 is conceivable. If 1 has a square pyramidal structure, the conceivable processes are depicted in Chart 1; the simultaneous rotation of two q′ ligands gives a mirror image complex B of the original complex A, thus the chirality at Al being lost dynamically.
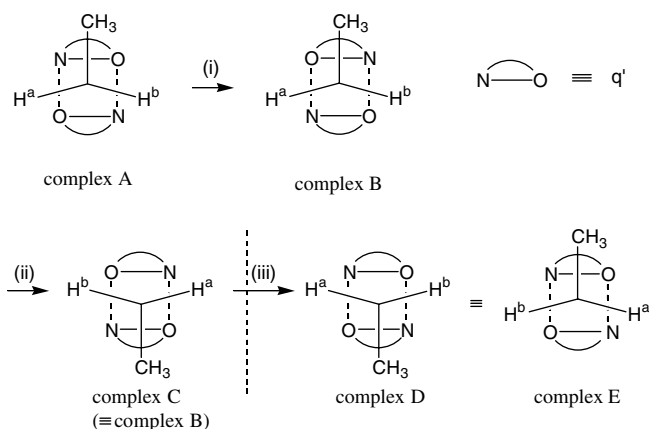

Chart 1. Conceivable processes to give H^a and H^b the magnetic equivalence. (i): rotation of the two q′ ligands. (ii): rotation of the Et ligand. (iii): formation of mirror image. After the rotation of the two q′ ligands, H^a in the mirror image complex (complex E) of the formed complex C becomes magnetically equivalent to H^b in the original complex (complex A). In contrast, simple rotation of the Et ligand attached to a chiral center does not give magnetically equivalent circumstances to H^a and H^b [14]. The complex A has the chirality at the Al center.

According to the shape analysis of the ^1H NMR peaks [15], the lifetime (τ) of the complex and the rate constant ($k = 1/\tau$) of the postulated rotation of the q′ ligand were obtained. From Arrhenius plots of ln k shown in Fig. 3, kinetic parameters of the dynamic process were estimated at $\Delta H^{\ddagger} = 135$ kJ mol^{-1} and $\Delta S^{\ddagger} = 159$ J K^{-1} mol^{-1} in $CDCl_2CDCl_2$ and at $\Delta H^{\ddagger} = 124$ kJ mol^{-1} and $\Delta S^{\ddagger} = 151$ J K^{-1} mol^{-1} in DMSO-d_6 [9], respectively, at 350 K. The large $\Delta S^{\ddagger}_{350}$ value suggests that the rotation proceeds through partial dissociation of the q′ ligand. Such a partial dissociation of bidentate ligands has been proposed for various dynamic processes in metal complexes [16]. The smaller $\Delta H^{\ddagger}$ value in DMSO-d_6 suggests that the partial dissociation of the q′ ligand (or dissociation of the Al–N bond) takes place more easily in the polar solvent. Rotation of one of the two q′ ligands seems to cause simultaneous rotation of another q′ ligand due to steric and/or electronic reasons.

Although various types of dynamic processes have been investigated by NMR spectroscopy [15], averaging of two NMR signals of such the diastereotropic α-CH_2 protons of the Et group attached at the chiral center has not been reported to our knowledge.

2.3. Reactivity of 1 toward OH compounds

The complex 1 showed good reactivity toward acidic OH compounds, especially toward acidic and chelating OH compounds. Reactions of 1 with qH, picolinic acid, (picH), and H_2O at room temperature afforded [Al(q′)$_2$q] (3), [Al(q′)$_2$(pic)] (4), and a binuclear complex [(q′)$_2$Al-μ-O-Al(q′)$_2$] (5), respectively, with evolution of ethane. In contrast to occurrence of the facile reaction of 1 with qH, 1 was not reactive toward q′H presumably due to steric reason.

