

Short communication

## Electron spin resonance of thin films of organic light-emitting material tris(8-hydroxyquinoline) aluminum doped by magnesium

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## ABSTRACT

We have successfully observed electron spin resonance (ESR) signals of radical anions in thin films of tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), a compound widely used as electron transporting and luminescent layers in organic light-emitting diodes. To obtain definitely defined radical-anion states in Alq<sub>3</sub>, we doped Alq<sub>3</sub> with Mg by co-evaporating these materials. The obtained *g* value and peak-to-peak ESR linewidth  $\Delta H_{pp}$  of Alq<sub>3</sub> radical anions are 2.0030 and 2.19 mT, respectively. Theoretical *g* value and hyperfine interactions were calculated by density functional theory method, which are in good agreement with the experimental results. A quantitative evaluation of doping concentration was performed. We confirmed that doped charges are localized at deep trapping sites by the lineshape analysis and temperature dependence of the ESR signals. Morphological investigation using transmission electron microscopy clarified that the co-evaporated Mg atoms form clusters.

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## 1. Introduction

Since the first multilayered organic light-emitting diode (OLED) was introduced by Tang et al. [1], there have been drastic improvements in their device performance, and OLEDs are now ready to be commercialized [2,3]. OLEDs are currently ones of the strong candidates for next-generation displays and lightings owing to their excellent characteristics [2]. However, there are still several problems remain to be clarified such as degradation mechanisms and charge carrier states in OLEDs [3]. Investigating charge-carrier states in organic thin films is also a fundamental subject in basic science in addition to significant contribution for understanding device operation in OLEDs.

Charge carriers in organic materials can be described as radical ions and are usually accompanied with spins. Electron spin resonance (ESR) spectroscopy is suitable for investigating charge carriers in organic semiconductors and their devices from microscopic viewpoints, because it can directly observe electron spins. We have applied this spectroscopy not only to organic semiconducting materials [4] but also to organic semiconductor devices

under operation such as organic field-effect transistors (OFETs) [5–7] and organic solar cells (OSCs) [8]. We also performed ESR study to investigate charge-carrier states of radical cations in *N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine (NPB), a typical hole transporting material in OLEDs [9]. Pawlik et al. demonstrated that ESR study is also effective for OLEDs [10].

Alq<sub>3</sub> is a compound widely used as a luminescent and electron transporting material in OLEDs [1]. The chemical structure of Alq<sub>3</sub> is shown in Fig. 1. In OLED devices, electrons are injected from cathode to Alq<sub>3</sub>, which forms radical anions (negative polarons). Characterizing these radical anions is one of the most important issues associated with charge-carrier states of the real devices. There have been several reports for ESR characterization of Alq<sub>3</sub> up to now [11–15]. However, these studies mainly observed residual paramagnetic species such as paramagnetic impurities or free radicals and did not identify the radical species in the ESR signals. Thus, a detailed ESR study on charge-carriers states in Alq<sub>3</sub> has not yet been reported.

In this study, we investigate the charge-carrier states of Alq<sub>3</sub> radical anions using the ESR method combined with density functional theory (DFT) calculation. To obtain definitely defined anion states of Alq<sub>3</sub>, doping by Mg was performed; such doping method is a common method to paramagnetize sample materials in the field of ESR study. Mg-doped Alq<sub>3</sub> films are also used as an electron injecting layer whereby the dopants seem to lower a potential barrier at Alq<sub>3</sub>/Al interface [16,17], and as an interconnecting layer in tandem-structure OLEDs [18]. In our ESR study, we clearly observed

