Research article

Characterisation of different polymorphs of tris(8-hydroxyquinolinato)aluminium(III) using solid-state NMR and DFT calculations

Mithun Goswami, Pabitra K Nayak, N Periasamy† and PK Madhu*†

Address: Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India

Email: Mithun Goswami - mithun@tifr.res.in; Pabitra K Nayak - pabitra@tifr.res.in; N Periasamy - peri@tifr.res.in; PK Madhu* - madhu@tifr.res.in

* Corresponding author    †Equal contributors

Abstract

Background: Organic light emitting devices (OLED) are becoming important and characterisation of them, in terms of structure, charge distribution, and intermolecular interactions, is important. Tris(8-hydroxyquinolinato)-aluminium(III), known as Alq3, an organomettalic complex has become a reference material of great importance in OLED. It is important to elucidate the structural details of Alq3 in its various isomeric and solvated forms. Solid-state nuclear magnetic resonance (NMR) is a useful tool for this which can also complement the information obtained with X-ray diffraction studies.

Results: We report here 27Al one-dimensional (1D) and two-dimensional (2D) multiple-quantum magic-angle spinning (MQMAS) NMR studies of the meridional (α-phase) and the facial (δ-phase) isomeric forms of Alq3. Quadrupolar parameters are estimated from the 1D spectra under MAS and anisotropic slices of the 2D spectra and also calculated using DFT (density functional theory) quantum-chemical calculations. We have also studied solvated phase of Alq3 containing ethanol in its lattice. We show that both the XRD patterns and the quadrupolar parameters of the solvated phase are different from both the α-phase and the δ-phase, although the fluorescence emission shows no substantial difference between the α-phase and the solvated phase. Moreover, we have shown that after the removal of ethanol from the matrix the solvated Alq3 has similar XRD patterns and quadrupolar parameters to that of the α-phase.

Conclusion: The 2D MQMAS experiments have shown that all the different modifications of Alq3 have 27Al in single unique crystallographic site. The quadrupolar parameters predicted using the DFT calculation under the isodensity polarisable continuum model resemble closely the experimentally obtained values. The solvated phase of Alq3 containing ethanol has structural difference from the α-phase of Alq3 (containing meridional isomer) from the solid-state NMR studies. Solid-state NMR can hence be used as an effective complementary tool to XRD for characterisation and structural elucidation.
Background
In organic based semiconductor devices, molecular solids of organic molecules are used in active layers [1]. The properties of amorphous solid thin films can be different from the properties of isolated molecule, due to interaction among the molecules in solid state. The properties of amorphous solid thin films are mainly decided at the molecular level and modulated by intermolecular interactions and other bulk properties. Hence, it is important to have information about the structure of the organic molecule, charge distribution on the molecular framework, and intermolecular interactions as they collectively govern the performance of the device.

Following the experimental demonstration by Tang et al. [2] Tris(8-hydroxyquinolinate)- aluminium(III), known as Alq3, has become a workhorse material for organic light emitting devices (OLED) and/or electron transporting material in OLED. Alq3 is an octahedrally coordinated chelate complex, with an Al^{3+} ion in the center and three 8-hydroxyquinolinate ions octahedrally coordinated around it. It has mainly two types of geometrical isomeric forms, meridional and facial. Brinkmann et al. investigated the light emitting properties of the isomeric states and the polymorphs of Alq3 and determined that molecular packing plays a significant role [3]. X-ray diffraction studies showed that the two crystalline polymorphs of Alq3, α and δ forms, are mainly composed of the meridional isomer [3]. Recently a new crystalline phase of Alq3, namely δ-Alq3, was discovered [4]. It shows blue luminescence which is markedly different from the meridional isomer which shows green luminescence. The quantum yield is also higher in the δ-phase. These results suggest that there is a clear correspondence between the crystal structure of Alq3 and the photoluminescence property. Extensive studies on the δ-phase of Alq3 have been carried out and it was suggested that δ-Alq3 is composed purely of facial Alq3 [5,6]. Again in the case of charge carrier transport in Alq3, intermolecular interactions play the most crucial role [7]. Also, it has been a practice to use different dopants in Alq3 emitting layers to obtain desired colours [1]. Such Alq3 systems which accommodate small solvent molecules within its crystal matrix are in general known as solvated Alq3. It was also reported that the unit crystal structure and the crystal packing change in Alq3 when it hosts small solvent molecules, which resulted in a small red shift in the fluorescence spectra [3].

