Division of Environmental Chemistry
– Molecular Materials Chemistry –

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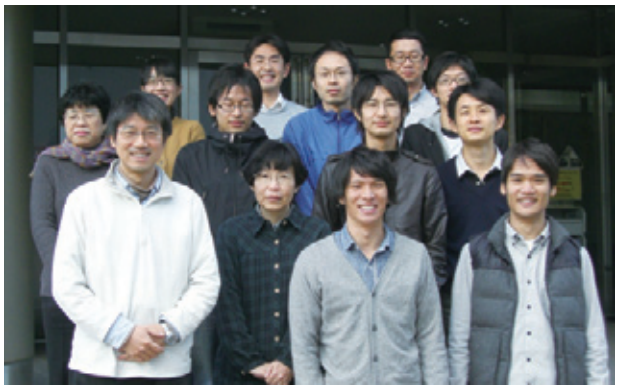
Mr ROTZOLL, Robert Georg-August-University of Göttingen, Germany, 4 November

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

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*., (in press).

Goto A, Hirai N, Nagasawa K, Tsujii Y, Fukuda T, Kaji H: Phenols and Carbon Compounds as Efficient Organic Catalysts for Reversible Chain Transfer Catalyzed Living Radical Polymerization (RTCP), *Macromolecules*, **43,** 7971-7978 (2010).

Nishiyama Y, Fukushima T, Takami K, Kusaka Y, Yamazaki T, Kaji H: Characterization of Local Structures in Amorphous and Crystalline Tris(8-hydroxyquinoline) Aluminum(III) (Alq_3) by Solid-State ^{27}Al MQMAS NMR Spectroscopy, *Chemical Physics Letters*, **471,** 80-84 (2009).

Goto A, Zushi H, Hirai N, Wakada T, Tsujii Y, Fukuda T: Living Radical Polymerizations with Germanium, Tin, and Phosphorus Catalysts–Reversible Chain Transfer Catalyzed Polymerizations (RTCPs), *J. Am. Chem. Soc*., **129,** 13347-13354 (2007).

Kaji H, Kusaka Y, Onoyama G, Horii F: CP/MAS ^{13}C NMR Characterization of the Isomeric States and Intermolecular Packing in Tris(8-hydroxyquinoline) Aluminum(III) (Alq_3), *J. Am. Chem. Soc.*, **128,** 4292-4297 (2006).

Revealing Bipolar Charge-Transport Property of 4,4'-N,N'-dicarbazolylbiphenyl (CBP) by Quantum Chemical Calculations

4,4'-*N*,*N*'-dicarbazolylbiphenyl (CBP) has both the hole- and electron-transport ability, that is, bipolar charge-transport property, and has been widely used for organic light-emitting diodes (OLEDs). In this study, we explain the bipolar charge-transport property of CBP by quantum chemical calculations for the crystal. Both the reorganization energies and the charge transfer integrals were investigated, and charge-transfer rate constants were calculated based on Marcus theory. The hole- and electron-transfer rate constants thus calculated were found to be similar in magnitude. This is in sharp contrast with the case of a structurally similar but a poor electron-transport material, *N*,*N*'-diphenyl-*N*,*N*'-di(*m*-tolyl)benzidine (TPD), for which the hole-transfer rate constants were calculated to be much larger than the electron-transfer rate constants. From the detailed analysis of the charge transfer integrals for CBP, it was found that holes transfer through all the segments of the molecules, using the delocalized HOMO over the whole molecule as in the case of TPD. On the other hand, electrons transfer advantageously through the delocalized LUMO on the carbazole moieties of CBP, which have close intermolecular contacts. The LUMO of TPD localizes on the central biphenylene moiety, resulting in small electron transfer integrals. The results clearly show the difference of the electron-transport property between CBP and TPD.

