Division of Environmental Chemistry
– Molecular Materials Chemistry –

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

Prof
KAJI, Hironori
(D Eng)

Assoc Prof
GOTO, Atsushi
(D Eng)

Techn Staff
OHMINE, Kyoko

Techn Staff
MAENO, Ayaka

PD
OHTSUKI, Akimichi
(D Sc)

Lect (pt)

NISHIYAMA, Yusuke (D Sc) JEOL Resonance

Researchers

FUKUSHIMA, Tatsuya
TANISHIMA, Miho

Students

SUZUKI, Furitsu (D3)
OIWA, Hajime (M2)
FUJIMURA, Subaru (M2)
FURUKAWA, Shinya (M2)
SUZUKI, Hajime (M1)
DETANI, Masahiro (M1)
OKUDA, Takashi(UG)
TANAKA, Fumiya (UG)

Scope of Research

Our research target is to develop high-performance organic electroluminescence devices, organic solar cells, and polymer materials. For the purpose, we have carried out syntheses, device fabrications, precise structure characterizations, and quantum chemical calculations for high functional organic materials. Along with exploring novel synthetic routes and novel devices, detailed analyses of structures and dynamics are performed mainly by sophisticated solid-state NMR spectroscopy in order to obtain structure-dynamics-property relationships.

KEYWORDS

Solid-State NMR
Amorphous Materials
Organic Light-Emitting Diodes
Organic Solar Cells
Living Radical Polymerization
Quantum Chemical Calculation

Selected Publications

Fukushima, T.; Kaji, H., Green- and Blue-Emitting Tris(8-hydroxyquinoline) Aluminum(III) (Alq_3) Crystalline Polymorphs: Preparation and Application to Organic Light Emitting Diodes, *Organic Electronics*, **13**, 2985-2990 (2012).

Nishiyama, Y.; Fukushima, T.; Fukuchi, M.; Fujimura, S.; Kaji, H., Sensitivity Boosting in Solid-State NMR of Thin Organic Semiconductors by a Paramagnetic Dopant of Copper Phthalocyanine, *Chem. Phys. Lett.*, (in press).

Sato, T.; Shizu, K.; Tanaka, K.; Kaji, H., Theoretical Design for Carrier-Transporting Molecules in View of Vibronic Couplings, *Journal of Photonics for Energy*, **2,** [021201-1]-[021201-10] **(**2012).

Goto, A.; Tsujii, Y.; Kaji, H., Reversible Complexation Mediated Polymerization (RCMP) of Methyl Methacrylate, *ACS Symp. Ser.*, **1100,** 305-315 (2012).

Yazawa, K.; Suzuki, F.; Nishiyama, Y.; Ohata, T.; Aoki, A.; Nishimura, K.; Kaji, H.; Asakura, T., Probing Intermolecular Structures of β Sheet of Alanine Oligomer and Silk Fibroin by High Resolution ^{1}H NMR Spectroscopy with Ultra Fast MAS under Ultra High Field ^{1}H Resonant Frequency, *Chem. Comm.*, **48,** 11199-11201 (2012).

Topics

Green- and Blue-Emitting Organic LED Materials: Preparation of Polymorphs and Application to Organic LEDs

Tris(8-hydroxyquinoline) aluminum(III) (Alq_3) is known to have two isomeric states, namely meridional and facial isomers. Typical Alq_3 crystals composed of meridional and facial isomers are α- and δ-form crystals, respectively. First, we investigate the temperature change in the crystalline forms of α-Alq_3 and δ-Alq_3 in X-ray diffraction experiments in a vacuum. α-Alq_3 remains in α-form up to 300ºC, immediately before sublimation. In contrast, δ-Alq_3 is found to transform into γ-form at ~180ºC, and remain in γ-form immediately before sublimation. Both γ-Alq_3 and δ-Alq_3 are composed of facial isomers and emit blue luminescence, which is different from the typical green emissions of α-Alq_3. Second, we fabricate organic light-emitting diodes (OLEDs) from different crystals as source powders; i.e., from 1) α-Alq_3, 2) δ-Alq_3, and 3) a mixture of α-, γ-, and δ-Alq_3. All the OLEDs exhibit green electroluminescence with almost the same maximum wavelength, suggesting that some facial isomers become meridional while Alq_3 is in the gas phase. In contrast, electroluminescence efficiency depends on the Alq_3 crystalline polymorph; the OLED fabricated from the mixture of α-, γ-, and δ-Alq_3 has up to 1.4 times the efficiency of the OLED fabricated from α-Alq_3 for the same device structure.

