55.1: Invited paper: the isomerism of the Alq3 molecule: evidence from structural, thermal and photophysical investigations

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55.1 Invited Paper: The Isomerism of the Alq3 Molecule: Evidence from Structural, Thermal and Photophysical Investigations

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Abstract

Tris(8-hydroxyquinolinato)aluminum(III) (Alq3) stands as one of the most successful materials used in organic light emitting devices (OLEDs) for display applications. In spite of its wide usage in these devices two key issues of the material, namely its isomerism and triplet state remained unresolved for many years. In this paper, we provide evidence for the existence of the facial isomer of Alq3 from a combination of structural, thermal and photophysical investigations. Moreover, we present experimental results on the energy and lifetime of the triplet state in Alq3.

1.   Introduction

From the viewpoint of chemistry, 8-hydroxyquinoline metal chelate complexes like Alq3 are old materials and were used already in the 1950s for a gravimetric determination of various metal cations in solution [1]. It was well-known that these 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 quinoline ligands, can occur in two different geometric isomers: meridional and facial, as shown in Figure 1. In spite of first indications from mass spectrometry, however, the clear identification and isolation of the facial isomer of Alq3 was not possible at that time [2].

Renewed interest in this class of materials came up with the report of efficient electroluminescent devices using Alq3 as the active medium [3]. These OLEDs opened the way for a new generation of flat panel displays. After nearly two decades of intensive research and development, Alq3 still continues to be the workhorse in low-molecular weight materials for these devices. It is used as electron transporting layer, as emission layer, where green light emission is generated by electron-hole recombination in Alq3, and it also serves as host material for various dyes to tune the emission color from green to red. Many studies in this field have focused on the optimization of device performance with respect to efficiency and long-term stability or on the understanding of charge transport properties of amorphous thin films [4-8]. Only recently, investigations started on the material's structural, electronic and optical properties in the crystalline state [9,10]. This turned out to be the key for the isolation and identification of the facial isomer of Alq3 [11-13].

Another unresolved issue was the triplet state in Alq3. Although its properties (energy and lifetime) are of outmost importance for understanding non-radiative losses and triplet energy transfer

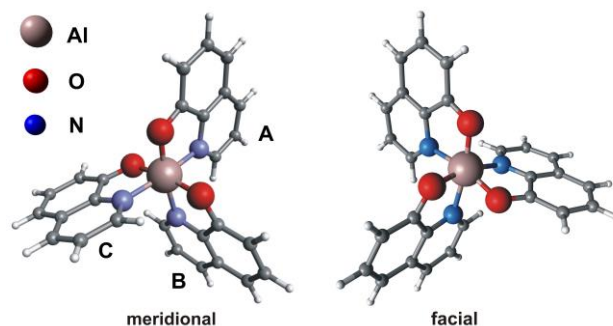processes in OLEDs, until recently there was no direct observation of the triplet state in Alq3.

Figure 1: Molecular structure of the meridional and facial isomer of Alq3.

2.   Preparation and Identification of Facial Alq3

Temperature gradient sublimation, a common method for the purification of organic materials, was used to induce growth of different phases of Alq3. As a result, polycrystalline powders of different appearance (color and shape of crystals) were found in the sublimation tube. A typical example of such a glass tube after sublimation is shown in Figure 2. The obtained fractions have different solubility in organic solvents. While fraction 3 and (apart from a small residue) also fraction 2 are readily dissolved in chloroform at relatively high concentration of more than 1% by weight, the solubility of fraction 1 is extremely poor. It takes several hours to dissolve a sizeable amount in chloroform, but then the color of the solution becomes similar to that of the other two fractions.