Considering the above stated facts, it becomes important to have insight about the structure of Alq3 in both the solvated and the unsolvated form and about the in-tramolecular and intermolecular interactions. Though X-ray diffraction is a powerful tool to yield insight into the structure of crystalline material, solid-state NMR can be as good in providing similar information. In addition, solid-state NMR is particularly suitable for studying disordered or amorphous materials [8-13]. Since Alq3 has an Al^{3+} ion in the centre, one can make use of it as a probe to monitor the electronic distribution in the molecule. 27Al is well suited for solid-state NMR because of its high natural abundance (100%) and relatively large gyromagnetic ratio. Since 27Al has spin I = 5/2, it possesses a quadrupolar moment [14]. It is possible to record and analyse solid-state 27Al MAS NMR spectra, observing the central m = +1/2↔-1/2 magnetic transition under magic-angle spinning (MAS), which, for well-resolved spectra, exhibits a characteristic second-order order broadening. High-resolution quadrupolar spectra can be obtained with two-dimensional (2D) methods such as multiple-quantum MAS (MQMAS) [15]. This can help in identifying the various quadrupolar sites in a system and in obtaining the quadrupolar parameters [16,17]. The study of quadrupolar parameters with solid-state NMR can provide a wealth of information about the local environment around quadrupolar nuclei, as the quadrupolar parameters show strong dependence on the neighbouring electronic environment [14,18].

Octahedral chelate complexes, which are structurally similar to Alq3, were studied by Schurko and co-workers using one-dimensional (1D) 27Al MAS NMR spectroscopy [19]. They showed that the change of structural environment about the aluminium centres can be easily investigated by studying the quadrupolar parameters of 27Al nuclei of the organic chelate complexes. They also reported how the distortion in the chelate rings leads to larger value of quadrupolar coupling constant in one of the complexes. Recently Utz et al. [10,11] have successfully used 1D MAS 27Al spectroscopy to differentiate between the α phase and the δ phase of Alq3, and to characterize the structural disorder of amorphous Alq3 deposited from vapour phase at different rates. They also estimated the EFG tensor on the basis of point charge model and predicted the asymmetry parameters of the α and the δ phase [10]. Kaji et al. have done a similar study by recording 1D 27Al spectra under static and MAS condition to characterise the α phase, the δ phase, and the γ phase of Alq3 and also amorphous Alq3 [20]. However unlike Utz et al. they have used DFT based quantum-chemical calculations to theoretically predict the value of the asymmetry parameters of the α phase and the γ phase. Their study suggested that whilst the α phase contains a non axially symmetric isomer both the δ phase and the γ phase of Alq3 contain an axially symmetric form.

Here, we have investigated three types of Alq3 samples: (a) α phase (containing the meridional isomer), (b) δ phase (containing the facial isomer), and (c) solvated phase (containing ethanol in the crystal lattice) using solid-state
NMR combined with density functional theory (DFT) [21] based quantum chemical calculation. We show with MQMAS experiments that in all the polymorphs, $^{27}$Al is present in a single crystallographic site. We further demonstrate that the local environment around $^{27}$Al in solvated phase is different from that in the $\alpha$ phase with the use of both 1D MAS and 2D MQMAS experiments. We also made use of Dmfit [22] program to model the 1D MAS spectra of all the polymorphs to extract the quadrupolar parameters and we have compared the results with the previous works. In addition the anisotropic slices of the peaks in 2D MQMAS spectra were modelled using the Dmfit program to extract the quadrupolar parameters and isotropic chemical shifts. We further report the result obtained from DFT based quantum-chemical calculation done on isolated molecule and show that the correspondence with the experimental results improve when the calculation is done under the solvation model.

**Experimental**

*Preparation of Alq$_3$ and X-ray diffraction measurements*

Alq$_3$ was prepared from 8-hydroxyquinoline and Al(NO$_3$)$_3$.9H$_2$O using an aqueous route by a standard procedure [23]. Briefly the procedure adopted was as follows: 1 g of aluminium nitrate (Al(NO$_3$)$_3$)_3.9H$_2$O was dissolved in 100 ml of water. The solution was warmed to 60°C. 1.5 g of 8-hydroxyquinoline was dissolved in a solvent mixture of 20 ml of water and 4 ml of glacial acetic acid. 8-hydroxyquinoline solution was slowly added to aluminium nitrate solution. The pH of the resulting solution was then increased to 10 by the addition of ammonia to precipitate Alq$_3$ out. The resulting precipitate was washed by hot (60°C) water. The bright yellow powder was dried in oven for overnight. Yield of Alq$_3$ obtained by this method was 95-100% with a melting point > 300°C. This procedure was adapted from Vogel [24].

