

Synthesis and Characterization of Monomeric, Oligomeric, and Polymeric Aluminum 8-Hydroxyquinolines

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We report the synthesis and characterization of monomeric, oligomeric, and polymeric aluminum 8-hydroxyquinolines. The new structures of aluminum quinolate are contrived for expanding the application of AlQ₃ in the area of solution process by modifying AlQ₃ structure for improving solution processibility and crystallization resistance. Oligomeric aluminum 8-hydroxyquinoline (OALQ) was obtained using methylaluminoxane (MAO) and 8-hydroxyquinoline (8-HQ). Polymeric aluminum 8-hydroxyquinoline (PALQ) consists of 8-HQ and a polymeric Al–O backbone, simply prepared by stoichiometrically reacting 8-hydroxyquinoline, pentaerythritol propoxylate, and triethyl aluminum in the presence of chloroform. The absorption and emission spectra of OALQ and PALQ bear a clear resemblance to those of AlQ₃, and the molecular orbitals of OALQ and PALQ are virtually identical to those of AlQ₃. In the SEM images of AlQ₃ and OALQ, cylindrical rods of >100 μm in length and 5–10 μm in diameter for AlQ₃ and 20–100 μm in length and 1–5 μm in diameter for OALQ were observed, respectively. The size of the cylindrical rods of OALQ decreased compared with that of AlQ₃. As for the image of PALQ, an amorphous phase with bulge spots (ca. 5 μm) was observed. These microscope data correspond well to the X-ray powder pattern results. The chemical shifts (31.1, 57.0 ppm) and peak broadness of ²⁷Al NMR of AlQ₃ and its DFT calculation results present that *mer*- and *fac*-AlQ₃ appear in equilibrium through pentacoordinated intermediates. With the combination of DFT optimization and NMR calculation, models of OALQ and PALQ, hexa-, penta-, and tetraordinated structures, were proposed, which exist in polymeric Al–O backbone and with inter- and intracoordination of Al–O bonds.

Introduction

Tris(8-hydroxyquinoline)aluminum (AlQ₃), one of the most successful electroluminescent materials, is widely used in organic light-emitting diodes (OLEDs) as an electron-transport layer or a green emitter.^{1,2} Despite its good electrical and photophysical properties, the application of AlQ₃ is limited in the area of chemical-vapor deposition.³ Crystal-

lization or morphological changes of AlQ₃ at elevated temperature or as function of time prevent the expansion of its application in the area of polymer light-emitting diodes (PLEDs), which are based on a solution process.^{4,5} PLED, a low-cost manufacturing method substituting for liquid crystal display, is basically fabricated by a solution-processing method such as spin-coating or ink-jetting at an inert atmosphere.⁴

Our study aims to expand the application of AlQ₃ in the area of PLED by modifying its structure to improve processibility and crystallization resistance on the basis of

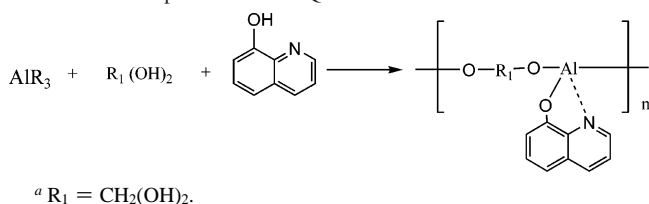
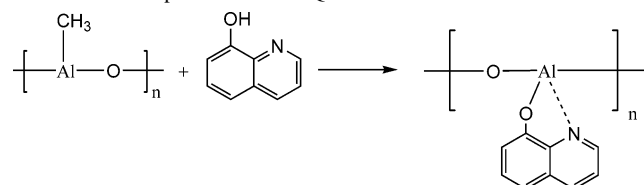
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Scheme 1. Preparation of PALQ^a**Scheme 2.** Preparation of OALQ

an aluminoxane backbone. Thus, a new structure of aluminum quinolate was contrived, which can be deposited on a variety of large-area flexible substrates for wearable and foldable electronic applications, such as thin-film transistors or displays.

