

# Division of Environmental Chemistry - Molecular Materials Chemistry -

<http://www.molmat.kuicr.kyoto-u.ac.jp/index-e.html>



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## Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminescence devices and different molecular hybrid materials. The structure formation process of bacterial cellulose is also characterized in detail and environmentally friendly cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

## Research Activities (Year 2008)

### Presentations

Structure of Materials in Organic Light-Emitting Diodes Studied by Solid State NMR, Kaji H, 235th ACS National Meeting, New Orleans, LA, 9 April 2008 (Invited).

Geometric and Electronic Structures of a Hole-Transport Material, TPD, Studied by DFT Calculations and Solid-State NMR, Kaji H, Yamada T, SPIE Symposium on Photonic Devices + Applications, "Organic Light-Emitting Materials and Devices XII", San Diego, CA, 10 August 2008 (Invited).

Organic Light-Emitting Diodes Fabricated from Alq<sub>3</sub> in Different Crystalline Polymorphs, Kaji H, Fukushima T, The 8th International Meeting on Information Display/International Display Manufacturing Conference 2008/Asia Display 2008 (IMID/IDMC/ASIA DISPLAY 2008), Gyeonggi, Korea, 15 October 2008 (Invited).

Effects of Added Electrolytes on the Phase Separation Behavior in Aqueous Suspensions of Bacterial Cellulose Microfibrils and on the Magnetic Alignment of the Chiral Nematic Phase, Hirai A, Inui O, Horii F, Yamamoto S, Tsuji M, 235th ACS National Meeting, New Orleans, LA, 7 April 2008 (Invited).

Future Vision and Roadmap of Organic and Molecular

Electronics/Bioelectronics, KAJI H et al., Special Program Symposium, "Future Vision of the Japan Society of Applied Physics—Academic Roadmap toward 2040", The 55th Annual Meeting of the Japan Society of Applied Physics, Chiba, Japan, 28 March 2008.

Phase Separation Behavior of Aqueous Suspensions of Tunicate Cellulose Nanofibers Prepared by HCl Hydrolysis and TEMPO-Mediated Oxidation, Hirai A, Iwata D, Horii F, Nomura A, Tsujii Y, Tsuji M, 15th Annual Meeting, Cellulose Soc., Japan, Kyoto, 10 July 2008.

### Grants

Kaji H, Synthesis of Novel Organic Electroluminescence Materials and the Application for Organic Devices, Research for Promoting Technological Seeds, Japan Science and Technology Agency (JST), 9 July 2008–13 March 2009.

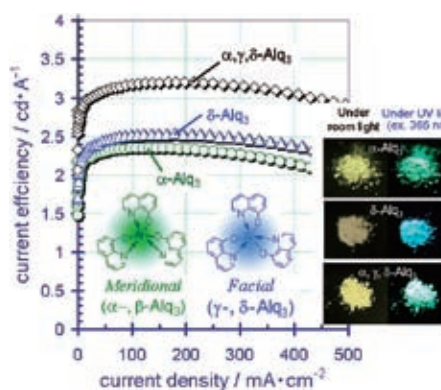
Kaji H, Science and Functions of Organic Amorphous Materials, Grant-in-Aid for Scientific Research (A), 1 April 2005–31 March 2008.

Kaji H, Electronic State Analysis of Organic Photoelectric Conversion Systems by Quantum Chemical Calculation and Nuclear Magnetic Resonance, Grant-in-Aid for

## Organic Light-Emitting Diodes Fabricated from Tris(8-hydroxyquinoline) Aluminum(III) ( $\text{Alq}_3$ ) in Different Crystalline Polymorphs

Tris(8-hydroxyquinoline) aluminum(III) ( $\text{Alq}_3$ ) has been one of the most widely used light-emitting electron-transport materials in organic lights emitting diodes (OLEDs). It is known that there are four polymorphs,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  forms, in crystalline  $\text{Alq}_3$  and that they show green or blue luminescence under UV-irradiation depending on their isomeric states (see Figure 1). However, their relationships with the performance of OLEDs have not been investigated.