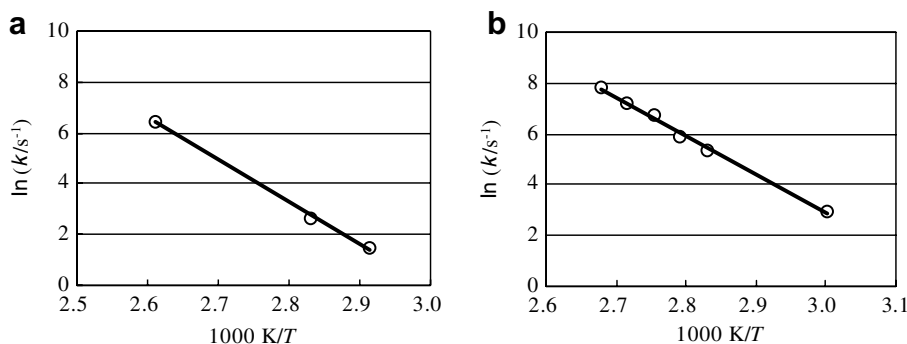$$1 + \text{8-quinolinol} \rightarrow [\text{Al}(\text{q}')_2\text{q}] \underset{\mathbf{3}}{} \tag{5}$$

$$1 + \text{pycolinic acid} \rightarrow [\text{Al}(\text{q}')_2(\text{pic})] \underset{\mathbf{4}}{} \tag{6}$$

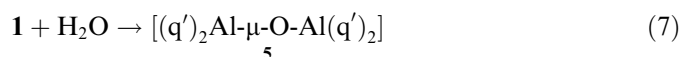$$1 + H_2O \rightarrow [(\text{q}')_2\text{Al-}\mu\text{-O-Al}(\text{q}')_2] \underset{\mathbf{5}}{} \tag{7}$$

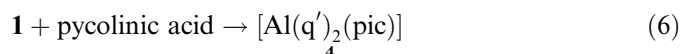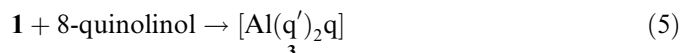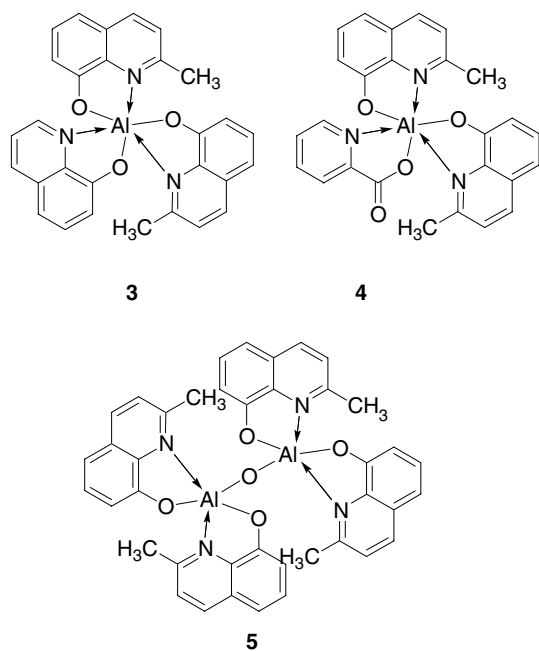Fig. 3. Arrhenius plots of ln k vs. T^{-1} for the ^1H NMR dynamic behavior of 1 in (a) $CDCl_2CDCl_2$ and (b) DMSO-d_6.

3   **4**

5

X-ray crystallographic molecular structure of **3** has been reported [8].

Fig. 4 shows an ORTEP diagram of **4** determined by X-ray crystallography. As shown in Fig. 4, the complex **4** has a six-coordinate octahedral geometry in a meridional configuration, similar to Alq$_3$ [17]. The Al–N bond distances (2.069–2.094 Å) in **4** are similar to those (2.017–2.087 Å) in Alq$_3$, whereas the Al–O bond lengths (1.831–1.866 Å) in **4** are somewhat shorter than those (1.851–1.860 Å) in Alq$_3$ [17].