Results and Discussion

Synthesis. Oligomeric aluminum 8-hydroxyquinoline (OALQ) and polymeric aluminum 8-hydroxyquinoline (PALQ) were prepared in a manner similar to the synthetic method for AlQ₃.⁶ The synthetic strategy for PALQ is based on the fact that only one quinoline unit among the three 8-hydroxyquinolines of AlQ₃ is needed for light-emitting and electron-transport;⁷ therefore, the other coordination sites of aluminum can be used for backbone structure to make the oligomeric or polymeric aluminoxane structure. PALQ, consisting of a polymeric Al–O backbone, was simply prepared by stoichiometrically combining 8-hydroxyquinoline (8-HQ), pentaerythritol propoxylate, and triethyl aluminum in the presence of chloroform at room temperature under a nitrogen atmosphere (Scheme 1). The reaction immediately provided a yellowish fluorescent precipitate. The product was washed with solvent (chloroform) to remove unreacted 8-HQ. PALQ was obtained as solid film. In another attempt, methylaluminoxane (MAO, oligomeric alkylaluminoxane), which consists of an aluminum alkyl and an oligomeric Al–O backbone, was employed instead of alkyl aluminum. The reaction between MAO and 8-HQ was carried out in a manner similar to the synthetic conditions for PALQ (Scheme 2), and OALQ was obtained as yellowish powder. The molecular weight was analyzed by gel permeation chromatography. The molecular weights of OALQ and PALQ were 1250 and 4570, respectively (Table 1).

Structural Study. The X-ray diffraction patterns of AlQ₃, OALQ, and PALQ showing the degree of crystallinity are shown in Figure 1. The peak intensity is decreased in the order AlQ₃ < OALQ < PALQ. The structure of AlQ₃, a

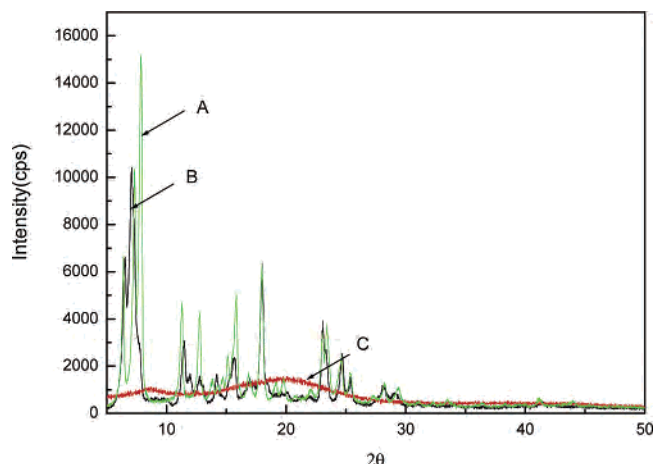


Figure 1. X-ray powder diffraction patterns (A, AlQ₃; B, OALQ; C, PALQ).

Table 1. Molecular-weight, Polydispersity, Absorption, and Emission Data

	<i>M_w</i>	polydispersity	absorption (nm)	emission (nm)
AlQ ₃	459	1.0	335, 393	513
OALQ	1250	1.98	335, 393	512
PALQ	4570	2.55	393	512

distorted octahedral coordination, exists as two geometrical isomers, facial (*fac*) and meridional (*mer*), in Figure 2a and b.^{4a,8} The octahedral geometry of AlQ₃, in which aluminum is coordinated with the three nitrogens of the pyridyl sides and the three oxygens of the phenoxy sides, turns to low-symmetry structures in OALQ, as well as in PALQ. In the PALQ pattern, broad peaks (8, 20 in 2θ) were observed, which show that PALQ has an amorphous structure.

The scanning-electron micrograph (SEM) images of AlQ₃, OALQ, and PALQ are shown in Figure 3. Cylindrical rods > 100 μm in length and 5–10 μm in diameter for AlQ₃ and 20–100 μm in length and 1–5 μm in diameter for OALQ were observed. The size of the OALQ crystal was decreased in comparison with that of AlQ₃. Bulge spots, of ca. 5 μm, were found in the amorphous phase of PALQ. These microscope data correspond well to the X-ray powder patterns.

²⁷Al NMR Measurement and DFT Calculations. AlQ₃ **Characterization.** Aluminum-27 (100% abundant, *I* = 5/2) has a moderately large electric quadrupole moment (*Q* = 0.149 × 10⁻²⁴ cm²), and the ²⁷Al NMR chemical shift is sensitive to aluminum geometry depending on the coordination geometry and number.⁹ The two basic parameters, chemical shift and line width, provide ligand and coordination information. The ²⁷Al NMR spectra of AlQ₃, OALQ, and PALQ measured in CDCl₃ are shown in Figure 4 and summarized in Table 2. [Al·6(H₂O)]³⁺ was used as an external reference. Two peaks in the AlQ₃ spectra, a narrow peak at 31.1 ppm and a broad peak at 57.0 ppm, were

