ChemComm
www.rsc.org/chemcomm

The structure of the blue luminescent δ-phase of tris(8-hydroxyquinoline)aluminium(III) (Alq_3)†

Michael Cölle,*[a] Robert E. Dinnebier[b] and Wolfgang Brütting‡[a]
[a] *Universität Bayreuth, Experimentalphysik II, Universitätsstr. 30, 95440 Bayreuth, Germany. E-mail: michael.coelle@uni-bayreuth.de; Fax: +49 (0)921-55 26 21; Tel: +49 (0)921 55 26 02*
[b] *Max-Planck-Institute for Solid-State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany. E-mail: R.Dinnebier@fkf.mpg.de; Fax: +49 711-689-1502; Tel: +49 711-689-1503*

Received (in Cambridge, UK) 19th September 2002, Accepted 8th October 2002
First published as an Advance Article on the web 5th November 2002

The existence of the facial isomer in the δ-phase of Alq_3 is proven by X-ray structural analysis, revealing that both the different molecular structure and the weaker overlap of the π-orbitals of hydroxyquinoline ligands belonging to neighboring Alq_3 molecules as compared to other phases (α, β) are likely to be the origin of the significantly different optical properties of δ-Alq_3.

Alq_3 is a stable metal chelate complex that can be sublimed to yield thin films and stands as one of the most successful materials used in organic light emitting devices for display applications. Although the partly nanocrystalline character of evaporated films used in these applications was known,[1,2] so far comparatively few investigations have been devoted to the crystalline state of this material.[3,4] A still unresolved issue concerns the isomery of the Alq_3 molecule. It is well-known that octahedral complexes of the type MN_3O_3, where M is a trivalent metal and N and O stand for the nitrogen and oxygen atoms in the hydroxyquinoline ligands, can occur in two different geometrical isomers: meridional and facial.[5–7,20] For the latter one quantum chemical calculations predict a larger energy gap which would result in a blue-shift of the fluorescence.[5,7] However, until recently all existing phases (α, β and γ) have been found to consist of the meridional isomer.[3,8]

In a previous publication we have reported a new crystalline phase of Alq_3 (δ-Alq_3) exhibiting strongly blue-shifted fluorescence.[4] Its significantly different optical properties have been tentatively discussed in terms of the isomery of the Alq_3 molecule. Vibrational analysis supported the assumption of the facial isomer in δ-Alq_3,[9,10]but from all methods used so far (*e.g.* photoluminescence, infrared and Raman measurements) it was not possible to distinguish clearly between intermolecular and intramolecular origin of the blue-shift. Very recent studies of the thermal and structural properties of Alq_3 gave more insight in the forming properties of the different phases, identifying a phase transition at about 385 °C to be the origin for the formation of δ-Alq_3.[11] Thus we are now able to produce pure powder of δ-Alq_3 without significant admixture of other phases in larger amounts by annealing α-Alq_3, *e.g.* for 6 h at 390 °C. It has therefore been possible to obtain well-resolved powder diffraction spectra using synchrotron radiation (see Fig. 1).

The unit cell§ obtained is different from that published by Braun *et al.* as in their samples some admixtures of other phases have been present giving 4 peaks instead of 3 peaks at low diffraction angles, which has lead to a wrong indexing.[4,11] We note that the unit cell volume for δ-Alq_3 of 1072.38 Å^3 is nearly the same value as reported for the β-phase of Alq_3,[3] however, lattice parameters and angles are significantly different for the δ-phase.

A global optimization method in direct space using simulated annealing followed by Rietveld refinement resulted in the crystal structure shown in Fig. 3.§ From the high quality of the refinement with a Rwp value of 6.5% as shown in the difference pattern in Fig. 1, there is strong evidence that the δ-phase consists of the facial isomer of Alq_3 shown in Fig. 2. Refinement under the assumption of the meridional isomer resulted in a distorted molecule, whereby the distance for one coordination bond (Al–N) was elongated compared to the isolated molecule and a 9% worse Bragg R value was obtained compared to the facial isomer (RF^2 = 10.5% facial, 19.4% meridional).¶ From these results δ-$Alq_3$is a nearly pure phase of the facial isomer.

