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A Theoretical and Experimental Study on meridional−facial Isomerization of Tris(quinolin-8-olate)aluminum (Alq_3)

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Rational behind the stereospecific synthesis of a facial isomer of tris(quinolin-8-olate)aluminum (Alq_3) is studied by density functional theory (DFT) calculations, which predict favourable influence of H_3O^+ ion on the distribution ratio between a meridional and a thermodynamically unstable facial isomer.

Tris(quinolin-8-olate)aluminum (Alq_3) has been referred to as a prototypical electroluminescent material in small molecule based organic light emitting diodes (OLEDs) due to its relatively low operational voltage to coax its characteristic green emission.[1] Its technological importance has drawn intensive research activities addressing synthesis,[2] structural characterization,[3] and physicochemical properties of Alq_3. Structurally,[4] three quinolin-8-olate (q^-) ligands are coordinated to aluminum(III) ion in Alq_3, existing in two isomeric forms: C_3 symmetrical facial Alq_3 (*fac*-Alq_3), and C_1 symmetrical meridional Alq_3 (*mer*-Alq_3). Each isomer exhibits quintessential optoelectronic properties.[4k] For example, the fluorescent emission spectrum of *fac*-Alq_3 is blue shifted and its quantum yield is higher than that of *mer*-Alq_3 in both solution and solid-state.[2a, 2c, 4e, 5] Different electron transporting abilities are predicted for two isomers.[4a, 4b, 4h, 4j, 4k] Thermodynamically more stable *mer*-Alq_3 is naturally the dominant species in solution phase synthesis,[2b, 2d, 4e] while *fac*-Alq_3 can be obtained as a by-product in sublimation purification of *mer*-Alq_3, or by annealing *mer*-Alq_3 at around 400 °C.[4e] However, *fac*-Alq_3 is notoriously elusive, and it converts to *mer*-Alq_3 at above -20 °C in chloroform. Hence, little has been known about the isomerization mechanism. Despite a keen interest in the blue emitting materials, *fac*-Alq_3 has been largely neglected for the lack of rational synthetic methods.

Previously, we have unexpectedly discovered that *fac*-Alq_3 can be isolated with an excellent yield by refluxing a water suspension of mineral boehmite (AlO(OH)) and 8-hydroxyquinolinol (Hq).[6] Boehmite is a naturally occurring mineral, in which Al^{3+} is coordinated by five oxides and a hydroxide ions. Terminal hydroxyl groups are readily replaced by various O- and N-donor ligands to yield corresponding aluminum coordination compounds, exemplified by reaction between boehmite and carboxylic acids to furnish the carboxylate-alumoxanes as demonstrated by Barron and co-workers.[7] Thus, boehmite can be employed as a quantitative and environmentally benign source of Al^{3+} in complexes formation. Unlike common aluminum salts, such as nitrate, sulfate, isopropoxide, and acetate,[2b, 2d, 8] we hypothesized that complexation of boehmite with Hq liberates only water-borne ions that may contributing to the promotion of a thermodynamically unfavorable *mer*- to *fac*-Alq_3 isomerization reaction (eq. 1).

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

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

This communication addresses theoretical and experimental studies on the isomerization of Alq_3 observed in a reaction between boehmite and Hq in water medium. Because authentic *mer*-Alq_3 was completely inert even after prolonged reflux in pure water,[11] the roles of water and water-borne ions (H_2O, H^+, H_3O^+, and OH^-) were evaluated using B3LYP level of DFT calculations.[4l, 12] 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.[13] Given their results, we performed a series of density functional theory (DFT) calculations to find that *mer*- to *fac*-Alq_3 isomerization is a two-state transition process with 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.

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.[14] Although equally satisfactory values are obtained for both 6-31G* and 6-31+G* level calculations (Table S1, and Figure S1 in ESI), we employed the one with diffuse functions (6-31+G*) throughout this research in expectation of better handling the anticipated intermediate species with elongated bonds.

Figure 1 shows the calculated reaction coordinate for isomerization of Alq_3. 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 rate-determining transition state geometry (TS1) has its imaginary frequency vectors (yellow arrows) pointing the direction of ligand rotation.[15] 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_3). Further TS geometry optimization between INT and *fac*-Alq_3 discovered that one of the imaginary frequency vectors of TS2 pointed the direction of ligand rotation to furnish the *fac*-Alq_3 configuration,[16] whose potential energy was estimated 5.4 kcal·mol^{-1} higher than *mer*-Alq_3, comparable to the values estimated by other studies.[4j, 4k, 13] Subsequently, solvent effects were included by performing the single point polarizable continuum model (PCM) calculations on each model in the reaction coordinate to find relatively substantial drop of the potential energy for the facial isomer (2.1 kcal·mol^{-1}).[17]