Synthesis of the μ-oxo complex **5** by reaction of AlCl$_3$ and q′H, as well as the molecular structure of **5**, was reported by Kushi and Fernando [18]. We have also con-

firmed the molecular structure of **5** by X-ray crystallography. Al in **5** has square pyramidal coordination circumstances with an axial O and the two q′ ligands in an *N,N*-trans configuration. The molecular structure of **5** gives support for the postulated square pyramidal structure of **1**.

2.4. Reaction of 1 with phenol resins

For a possible industrial application of **1**, reactions of **1** with phenol resin, one of the most widely used polymeric materials, have been investigated. Reactions of **1** with a novolac resin [19], in 1:1 and 1:3 molar ratios between **1** and the OH group in the novolac resin, gave the polymer complexes **6-a** and **6-b**, respectively, as expressed in Eq. (8). Polymers having light emitting Al complexes in pendant groups of the polymer are the subject of recent interest [20].

1   novolac resin

(a) Al:OH = 1:1
(b) Al:OH = 1:3

(8)

6-a
6-b
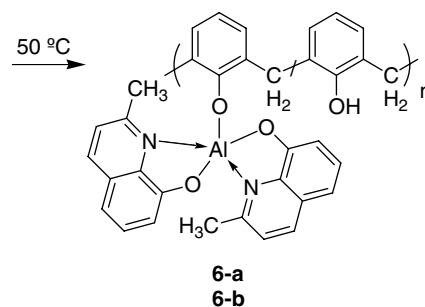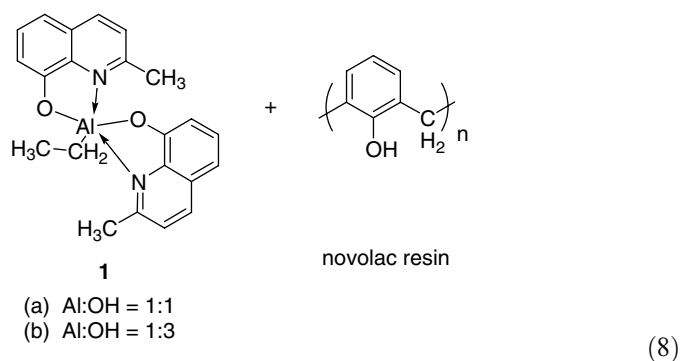
The Al contents in **6-a** and **6-b** revealed that about 50% and 15% of the phenolic OH group of the novolac resin were converted into the –O-Al(q′)$_2$ group in the 1:1 and 1:3 reactions, respectively. The strong v(O–H) peak of the novolac resin at around 3350 cm^{-1} decreased and characteristic peaks of the q′ ligand appeared in the region of 1600–1200 cm^{-1} after the complex formation, as shown in Fig. 5. Complex **6-a** was soluble in CHCl$_3$ and THF, and **6-b** and was soluble in THF and DMSO. Casting THF solutions of **6-a** and **6-b** afforded smooth films. Preparation of Alq$_2$(OPh–R) (OPh–R = phenolato ligand) type complexes *via* different pathways has been reported [21]. A resol resin [19], another type of phenol resin, also reacted with **1** to give a polymer-Al complex **7**, which showed an Al content of 2.78%. **7** also gave a smooth film by casting from a THF solution.
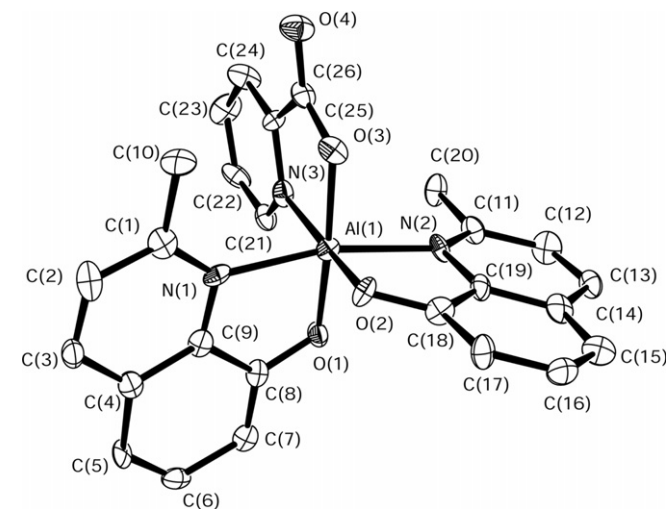