In our former work, based on vibrational analysis by IR and Raman measurements, the significantly blue-shifted photoluminescence and the reduced intersystem crossing rate, we suggested δ-Alq_3 to consist of the facial isomer.[4,9,10] However, the structural analysis presented here is the first clear evidence for the facial isomer in Alq_3. The structure of δ-Alq_3 obtained from synchrotron powder diffraction measurements is shown in Fig. 2 and Fig. 3. The molecule is only slightly distorted

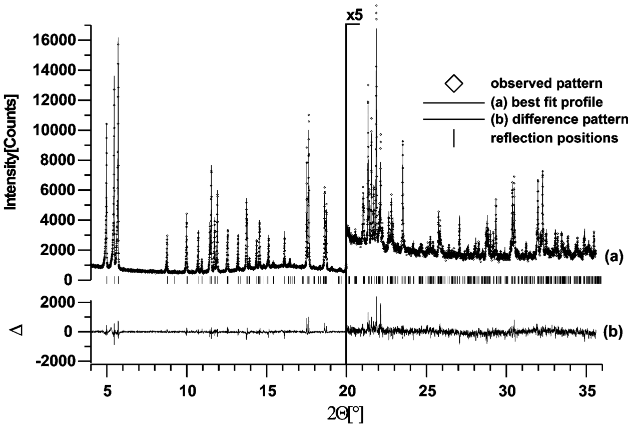

Fig. 1 Scattered X-ray intensity for δ-Alq_3 at ambient conditions as a function of diffraction angle 2θ. Shown are the observed patterns (diamonds), the best Rietveld-fit profiles (line) and the enlarged difference curves between observed and calculated profiles in an additional window below. The high angle part is enlarged by a factor of 5, starting at 20°. The wavelength was λ = 1.15 Å.

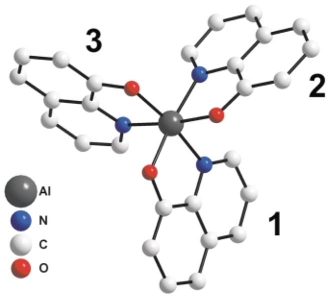

Fig. 2 Alq_3 molecule of the δ-phase with the three hydroxyquinoline ligands labelled with **1**, **2** and **3**.

---

† Electronic supplementary information (ESI) available: experimental section and crystallographic data. See http://www.rsc.org/suppdata/cc/b2/b209164j/

‡ Present address: University of Saarland, Electronics and Semiconductor Devices, 66041 Saarbrücken, Germany.

DOI: 10.1039/b209164j

reducing weakly its symmetry and the planes defined by the O and N-atoms, respectively, are parallel.§

Another factor is molecular packing in the crystal. Interestingly the molecules are arranged in a manner minimising the possible overlap of the π-orbitals between pairs of hydroxyquinoline ligands belonging to neighbouring Alq$_3$ molecules as shown in Fig. 3. As demonstrated by Brinkmann *et al*. the orbital overlap influences the optical properties and can explain shifts in the photoluminescence spectra of different phases of Alq$_3$. Here the pyridine rings of antiparallel ligands **1** face each other with an interligand distance of 3.4Å (Fig. 3(a)). The partial overlap of the rings is smaller as compared to the other known phases‖ [3] and the atoms are slightly displaced, further reducing the overlap of the π-orbitals. Fig. 3(b) and 3(c) show the projection perpendicular to the planes of ligand **2** and ligand **3**, respectively. The interligand distance is about 3.45 Å and these ligands do not overlap at all. Thus we find a strongly reduced π-orbital overlap of neighbouring ligands in δ-Alq$_3$ as compared to the α- and β-phase. As only one ligand of each molecule overlaps with a neighboured molecule there are no π–π links generating an extended one-dimensional chain as reported for the β-phase, so the interaction is limited to two molecules. We believe that this packing effect together with the changed symmetry of the molecule are responsible for the large blue-shift of the photoluminescence by 0.2 eV, which is in the same range as predicted theoretically by Curioni *et al*. for the two isomers.[5]