Alq$_3$, as prepared, was subjected to train sublimation under vacuum and purified [23]. Alq$_3$ gets deposited in different temperature zones. The portion which was deposited at ~175°C was collected. Powder XRD pattern of the sample matched with the reported pattern for the $\alpha$ phase of Alq$_3$ [3], which is well established to be the meridional isomer of Alq$_3$. Fluorescence emission spectra in thin film showed a maximum at 510 nm (Figure 1). Powder XRD pattern of the $\delta$ phase of Alq$_3$ matched with the previously reported pattern [5]. Fluorescence emission spectra in thin film showed a maximum at 468 nm (Figure 1). XRD pattern and fluorescence spectrum confirmed the sample to be the facial isomer of Alq$_3$. The ethanol solvated phase was prepared by recrystallising Alq$_3$ from ethanol. Fluorescence emission spectra in thin film showed a maximum at 510 nm (Figure 1). Powder XRD pattern showed a close resemblance with the reported solvated phase of the form Alq$_3$ (C$_6$H$_5$Cl)$_{1/2}$ where C$_6$H$_5$Cl acts as an inclusion or guest compound within Alq$_3$ crystal [3]. Alq$_3$-ethanol solvated phase was annealed at ~200°C under nitrogen atmosphere for 2 hrs to remove ethanol from the crystal lattice. X-ray powder diffraction data were obtained with Philips instrument (panalytica) with a Cu K$\alpha$ ($\lambda = 1.5418\text{Å}$) radiation source. Data were recorded at room temperature in 2$\theta$ mode ($\Delta 2\theta = 0.017$).

*Fluorescence measurements*

Steady-state fluorescence of powdered Alq$_3$ samples was recorded at room temperature using a Spex Fluorolog
fluorimeter. The excitation wavelength was 340 nm and scanned at a step of 1 nm.

**Thermo-gravimetric measurements**

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with a NETZSCH instrument. The temperature was varied at 5 K/min under nitrogen atmosphere.

**NMR experiments**

All NMR experiments were carried out on a Bruker Avance 500 MHz spectrometer operating at a field strength of 11.7 T with a Bruker 4 mm triple-resonance probe. Experiments were performed observing the central transition of $^{27}$Al ($I = 5/2$) of the different forms of Alq$_3$, sample at a Larmor frequency of 130.28 MHz. Magic-angle spinning was performed at 10 kHz. The nutation frequency of the excitation pulse for the 1D MAS experiments was 120 kHz. For the 2D experiments the split-frequency of the excitation pulse for the 1D MAS experiments was 120 kHz. For the 2D experiments the split-$t_1$ sequence proposed by Brown and Wimperis was used [26]. A nutation frequency of 80 kHz was applied for excitation and conversion pulses. The echo time was 2.5 ms. The pulse width of the selective 180° pulse was 27.8 $\mu$s. Further experimental details are given in the figure captions of Figs. Three-Six. The chemical shifts were referenced to aqueous 1 M AlCl$_3$ solution. The isotropic quadrupolar shifts from the MQMAS spectra, $\nu_Q^{iso}$, were calculated using the method given in Ref. [16]. In all the experiments swept-frequency two pulse phase modulation (SW$_B$TPPM) [27] heteronuclear dipolar scheme was applied to remove the $^1$H-$^{27}$Al dipolar couplings [28].

