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## A theoretical and experimental study on meridional–facial isomerization of tris(quinolin-8-olate)aluminum (Alq<sub>3</sub>)†

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The rationale behind the stereospecific synthesis of a facial isomer of tris(quinolin-8-olate)aluminum (Alq<sub>3</sub>) is studied by density functional theory (DFT) calculations, which predict the favourable influence of an  $H_3O^+$  ion on the distribution ratio between a meridional and a thermodynamically unstable facial isomer.

Tris(quinolin-8-olate)aluminum (Alq<sub>3</sub>) has been referred to as a prototypical electroluminescent material in small moleculebased organic light-emitting diodes (OLEDs) due to its relatively low operational voltage to coax its characteristic green emission.<sup>1</sup> Its technological importance has drawn intensive research activities addressing synthesis,<sup>2</sup> structural characterization,<sup>3</sup> and physicochemical properties of Alq<sub>3</sub>. Structurally,<sup>4</sup> three quinolin-8-olate (q<sup>-</sup>) ligands are coordinated to aluminum(m) ion in Alq<sub>3</sub>, existing in two isomeric forms:  $C_3$  symmetrical facial Alq<sub>3</sub> (fac-Alq<sub>3</sub>) and C<sub>1</sub> symmetrical meridional Alq<sub>3</sub> (mer-Alq<sub>3</sub>). Each isomer exhibits quintessential optoelectronic properties.<sup>4k</sup> For example, the fluorescent emission spectrum of fac-Alq<sub>3</sub> is blue shifted, and its quantum yield is higher than that of mer-Alq<sub>3</sub> in both solution and solid state.<sup>2a,c,4e,5</sup> Different electron-transporting abilities are predicted for two isomers.<sup>4a,b,h,j,k</sup> Thermodynamically more stable mer-Alq<sub>3</sub> is naturally the dominant species in solution-phase synthesis,<sup>2b,d,4e</sup> whereas fac-Alq<sub>3</sub> can be obtained as a byproduct in the sublimation purification of mer-Alq<sub>3</sub>, or by annealing mer-Alq<sub>3</sub> at around 400 °C.<sup>4e</sup> However, fac-Alq<sub>3</sub> is notoriously elusive, and it converts to mer-Alq<sub>3</sub> at higher than -20 °C in chloroform. Hence, little has been determined about the isomerization mechanism. Despite a keen interest in the blue-

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emitting materials, fac-Alq<sub>3</sub> has been largely neglected for a lack of rational synthetic methods.

Previously, we have unexpectedly discovered that fac-Alq<sub>3</sub> can be isolated with an excellent yield by refluxing a water suspension of mineral boehmite [AlO(OH)] and 8-hydroxyquinolinol (Hq).<sup>6</sup> Boehmite is a naturally occurring mineral, in which Al<sup>3+</sup> is coordinated by five oxides and a hydroxide ion. Terminal hydroxyl groups are readily replaced by various O- and N-donor ligands to yield corresponding aluminum coordination compounds, exemplified by the reaction between boehmite and carboxylic acids to furnish the carboxylate-alumoxanes as demonstrated by Barron et al.7 Thus, boehmite can be employed as a quantitative and environmentally benign source of Al<sup>3+</sup> in the formation of complexes. Unlike common aluminum salts, such as nitrate, sulfate, isopropoxide, and acetate,<sup>2b,d,8</sup> we hypothesized that the complexation of boehmite with Hq liberates only water-borne ions that may contribute to the promotion of a thermodynamically unfavorable mer- to fac-Alq<sub>3</sub> isomerization reaction (eqn (1)).

$$AlO(OH) + 3Hq (\rightarrow H^+ + q^-) \rightarrow Alq_3 + 2H_2O$$
 (1)

Given that boehmite is hardly soluble in pure water,<sup>9</sup> it is surmised that heterogeneous reactions between boehmite and Hq may be occurring with high efficiency and stereo selectivity in a water medium. Analogous efficiency improvement was detected in a stereoselective bromination reaction of stilbene in water suspension.<sup>10</sup>