Due to its importance for applications such as organic light emitting devices (OLEDs), intense research has been performed on Alq$_3$. The facial isomer has been searched for many years and now it is clearly identified in the δ-phase of Alq$_3$. Its different geometry, higher dipole moment and different electronic properties are expected to be of high relevance for film forming and transport properties and thus for the performance of OLEDs. With our simple preparation method it is now possible to obtain large amounts of pure facial Alq$_3$ for further measurements. In preliminary experiments we have successfully converted amorphous thin films of yellowish green Alq$_3$ into films showing blue fluorescence.[11]** Their application in OLEDs is under investigation.

Research was carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory (supported by the US Department of Energy under Grant No. DE-FG02-86ER45231). Special thanks are due to P. Stephens (Stony Brook) for his help during data collection, J. Gmeiner (Bayreuth) for sample preparation and S. Forero (Bayreuth) for helpful discussions. Financial support by the DFG, the BMBF and the FCI is gratefully acknowledged.

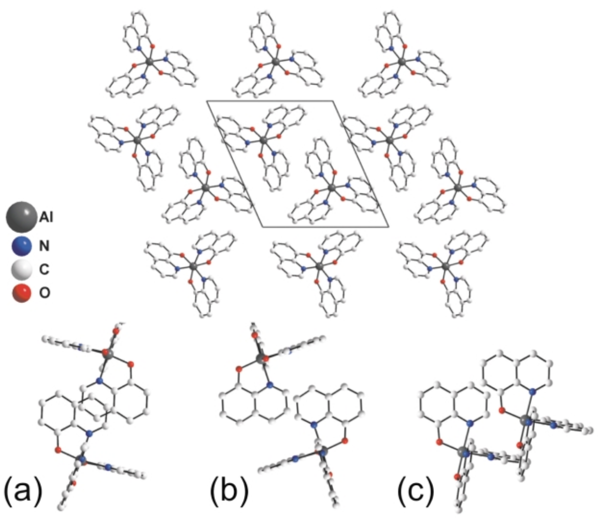

Fig. 3 Crystal structure of δ-Alq$_3$ in a projection along the *c*-axis. (a), (b) and (c) are projections perpendicular to the planes of the hydroxyquinoline ligands **1**, **2** and **3**, respectively, showing the overlap between ligands of neighbouring Alq$_3$ molecules.

Notes and references

§ a) Crystal structure data of δ-Alq$_3$: triclinic unit cell, space group $P\bar{1}$, $a = 13.24116(11)$, $b = 14.42446(12)$, $c = 6.1768(4)$ Å, $\alpha = 88.5553(7)°$, $\beta = 95.9230(6)°$, $\gamma = 113.9332°(5)$, $V = 1072.382(15)$ Å^3, $\rho_{\mathrm{calc}} = 1.423$ gcm^{-3}, $Z = 2$, $\mu = 2.48$ cm^{-1}. b) Devices for X-ray diffraction experiments: 2-circle Huber diffractometer at the Suny X3B1 beamline at Stony Brook double Si(111) monochromator, Ge(111) crystal analyzer, $\lambda = 1.14982(2)$Å, Na(T1)I scintillation counter with pulse height discriminator, $T = 295$ K, $4.0° < 2\theta < 35.7°$ in steps of 0.005° 2θ, glass capillary of 0.7 mm diameter. c) Structure determination process: Data reduction and background modeling by using the GUFI program,[12] indexing with Visser,[13] peak profiles and precise lattice parameters were determined by LeBail-type fits[14] using the programs GSAS[15] and FULLPROF.[16,17] Structure determination by a global optimization method in direct space[18] using the DASH program (CCDC, 12, Union Road. Cambridge. CB2 1EZ. UK). Rietveld refinements[19] using GSAS led to agreement factors of Rp = 0.05, Rwp = 0.065, RF^2 = 0.105, $\chi^2 = 1.6$, 357 reflections, number of variables 115, slack soft constraints for bond lengths, angles and the planarity of the functional hydroxyquinoline groups to stabilize the refinement. d) Further details on the crystal structure investigation as well as tables of crystallographic data, positional parameters, temperature factors as well as selected bond lengths and angles for δ-Alq$_3$ are available as electronic supplementary information (ESI). See http://www.rsc.org/suppdata/cc/b2/b209164j/.