Fig. 4. Crystal structure of **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(1), 1.831(6); Al(1)–O(2), 1.833(7); Al(1)–O(3), 1.866(7); Al(1)–N(1), 2.094(8); Al(1)–N(2), 2.093(8); Al(1)–N(3), 2.069(7); O(1)–Al(1)–N(1), 83.9(3); O(2)–Al(1)–N(2), 83.5(3); O(3)–Al(1)–N(3), 79.9(3).
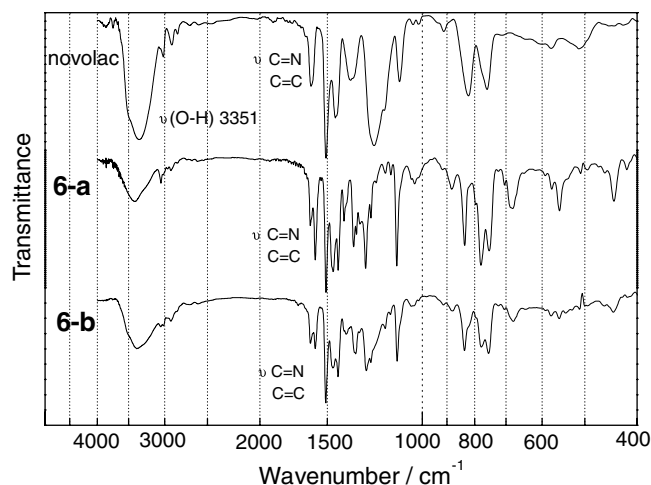
Fig. 5. IR spectra of the novolac resin, **6-a**, and **6-b**.

Table 1
Optical data of the aluminum complexes

Entry	Complex	Absorption[a]	Photoluminescence[a]	
		λ_{max}, nm	λ_{EM}, nm (λ_{EX}, nm)	$\Phi/\%$[b]
1	2-methyl-8-quinolinol	308, 372		
2	[Alq$_3$]	260, 384	521 (383)[c]	13[d]
3	**1** [Al(Et)(q')$_2$]	259, 359	497 (358)	3
4	**3** [Al(q')$_2$q]	259, 375	507 (369)	7
5	**4**: [Al(q')$_2$(pic)]	260, 315, 369	493 (360)	18
6	**5**: [(q')$_2$Al-μ-O-Al(q')$_2$]	259, 311, 358	492 (360)	23
7	**6-b**	279, 354[e]	495 (366)[e]	9
9	**6-b** in cast film	350[f]	503 (356)	–

[a] In chloroform unless otherwise noted. The photoluminescence spectrum was obtained by excitation at the λ_{max} position.
[b] Quantum yield of photoluminescence relative to quinine sulfate (*ca.* 10^{-5} M solution in 0.5 M sulfuric acid having a quantum yield of 54.6%).
[c] The peak position of the excitation spectrum is shown in the parentheses.
[d] A similar value was reported [22].
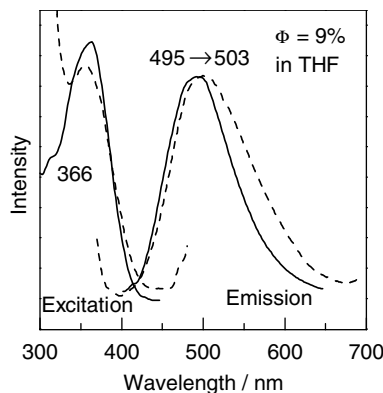[e] In THF.
[f] Broad peak.

Fig. 6. Excitation and photoluminescence spectra of **6-b** in THF (solid line) and in cast film (dashed line).