This communication addresses theoretical and experimental studies on the isomerization of Alq<sub>3</sub> observed in a reaction between boehmite and Hq in a water medium. Because authentic *mer*-Alq<sub>3</sub> was completely inert even after prolonged reflux in pure water,<sup>11</sup> the roles of water and water-borne ions (H<sub>2</sub>O, H<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, and OH<sup>-</sup>) were evaluated using the B3LYP level of DFT calculations.<sup>4l,12</sup> An elegant study by Amati and Lelj has revealed that the fastest isomerization proceeds *via* the Al–N bond cleavage and formation of five-coordinate intermediate.<sup>13</sup> Considering their results, we performed a series of density functional theory (DFT) calculations to find that *mer*to *fac*-Alq<sub>3</sub> isomerization is a two-state transition process with

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a high-energy intermediate species, and the pathway transforms to a single-state transition process upon  $H_3O^+$  complexation. The role of  $H_3O^+$  was experimentally verified by refluxing reactants in acidic water that drastically accelerated the reaction.

The integrity of calculations were assessed using different basis sets (LANL2DZ, 6-31G\*, 6-31+G\*) and compared the resulting geometries with corresponding X-ray crystallographic data.<sup>14</sup> Although equally satisfactory values are obtained for both 6-31G\* and 6-31+G\* level calculations (Table S1 and Fig. S1 in ESI†), we employed the one with diffuse functions (6-31+G\*) throughout this research in the expectation of better handling the anticipated intermediate species with elongated bonds.

Fig. 1 shows the calculated reaction coordinate for isomerization of Alq<sub>3</sub>. The initial guess for the five-coordinate transition state (TS) geometry was prepared by breaking the Al–N bond in a ligand L1 (shown in green) and twisted 90° about the Al–O bond. A converged calculation shows that the ratedetermining transition state geometry (TS1) has its imaginary frequency vectors (yellow arrows) pointing the direction of ligand rotation.<sup>15</sup> Intrinsic reaction coordinate (IRC) calculations were performed by perturbing the coordinates of TS1 to create a stable intermediate (INT) along the reaction coordinate going forward (*mer*- to *fac*-Alq<sub>3</sub>). Further, TS geometry optimization between the INT and *fac*-Alq<sub>3</sub> discovered that one of the imaginary frequency vectors of TS2 pointed the direction of ligand rotation to furnish the *fac*-Alq<sub>3</sub> configuration,<sup>16</sup> the potential energy of which was estimated to be 5.4 kcal mol<sup>-1</sup> higher than *mer*-Alq<sub>3</sub>, which is comparable to the values estimated by other studies.<sup>4*j*,*k*,13</sup> Subsequently, solvent effects were included by performing the single-point polarizable continuum model (PCM) calculations on each model in the reaction coordinate to find a relatively substantial drop of the potential energy for the facial isomer (2.1 kcal mol<sup>-1</sup>).<sup>17</sup>

The association models are created by placing  $H^+$ ,  $H_3O^+$ ,  $OH^-$ , or  $H_2O$  at the sterically least-congested sites around the  $Al^{3+}$  centre of each isomer. Calculations reached convergence, except for the  $OH^-$  association model (see Fig. S2 in ESI† for optimized coordination geometries). The smallest potential energy difference between *mer*- and *fac*-Alq<sub>3</sub> (3.3 kcal mol<sup>-1</sup>) is obtained for  $H_3O^+$  association models (Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>), in which two out of three hydrogen atoms are bonded to the oxygen atoms in *mer*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>, and the third hydrogen atom is pointing away from  $Al^{3+}$ . For symmetrically coordinated *fac*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>, H<sub>3</sub>O<sup>+</sup> occupies the centre of the triangular face defined by the three ligand oxygen atoms. This geometry can accommodate a relatively large interstitial space around L1, which is responsible for isomerization through rotation about the Al–O bond.