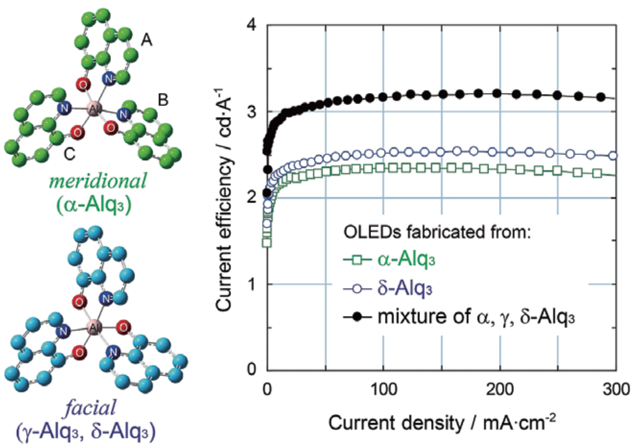

Figure 1. Current efficiency-current density characteristics of OLEDs fabricated from α-Alq_3, δ-Alq_3, and the mixture of α-, γ-, and δ-Alq_3.

Visible-Light-Induced Living Radical Polymerization with Organic Catalysts

A photo-induced living radical polymerization (photo-LRP) using organic catalysts was developed. It is among the most simple and robust photo-LRPs, as it uses iodine as a capping agent and the catalysts are such common compounds as tributylamine. Under visible-light-irradiation at 350-600 nm, the polymer molecular weight and its distribution (M_w/M_n = 1.1–1.4) were well controlled for methyl methacrylate and some functional methacrylates up to fairly high conversions in many cases. Perfectly no polymerization took place without photo-irradiation, meaning that the system is an ideal polymerization switched "on" and "off" by external photo-stimulus. The polymerization rate was also finely tunable by the external irradiation power. The uses of inexpensive compounds and visible light, good polydispersity control, good tolerance to functional groups, and fine response to external photo-irradiation may be useful features of this system.

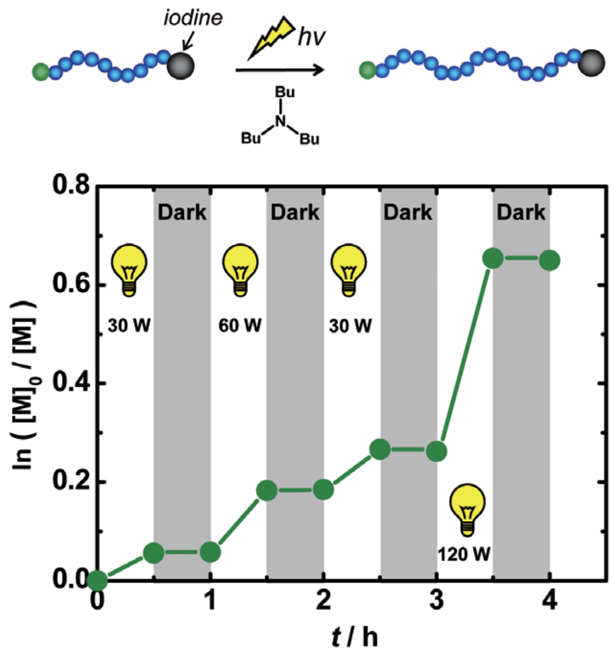

Figure 2. Schematic illustration of photo-LRP using iodine as a capping agent and tributylamine as a catalyst, and first-order-plot of monomer concentration (monomer conversion index) for temporal control by external visible-light-irradiation.