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Volume 82, Number 3, March 2009

Award Accounts

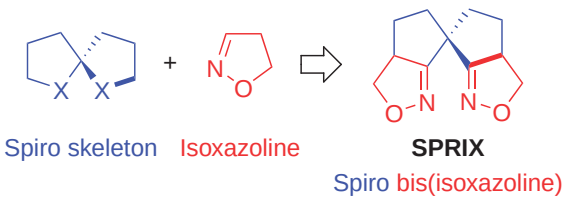
The Chemical Society of Japan Award for Creative Work for 2005

Development of Chiral Spiro Ligands for Metal-Catalyzed Asymmetric Reactions

G. B. Bajracharya, M. A. Arai, P. S. Koranne, T. Suzuki, S. Takizawa, and H. Sasai*

Bull. Chem. Soc. Jpn. **2009**, *82*, 285–302

We have developed a range of novel chiral spiro ligands bearing N-heterocycles as metal-coordinating units. The metal complexes of these ligands displayed unprecedented activation of olefins that allowed us to develop several asymmetric transformations.



Award Accounts

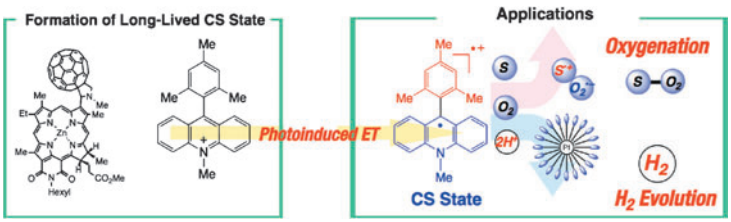
The Chemical Society of Japan Award for Young Chemists for 2006

Rational Design and Functions of Electron Donor–Acceptor Dyads with Much Longer Charge-Separated Lifetimes than Natural Photosynthetic Reaction Centers

K. Ohkubo* and S. Fukuzumi

Bull. Chem. Soc. Jpn. **2009**, *82*, 303–315

Simple electron donor–acceptor dyads with a short spacer have been developed to attain a long-lived charge-separated state. The use of 9-mesityl-10-methylacridinium ion, which has 2 h charge-separation lifetime, enables the construction of highly efficient photocatalytic systems.



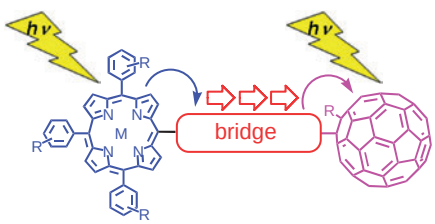
Accounts

Roles of Molecular Wires between Fullerenes and Electron Donors in Photoinduced Electron Transfer

O. Ito* and K. Yamanaka

Bull. Chem. Soc. Jpn. **2009**, *82*, 316–332

Roles of molecular wires connecting electron donors such as porphyrin and electron acceptors such as fullerene in photosensitizing electron-transfer processes are summarized in this account. High electron-transferring abilities of the π-conjugated molecular wires are revealed in connection with the MO energy levels and shape of the LUMO and HOMO of these molecular wires.



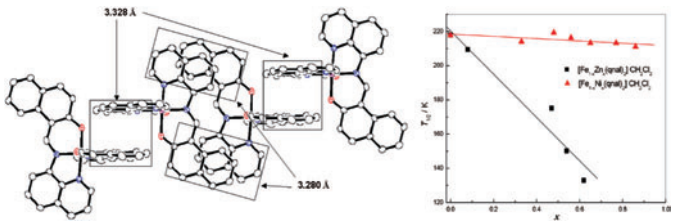
BCSJ Award Article

Effects of Metal Doping on the Spin-Crossover Properties of an Iron(II) Complex with Extended π-Conjugated Schiff-Base Ligand Having an N_4O_2 Donor Set

Z. Yu, T. Kuroda-Sowa,* H. Kume, T. Okubo, M. Maekawa, and M. Munakata

Bull. Chem. Soc. Jpn. **2009**, *82*, 333–337

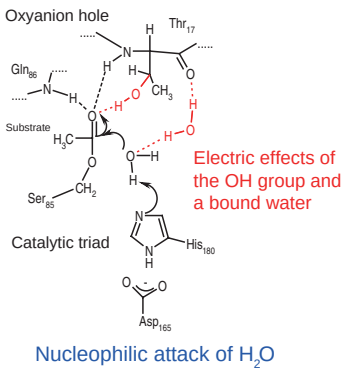
Metal-doping experiments in a spin-crossover system $[Fe_{1-x}M_x(qnal)_2]\cdot CH_2Cl_2$ with M = zinc(II) or nickel(II) reveal that the decrease of cooperativity in the spin transition occurred in both cases while only zinc(II) doping induces the decrease of critical temperature $T_{1/2}$.