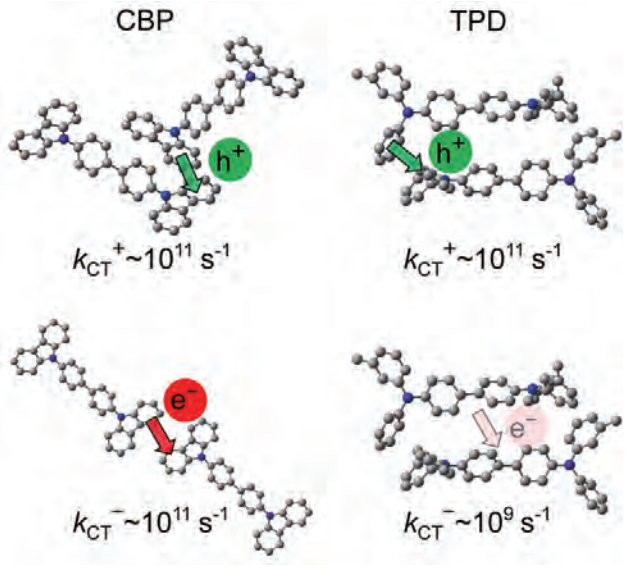


Figure 1. Structures of CBP and TPB and the charge transfer rate constants.

Phenols and Carbon Compounds as Efficient Organic Catalysts for Living Radical Polymerization

Simple phenols and hydrocarbons were successfully used as novel and efficient organic catalysts for reversible chain transfer catalyzed living radical polymerization (RTCP). This is the first use of oxygen- and carbon-centered compounds as catalysts of living radical polymerization. Low-polydispersity polystyrenes and polymethacrylates with predicted molecular weight were obtained with a fairly high conversion in a fairly short time. The catalysts include such common compounds as phenol itself, phenol-based antioxidants for foods and resins (e.g., 3,5-di-*t*-butyl-4-hydroxytoluene (BHT)), phenol-based natural antioxidants (e.g., vitamin E), and dienes (e.g., 1,4-cyclohexadiene). Their commonness (hence low cost) and environmental safety may be attractive for practical applications. They also exhibited good tolerance to functional groups, being useful to a variety of functional monomers.

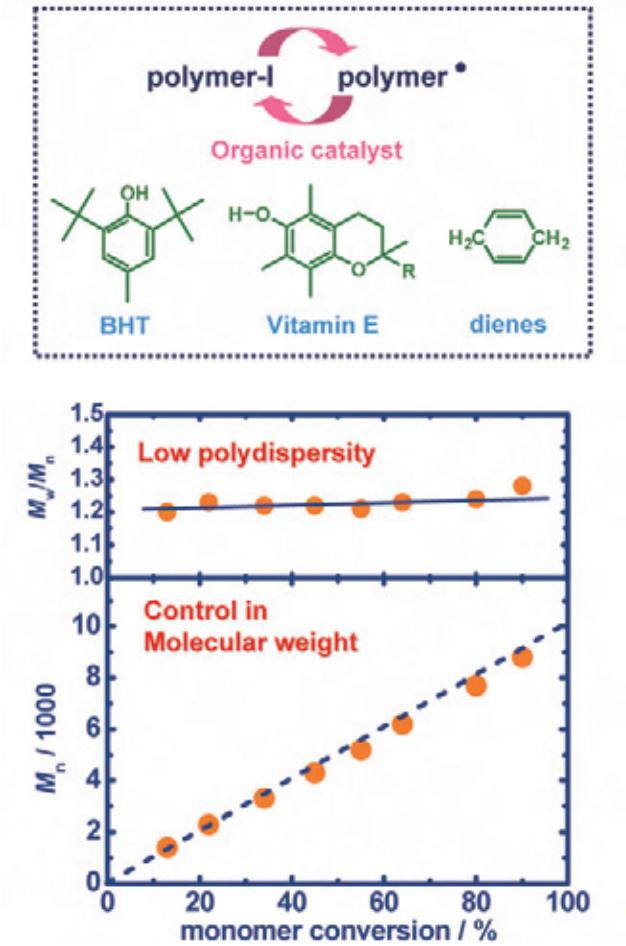


Figure 2. Plots of molecular weight (M_n) and molecular weight distribution (M_w/M_n) vs monomer conversion for a polymerization of methyl methacrylate with 1,4-cyclohexadiene (carbon-centered catalyst).