**Computation**

Density functional theory (DFT) was used in all the quantum-chemical calculations using Gaussian 03 [29]. The DFT method used here is based on hybrid B3LYP functional. The geometry optimisation of Alq$_3$ (both the facial and the meridional isomer) was done using 6-31G(d) basis set for all the atoms. The gas phase geometry optimised structure was used to calculate the electric field gradients (EFG). The EFG calculation was done using DFT with B3LYP functional. 6-31G(d) basis functions for C, H atoms and 6-311+G(3df) basis set for Al, N and O atoms were taken during the calculation. The more diffused basis sets were used for Al, N, and O due to our interest in the quadrupolar parameters at the Al center of Alq$_3$. The calculated values are given in Table 1. In organic powder/thin-film samples the organic molecule can be considered as solvated by the molecules of its own type. Hence, it is more realistic to take solid “solvation” into account whilst doing the EFG calculation for the molecules in thin films. For this, the isodensity polarisable continuum model (IPCM) provides an efficient way to consider the solvent effect as it defines the molecular cavity as a contour surface of constant electron probability density of the molecule [30]. Our theoretical calculation of dielectric constants, $\varepsilon$, for facial and meridional isomers came out to be 2.62 and 2.69 respectively. Dielectric constant of a material can be obtained from Clausius-Mossot equation [31]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = 4\pi\rho N_A \alpha / 3M$$

where $\alpha$ is the isotropic polarisability, $\rho$ is the density, $M$ is the molecular mass, $N_A$ is the Avogadro number, and $\varepsilon$ is the dielectric constant. Isotropic polarisability ($\alpha$) and reciprocal of Molar volume ($\rho/M$) were calculated from geometry optimised structure of the isomers using the DFT method (B3LYP/6-31G(d)). The experimentally determined value of $\varepsilon$ for thin film, which predominantly contains the meridional isomer, was found to be 3.0 ± 0.3 [32]. As the computationally determined values for both the isomers were nearly the same, the experimentally determined value of $\varepsilon$ for thin film was used in the IPCM calculation for both the isomers. The levels of basis functions were the same for both the gas phase and the solid solvated phase.

**Results and discussion**

We present here the results obtained from the $\alpha$ and the $\delta$ forms of Alq$_3$ and also from the solvated phase of Alq$_3$ using 1D MAS and 2D MQMAS NMR experiments. The quadrupolar parameters were obtained by fitting the 1D MAS spectra and the anisotropic slices of the 2D spectra of the three phases using the DMFIT program. We also report the theoretically calculated values of the quadrupolar parameters using the DFT calculations of the $\alpha$ and the $\delta$ forms of Alq$_3$.

### Table 1: The $^{27}$Al quadrupolar parameters obtained from the DFT quantum-chemical calculation under the isolated molecule and the isodensity polarisable continuum model (IPCM).

| Model   | Isomer | $\delta_{iso}$ (ppm) | $\eta_Q$ | $\nu_Q^{iso}$/MHz |
|---------|--------|----------------------|----------|-------------------|
| Isolated Molecule | $\alpha$-Alq$_3$ | - | 0.77 | 7.7 |
|          | $\delta$-Alq$_3$ | - | 0.03 | 7.0 |
| IPCM    | $\alpha$-Alq$_3$ | - | 0.81 | 7.2 |
|          | $\delta$-Alq$_3$ | - | 0.10 | 5.8 |

**NMR and XRD of isomeric forms of Alq$_3$**

Figure 2a shows the comparison between the experimental 1D spectra of the $\alpha$-phase and 2b shows the $\delta$-phase of Alq$_3$ with the theoretical line generated using the DMFIT program which gave the quadrupolar coupling constant...
\( \chi \) in MHz, the asymmetry parameter \( \eta_Q \), and the average value of isotropic shift which is a combination of both the isotropic chemical shift \( \delta_{\text{iso}} \) and the isotropic quadrupolar shift. The uncertainties in the values of \( \chi, \eta_Q, \) and \( \delta_{\text{iso}} \) were estimated by visual comparison of experimental and modelled spectra by employing small changes in the parameters and observing the matching of modelled spectra with the experimental ones.

The quadrupolar parameters obtained from the 1D spectra (Table 2) conclusively prove that Al\(^{3+} \) ion is situated in an axially symmetric environment in the \( \delta \)-phase whilst it is in a non-axially symmetric environment in the \( \alpha \)-phase of Alq\(_3\). (A low asymmetry value generally signifies axial symmetry and a high asymmetry value denotes otherwise.) This agrees well with the previously reported results [10,11,20]. Figs. 2c and 2d show the 1D spectrum of solvated Alq\(_3\) after the removal of ethyl alcohol.