Further differences between the three fractions are found in their photoluminescence (PL) spectra. Figure 3 shows the spectra measured with an excitation wavelength of 350nm at room temperature. All fractions show one broad, featureless PL band. Their main difference is the large blue shift of the PL maximum of about 0.19eV (36nm) from fraction 3 to fraction 1 with a PL maximum at about 506nm (2.45eV) and 470nm (2.64eV), respectively. For comparison: an evaporated Alq3 film on glass has a PL maximum at about 515nm (2.4eV). The emission color is shifted from green for fraction 3 (CIE coordinates: x=0.27, y=0.5) to blue in fraction 1 (x=0.16, y=0.26). The PL quantum efficiencies obtained for blue Alq3, yellowish-green powder and an evaporated

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film were 51%, 40% and 19%, respectively. This is a direct indication that structural ordering could lead to higher luminescence yield also in OLEDs.
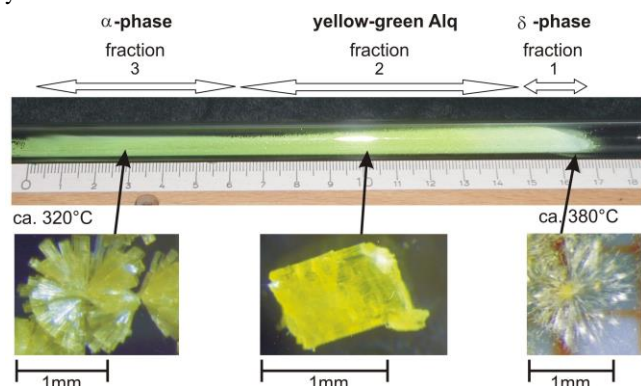

Figure 2: Picture of a temperature gradient sublimation tube. Due to the temperature gradient in the sublimation tube, the material obtained is separated into three zones, which are labeled by fraction 1, fraction 2 and fraction 3. Crystals of these fractions in the tube are also shown.
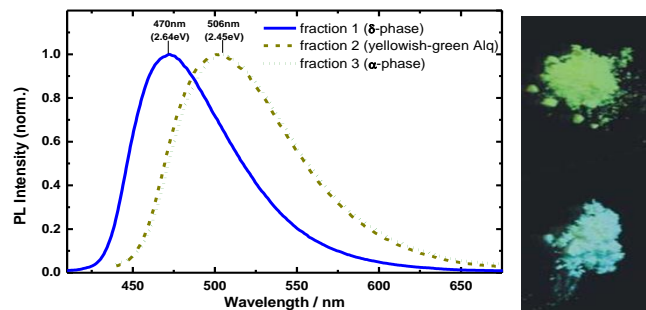

Figure 3: Photoluminescence spectra of polycrystalline Alq$_3$ samples taken from different regions of the sublimation tube. The visual appearance of powders from fraction 1 and 3 under UV light is shown to the right.

	α-phase (fraction 3)	γ-phase	δ-phase (fraction 1)
crystal system	triclinic	trigonal	triclinic
space group	P-1	P-31c	P-1
Z	2	2	2
a [Å]	12.91	14.41	13.24
b [Å]	14.74	14.41	14.43
c [Å]	6.26	6.22	6.18
α [°]	89.7	90	88.55
β [°]	97.7	90	95.9
γ [°]	109.7	120	113.9
V [Å^3]	1111	1118	1072.5

Table 1: Crystallographic data of the obtained crystalline phases of Alq$_3$ together with another high-temperature phase obtained by Brinkmann et al. [9].

In order to investigate the origin of these differences, the crystallographic data of the three fractions were determined by using X-ray powder diffraction [10,12]. As a result two different phases were found: the well-known α-phase of Alq$_3$ (fraction 1) and a new high-temperature phase (δ-Alq$_3$). Their unit cell parameters are summarized in Table 1 together with another high-temperature phase (γ-Alq$_3$) found by Brinkmann et al. [9]. The X-ray data also

show that fraction 2 mainly consists of α-Alq$_3$ with small admixtures of the δ-phase.