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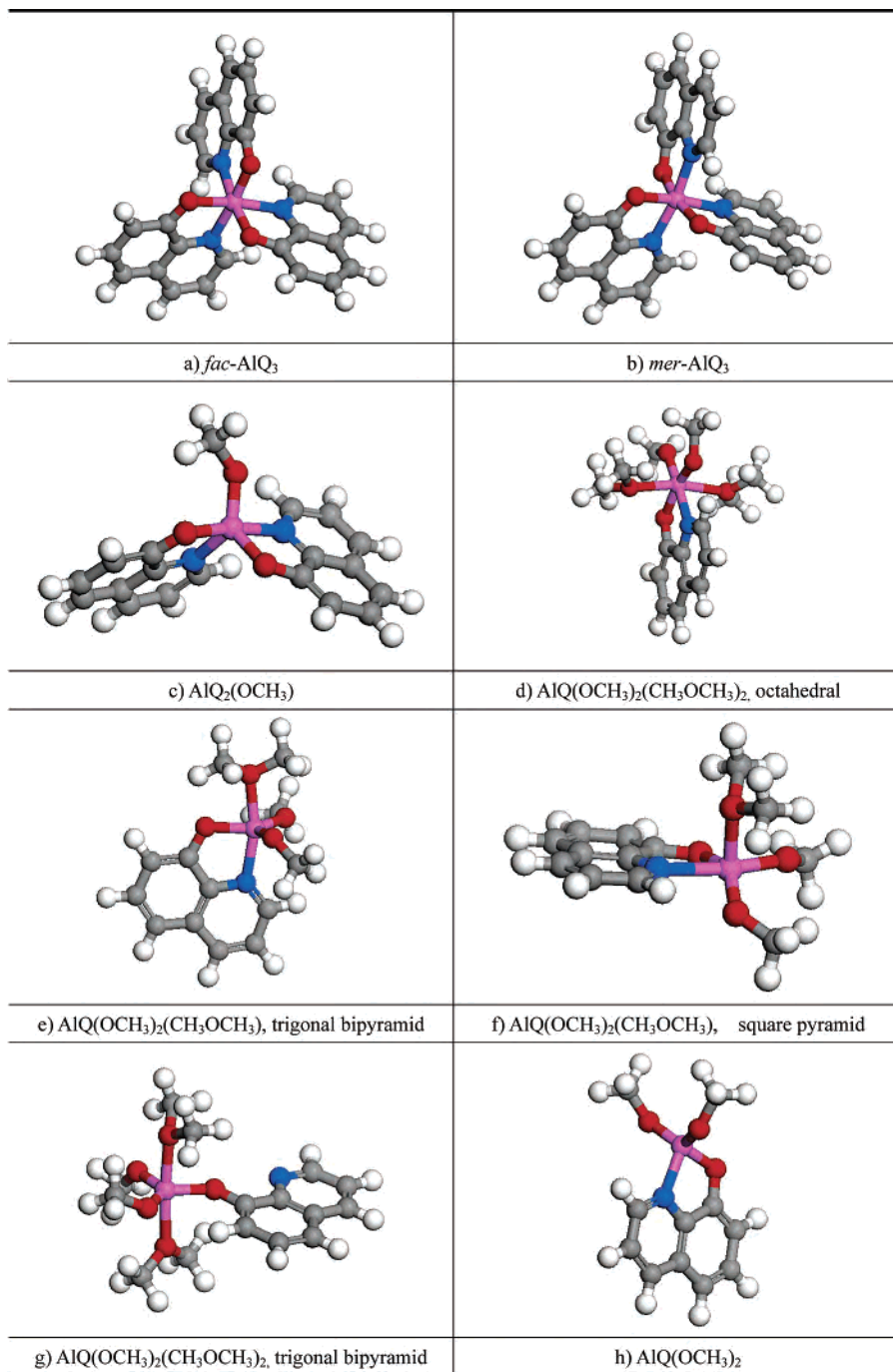


Figure 2. Structures of (a) *fac*-AlQ₃, (b) *mer*-AlQ₃, (c) AlQ₂(OCH₃), (d) AlQ(OCH₃)₂(CH₃OCH₃)₂, (e) AlQ(OCH₃)₂(CH₃OCH₃), and (f) AlQ(OCH₃)₂.

observed (aluminosilicate peak of NMR tube appeared at 62.5 ppm). The narrow peak (half width, $w_{1/2}$, 1355 Hz) at 31.1 ppm indicates hexa-coordination, which is attributed to the two geometric isomers of “meridional” and “facial” AlQ₃.¹⁰ The *fac*-AlQ₃ possesses C₃ symmetry and *mer*-AlQ₃ has C₁ geometry, and there is an equilibrium in solution between the two isomers through pentacoordination.¹¹ The broad peak (half width, $w_{1/2}$, 5090 Hz) at downfield 57.0 ppm indicates the pentacoordinated species, which would be the intermediates between *fac*- and *mer*-AlQ₃, appear through the dissociation of the Al–N bond and free rotation.

