



Letter

Negative giant surface potential of vacuum-evaporated tris(7-propyl-8-hydroxyquinolinolato) aluminum(III) [Al(7-Prq)₃] film



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ABSTRACT

Negative giant surface potential was realized in a vacuum-evaporated film of tris(7-propyl-8-hydroxyquinolinolato) aluminum(III) [Al(7-Prq)₃]. Electroabsorption response of the film presented an inverted polarity to that of tris(8-hydroxyquinolinolato) aluminum (Alq₃), suggesting opposite noncentrosymmetry of molecular orientation. Asymmetric dice model with molecular geometric effect has been proposed, and propyl substitution at 7 position of the ligands was indicated to affect the molecular posture on the surface to invert the polarity of noncentrosymmetry. Our results opened a new possibility of controlling molecular orientation in a film for device applications.

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Tris(8-hydroxyquinolinolato) aluminum(III) (Alq₃, Fig. 1a) and its derivatives are one of the promising material families for organic light-emitting diodes (OLEDs), and many investigations on the film structures, electric properties, and optical properties have been reported [1–6]. A peculiar phenomenon is giant surface potential (gSP) build-up reaching +50 V/μm in an Alq₃ film evaporated under dark condition [7–15]. Such huge polarization in an organic film is applicable to electronic devices and non-linear optical devices, if we can control the polarity and magnitude. The gSP build-up originates from the spontaneous noncentrosymmetric orientation of the molecular dipoles [7,8], although an evaporated Alq₃ film has an amorphous form. The degree of anisotropy was estimated to be small (order parameter $\langle \cos\theta \rangle \sim 1 \times 10^{-2}$) [7,9,13] and the mechanism of such small anisotropy is not fully understood yet. We have recently reported that the sense of

spontaneous dipole orientation of Alq₃ molecules does not depend on the substrate even when the substrate is the backside of the Alq₃ film, which has an opposite orientation of Alq₃ molecules [14,15]. Therefore, the interfacial interaction between the 1st Alq₃ layer and the substrate is not the trigger for the macroscopic molecular orientational anisotropy and thus emergence of gSP. We have proposed that the molecular geometric effect originating from the molecular shape of Alq₃ is the origin of the noncentrosymmetric molecular orientation [15]. The molecule can be regarded as an asymmetric dice rolled on the table, presenting an uneven distribution of the postures. Fig. 1c schematically illustrates this “asymmetric dice model”. Intuitively, most favorable postures of an Alq₃ molecule on a flat surface are those in which each one position in three ligands (shown as thick black circles) attaches to the surface. There are two such postures, but those two attachment planes (shown as a dark yellow line at the bottom and light yellow triangle at the top) are not parallel to each other. Following this consideration, we can predict

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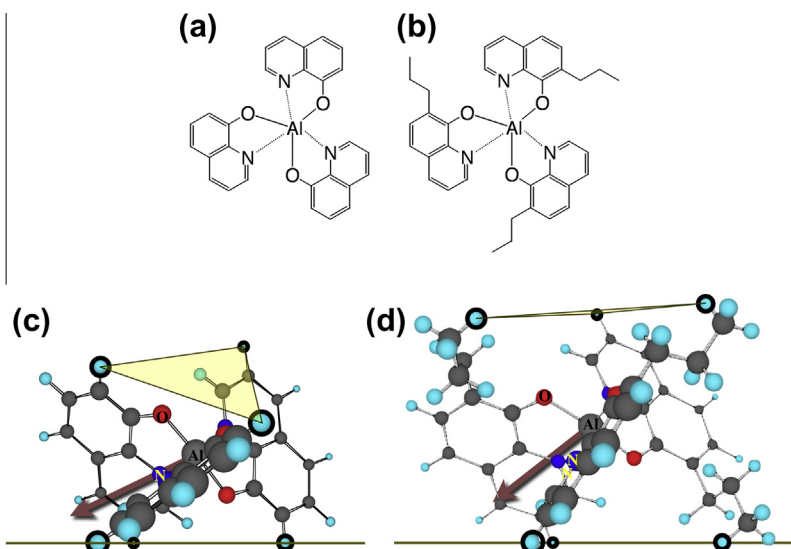


Fig. 1. Top: molecular structure of (a) Alq₃ and (b) Al(7-Prq)₃. Bottom: schematic steric view of (c) mer-Alq₃ and (d) mer-Al(7-Prq)₃ sitting on flat surfaces (dark yellow lines at the bottom of the figures). Circles represent atoms in the molecules, colored by elements (light blue for H, grey for C, dark blue for N, red for O, and grey with label “Al” for the central Al atoms). Circles drawn with thick lines represent adsorption points, each belonged to the three ligands. Yellow triangles at the top of the figures show another adsorption planes when the molecules are flipped upside down. Dark red arrows show the molecular dipole moments (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that a peripheral substitution in the ligands of Alq₃, especially at three and/or 7 position where the ligands attach to the surface, may significantly affect the molecular orientation.