The phases discussed above were grown in different areas of the sublimation tube in regions of different temperature. Thus, temperature obviously has a strong influence on the growth of these phases. Therefore the formation conditions of the different phases of Alq$_3$ were investigated using differential scanning calorimetry (DSC) measurements [12]. As displayed in Figure 4, upon heating Alq$_3$ two phase transitions can be observed: an exothermic one at about 380°C and an endothermic transition at 415°C, where the latter is clearly ascribed to the melting of Alq$_3$.
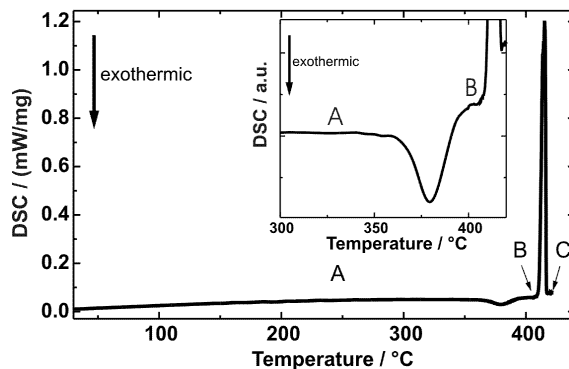

Figure 4: DSC trace of Alq$_3$ measured at a heating rate of 2°C/min. The clearly pronounced exothermic phase transition at 380°C prior to the melting point is enlarged in the inset.

In these DSC measurements three different regions are distinguished. In the first region (A), below the exothermic phase transition, Alq$_3$ is the usual yellowish green powder (α-phase). In the second region (B), between this phase transition and the melting peak, Alq$_3$ is a whitish powder showing blue fluorescence, which is identified to be the δ-phase. Finally, in region (C), Alq$_3$ is a liquid melt. Repeated thermal cycling has revealed that α-Alq$_3$ and δ-Alq$_3$ can be fully converted into each other. Yellowish-green Alq$_3$ annealed above the phase transition at 380°C results in blue Alq$_3$, whereas annealing blue Alq$_3$ above the melting point and cooling it down slowly yields yellowish-green powder again. The successful conversion from one phase into the other was confirmed by measurements of the PL spectra, FT-IR spectra, Raman spectra, and X-ray diffraction [12-14]. Further, these measurements could show that blue luminescent Alq$_3$ obtained by train sublimation as described above and by annealing show the same behavior. Therefore it is possible to obtain pure δ-phase material without any visible admixtures of other phases under appropriate annealing conditions (390°C, inert atmosphere). Thus, by a simple annealing process large amount (several grams) of pure δ-Alq$_3$ can be fabricated in a well-controlled manner.

According to quantum chemical calculations by Curioni et al. [15], the observed blue shift of the PL in δ-Alq$_3$ was a strong indication for the presence of the facial isomer in this phase. The final proof, however, was given by structure determination. Using modern powder diffraction methods based on high-resolution synchrotron data, we have been able to resolve the molecular structure of the δ-phase of Alq$_3$ [11]. It could unambiguously be shown that it consists of the facial isomer. The assignment of the facial isomer as being the only constituent of the δ-phase of Alq$_3$ was also confirmed by infrared measurements where the higher symmetry of the facial isomer can be seen in a reduced number of

stretching vibrations around the central Al atom [14]. Further evidence comes from recent NMR measurements where the different electric field gradient tensors for the two isomers give characteristic fingerprints for their identification in solid state Al-NMR spectra [16]. Moreover, the group at Eastman Kodak has been able to grow single crystals of δ-Alq3 large enough for a single crystal structure analysis confirming our results [17].
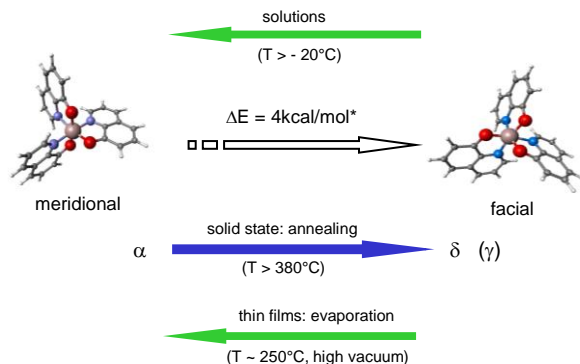

Figure 5: Schematic phase transformation diagram of Alq3. (*Value for ΔE taken from Ref. [15])