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We made a model of *pentacoordinated* species AlQ₂(OCH₃) consisting of two 8-HQs and one methoxy group representing one 8-HQ with the dissociated pyridyl unit from aluminum, through DFT optimization, in Figure 2c. The calculated ²⁷Al chemical shifts are given in Table 3. The chemical shifts are obtained using the relationship $\delta = \sigma^{\text{ref}} - \sigma^{\text{molecule}}$, where σ^{ref} is the chemical shielding value of [Al·6(H₂O)]³⁺, 615.0

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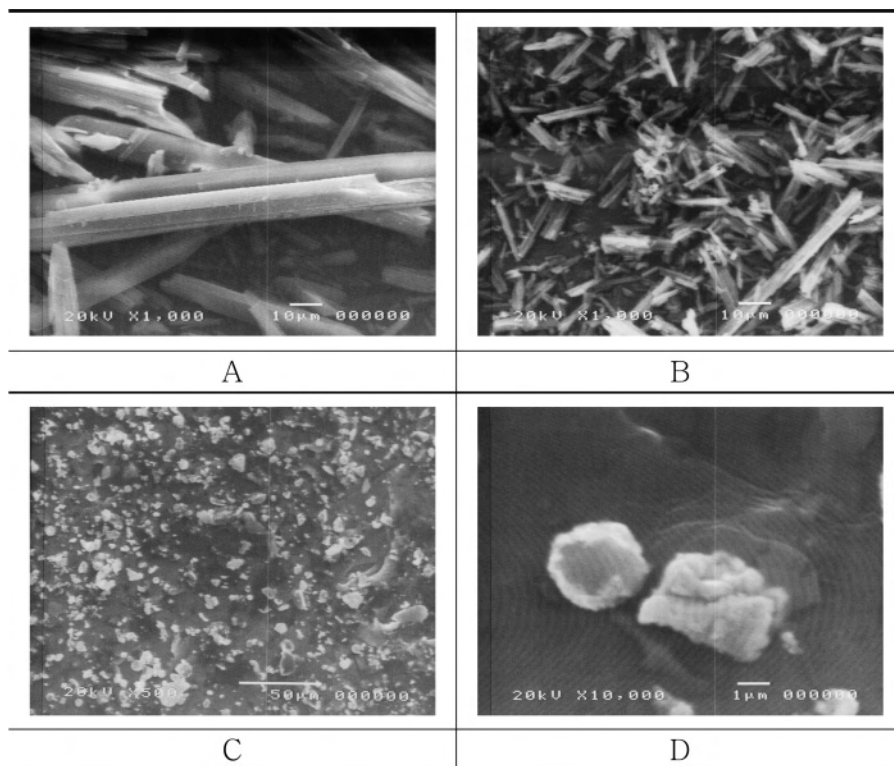


Figure 3. SEM images of (A) AlQ₃, (B) OALQ, and (C, D) PALQ.

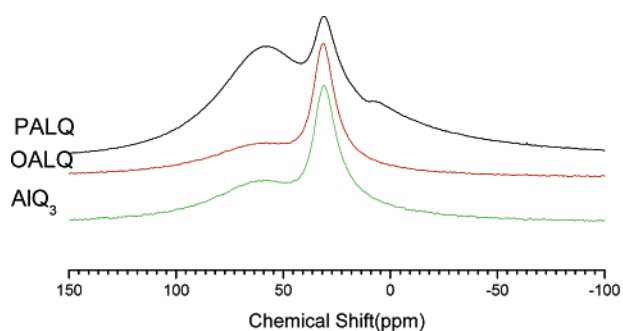


Figure 4. ²⁷Al NMR spectra of AlQ₃, OALQ, and PALQ.

Table 2. ²⁷Al NMR Peak Position and Integration Data

	peak position (ppm)	line width (Hz)
AlQ ₃	31.1(n)	1355
	57.5(br)	5090
OALQ	31.2(n)	1563
	57.9(br)	5627
PALQ	7.0 (n)	
	31.1 (n)	2605
	57.3(br)	5960

ppm.¹² The calculated ²⁷Al shifts of *mer*- and *fac*-AlQ₃ are 36.2 and 37.7 ppm, respectively, which correspond well to the experimental peak at 31.1 ppm in the NMR spectrum of AlQ₃. The calculated ²⁷Al shift of AlQ₂(OCH₃) is 62.5 ppm, similar to that of measured one (57 ppm). The broad peak at around 57 ppm is attributed to the signals of the pentacoordinated isomers and conformers.