Table 2: The \( ^{27}\text{Al} \) quadrupolar parameters obtained from the 1D MAS and the 2D MQMAS experiments using the DMFIT program.

| Experiment     | Isomer       | \( \delta_{\text{iso}} \) (ppm) | \( \eta_Q \)       | \( \chi \) (MHz) |
|----------------|--------------|---------------------------------|--------------------|-----------------|
| 1D MAS         | \( \alpha \)-Alq\(_3\) | 55.4 ± 1.0                      | 0.80 ± 0.04        | 7.0 ± 0.1       |
|                | \( \delta \)-Alq\(_3\) | 43.6 ± 1.0                      | 0.18 ± 0.03        | 4.9 ± 0.1       |
|                | Solvated Alq\(_3\) | 50.5 ± 1.0                      | 0.62 ± 0.04        | 6.4 ± 0.1       |
|                | Solvated Alq\(_3\) after the removal of ethanol | 55.1 ± 2.0 | 0.85 ± 0.05 | 6.5 ± 0.3 |
| 2D MQMAS       | \( \alpha \)-Alq\(_3\) | 54.7 ± 1.0                      | 0.85 ± 0.04        | 6.9 ± 0.1       |
|                | \( \delta \)-Alq\(_3\) | 43.1 ± 1.0                      | 0.15 ± 0.03        | 5.1 ± 0.1       |
|                | Solvated Alq\(_3\) | 50.4 ± 1.0                      | 0.60 ± 0.04        | 6.4 ± 0.1       |
|                | Solvated Alq\(_3\) after the removal of ethanol | 55.0 ± 2.0 | 0.81 ± 0.04 | 6.9 ± 0.3 |

Figure 2
1D \( ^{27}\text{Al} \) spectra of different modifications of Alq\(_3\) under MAS. Experimental data (black) and fitted spectra (red) of (a) \( \alpha \)-Alq\(_3\), (b) \( \delta \)-Alq\(_3\), (c) solvated Alq\(_3\), and (d) solvated Alq\(_3\) after the removal of ethyl alcohol.
vated Alq$_3$ before and after removal of the ethanol respectively along with the fitted lines. The 1D spectra of the $\alpha$-phase of Alq$_3$, the $\delta$-phase of Alq$_3$, and the solvated Alq$_3$ have distinctly different second-order quadrupolar broadened line shapes. The quadrupolar parameters obtained using the DMFIT program also show significant difference between the $\alpha$-phase and the solvated Alq$_3$, which clearly suggests that the introduction of an ethanol molecule inside the Alq$_3$ matrix changes the local environment around Al$^{3+}$ in the centre. Further, the line shape of the apohost Alq$_3$ (i.e., after the removal of ethanol from the solvated phase) has similar features to that of the $\alpha$-phase of Alq$_3$ which is also evident from their nearly similar quadrupolar parameters (Table 2).

Figs. 3, 4, 5, and 6 show the 2D 3QMAS spectrum of the $\alpha$ phase, the $\delta$ phase, and the solvated phase before and after the removal of ethanol respectively of Alq$_3$. Side-bands appear along the $F_1$ dimension of the 2D spectra as the $t_1$ increments were not synchronised with the MAS rotor period. The isotropic spectrum is obtained from a projection on to $F_1$ which in all cases consists of only a single resonance. This indicates that all the phases studied here have $^{27}$Al in an unique crystallographic site. The cross section extracted along the ridge line shape parallel to the $F_2$ axis was fitted using the DMFIT program. From the fit the quadrupolar parameters were extracted and are given in Table 1. Figure 7 shows a comparison of the 2D MQMAS experimental anisotropic slice with the theoretical line generated using the DMFIT program. Since the DMFIT program gives the model spectrum of a site under ideal excitation, there will be some difference in the line shapes of the model and the experimental spectra, nevertheless the procedure for the model calculation is quite robust and gives fairly accurate results [22].

The quadrupolar parameters in Table 2 indicate that the $\alpha$ phase of Alq$_3$ contains only the meridional isomer as reported from the XRD study [3] and the $\delta$ phase of Alq$_3$ is composed of purely facial isomer as reported from the XRD study [5].