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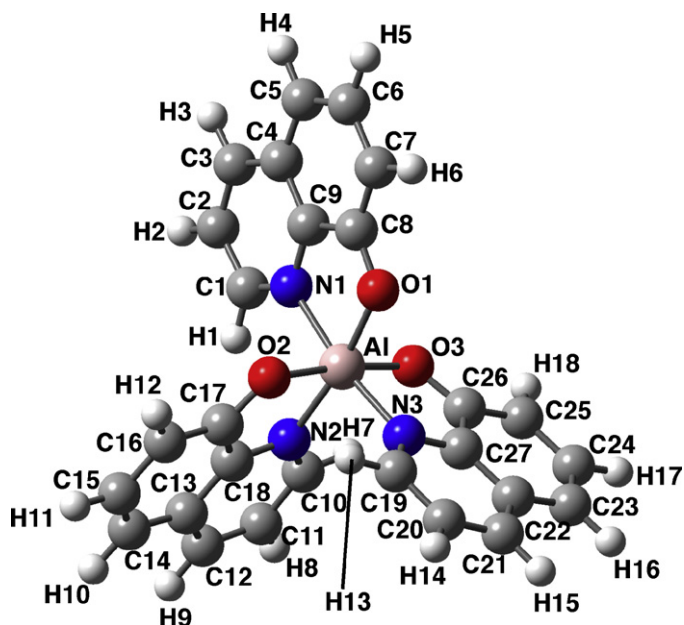


Fig. 1. Chemical structure and atomic numbering of AlQ<sub>3</sub>.

ESR signals due to AlQ<sub>3</sub> radical anions in Mg-doped AlQ<sub>3</sub> films. The observed *g* value and ESR linewidth are well explained by theoretical results based on the DFT calculation. We also present the doping concentration of charge carriers by ESR intensity. Lineshape analysis and temperature dependence of the ESR signals indicate that observed spins are localized. Transmission electron microscopy (TEM) observation showed that doped Mg atoms form clusters.

## 2. Experimental

Mg-doped AlQ<sub>3</sub> film samples were prepared in a vacuum chamber under pressure of  $2 \times 10^{-4}$  Pa by co-evaporating AlQ<sub>3</sub> and Mg on quartz substrates which were cleaned with isopropyl alcohol and acetone. Doping concentration was controlled by varying co-evaporation rate of AlQ<sub>3</sub> molecule and Mg atom. Subsequently, we deposited an additional Al layer on the Mg-doped AlQ<sub>3</sub> layer to protect Mg from oxidation. The thickness of layer for Mg-doped AlQ<sub>3</sub> and Al was 200 and 100 nm, respectively. The area of the layer was 0.84 cm<sup>2</sup>. Each sample was then put in an ESR sample tube, which was evacuated down to  $2 \times 10^{-5}$  Pa, and then finally sealed under vacuum conditions or He gas atmosphere at  $1.33 \times 10^4$  Pa. ESR measurements on these samples were performed with a JEOL FA200 ESR spectrometer. The absolute values of the *g* value, the ESR linewidth, and the number of spins of the samples were calibrated using a Mn<sup>2+</sup> marker as a standard sample. The number of spins of the samples was obtained by integrating the ESR signal twice and by comparing with that of the Mn<sup>2+</sup> marker in which the number of spins is known. TEM measurements were performed on AlQ<sub>3</sub>:Mg films that were deposited on a microgrid without Al layers.

DFT calculations were performed for an isolated AlQ<sub>3</sub> radical anion with the B3LYP functional and the 6-31G(d) basis set. The geometry is fully optimized for its meridional isomer. The calculations were carried out with the Gaussian 09 package [19].

## 3. Results and discussion

By using Mg doping, we have successfully observed ESR spectra of AlQ<sub>3</sub> radical anions in Mg-doped AlQ<sub>3</sub> thin films. This indicates that charge transfer between Mg and AlQ<sub>3</sub> takes place. The observed ESR spectra are shown in Fig. 2 for the films deposited