OALQ and PALQ Characterization. Two peaks in the OALQ spectrum, a narrow peak at 31.1 ppm and a broad peak at 57.0 ppm and three peaks in the PALQ spectrum at

57.3, 31.1, 7.0 ppm were observed. The peak at 7 ppm in the spectrum of PALQ indicates hexa-oxy-coordinated aluminum, which is Al(OR)₃(OR)₃ or its aggregate. The broadness of peaks at 57 and 31 ppm explains the low symmetry of OALQ and PALQ.^{9c} To understand the NMR spectra of OALQ and PALQ, the model structures, AlQ(OCH₃)₂(CH₃OCH₃)₂, AlQ(OCH₃)₂(CH₃OCH₃), and AlQ(OCH₃)₂ for the hexa-, penta-, and tetra-coordinated species were proposed, where methoxy and dimethyl ether ligands were considered as backbone oxygens available to be inter- or intramolecularly coordinated to aluminum. The optimized structures of the model compounds are shown in Figure 2d–h. The calculated ²⁷Al shift of hexacoordinated AlQ(OCH₃)₂(CH₃OCH₃)₂ was determined to be 32.8 ppm and that of tetra-coordinated AlQ(OCH₃)₂ was downfield 82.3 ppm, which represents the sensitivity of the chemical shift for coordination number.⁹ The calculated shift of AlQ(OCH₃)₂(CH₃OCH₃)₂ corresponds well to the experimental value, 31.1 ppm. The pentacoordinated complex, AlQ(OCH₃)₂(CH₃OCH₃), will be either trigonal bipyramidal (tbp) or square pyramidal (sqp) depending on the coordination of quinolate and methoxy ligands. The tbp geometry positions the oxygen and the nitrogen of quinolate at one equatorial position and at one axial position, respectively, in Figure 2e. The calculated ²⁷Al shift of the tbp structures is given at 56.6 ppm. The sqp structure of AlQ(OCH₃)₂(CH₃OCH₃) is shown in Figure 2f. The bottom square, a slightly distorted plane, is composed of a quinolate and two methoxy ligands. Vibrational frequency calculation gives no imaginary frequency, indicating the sqp geometry is considered to be one of the intermediates between two tbp isomers. The relative energy and structure of the

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Table 3. Calculated ^{27}Al Chemical-Shielding Data

molecule	coordination	structure	chemical shielding σ (ppm)	chemical shift δ (ppm)	
				calculated ^a	observed
<i>fac</i> -AlQ ₃	6 (octahedral)	Figure 2a	577.3	37.7	31.1
<i>mer</i> -AlQ ₃	6 (octahedral)	Figure 2b	578.8	36.2	
AlQ ₂ (OCH ₃)	5	Figure 2c	552.5	62.5	57.0 (AlQ ₃)
AlQ(OCH ₃) ₂ (CH ₃ OCH ₃) ₂	6 (octahedral)	Figure 2d	582.2	32.8	
	5 (trigonal bipyramid)	Figure 2g	561.9	53.1	
AlQ(OCH ₃) ₂ (CH ₃ OCH ₃)	5 (trigonal bipyramid)	Figure 2e	558.4	56.6	57.9 (OALQ)
	5 (square pyramid)	Figure 2f	562.2	52.8	57.2 (PALQ)
AlQ(OCH ₃) ₂	4 (tetrahedral)	Figure 2h	532.7	82.3	

^a Chemical shift is calculated by the relationship $\delta = \sigma^{\text{ref}}(615.0 \text{ ppm}) - \sigma^{\text{molecule}}$.