In this work, we investigated tris(7-propyl-8-hydroxyquinolinolato) aluminum(III) [Al(7-Prq)₃, Fig. 1b] [16] to examine our asymmetric dice model. As shown in Fig. 1d, the posture of Al(7-Prq)₃ on the surface is significantly tilted from that of Alq₃. Indeed, an average of the molecular dipole moment projected to the surface normal over the two postures was +0.72 Debye and −0.15 Debye for Alq₃ and Al(7-Prq)₃, respectively, suggesting that the polarity of gSP can be inverted (i.e. negative) in Al(7-Prq)₃ thin films. We measured surface potential (SP) and first-order electroabsorption (EA) response of Alq₃ and Al(7-Prq)₃ thin films to examine the noncentrosymmetry in Al(7-Prq)₃ and Alq₃ films.

Experimentally, Al(7-Prq)₃ was synthesized by reaction between triethylaluminum and 7-*n*-propyl-8-hydroxyquinoline in the presence of triethylamine in high yields, and purified by recrystallization from chloroform and petroleum ether [16]. Alq₃ was purchased from Tokyo Chemical Industry, Co., Ltd., and used without further purification. They were evaporated using a conventional vacuum evaporator (SVC-700TM, Sanyu Electron, Co.) onto indium tin oxide (ITO)-coated glass (100 Ωsq, Kinoene Kogaku, Co., Ltd.), fused silica, and silicon substrates. The evaporation rate was controlled to be *ca.* 1 nm/s, monitored by a quartz thickness monitor (XTC/2, Inficon, Inc.). SP values of the samples were measured in air with a Kelvin probe (KP) measurement system (KP-6500, McAllister Technical Service, Inc.). These experiments were performed under dark condition. The film thickness was

determined by a spectroscopic ellipsometer (M-2000UI, J. A. Woollam Co., Inc.). UV-Visible absorption spectrum of the films was measured using a CCD optical multichannel analyzer (USB-2000, Ocean Optics, Inc.). Semitransparent Al electrodes of 27 nm thick were evaporated using the same vacuum evaporator to fabricate sandwich-structured devices for EA measurement. EA measurement was performed using a home-made setup, applying an AC external electric field of 1.2×10^5 V/cm at 138 Hz [13]. Wavelength was scanned from 360 nm to 800 nm. First-order EA response was obtained by detecting the component in the transmitted light intensity changing at the same frequency as the external AC electric field using a lock-in amplifier (SR830, Stanford Research, Inc.). First-order EA response originates from the second-order non-linear optical process, reflecting the noncentrosymmetry of the material. Molecular dipole moments of meridional Al(7-Prq)₃ and Alq₃ were theoretically obtained by DFT calculation on Gaussian09 using RB3LYP/6-31G(d,p) basis set.

Fig. 2a shows absorption coefficient spectra α of Al(7-Prq)₃ and Alq₃ films, and Fig. 2b shows refractive indices n and extinction coefficients k of them determined by the spectroscopic ellipsometry. Al(7-Prq)₃ presented an absorption peak at 407 nm with a profile similar to but slightly red-shifted (14 nm) from that of Alq₃, suggesting that the electronic states of Al(7-Prq)₃ and Alq₃ are similar to each other. However, the magnitude of α , n and k of Al(7-Prq)₃ are significantly smaller than those of Alq₃, due to lower density of the film originating from the bulky propyl groups. Indeed, the ratio of the actual film thickness determined by the ellipsometry over the apparent thickness obtained by the uncalibrated quartz thickness monitor was 0.75 for Al(7-Prq)₃ and 0.60 for Alq₃, indicating that the density of

