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Communication

Configuration-Specific Synthesis of the Facial and Meridional Isomers of Tris(8-hydroxyquinolinate)aluminum (Alq_3)

Ryo Katakura and Yoshihiro Koide*

Department of Applied Chemistry, Kanagawa University, Yokohama 221-8686, Japan

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Treatment of AlO(OH) with 3 equiv of 8-hydroxyquinolinol in refluxing deionized water provided the meridional and facial isomers of tris(8-hydroxyquinolinate)aluminum (Alq_3) with good yields as solid deposits after 1 and 90 h, respectively. X-ray diffraction and solid-state ^{13}C NMR studies revealed that *mer*-Alq_3 is formed in the early stage of the reaction and then gradually converts to *fac*-Alq_3, which is thermodynamically less stable, although no existence of a catalyst substance is implied.

Tris(8-hydroxyquinolinate)aluminum (Alq_3) is widely used in organic light-emitting diodes (OLEDs) as the cost-efficient green light-emitting material since the late 1980s,[1] and its physicochemical properties are still under active investigation. The molecule consists of three chelating oxyquinoline ligands, occurring in the facial (*fac*) and meridional (*mer*) isomers (Figure 1). Although isomerization of Alq_3 is an important issue with respect to the emission behavior, spectroscopic characterization of the five crystalline phases (α, β, γ, δ, and ϵ) has only recently become available.[2] According to the reports, the β and ϵ phases contain *mer*-Alq_3, crystallized in the two different molecular packing modes,[2a,f] while the α, γ, and δ phases consist of *fac*-Alq_3.[2b−g] Recent studies designate the α phase to *fac*-Alq_3,[2f] although the issue remains unsettled.[2b−d,e,g] Among the two structural isomers, *fac*-Alq_3 is particularly desirable for its blue-shifted fluorescence[2d,3] and a high quantum yield.[2c] However, *fac*-Alq_3 has been obtained only in the subgram order by sublimation[2c] of mixed polymorphs of Alq_3 or by thermal conversion of commercial Alq_3 followed by acetone[2d] and chloroform[4] treatment because synthetic control of a ligand configuration has been considered difficult as a result of the favorable formation of the thermodynamically stable *mer* isomer.[2d,5] Conventionally, Alq_3 is prepared by reaction of either $AlCl_3$, $Al(NO_3)_3{\cdot}9H_2O$, or $Al_2(SO_4)_3{\cdot}nH_2O$ with 8-hydroxyquinolinol (8-Hq), which provides the *mer* isomer as a major product, giving rise to the characteristic green fluorescence.[6] Mixed isomers are also prepared in the solid state by heating a mixture of aluminum propoxide ($Al[OCH(CH_3)_2]_3$) and 8-Hq to yield a product virtually identical with that of the solution methods.[7] Thermal interconversion between the polymorphs is extensively investigated by both spectroscopic methods[2b−d,3,8] and quantum chemical calculations.[5,9] However, *fac*-Alq_3 has been a difficult species to capture for its relatively short lifetime in solution.[8] Solution NMR studies revealed that *fac*-to-*mer* isomerization via the ligand-flip mechanism is exceedingly fast compared to the reverse step. In addition, because *fac*-Alq_3 is poorly soluble as a result of the larger dipole moment compared to *mer*-Alq_3,[10] ^1H and ^{13}C NMR detected only *mer*-Alq_3 at room temperatures. Despite a plethora of research activities on

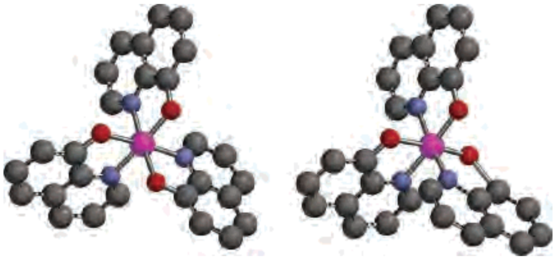

Figure 1. Two configuration isomers, *fac*-Alq_3 (left) and *mer*-Alq_3 (right). O and N atoms are shown in red and blue, respectively.

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* To whom correspondence should be addressed. E-mail: ykoide01@kanagawa-u.ac.jp.