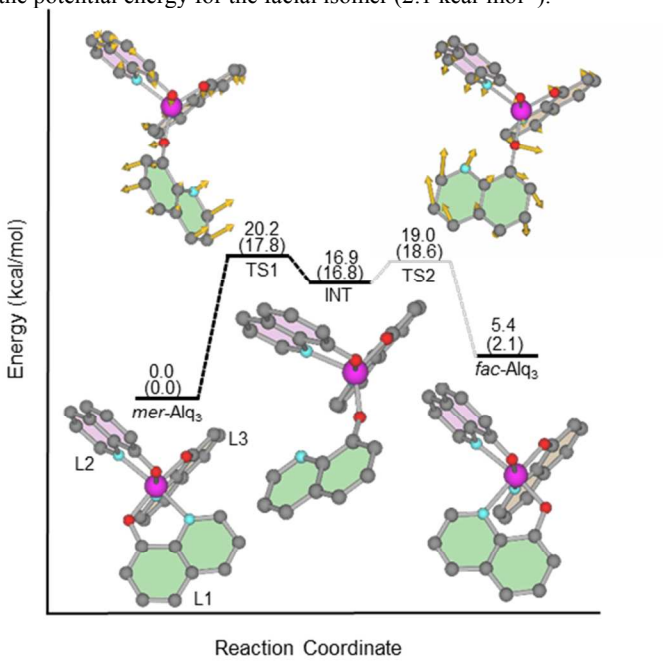

Figure 1. Reaction coordinate for isomerization of Alq_3. The potential energy values after applied single point PCM calculations are shown in parentheses. Yellow arrows on the calculated molecular structures indicate the direction of imaginary frequency vectors. Colour scheme: Al= purple, O = red, N = blue, C = grey. Hydrogen atoms are omitted for clarity.

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 the OH^- association model (see Figure S2 is ESI for optimized coordination geometries). The smallest potential energy difference between *mer*- and *fac*-Alq_3 (3.3 kcal·mol^{-1}) is obtained for H_3O^+ association models (Alq_3/H_3O^+), in which two out of three hydrogen atoms are bonded to the oxygen atoms in *mer*-Alq_3/H_3O^+, and the third hydrogen is pointing away from Al^{3+}. For symmetrically coordinated *fac*-Alq_3/H_3O^+, H_3O^+ 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. Search for the reaction coordinate of Alq_3/H_3O^+ started from preparation of the five coordinate TS geometry of *mer*-Alq_3/H_3O^+ by cleaving the Al–N bond of L1 and twisted 90° so the pyridine moiety moves away from the Al^{3+} center, and H_3O^+ 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 (Figure 2). The imaginary frequency vectors on L1 are in accord with the ligand rotation toward the facial configuration. IRC calculations on the TS3 found two local minima,[18] one each on going forward and backward. The former configuration coincides with that of *fac*-Alq_3/H_3O^+, while the latter is practically identical to the starting *mer*-Alq_3/H_3O^+. Although the single point PCM calculations predicted lower potential energies for TS3 and *fac*-Alq_3/H_3O^+, 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_3,[4e] which will precipitate out as a crystalline solid. Indeed, *fac*-Alq_3 is confirmed less soluble in water than *mer*-Alq_3, and disparities grow bigger in acidic water (Table 1).

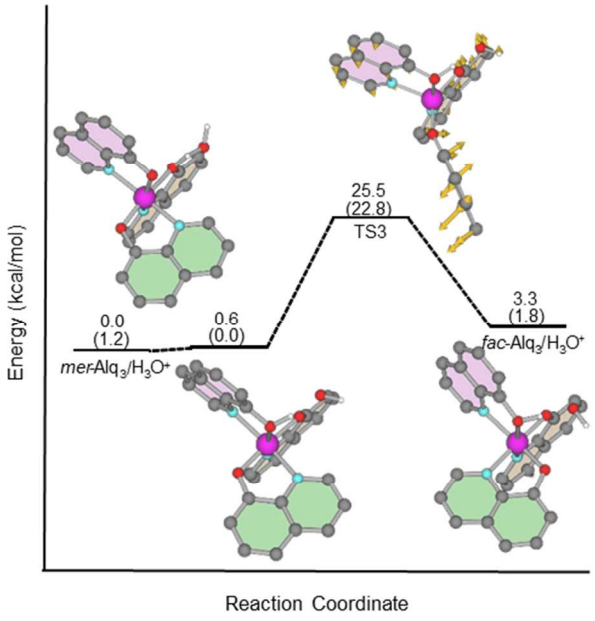

Figure 2. Reaction coordinate for isomerization of Alq_3/H_3O^+. The potential energy values after applied single point PCM calculations are shown in parentheses. Yellow arrows on the calculated molecular structures indicate the direction of imaginary frequency vectors. Color scheme: Al= purple, O =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

Table 1. Comparison of the amount of Alq_3 isomers dissolved in pure and in acidic water (2.0×10^{-2} M HCl) at 25 °C and 100 °C. 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.

	mer-Alq_3 (mg)	*fac*-Alq_3 (mg)
H_2O (25 / 100 °C)	75.5 / 110	20.0 / 73.5
2.0×10^{-2} M HCl (25 / 100 °C)	110 / 130	18.0 / 70.5

In order to experimentally verify the role of H_3O^+ boehmite and Hq are reacted in a dilute HCl solution (2.0×10^{-2} M). A bright yellow precipitate formed within 1 h, then the color faded to yellowish cream in 3 h that is substantially faster than in pure water where it took at least 24 h. The ^{13}C NMR spectrum of the solid product confirmed the formation of *fac*-Alq_3 (Figure S3).[6] More significantly, even though a suspension of *mer*-Alq_3 in pure water

was never converted to the facial isomer that happened in an acidic water after refluxed for 48 h.

In conclusion, we have conducted theoretical studies on the isomerization mechanisms of Alq_3 in aqueous medium, and showed that there are two transition states and 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 that lead to great increase in the reaction rate.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, supplementary calculation results and graphics, solid-state ^{13}C NMR spectra. See DOI: 10.1039/c000000x/

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