The search for the reaction coordinate of  $Alq_3/H_3O^+$  started from the preparation of the five-coordinate TS geometry of *mer*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup> by cleaving the Al–N bond of L1 and twisted 90°; therefore, the pyridine moiety moves away from the Al<sup>3+</sup> center, and H<sub>3</sub>O<sup>+</sup> was fixed between the oxygen atoms. A successfully converged geometry (TS3) shows that three equatorial oxygen atoms are slightly puckered to bring them closer to each other (Fig. 2). The imaginary frequency vectors on L1 are



**Reaction Coordinate** 



Reaction Coordinate

Fig. 1 Reaction coordinate for isomerization of Alq<sub>3</sub>. The potential energy values after applying single-point PCM calculations are shown in parentheses. Yellow arrows on the calculated molecular structures indicate the direction of imaginary frequency vectors. Colour scheme: Al = purple, O = red, N = blue, and C = grey. Hydrogen atoms are omitted for clarity.

**Fig. 2** Reaction coordinate for isomerization of  $Alq_3/H_3O^+$ . The potential energy values after applying single-point PCM calculations are shown in parentheses. Yellow arrows on the calculated molecular structures indicate the direction of imaginary frequency vectors. Color scheme: Al = purple, O = red, N = blue, and C = grey. Hydrogen atoms on the ligands are omitted for clarity.

**Table 1** Comparison of the amount of Alq<sub>3</sub> isomers dissolved in pure and acidic water ( $2.0 \times 10^{-2}$  M HCl) at 25 °C and 100 °C, respectively. A sample (500 mg) was stirred in 60 mL of water and collected after 60 min (25 °C) or 10 min (100 °C). The amounts of the isomer dissolved were calculated from a dry weight of the retrieved solid

	<i>mer</i> -Alq $_3$ (mg)	<i>fac</i> -Alq <sub>3</sub> (mg)
H <sub>2</sub> O (25/100 °C)	75.5/110	20.0/73.5
2.0 × 10 <sup>-2</sup> M HCl (25/100 °C)	110/130	18.0/70.5

in accordance with the ligand rotation toward the facial configuration. IRC calculations on the TS3 found two local minima,<sup>18</sup> one each going forward and backward. The former configuration coincides with that of *fac*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>, whereas the latter is practically identical to the starting *mer*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>. Although the single-point PCM calculations predicted lower potential energies for TS3 and *fac*-Alq<sub>3</sub>/H<sub>3</sub>O<sup>+</sup>, the forward reaction remained thermodynamically uphill. Muccini *et al.* attributes the driving force of this uphill reaction to the higher lattice free energy of *fac*-Alq<sub>3</sub>,<sup>4e</sup> which will precipitate out as a crystalline solid. Indeed, *fac*-Alq<sub>3</sub> is confirmed to be less soluble in water than *mer*-Alq<sub>3</sub>, and disparities grow larger in acidic water (Table 1).

In order to experimentally verify the role of  $H_3O^+$ , boehmite and Hq are reacted in a dilute HCl solution  $(2.0 \times 10^{-2} \text{ M})$ . A bright yellow precipitate formed within 1 h, and the color then faded to a yellowish cream in 3 h, which was substantially faster than in pure water, in which it took at least 24 h. The <sup>13</sup>C NMR spectrum of the solid product confirmed the formation of *fac*-Alq<sub>3</sub> (Fig. S3†).<sup>6</sup> More significantly, even though a suspension of *mer*-Alq<sub>3</sub> in pure water was never converted to the facial isomer that occurred in acidic water after refluxing for 48 h.

In conclusion, we have conducted theoretical studies on the isomerization mechanisms of  $Alq_3$  in an aqueous medium and showed that there are two transition states in addition to a high-energy intermediate species along the reaction coordinate. The studies also found that  $H_3O^+$  association modifies the two-state TS to a single TS process. Theoretical predictions were experimentally confirmed by performing the reaction under acidic conditions, which lead to a great increase in the reaction rate.

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- 15 Imaginary rotation vectors have relatively low intensities for all TS structures presumably because the ligands are directly coordinated to the metal center. Thus, the resulting structures may not necessarily reflect those of TSs. The calculated activation energies are considered qualitative rather than quantitative.
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