2.5. Optical properties

Table 1 summarizes UV–vis and photoluminescence (PL) data of the Al complexes, and an example of the PL spectrum is shown in Fig. 6.

The UV–vis spectra of complexes **1**, **3**, **4**, **5**, and **6-b** exhibited absorption peaks at $\lambda_{max} = 359$, 375, 369, 358, and 354 nm, respectively, near the absorption peak of Alq$_3$ at 384 nm. The UV–vis absorption of the Alq$_3$ type complex has been assigned to π–π^* transition in the q ligand and it is reported that introduction of an electron-donating substituent at C-2 or C-4 position of the 8-quinolinolato ligands causes a blue shift of the UV–vis peak [22]. The observation of the UV–vis peak of **3** at a shorter wavelength than that of Alq$_3$ agrees with the previous report.

The Al complexes were photoluminescent, similar to Alq$_3$, and the PL peak, λ_{EM} in Table 1, appears near the onset position of the UV–vis absorption band as usually observed with photoluminescent compounds. As shown in Table 1, complexes **4** and **5** gave quantum yields higher than that of Alq$_3$. The polymer complex **6-b** was also photoluminescent, however, the PL spectrum of **6-b** in cast film became broad and somewhat red shifted.

3. Conclusion

The complex **1** with the reactive Al–Et group was isolated. **1** readily reacted with active OH compounds such as picolinic acid and phenol resin to give new aluminum complexes. The obtained Al complexes were photoluminescent and gave quantum yields comparable to or higher than that of Alq$_3$. The complex **1** is expected to be a starting material for various light emitting aluminum complexes and polymer materials.

4. Experimental

4.1. Materials and general procedures

The novolac resin (code number: tamanol 758) was purchased form Arakawa Chemical Industries, Ltd. The resol resin was purchased from Hitachi Chemical Co. Ltd. Other chemicals were purchased from Aldrich Co., Kanto Chemical Co., and Tokyo Chemical Industry Co. Ltd., and used as purchased. Reactions were carried out under inert gas using standard Schlenk techniques. IR and NMR spectra were recorded on JASCO-IR 810 and JEOL EX-400 or JNM La-500 spectrometers, respectively. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder. UV–vis and photoluminescence spectra were recorded on Shimadzu UV-3100 and Hitachi F-4010 spectrometers, respectively. Mass spectra were measured with a JEOL JMS-700 spectrometer. Analysis of Al by ICP atomic emission spectrometry was carried out with a Shimadzu ICPS-8100 spectrometer.

4.2. Synthesis of [Al(Et)(q')₂] (1) and [Al(Et)₂q]₂ (2)

The complexes **1** and **2** were synthesized as reported previously [8]. The following additional data have been obtained for the complex **1**. ^{13}C NMR (CDCl₃, 125 MHz): δ 156.7, 156.5, 139.6, 138.9, 128.9, 126.8, 124.4, 113.9, 112.4, 23.2, 9.6, 2.6. FAB MS [M + H$^+$] = 373. The ^{1}H-^{13}C COSY NMR spectrum is shown in Fig. 1.

4.3. Reaction of 1 with the OH compounds

Results of the reaction of **1** with qH expressed in Eq. (5) has been reported previously [8]. Synthesis of **4** by the reaction with picolinic acid is described below.

4.4. Synthesis of [Al(q')₂(pic)] (4)

To a THF solution (10 mL) of **1** (0.26 g, 0.71 mmol) was added dropwise an ethanol solution (10 mL) of picolinic acid (0.08 g, 0.71 mmol). The reaction mixture was stirred at 50 °C for 4 h. After removal of the solvent under vacuum, the product was recrystallized from CH₂Cl₂/hexane to give **4** as yellow needles. Yield: 0.24 g, 72%. The molecular structure of **4** is shown in Fig. 4. FAB MS [M + H$^+$] = 466.

