

# 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

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

Living Radical Polymerization  
Quantum Chemical Calculation

## Selected Publications

Fukushima, T.; Kimura, H.; Shimahara, Y.; Kaji, H., Solid-State Nuclear Magnetic Resonance Analysis of Phase Separation Behavior of Regioregular Poly(3-hexylthiophene) and [6,6]-Phenyl-C<sub>61</sub>-Butyric Acid Methyl Ester in Bulk Heterojunction Organic Solar Cells, *Appl. Phys. Lett.*, **99**, [223301-1]-[223301-3] (2011). (Selected for the November 2011 Issue of APL: Organic Electronics and Photonics.)

Goto, A.; Suzuki, T.; Ohfuji, H.; Tanishima, M.; Fukuda, T.; Tsujii, Y.; Kaji, H., Reversible Complexation Mediated Living Radical Polymerization (RCMP) Using Organic Catalysts, *Macromolecules*, **44**, 8709-8715 (2011).

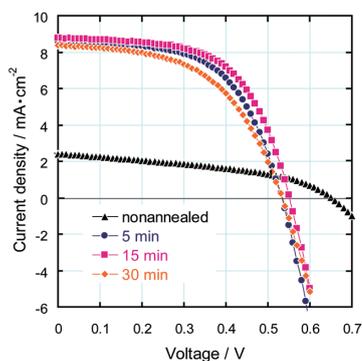
Tokudome, Y.; Fukushima, T.; Goto, A.; Kaji, H., Enhanced Hole Injection in Organic Light-Emitting Diodes by Optimized Synthesis of Self-Assembled Monolayer, *Org. Electron.*, **12**, 1600-1605 (2011).

Kaji, H.; Hayashi, H.; Yamada, T.; Fukuchi, M.; Fujimura, S.; Ueda, M.; Kang, S.; Umeyama, T.; Matano, Y.; Imahori, H., Local Stoichiometry in Amorphous Supramolecular Composites Analyzed by Solid-State <sup>13</sup>C Nuclear Magnetic Resonance, *Appl. Phys. Lett.*, **98**, [113301-1]-[113301-3] (2011). (Selected for the March 2011 Issue of APL: Organic Electronics and Photonics. Selected for the March 28, 2011 Issue of Virtual Journal of Nanoscale Science & Technology.)

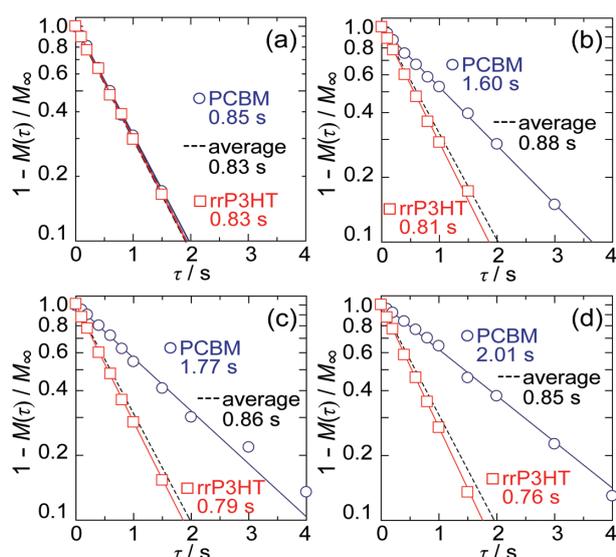
Yamada, T.; Suzuki, F.; Goto, A.; Sato, T.; Tanaka, K.; Kaji, H., Revealing Bipolar Charge-Transport Property of 4,4'-N,N'-dicarbazolylbiphenyl (CBP) by Quantum Chemical Calculations, *Org. Electron.*, **12**, 169-178 (2011).

## Solid-State NMR Analysis of Donor-Acceptor Structure in Bulk Heterojunction Organic Solar Cells

The origin of the improvement in power conversion efficiency (PCE) by the thermal annealing of bulk heterojunction organic solar cells, based on regioregular poly(3-hexylthiophene-2,5-diyl) (rrP3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), is analyzed by solid-state nuclear magnetic resonance (NMR). <sup>1</sup>H spin-lattice relaxation experiments of solid-state NMR clearly reveal that the phase-separated heterojunction structure develops on the order of several tens of nanometers in rrP3HT/PCBM blend films with thermal annealing at 150°C. The development of the phase-separated structure explains the increase in the PCE for the solar cell system from 0.7% to nearly 3% through the thermal annealing.



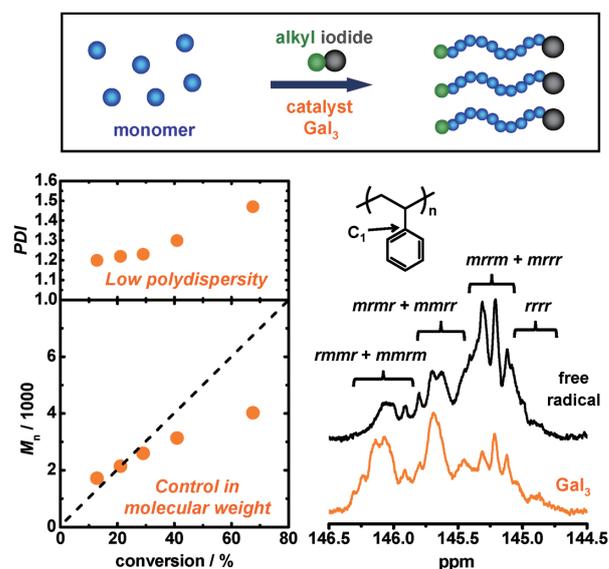
**Figure 1.** J–V curves obtained from rrP3HT/PCBM bulk heterojunction OSCs under AM 1.5 illumination at an irradiation intensity of 100 mW/cm<sup>2</sup>. The annealing temperature is 150°C. The annealing times are shown in the figure.



**Figure 2.** <sup>1</sup>H spin-lattice relaxation curves of rrP3HT (□) and PCBM (○) components in rrP3HT/PCBM blends; (a) as-cast, annealed at 150°C for (b) 5 min, (c) 15 min, and (d) 30 min. The average relaxation curves for rrP3HT and PCBM are also shown as broken lines.

## Living Polymerization of Styrene with Gallium Catalyst towards Control of Molecular Weight and Tacticity

A living polymerization using iodine as a capping agent and a gallium compound (GaI<sub>3</sub>) as a catalyst was studied. The polymerization of styrene yielded well-defined polymers with predetermined molecular weights and narrow molecular weight distribution (PDI=1.2–1.5) up to about 70% monomer conversion. Interestingly, the catalyst did not only achieve small PDI but also changed tacticity (stereoregularity) from that of a free radical propagating species. This indicates the (co)existence of another type of propagating species and a potential for dual control of PDI and tacticity with a single catalyst.



**Figure 3.** Schematic illustration of gallium-catalyzed polymerization, plots of  $M_n$  (molecular weight) and PDI vs monomer conversion, and <sup>13</sup>C NMR spectra for phenyl C1 carbon taken by 800 MHz NMR (200 MHz <sup>13</sup>C NMR) spectrometer.