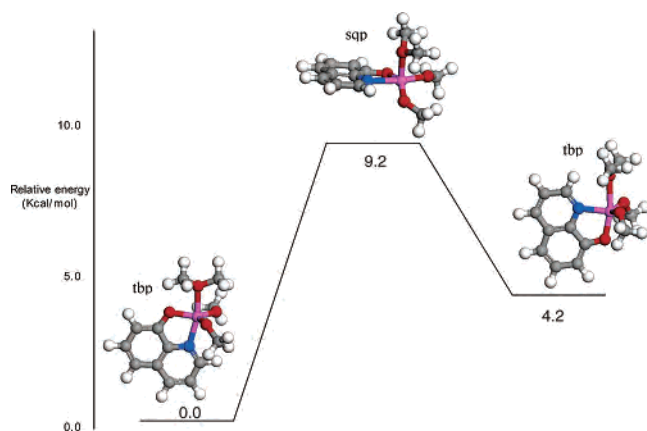


Figure 5. Energy profile of AlQ(OCH₃)₂(CH₃OCH₃), the pentacoordinated model of OALQ and PALQ.

intermediate sqp and the two tbp geometries are presented in Figure 5. The sqp geometry gives a little upfield shift at 52.8 ppm. The hexacoordinated AlQ(OCH₃)₂(CH₃OCH₃)₂ can also be changed into a pentacoordinated structure, if the pyridyl unit of quinolate ligand is dissociated from aluminum. The optimized pentacoordinated AlQ(OCH₃)₂(CH₃OCH₃)₂ is shown in Figure 2g, and its calculated ^{27}Al shift is 53.1 ppm. The experimental ^{27}Al shift, in the range of 45–75 ppm, falls within the calculated range for various kinds of pentacoordinated complexes, and the broadness of the peak indicates many isomers and conformers exist with such representative isomers.

The broad area of chemical shifts over 75.0 ppm is thought to be exclusively the result of the tetracoordinated complexes of PALQ, and a model compound AlQ(OCH₃)₂ is shown in Figure 2h. Because the dissociation energy of AlQ(OCH₃)₂(CH₃OCH₃) into AlQ(OCH₃)₂ and CH₃OCH₃ is 7.0 kcal/mol, the pentacoordinated AlQ(OCH₃)₂(CH₃OCH₃) is more favorable than the tetracoordinated AlQ(OCH₃)₂. In addition, the dissociation energy of the hexacoordinated complex, AlQ(OCH₃)₂(CH₃OCH₃)₂, is favored (ca. 3 kcal/mol) over that of the pentacoordinated one. These data indicate various hexa-, penta-, and tetracoordinated isomers and conformers exist in the oligomeric and polymeric aluminoxane backbone.

Optical Property. The photophysical phenomena of OALQ and PALQ (absorption, 393 nm; emission, 512 nm) were similar to those of AlQ₃ (absorption, 335, 393 nm; emission, 513 nm) (Figure 6 and Table 1). The relative fluorescence intensity in solution was in the order PALQ >

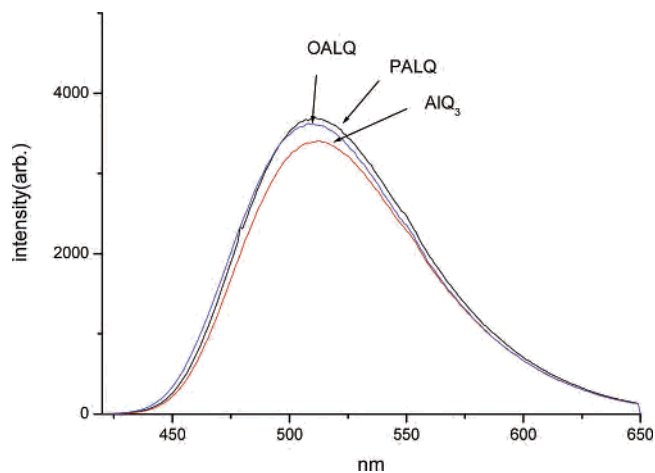


Figure 6. Emission spectra of AlQ₃, OALQ, and PALQ.

OALQ > AlQ₃.¹³ The peak positions of absorption or emission data do not show any significant differences, corresponding to the structural changes from AlQ₃ to OALQ and PALQ. This result suggests that OALQ and PALQ also display 8-HQ-oriented photophysical properties. Figure 7 illustrates the frontier orbitals of AlQ₃ (Figure 7a) and the hexa-, penta- and tetracoordinated models of OALQ and PALQ (Figures 7b, 7c, 7d), which bear a clear resemblance to those of 8-HQ and are expected to perform similarly in optical absorption and emission.¹⁴ The filled π orbitals (HOMO) are located on the phenoxide and the unfilled π^* orbitals (LUMO) are on the pyridyl group, in which the electronic transitions are $\pi \rightarrow \pi^*$ transitions in the quinolate rings, involving partial charge transfer from the phenoxide to the pyridyl group with little contribution from aluminum.^{2,15} Thus, OALQ and PALQ, consisting of only one 8-HQ, show a performance in both absorption and emission similar to that of AlQ₃.