Based on these findings, a phase transformation diagram of Alq3 can be constructed as shown schematically in Figure 5. Starting from the usual yellowish-green α-phase (meridional isomer) the blue-fluorescent δ-phase of Alq3 (facial isomer) can be obtained by a solid-state transition at 380°C. After cooling to room temperature, δ-Alq3 is fully stable without any indication of a back reaction. However, this stability gets lost as soon as the structure is no longer stabilized by packing effects in the solid state. In solution or in the vapor phase the facial isomer readily converts back to the meridional one. In particular the evaporation of δ-Alq3 to fabricate thin films as used in OLEDs always results in the usual yellowish-green light emission known from the meridional isomer. Thus the fabrication of blue OLEDs from facial Alq3 has not yet been successful. We note that Muccini et al. have reported on the stabilization of the facial isomer in solution at low temperature (<-20°C) and the fabrication of thin films showing blue fluorescence [18], however, it remains questionable whether these experiments were really dealing with molecular solutions or just suspensions of very small grains. Brinkmann et al. used the preparation method that is described here to obtain different phases of tris(8-hydroxyquinoline) gallium (Gaq3) [19]. Thereby the same properties as with Alq3 were observed. Thus the described scenario seems to be a general feature of this class of metal chelate complexes.

3.   The Triplet State of Alq3

A characteristic property in the photophysics of organic semiconductor materials is the existence of distinct singlet and triplet states as shown in Figure 6. Whereas light absorption and emission via fluorescence between the S_0 and S_1 states are allowed processes having high oscillator strength and short lifetime of a few nanoseconds, transitions between the singlet and triplet manifold are disallowed and thus very weak. In particular the direct $T_1 \rightarrow S_0$ transition via phosphorescence is usually not seen at room temperature in materials that do not contain heavy elements.
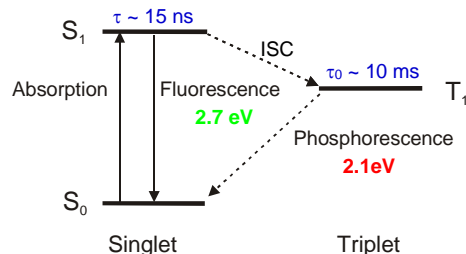

Figure 6: Photophysical processes in an organic molecule. The given numbers are for the meridional Alq3 isomer.

Therefore, until recently, the determination of the triplet properties of Alq3 has been based on indirect methods. For example, Baldo et al. determined a lifetime of the triplet state of about 25µs from measurements of the exciton diffusion length at room temperature using a phosphorescent sensing layer and the triplet energy was inferred from similar metal-chelate complexes [20]. Burrows et al. published a phosphorescence spectrum of Alq3 in an ethyl iodide glass matrix [21]. Very recently, we measured the electro-phosphorescence of Alq3-based OLEDs by using delayed electroluminescence [22], further, phosphorescence was found for all crystalline phases and for the evaporated amorphous film [23-25]. Here we summarize the results that were mainly obtained by delayed fluorescence as well as by phosphorescence measurements of Alq3.
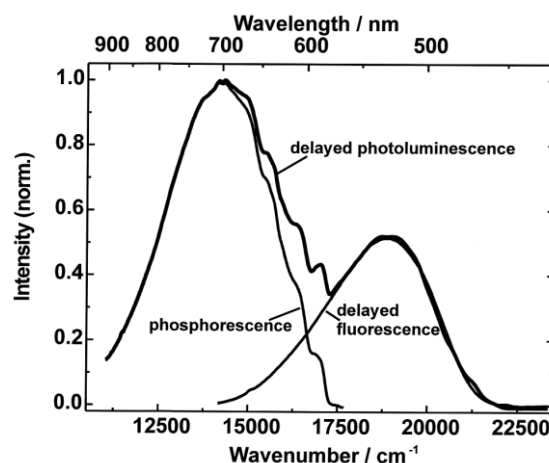

Figure 7: Delayed photoluminescence spectrum of α-Alq3 at 10 K. The excitation wavelength was 442 nm.