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Alq$_3$, those properties have hampered the detection and isolation of *fac*-Alq$_3$, and major efforts were devoted to the emission optimization and stability enhancement of the green-fluorescent aspect of *mer*-Alq$_3$. Recent isolation and characterization of *fac*-Alq$_3$ have invigorated researchers' interest in Alq$_3$ as a new class of blue-fluorescent material,[2b−d,3] and it is important to establish rapid, efficient, and quantitative synthesis methods of the single isomers of *fac*- and *mer*-Alq$_3$ that will advance the development of the next-generation Alq$_3$-based multicolor OLEDs[11] and lasers.[12]

In this Communication, we introduce a surprisingly straightforward configuration-specific synthesis of *fac*- and *mer*-Alq$_3$ by solid-state reaction between aluminum oxide−hydroxide[13] and 8-Hq[14] under acid-free conditions.[15] AlO(OH) is a water-insoluble colorless powder in which the Al atom is octahedrally coordinated by five oxide and one hydroxide anions, forming sheets of the edge-shared AlO$_6$. In a typical synthesis, 0.20 g (3.3 mmol)[16] of AlO(OH) and 1.45 g (10.0 mmol) of 8-Hq were charged in a flask with 30 mL of deionized water (pH 7.1) and stirred vigorously under reflux in an oil bath maintained at 110 °C. The reaction mixture spontaneously developed a yellow color that intensified to bright yellow in 30 min, and the color lasted for more than 24 h. However, the color gradually faded to pale yellow in a reaction over an extended period of time (90 h). The resulting pale-yellow deposits were filtered and rinsed with cold acetone to remove residual 8-Hq to obtain 1.26 g of the product, equivalent to 2.75 mmol of Alq$_3$ or 83% yield. The samples prepared with different reaction times are treated in the same manner.

Room-temperature solid-state ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR spectra of the two samples prepared by refluxing 1 and 90 h are shown in parts a and b of Figure 2, respectively. The spectrum of the 1-h sample exhibits a complex set of multiplets in the range 110−165 ppm arising from three magnetically inequivalent oxyquinoline ligands in *mer*-Alq$_3$.[2g,4] In the 90-h sample, however, all of the resonances have been converted into sharp singlets that are consistent with magnetic equivalence of the ligands in *fac*-Alq$_3$ having C_3 symmetry.

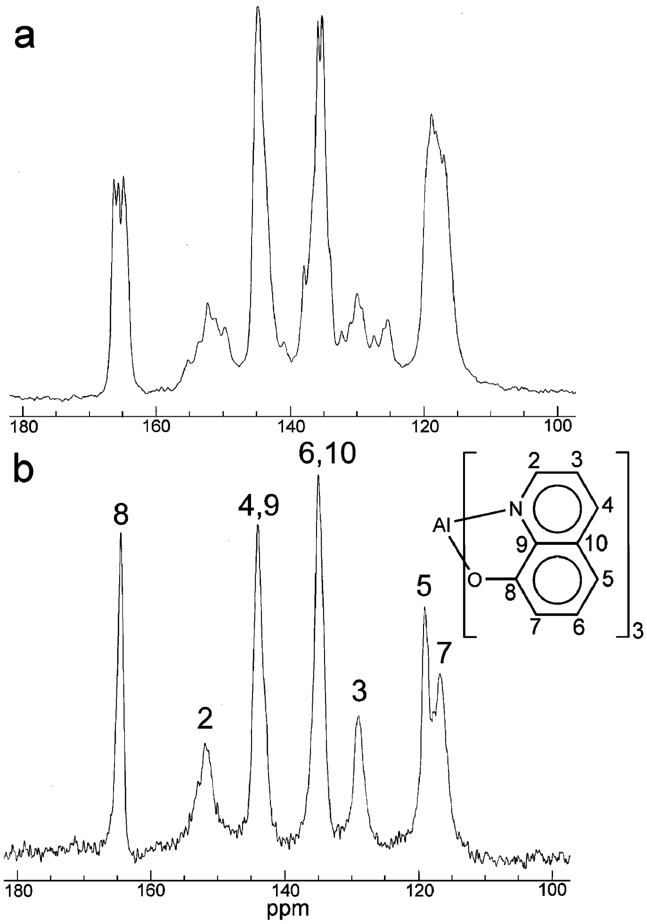

Figure 2. Solid-state ^{13}C CPMAS NMR spectra of as-prepared powders obtained after reacted for 1 h (a) and 90 h (b). Inset shows the assignments of carbons.

Strong evidence of the structural transformation is obtained by X-ray powder diffraction (XRPD) measurements of the same powder samples as those used for NMR data acquisition (Figure 3).[17] All of the prominent peaks in a diffractogram of the 1-h sample coincide with those of the meridional isomer (either β- or ϵ-Alq$_3$) reported by Rajeswaran and Blanton,[2f] although further characterization was difficult because of the noisy baseline typical for the 1-h sample. On the other hand, a diffractogram of the 90-h sample shows excellent agreement with that of δ-Alq$_3$ with a trace of γ-Alq$_3$ (both facial),[3] supporting the change in configuration observed in NMR experiments. The sharper peaks and subdued background noise are indicative of the highly crystalline nature of the sample prepared after prolonged reaction. Furthermore, a powder sample obtained after refluxing for 48 h displayed a mixed pattern of the two phases. Reportedly, solid-state phase conversion from *mer*- to *fac*-Alq$_3$ occurs at temperatures above 380 °C,[2c,d] although our samples were never exposed to such high temperatures at any point. To test the possible thermodynamic isomerization, the 1-h sample was refluxed for an additional 100 h (Figure 4). Interestingly, the meridional isomer persisted in the resulting powder and improved crystallinity allows identification of a crystalline phase as ϵ-Alq$_3$. Although the molecule

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(16) Commercially available AlO(OH) is hydrated by an unknown number of water molecules, which is excluded from the molecular weight calculation.