Conclusions

Oligomeric and polymeric aluminum 8-hydroxyquinolines (OALQ and PALQ) were prepared with the same synthetic method as AlQ₃ in a one-pot reaction under mild conditions. OALQ and PALQ consist of an aluminoxane backbone and an 8-hydroxyquinoline grafting unit. The absorption and emission spectra of OALQ and PALQ are

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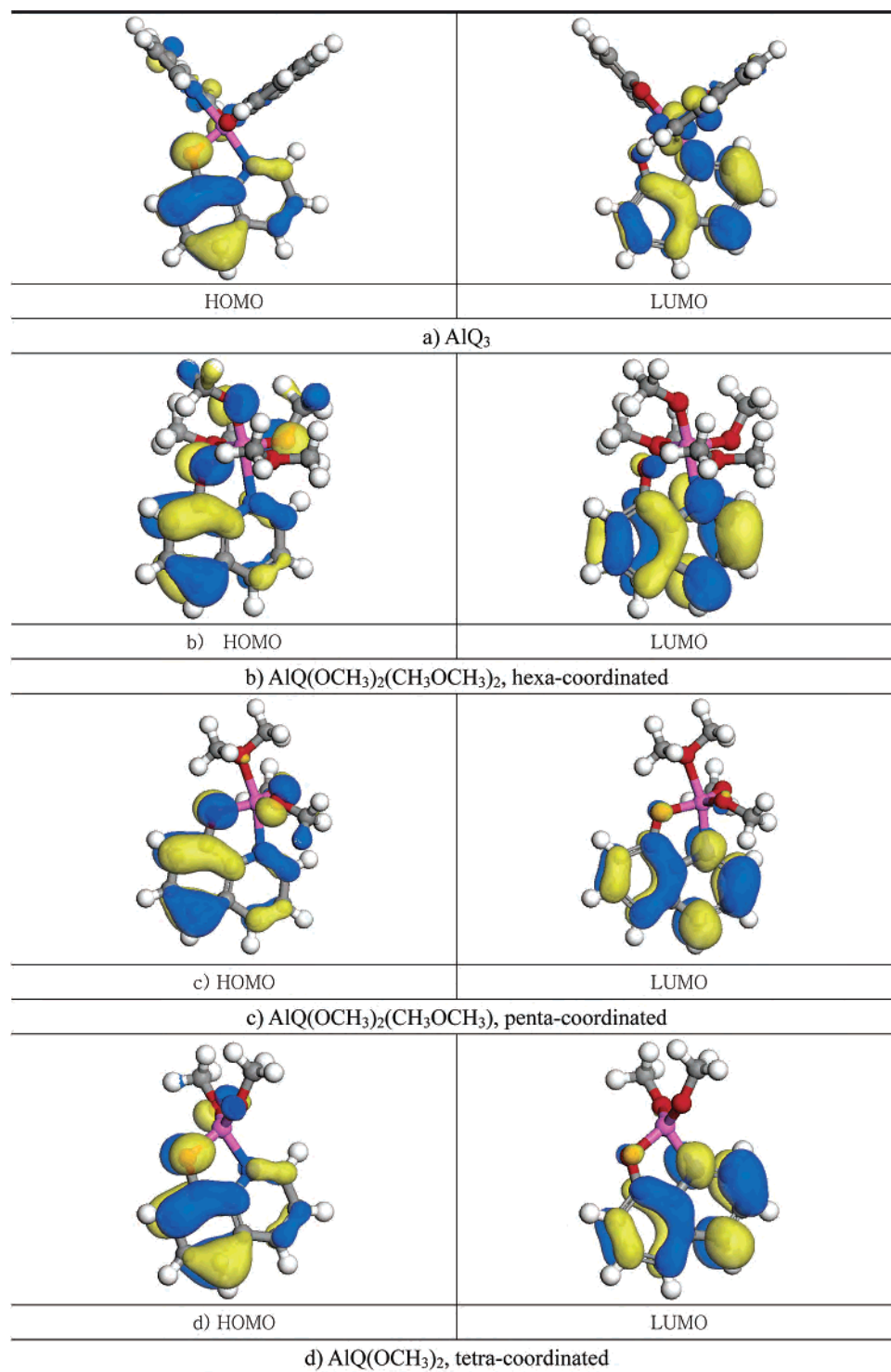


Figure 7. Illustration of highest-occupied and lowest-unoccupied molecular orbitals (HOMO and LUMO) of (a) AlQ₃, (b) AlQ(OCH₃)₂(CH₃OCH₃)₂, (c) AlQ(OCH₃)₂(CH₃OCH₃), and (d) AlQ(OCH₃)₂. Yellow and blue regions indicate opposite phases of the one-electron wave functions.