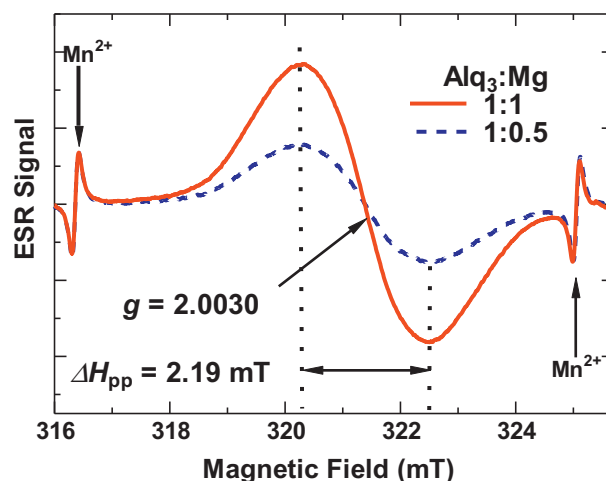


Fig. 2. ESR spectra of Mg-doped AlQ<sub>3</sub> thin films. Solid and dashed lines show the ESR spectrum of the sample co-evaporated in the ratio of 1:1 and 1:0.5 for AlQ<sub>3</sub> molecule and Mg atom, respectively.

by co-evaporating AlQ<sub>3</sub> and Mg in the ratio of 1:1 (solid curve) and 1:0.5 (dashed curve) for AlQ<sub>3</sub> molecules and Mg atoms. Signals around 316 mT and 325 mT are marker signals of a standard sample of Mn<sup>2+</sup>. AlQ<sub>3</sub> molecules are originally nonmagnetic, while magnetic moments arise when electrons are injected into AlQ<sub>3</sub> molecules [20]. Actually, our ESR measurement on a pure AlQ<sub>3</sub> thin film did not show any ESR signals, which means the amount of paramagnetic species in the undoped sample is under detection sensitivity. Our observation of the spectra in the doped samples is consistent with previous report that the AlQ<sub>3</sub>/Mg interface forms an ohmic contact under vacuum condition and a large amount of charge carriers enter the AlQ<sub>3</sub> layer without applying voltage [21].

As seen in Fig. 2, both *g* value (2.0030) and peak-to-peak ESR linewidth  $\Delta H_{pp}$  (2.19 mT) do not change with each other in spite of the different doping ratios. Both samples did not show any angular dependence to external magnetic field, reflecting amorphous nature of molecular orientation in thin films. The three principal *g* values are calculated as 2.0024, 2.0029, and 2.0032 at the B3LYP/6-31G(d) level. These theoretical values are excellently consistent with the observed *g* value. This consistency strongly supports our assignment of AlQ<sub>3</sub> radical anions in the ESR spectra, since the *g* value is a fingerprint to identify the molecular species in ESR measurements. The observed single ESR spectrum is reasonable, when we consider the *g* shifts small enough compared with the linewidth in the samples of amorphous nature.

Next, we discuss the linewidth of the ESR spectra. The  $\Delta H_{pp}$  of 2.19 mT of (AlQ<sub>3</sub>)<sup>-</sup> looks somewhat broad compared to other organic materials. For example,  $\Delta H_{pp}$  of 0.19 mT and 0.01 mT was reported for hole carriers in pentacene and rubrene FETs, respectively [6,7]. An ESR linewidth reflects the motion of charge carriers and the magnitude of hyperfine interactions. For example, the ESR linewidths in pentacene and rubrene FETs are narrowed because of the mobile nature of carriers in addition to small hyperfine interactions. Here, we examine the hyperfine interaction in (AlQ<sub>3</sub>)<sup>-</sup> molecule. (We will discuss the effects of motion of charges later.) Table 1 summarizes calculated anisotropic hyperfine coupling constants for the atoms that have nuclear spins in natural abundance. The table also includes the charge and spin densities,  $\rho$  and *s*, on each atom of an AlQ<sub>3</sub> anion evaluated by the natural population analysis. Fig. 3 shows spin density profile calculated by the DFT method. Large spin density on an atom gives rise to a large hyperfine interaction. For a carbon atom, an electron interacts not with this carbon nucleus itself but with a hydrogen nucleus covalently bonded to it. As seen in Table 1, the calculated hyperfine interactions in (AlQ<sub>3</sub>)<sup>-</sup> show that one nitrogen atom (N2)

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