From Figs. 5 and 6, it can be observed that the isotropic projection for solvated Alq$_3$ is much narrower compared to the $\alpha$-phase, the $\delta$-phase, and the solvated Alq$_3$ from which ethanol was removed. It is well known that chemical and/or rotational exchange processes can influence the powder patterns of half-integer spin quadrupolar nuclei [33]. In general, the higher the rate and symmetry of the exchange process the narrower will be the line width. Hence, the reason for the narrowing down of isotropic projection of solvated Alq$_3$ could be due to the high mobility of the quinoline ligands between chemically equivalent orientations around the $^{27}$Al site due to the introduction of ethanol into the crystal structure. Also it was observed that the shape of the cross section extracted along the $F_2$ dimension of the solvated Alq$_3$ is completely different from that of the $\alpha$-phase of Alq$_3$ which was earlier indicated by their 1D MAS spectra as well. This also clearly indicates that the local electronic environment

![Figure 3](http://journal.chemistrycentral.com/content/3/1/15/fig3)

**Figure 3**

(a) 2D 3QMAS spectra of meridional Alq$_3$ ($\alpha$-phase). The optimized excitation pulse and conversion pulse lengths were 3.8 $\mu$s and 1.8 $\mu$s. A total of 64 $t_1$ increments was taken with 10 $\mu$s of dwell time with 288 transients per increment. The recycling delay was 1 s. Total experiment time was 5 hours. (b) The anisotropic slice along the direction parallel to the $F_2$ dimension. (c) The isotropic projection along the $F_1$ dimension.
around the $^{27}\text{Al}$ centre undergoes significant change upon the introduction of ethanol into the matrix. Similar results were reported by Brinkmann et al. [3] where they showed that the unit crystal structure of the $\alpha$-phase (triclinic) is different from that of a solvated phase of the form $\text{Alq}_3(\text{C}_6\text{H}_5\text{Cl})_{1/2}$ (monoclinic). On the other hand the fluorescence emission spectra (Fig. 1) interestingly show practically no difference between the $\alpha$-form (meridional) of Alq$_3$ and the solvated Alq$_3$ containing ethyl alcohol. It shows fluorescence in Alq$_3$ is determined at molecular level and hardly influenced by molecular packing. Further the shape of the anisotropic slice of the apohost Alq$_3$ has remarkable resemblance to that of the $\alpha$-phase. However, the isotropic projection is broader in the apohost form compared to the later. In a recent study on the polymorphism of a hexa-substituted benzene derivative, Hexakis

![Figure 4](image1)

**Figure 4**
(a) 2D 3QMAS spectra of facial Alq$_3$ ($\delta$-phase). The optimised excitation pulse and conversion pulse lengths were 4.4 $\mu$s and 1.9 $\mu$s. Rest of the experimental parameters are as in Figure 3. (b) The anisotropic slice along the direction parallel to the $F_2$ dimension. (c) The isotropic projection along the $F_1$ dimension.

![Figure 5](image2)

**Figure 5**
(a) 2D 3QMAS spectra of solvated Alq$_3$ (containing ethanol). Optimised excitation and conversion pulse lengths were 4.6 $\mu$s and 2.5 $\mu$s. A total of 192 $t_1$ increments was taken with 8 $\mu$s of dwell time with 96 transients per increment. The recycling delay was 1 s. Total experiment time was 5 hours 18 mins. (b) The anisotropic slice along the direction parallel to the $F_2$ dimension. (c) The isotropic projection along the $F_1$ dimension.
(4-cyanophenyl oxy) benzene, it was suggested that one can get four different polymorphic forms of the above mentioned compound when crystallising it from melt [34]. It can be argued qualitatively that removal of ethanol from the solvated Alq3 is akin to the process of crystallising from melt, as the number of ethanol molecules existing per unit Alq3 to solvate it is very small. Therefore it is possible that more than one polymorph may appear from the re-crystallisation process giving rise to a distribution of NMR parameters resulting in the broadening of the ridges in the 3QMAS experiments. The quadrupolar parameters obtained for the α-phase of Alq3 and the apohost Alq3 are similar to each other indicating a similar environment around 27Al in the two forms. Similar observations were also made from the XRD analysis, Figure 8, where the solvated form of Alq3 containing ethanol has distinctly different feature from that of the α-phase. However, when the ethanol was removed from the solvated phase it gave XRD feature similar to that of the α-phase.