similar to those of AlQ₃, and the molecular orbitals of OALQ and PALQ are also almost identical to those of 8-HQ. AlQ₃ and OALQ have cylindrical rod structures in micron scale, while PALQ shows an amorphous phase. The crystallinity of OALQ decreases compared to that of AlQ₃. Various penta- and hexacoordinated structures exist in OALQ and amorphous PALQ because of intra- and intermolecular interactions between aluminum and oxygen in aluminoxane backbone. The amorphous PALQ would prevent the continued growth

of crystals or grains during device operation, which causes dimensional instability and luminance decay.

Experimental Section

General Methods. 8-Hydroxyquinoline, pentaerythritol propoxylate (mw ca. 426), THF, chloroform, triethyl aluminum (1.0 M in *n*-hexane), and MAO were purchased from Aldrich.

Synthesis. AlQ₃ was prepared according to a literature method.^{6a} OALQ and PALQ were prepared using a modified AlQ₃ procedure.

Preparation of OALQ. Methylaluminoxane (5.4 mL, 5.7% Al, MMAO) was slowly added to 100 mL of a tetrahydrofuran solution of 8-hydroxyquinoline (4.5 g), and the mixture was stirred at room temperature for 5 h. The precipitate was collected by filtration, washed with chloroform, and dried in a vacuum. ^1H NMR (200 MHz, CDCl_3): δ 8.90–8.80 (m), 8.33–8.23(d), 8.22–8.14(t), 7.50–7.01(m), 3.78–3.70(t), 1.88–1.81(m). ^{27}Al NMR (104.2 MHz, CDCl_3): δ 57.9 (br, $w_{1/2}$ = 5627 Hz), 31.4 (n, $w_{1/2}$ = 1563 Hz).

Preparation of PALQ. Triethylaluminum (10 mL, 1.0 M in *n*-hexane) was slowly added to 100 mL of a chloroform solution of 8-hydroxyquinoline (1.4 g) and pentaerythritol propoxylate (2.1 g), and the mixture was refluxed at 70 °C overnight. The precipitate was collected by filtration, washed with chloroform, and dried in a vacuum. ^1H NMR (200 MHz, CDCl_3): δ 8.90–8.80 (m), 8.33–8.23(d), 8.22–8.14(t), 7.50(m), 7.10 (m), 3.96(br, m), 3.60 (br, m), 3.42(br, m), 3.27(br, m), 1.80–1.60(br), 1.13(m, br). ^{27}Al NMR (104.2 MHz, CDCl_3): δ 57.2 (br, $w_{1/2}$ = 5960 Hz), 31.4 (n, $w_{1/2}$ = 2605 Hz), 7.0 (n).

Characterization. AlQ_3 , OALQ, and PALQ were characterized by powder X-ray diffraction on a MAC model diffractometer with graphite monochromator and $\text{Cu K}\alpha$ radiation (λ = 0.15418 nm). A scanning rate of 0.05 s^{-1} was applied to record the patterns and data in a 2θ range of 10–60°. The samples were gently ground and deposited in a sample holder. Scanning-electron microscopy (SEM) images were collected using a JEOL JSM-5400. Samples were sputter-coated with gold prior to examination. Molecular weights were determined by GPC analysis (Viscotek), calibrated with polystyrene and AlQ_3 as reference, and THF was as solvent at 40 °C. JASCO V-570, Varian Unit Inova 200, and Varian Unit Inova 400 were used to measure UV–vis, ^1H NMR, and ^{27}Al NMR spectra, respectively. The chemical shifts of ^{27}Al NMR were reported relative to the external reference, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Fluorescence spectra were obtained with a SLM-AMINCO 4800 spectrofluorometer, in which rhodamine was used as the quantum counter.

Calculations. AlQ_3 , OALQ, and PALQ models were fully optimized with the BLYP functional.¹⁶ The geometry optimizations of the molecules were carried out with the program package DMOL³ without any symmetry constraints.¹⁷ Aluminum, carbon, nitrogen, and hydrogen were treated with all-electron double-numerical polarized (DNP) basis sets.¹⁸ ^{27}Al absolute shieldings were calculated for all of the optimized molecules above using the GIAO method¹⁹ at the restricted Hartree–Fock level with the 6-311+G(2df,p) basis set.²⁰ Gaussian98 was used for all ^{27}Al shift calculations.²¹

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