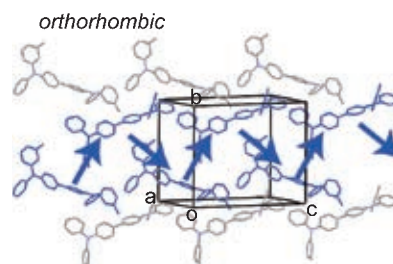
We prepared three kinds of  $\text{Alq}_3$  crystals,  $\alpha$ - $\text{Alq}_3$ ,  $\delta$ - $\text{Alq}_3$ , and mixture of  $\alpha$ ,  $\gamma$ ,  $\delta$ - $\text{Alq}_3$ , by temperature gradient sublimation and thermal annealing. The crystals show different colors under UV-irradiation as shown in Figure 1. By evaporating each crystal under vacuum, three OLEDs with the configuration of ITO / NPD 40nm /  $\text{Alq}_3$  60 nm /  $\text{Cs}_2\text{CO}_3$  / Al were fabricated. All the devices exhibit yellowish-green electroluminescence (EL) emissions, irrespective of the polymorphs before the vacuum evaporation. However, the three devices show different EL performances as shown in Figure 1. The current efficiency of the device fabricated from the mixture of  $\alpha$ ,  $\gamma$ ,  $\delta$ - $\text{Alq}_3$  is larger than the other two devices fabricated from  $\alpha$ - $\text{Alq}_3$  and  $\delta$ - $\text{Alq}_3$ . We carried out the same experiments several times to confirm the reproducibility. The enhancement factors slightly change, but the current efficiencies of the three devices are always in the order of  $\alpha$ ,  $\gamma$ ,  $\delta$ - $\text{Alq}_3$  >  $\delta$ - $\text{Alq}_3$   $\cong$   $\alpha$ - $\text{Alq}_3$ .



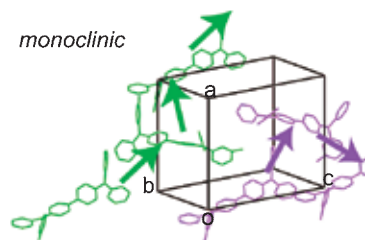
**Figure 1.** Current efficiency-current density characteristics for the OLEDs fabricated from three kinds of  $\text{Alq}_3$  crystals;  $\alpha$ - $\text{Alq}_3$ ,  $\delta$ - $\text{Alq}_3$ , and the mixture of  $\alpha$ ,  $\gamma$ ,  $\delta$ - $\text{Alq}_3$ .

## Charge Transport Paths in Organic Solids, $N,N'$ -diphenyl- $N,N'$ -di(*m*-tolyl) Benzidine (TPD)

Charge transports in organic materials are of immense interest for device applications such as OLEDs. For OLEDs,  $N,N'$ -diphenyl- $N,N'$ -di(*m*-tolyl)benzidine (TPD) is widely used as a hole-transport material. We investigated the paths for charge transports in the orthorhombic and monoclinic polymorphs of TPD. Based on Marcus theory, we calculated charge transfer rate constants for all the neighboring molecular pairs in both polymorphs by density functional theory (DFT) method. The electron transfer rate constants were less than  $3 \times 10^{11} \text{ s}^{-1}$  for any pairs in both polymorphs, due to its large reorganization energy for electron transfer. In contrast, the small reorganization energy for hole transfer resulted in large hole transfer rate constants. Moreover, percolation paths were found for hole transfer with large rate constants in both polymorphs. In the orthorhombic polymorph, the paths are along the *c* axis with the hole transfer rate constant of  $5 \times 10^{12} \text{ s}^{-1}$  (Figure 2). In the monoclinic polymorph, holes can be transported in various directions with the rate constants of  $2 \times 10^{12}$ – $4 \times 10^{12} \text{ s}^{-1}$  (Figure 3). In addition to the small reorganization energy and the large charge transfer integrals, the existence of percolation paths is found to be a crucial factor for high carrier-transport property.



**Figure 2.** Hole transport paths in the orthorhombic polymorph of TPD.



**Figure 3.** Hole transport paths in the monoclinic polymorph of TPD.

Scientific Research on Priority Areas, 1 April 2007–31 March 2008.

Hirai A, Structure Control of Native Polymer Nano-

Assemblies by Magnetic Field, Grant-in-Aid for Scientific Research, 1 April 2007–31 March 2010.