¶ Detailed data and tables of crystallographic data, positional parameters, temperature factors as well as selected bond lengths and angles for the assumption of the meridional isomer are available as ESI. See http://www.rsc.org/suppdata/cc/b2/b209164j/.

‖ Measurements, simulated annealing and Rietveld refinements of samples prepared by sublimation method as described in Ref. 4 (there called fraction 3) verified the data published by Brinkmann *et al*. for the α-phase of Alq$_3$ including the spatial overlap of the π-orbitals of neighbouring molecules (ligands B/B′).

** We note that the facial molecule in the δ-phase of Alq$_3$ reconverts for the most part to the meridional molecule during evaporation onto unheated substrates or after dissolving it in polar solvents like chloroform. When stored at ambient conditions, however, the δ-phase is stable for months.

1 C. Tang and S. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
2 C. Jonda, A. B. R. Mayer, U. Stolz, A. Elschner and A. Karbach, *J. Mater. Sci.*, 2000, **35**, 5645.
3 M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi and A. Sironi, *J. Am. Chem. Soc.*, 2000, **122**, 5147.
4 M. Braun, J. Gmeiner, M. Tzolov, M. Cölle, F. Meyer, W. Milius, H. Hillebrecht, O. Wendland, J. von Schütz and W. Brütting, *J. Chem. Phys.*, 2001, **114**, 9625.
5 A. Curioni, M. Boero and W. Andreoni, *Chem. Phys. Lett.*, 1998, **294**, 263.
6 R. Martin, J. Kress, I. Campbell and D. Smith, *Phys. Rev. B*, 2000, **61**, 15804.
7 M. Amati and F. Lelj, *Chem. Phys. Lett.*, 2002, **358**, 144.
8 G. Kushto, Y. Iizumi, J. Kido and Z. H. Kafafi, *J. Phys. Chem. A*, 2000, **104**, 3670.
9 M. Cölle, J. Gmeiner, W. Milius, H. Hillebrecht and W. Brütting, *Proceedings of the EL2002*, Ghent, 2002, 133.
10 M. Cölle, S. Forero-Lenger, J. Gmeiner and W. Brütting, submitted to *J. Chem. Phys*.
11 M. Cölle, J. Gmeiner, W. Milius, H. Hillebrecht and W. Brütting, *Adv. Funct. Mat.*, 2002 accepted.
12 R. E. Dinnebier and L. Finger, *Z. Krist. Suppl.*, 1998, **15**, 148GUFI 5.0 available at http://www.mpi-stuttgart.mpg.de/xray/.
13 J. W. Visser, *J. Appl. Cryst.*, 1969, **2**, 89–95.
14 A. Le Bail, H. Duroy and J. L. Fourquet, *Mat. Res. Bull.*, 1988, **23**, 447–452.
15 A. C. Larson and R. B. von Dreele, *GSAS—General Structure Analysis System, Los Alamos National Laboratory Report LAUR*, 1994, 86–748 available by anonymous FTP from ftp://ftp.lanl.gov/public/gsas/.
16 J. R. Carvajal, *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France*, 1990, 127.
17 J.R. Carvajal, 2001, PROGRAM FullProf.2k, Version 1.9c May2001-LLB JRC; available at http://www-llb.cea.fr/fullweb/fp2k/fp2k.htm.
18 W. I. F. David, K. Shankland and N. Shankland, *Chem. Commun*, 1998, 931–932.
19 H. M. Rietveld, *J. Appl. Cryst.*, 1969, **2**, 65–71.
20 M. Amati and F. Lelj, *Chem. Phys. Lett.*, 2002, **363**, 451.