Figure 9 shows the data from the thermo gravimetric analysis of the solvated phase indicating a mass loss of 9.4% at 185 °C which corresponds to loss of one molecule of ethanol from Alq3(C2H5OH)1. It should be noted that Mq3 where M is a trivalent metal can host small molecules in its solvated phase [3]. The removal of ethanol at a temperature higher than its boiling point confirms its participation in the crystal lattice. Though ethanol is not chemically bonded to Alq3 its presence within the lattice affects the electronic distribution around Al and as a result the quadrupolar parameters of the solvated phase are different from either the α or the δ phase.

**Quantum-chemical calculation**
Quantum-chemical calculations yield principal components of EFG tensor, q_{ii} in atomic unit, with |q_{zz}| ≥ |q_{yy}| ≥ |q_{xx}|. The calculated q_{ii} values were used to obtain the quadrupolar parameters manually [17], where Q is the quadrupolar moment of 27Al nuclei. The atomic Q(27Al) value is 14.66 × 10^{-30} m^2 [35]. The calculated values of quadrupolar parameters are tabulated in Table 1.

DFT calculation of EFG principal values were done for isolated Alq3 molecule. The asymmetry parameter η_Q obtained for the α-form was 0.77 while η_Q for the δ-phase of Alq3 came to be 0.03. Previously Kaji et al. [20] also did similar kind of DFT calculations where they predicted that the η_Q values for the α-form and the γ form of Alq3 are 0.72 and 0.0 respectively. They also reported that the DFT calculation for the δ-phase yielded inconsistent results. Utz et al. [11] carried out a simple calculation for the estimation of EFG tensor on the basis of the assumption that the EFG tensor is determined by three point charges of -e at the oxygen sites. However, the values of η_Q predicted by this model (0.91 for meridional and 0.26 for facial) over-
shoot the experimental values obtained by us for both the isomers.

Here we propose a model for DFT calculation where molecules are considered under the influence of a continuum dielectric medium (IPC model) which is a more realistic situation. Under this model it is observed that the theoretically predicted values (0.81 for meridional and 0.10 for facial) show a relatively good agreement with the experimental values. In the case of solvated Alq$_3$, it was not possible to take a suitable model for the DFT calculation.

**Conclusion**

We have performed 1D MAS and 2D MQMAS experiments to obtain high-resolution spectra of meridional (α-phase) and facial (δ-phase) isomers of Alq$_3$. We have determined the quadrupolar parameters from 1D MAS spectra using the DMTFIT program. The 2D MQMAS experiments have shown that all the different modifications of Alq$_3$ have $^{27}$Al in single unique crystallographic site which is evident from the single isotropic peak along $F_1$ dimension. The quadrupolar parameters were also predicted using the DFT calculation under isolated molecule assumption and also under the IPC model. The theoretically calculated values of quadrupolar parameters improve and come close to the experimentally obtained values when calculations are done under the IPC model where an Alq$_3$ molecule is assumed to be solvated in a surrounding of similar Alq$_3$ molecules, which is the closest to the actual situation. Solid-state NMR data indicate that the solvated phase of Alq$_3$ containing ethanol has structural difference from the α-phase of Alq$_3$ (containing meridional isomer). This was also confirmed by the XRD features, though the fluorescence spectra did not show any significant difference between them which again reaffirms the fact that fluorescence is determined at molecular level in Alq$_3$ and does not depend on the crystal structure. Further the isotropic projection of the solvated Alq$_3$ is much narrower than all the other polymorphs, which could be due to dynamic exchange processes. Thermo-

![Figure 7](image-url)
The authors declare that they have no competing interests.

Acknowledgements
We acknowledge the use of National Facility for High-Field NMR, TIFR, for the use of the Bruker AV500 spectrometer, Thomas Bräuniger for discussions and a careful reading of the manuscript, and M. V. Naik for technical assistance.