Figure 7 shows a typical spectrum of delayed PL for a crystalline sample of α-Alq3 measured at low temperature. The spectrum consists of two components: one is delayed fluorescence (DF) at the same spectral position where the spontaneous PL is located (Figure 3), the second one in the long wavelength range is due to phosphorescence from the triplet state. The deconvolution of the two contributions allows determining the onset of phosphorescence which directly yields the energy of the lowest triplet state T_1. From the data in Figure 7 a value of (2.11 ± 0.1)eV is determined for α-Alq3. This has to be compared with the energy of the first excited singlet state S_1 being 2.7eV [10].

Further information about the triplet state in Alq3 was obtained by investigating the time dependent decay of DF and phosphorescence as shown in Figure 8. For both components we observe monoexponential decays, however, with different decay times. It

is instructive to recall that DF results from the annihilation of two triplets resulting in one excited singlet state which then emits DF. Thus DF is a bimolecular process and its intensity is proportional to the square of the number of triplets: $I_{DF} \propto [T_1]^2$. Therefore, for an exponential decay of the triplet population with a lifetime τ_0 one expects to see also an exponentially decaying DF signal with a decay constant τ_{DF} being just one half of the triplet lifetime.

As can be seen from Figure 8 and Table 2 the determined decay times of the two components are in agreement with this model for all crystalline Alq$_3$ samples and also an evaporated film [23]. Furthermore, temperature dependent investigations have revealed that this relation is fulfilled over the whole temperature interval from 10 to 120K where DF and phosphorescence were detectable [24].
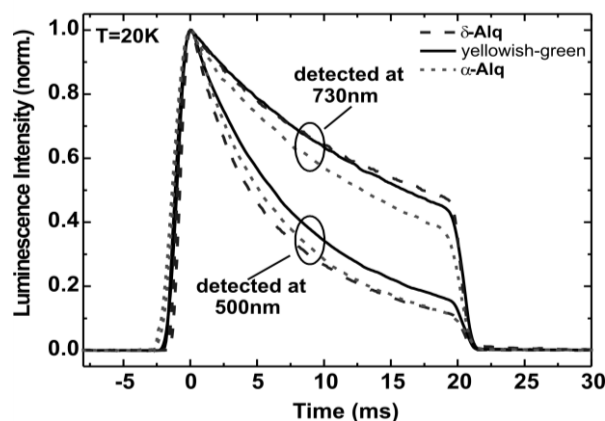

Figure 8: Decay of the delayed photoluminescence signals for different samples.

	τ_{DF} [ms]	$\tau_0 = 2\tau_{DF}$ [ms]	τ_{730} [ms]	τ_{730}/τ_{DF}
α-Alq$_3$	6.6±0.5	13.2±1	13.6±0.5	2.05
Yellow-ish-green	7.8±0.5	15.6±1	16.2±0.5	2.08
δ-Alq$_3$	6.2±0.5	12.4±1	13.2±0.5	2.13
Film	4.33±0.5	8.66±1	9.3±0.5	2.15

Table 2: Lifetimes obtained from the transient measurements of delayed photoluminescence shown in Figure 8.

It can be seen that the triplet lifetimes of all polycrystalline phases of Alq$_3$ as well as of the amorphous film are very similar. The most important difference in the triplet properties is again between the meridional isomer (α-phase) and the facial one (δ-phase). The latter has a slightly higher triplet energy of (2.16±0.1)eV and a significantly reduced intersystem crossing as demonstrated in transient PL measurements [10].

4.   Conclusion

We have been able to resolve two key questions related to Alq$_3$ as an OLED material. One is the identification and isolation of the facial isomer in a high temperature phase (δ-phase). The second one concerns the triplet energy and lifetime of Alq$_3$. Both issues are directly related to the use of Alq$_3$ in OLEDs as the presence of the facial isomer might have an influence on film growth, charge transport and light emission in these devices. Moreover, the facial

isomer might allow to prepare blue OLEDs from Alq$_3$. The knowledge of the triplet state is required to understand nonradiative losses as well as to improve light output by making use of triplet energy transfer. We anticipate that a deeper understanding of molecular and solid state properties of Alq$_3$ will help to further improve OLEDs based on these materials [26].

5.   Acknowledgements

6.   References

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