4.5. Synthesis of [(q')₂Al-μ-O-Al(q')₂] (5)

To a THF solution (10 mL) of **1** (0.29 g, 0.78 mmol) was added dropwise H₂O (7.0 μL, 0.39 mmol). The reaction mixture was stirred at room temperature for 17 h. After removal of the solvent by vacuum evaporation, the solid was recrystallized from a CH₂Cl₂/diethyl ehter solution to give **5** as yellow crystals. Yield: 50 mg, 18%. Molecular structure of **5** was confirmed by X-ray crystallography as described in the main text.

4.6. Synthesis of 6-a

To a THF solution (20 mL) of the novolac resin (0.27 g, corresponding to 2.5 mmol of the OH group based on the repeating unit expressed in Eq. (8)) was added a THF solution (15 mL) of **1** (0.93 g, 2.5 mmol). The reaction mixture was stirred at 50 °C for 24 h. After removal of the solvent by evaporation, the obtained solid were washed with acetone. The residual solid was dissolved in THF and the solution was poured (or reprecipitated) into hexane. The precipitate was separated by filtration and dried under vacuum to give **6-a** as a yellow solid. Yield: 0.98 g. Anal. Found: Al, 4.87. Calcd for (C₇H₆O)₀.₅(C₂₇H₂₁AlN₂O₃)₀.₅: Al, 4.87.

4.7. Synthesis of 6-b

To a THF solution (30 mL) of the novolac resin (0.61 g, 5.8 mmol) was added a THF solution (15 mL) of **1** (0.78 g, 2.1 mmol). The reaction mixture was stirred at 50 °C for

18 h. After removal of the solvent by evaporation, the obtained solid were washed with acetone. The residual solid was dissolved in THF and the solution was poured into hexane. The precipitate was separated by filtration and dried under vacuum to give **6-b** as a yellow solid. Yield: 0.32 g. Anal. Found: Al, 2.44. Calcd for (C₇H₆O)₀.₈₅(C₂₇H₂₁AlN₂O₃)₀.₁₅: Al, 2.57.

4.8. Synthesis of 7

To a THF solution (15 mL) of the resol resin (1.33 g) was added a THF solution (15 mL) of **1** (0.92 g, 2.5 mmol). The reaction mixture was stirred at 50 °C for 18 h. After removal of the solvent by evaporation, the obtained solid were washed with toluene. The residual solid was dissolved in chloroform and the solution was poured into hexane. The precipitate was separated by filtration and dried under vacuum to give **7** as a yellow solid. Yield: 1.66 g. Anal. Found: Al, 2.78.

4.9. Crystal structure determination

Crystals suitable for X-ray diffraction study were obtained by recrystallizaiton from CH₂Cl₂/hexane solutions for all the Al complexes, and mounted in glass capillary tubes on a Rigaku AFC-7R automated CCDC diffractometer equipped with Mo Kα radiation (λ = 0.7107 Å). The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation image were collected. A sweep of data was done using ω scans from −110.0° to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. The detector swing angle was −20.38°. A second sweep was performed using ω scans from −110.0° to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. The crystal-to-detector distance

Table 2
X-ray crystallographic data of 4

	[Al(q')₂(pic)] (4)
Formula	C₂₆H₂₀N₃O₄Al
Formula weight	465.44
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	7.966(7)
b (Å)	24.68(2)
c (Å)	11.184(9)
β (°)	105.02(1)
V (Å^3)	2123.6(3)
Z	4
μ(Mo Ka) (cm^{-1})	1.37
$F(000)$	968
Number of reflections measured	13956
Number of unique reflections	4635
Number of parameters	327
D_{calc} (g/cm^3)	1.456
Structure solution	Direct Methods (SIR92)
R ($I > 3\sigma(I)$)	0.087
R_w	0.143
Goodness of fit	1.00
Residual extrema in final diff. map (e Å^{-3})	0.77 to −0.74

was 44.76 mm. Readout was performed in the 0.070 mm pixel mode. Calculations were carried out by using the program package Crystal Structure for Windows. The structure was solved by direct methods SIR92 and expanded using Fourier techniques. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. Crystal structure data and refinement details are shown in Table 2.

Acknowledgements

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