References
1. Adachi C, Tsutsui T: Organic Light Emitting Devices Edited by: Shinar J. New York: Springer-Verlag; 2004.
2. Tang CW, Van Slyke SA: Organic electroluminescent diodes. Appl Phys Lett 1987, 51:913-916.
3. Brinkmann M, Gadret G, Muccini M, Taliani C, Masicocchi N, Sironi A: Correlation between molecular packing and optical properties in different crystalline polymorphs and amorphous thin films of mer-tris(8-hydroxyquinoline)aluminum(III). J Am Chem Soc 2000, 122:5147-5157.
4. Braun M, Gmeiner J, Tzolov M, Coelle M, Meyer FD, Milius W, Hillebrecht H, Wendland O, Schutz JUV, Brütting W: A new crystalline phase of the electroluminescent material tris(8-hydroxyquinoline) aluminum exhibiting blueshifted fluorescence. J Chem Phys 2001, 114:9625-9632.
5. Coelle M, Dinnebier RE, Brütting W: The structure of the blue luminescent d-phase of tris(8-hydroxyquinoline)aluminum(III) (Alq3). Chem Commun 2002, 23:2908-2909.
6. Coelle M, Gmeiner J, Milius W, Hillebrecht H, Brütting W: Preparation and characterization of blue-luminescent tris(8-hydroxyquinoline)-aluminum (Alq3). Adv Funct Mater 2003, 13:108-112.
7. Lin BC, Cheng CP, You ZQ, Hsu CP: Charge transport properties of tris(8-hydroxyquinolinato)aluminum(III): Why it is an electron transporter. J Am Chem Soc 2005, 127:66-67.
8. Lesage A, Bardet M, Emsley L: Through-bond carbon-carbon connectivities in disordered solids by NMR. J Am Chem Soc 1999, 121:10987-10993.
9. Kaji H, Schmidt-Rohr K: Conformation and dynamics of atactic poly(acrylonitrile). I. Trans/Gauche ratio from double-quantum solid-state 13C NMR of the methylene groups. Macromolecules 2000, 33:5169-5180.
10. Utz M, Nandagopal M, Mathai M, Papadimitrakopoulos F: Characterization of isomers in aluminium tris(quinoline-8-olate) by
one-dimensional $^{27}\text{Al}$ NMR under magic angle spinning. Appl Phys Lett 2003, 83:4023-4025.

11. Utz M, Nanagopalan M, Mathias W, Papadimitrakopoulos F: Characterization of molecular disorder in vapor-doped thin film of aluminum tris(8-hydroxyquinolate-8-olate) by one-dimensional $^{27}\text{Al}$ NMR under magic angle spinning. J Chem Phys 2006, 124:0347051-0347058.

12. Brauner T, Poupko R, Luz Z, Gutsche P, Meinel C, Zimmermann H, Haeberlen U: The dynamic disorder of azulene: A single crystal deuterium nuclear magnetic resonance study. J Chem Phys 2000, 112:10858-10870.

13. Goldbourt A, Madhu PK: Multiple-quantum magic-angle spinning: High-resolution solid state NMR spectroscopy of half-integer quadrupolar nuclei. Annu Rep NMR Spectrosc 2004, 54:81-153.

14. Laws DD, Bitter Hans-Marcus L, Jerschow A: Solid-state NMR spectroscopic methods in chemistry. Angew Chem Int Ed 2002, 41:3096-3129.

15. Schurko RW, Wasylishen RE, Foerster H: Characterization of anisotropic aluminum magnetic shielding tensors. Distorted octahedral complexes and linear molecules. J Phys Chem A 1998, 102:9750-9760.

16. Kajiwara Y, Ono S, Horii F: Relationships between light-emitting properties and different isomers in polymorphs of tris(8-hydroxyquinoline) aluminum(III) (Alq3) analyzed by solid-state $^{27}\text{Al}$ NMR and Density Functional Theory (DFT) calculations. Jpn J Appl Phys 2003, 42:3706-3711.

17. Neyer CJ: Essentials of Computational Chemistry-Theories and Models, 3rd edition. Chichester: John Wiley and Sons; 2003.

18. Massiot D, Fayon F, Capron M, King I, Calve SL, Alonso B, Durand Jean-Olivier, Bujoli B, Gan Z, Hoatson G: Characterization of local structures in amorphous and crystalline tris(8-hydroxyquinoline) aluminum(III) (Alq3) by solid-state $^{27}\text{Al}$ MQMAS NMR spectroscopy. Chem Phys Lett 2009, 471:80-84.

Publish with ChemistryCentral and every scientist can read your work free of charge

“Open access provides opportunities to our colleagues in other parts of the globe, by allowing anyone to view the content free of charge.”

W. Jeffery Hurst, The Hershey Company.

- available free of charge to the entire scientific community
- peer reviewed and published immediately upon acceptance
- cited in PubMed and archived on PubMed Central
- yours — you keep the copyright

Submit your manuscript here:
http://www.chemistrycentral.com/manuscript/