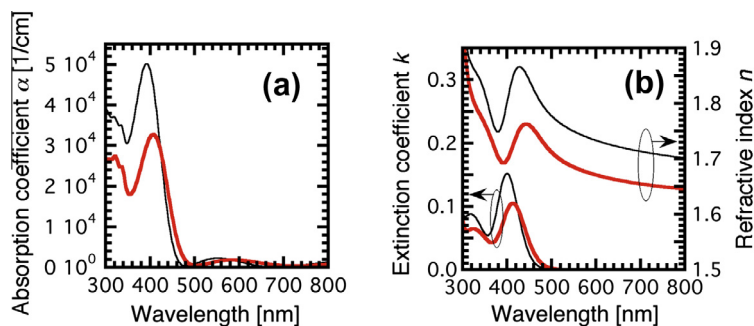


Fig. 2. (a) Absorption coefficient spectra of Al(7-Prq)₃ (red thick line) and Alq₃ (black thin line) thin films vacuum-evaporated on quartz substrates. Small peaks around 600 nm originated from optical interference in the films. (b) Refractive indices *n* and extinction coefficients *k* of Al(7-Prq)₃ (red thick lines) and Alq₃ (black thin lines) determined by spectroscopic ellipsometry (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

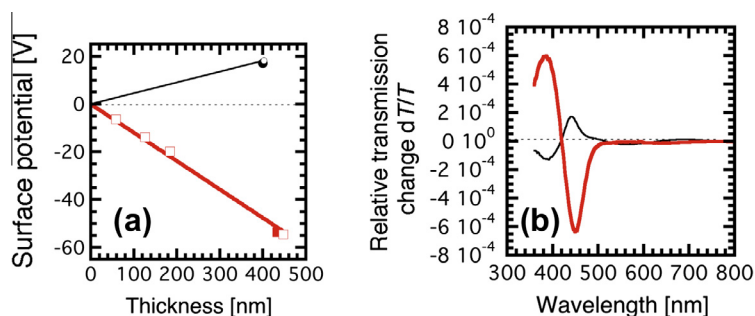


Fig. 3. (a) Thickness dependence of surface potential of Al(7-Prq)₃ on Si (red open circles) and on ITO-coated glass (red filled square), and Alq₃ on Si (black open circle) and on ITO (black filled square). Lines present results of linear fitting, red thick line for Al(7-Prq)₃ and black thin line for Alq₃. The slope of the lines stand for the normalized surface potential values, $-118 \text{ V}/\mu\text{m}$ for Al(7-Prq)₃ and $+45 \text{ V}/\mu\text{m}$ for Alq₃. Thin dotted line corresponds to 0 V for guiding eyes. (b) Electroabsorption spectra of Al(7-Prq)₃ (red thick line) and Alq₃ (black thin line) thin films vacuum-evaporated on ITO-coated glass substrates. Thin dotted line corresponds to 0 for guiding eyes (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the former is much smaller than the latter. This is also consistent with the report that Al(7-Prq)₃ presented significantly smaller electroluminescence than Alq₃ [16].

SP of the Al(7-Prq)₃ thin films were negative and their magnitude was significantly larger than that of the Alq₃ thin films, as shown in Fig. 3a. SP normalized by the film thickness was $-118 \text{ V}/\mu\text{m}$ for Al(7-Prq)₃ and $+45 \text{ V}/\mu\text{m}$ for Alq₃. The EA response of the Al(7-Prq)₃ thin film also presented an opposite polarity and significantly (about 3.7 times) larger magnitude, as shown in Fig. 3b. These results are qualitatively consistent with the prediction of the asymmetric dice model. However, the magnitudes of gSP and EA response of Al(7-Prq)₃ were a few times larger than those of Alq₃. Considering the magnitude of molecular dipole moment (3.7 Debye for Al(7-Prq)₃ and 5.2 Debye for Alq₃) and the density of Al(7-Prq)₃ which is lower than that of Alq₃, the order parameter of molecular orientation in the Al(7-Prq)₃ films is significantly larger than that of Alq₃ films. This is not elucidated by the asymmetric dice model, suggesting that the model requires improvement for quantitative prediction. However, the asymmetric dice model provides a qualitative guideline for molecular design of Alq₃ derivatives to control the noncentrosymmetry in their vacuum-evaporated films.

In summary, we investigated SP and EA response of vacuum-evaporated Al(7-Prq)₃ films, expecting that

substitution at 7 position of the ligands may significantly affect to the molecular posture on the surface based on our asymmetric dice model. It was revealed that the Al(7-Prq)₃ films presented negative gSP, opposite to the Alq₃ films, and the EA response of the films also presented consistent results. Our finding demonstrated that the molecular geometric consideration – asymmetric dice model – is a plausible elucidation for the origin of gSP and spontaneous noncentrosymmetric molecular orientation, and it is suggested that gSP and molecular orientational noncentrosymmetry in the film can be controlled by substitution in the ligands. This finding leads to a useful molecular design guideline for various electronic and optical devices.

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