(17) Diffractograms are acquired with monocromated Cu Kα radiation (λ = 1.540 56 Å) on a Rigaku Multiflex powder diffractometer. Ground powder samples were mounted on glass slides, and data collection was conducted at room temperature in the 2θ range of 5−35° with sampling width $\Delta 2\theta = 0.020°$.

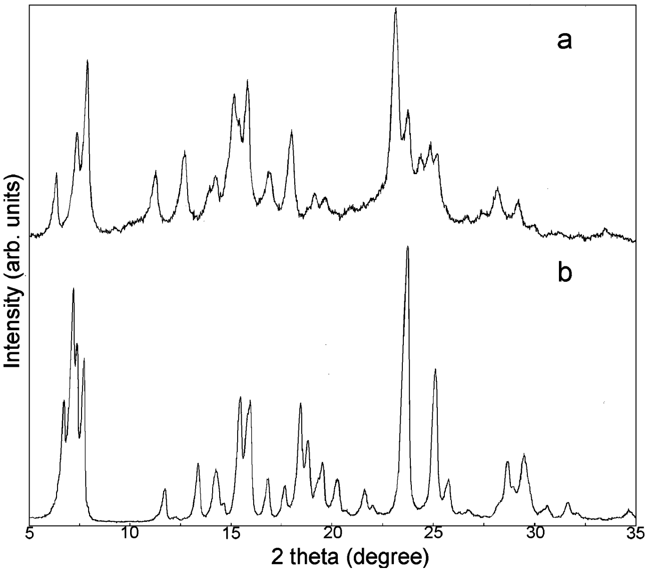

Figure 3. XRPD diffractograms of as-prepared powders obtained after reacting for 1 h (a) and 90 h (b).

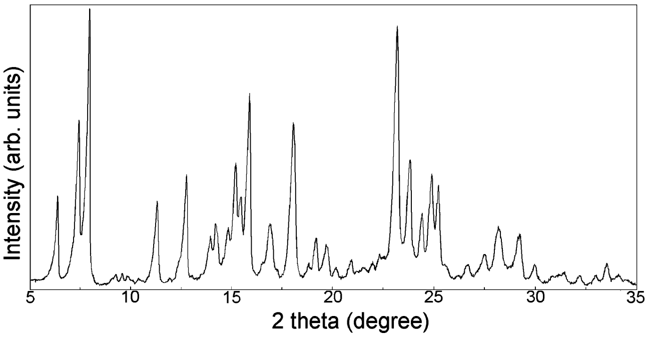

Figure 4. XRPD diffractogram of the 1-h sample after refluxing for an additional 100 h.

maintains a meridional configuration, the molecular packing may be different before and after the prolonged heat treatment, and we are currently investigating this point. Indeed, because *mer*-to-*fac* isomerization entails a higher activation energy compared to the local fluctuations between two enantiomers (Λ and Δ) of *mer*-Alq$_3$,[8,9b] the thermodynamic conversion is not likely the case for Alq$_3$. It can be contrasted to the temperature-dependent control over the *fac*-to-*mer* isomerization observed for trischelated Ir(III) complexes.[18] To probe the existence of a catalyst ingredient in the reactants, the 1-h sample was refluxed in the presence of AlO(OH) or 8-Hq (10 mol %), but no isomerization occurred.

The presented methods allow controlled synthesis of *fac*- and *mer*-Alq$_3$ under stoichiometric conditions with good yield. Preparation of the Alq$_3$ single isomer may facilitate the recrystallization of the molecule that will be considerably important when a device performance is significantly affected by the presence of the ppm order of the impurities. Contrary to the common belief that *fac*-Alq$_3$ is formed by high-temperature thermal conversion, our method should open the way to the development of low-temperature wet fabrication of blue-fluorescent Alq$_3$ films by dip-coating and spin-coating techniques. Furthermore, if this method could be applicable to the preparation of a single isomer of trischelate Al complexes in general, it will be an extremely useful synthesis technique.

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Supporting Information Available: ^{13}C CPMAS NMR with dipolar dephasing, TG/DTA data, the EI-MS spectrum of *fac*-Alq$_3$, and XRPD of the sample refluxed for 48 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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