ONIOM Study of the Mechanism of the Enzymatic Hydrolysis of Biodegradable Plastics

Y. Sakae, T. Matsubara,* M. Aida, H. Kondo, K. Masaki, and H. Iefuji

Bull. Chem. Soc. Jpn. **2009**, *82*, 338–346



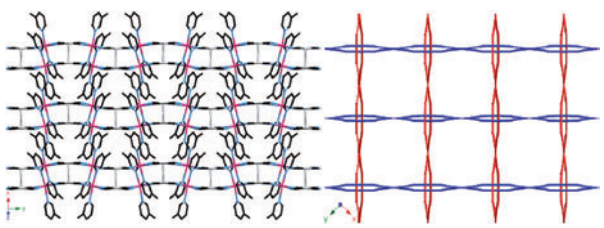
We theoretically examined the reaction mechanism of the cutinase-like enzyme (CLE), which degrades biodegradable plastics very efficiently, using the ONIOM method. We revealed the electronic effects of amino acid residues and bound water in the catalytic reaction.

Structural Isomers of $\{Mn^{II}(L)_2[Ag^{I}(CN)_2]_2\}$ (L = 3-Methylpyridine or 4-Methylpyridine), Bilayer Structure with Binuclear Argentophilic Interaction and Interpenetrated Structure with 1D Chain Argentophilic Interaction; Synthesis, Crystal Structure, and Magnetic Properties

T. Kosone, Y. Suzuki, C. Kanadani, T. Saito, and T. Kitazawa*

Bull. Chem. Soc. Jpn. **2009**, *82*, 347–351

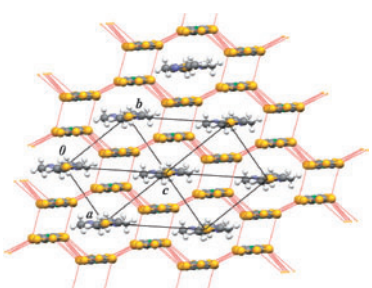
Two novel 2D network coordination polymers $\{Mn(L)_2[Ag(CN)_2]_2\}_n$ (L = 3-methylpyridine or 4-methylpyridine) were synthesized and characterized by using single-crystal X-ray analysis and magnetic measurements. The coordination environment of the Mn^{II} ions and Ag^{I} atoms in complexes **1** and **2** are almost similar. However, coordination polymers for **1** and **2** are structural isomers with each other.



Honeycomb Sheet Structures Achieving High Electrical Conductivities in Alkyl-Substituted Thiazolium Bis(2-thioxo-1,3-dithiole-4,5-dithiolato)nickelate(III) Complex Salts

E. Tomiyama,* K. Tomono, D. Hashizume, T. Wada, and K. Miyamura

Bull. Chem. Soc. Jpn. **2009**, *82*, 352–357



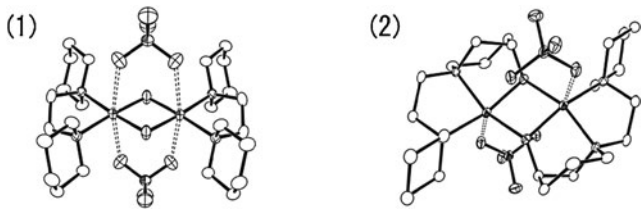
Three 1:1 complex salts of $[Ni(dmit)_2]$ anion with alkyl-substituted thiazolium cations formed honeycomb sheet structures that exhibited high electrical conductivities. The IR spectra showed that the formal charge of anion is shifted positively from −1.

Structures and Magnetic Properties of Dinuclear Copper(II) Complexes Containing a Bulky Diamine Ligand, 1,2-Dipiperidinoethane

M. Arakawa-Itoh, K. Tokuman, Y. Mori, T. Kajiwara, M. Yamashita, and Y. Fukuda*

Bull. Chem. Soc. Jpn. **2009**, *82*, 358–363

A reaction of copper(II) perchlorate with a bulky diamine, 1,2-dipiperidinoethane yields two dinuclear complexes: di-μ-hydroxo dinuclear complex **1** and di-μ-alkoxo dinuclear complex **2**. Structures and magnetic properties of both complexes are studied.

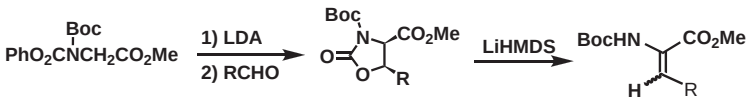


Stereoselective Syntheses of (*E*)-α,β-Didehydroamino Acid and Peptide Containing Its Residue Utilizing Oxazolidinone Derivative

M. Kometani, K. Ihara, R. Kimura, and H. Kinoshita*

Bull. Chem. Soc. Jpn. **2009**, *82*, 364–380

Reaction of methyl *N*-Boc-*N*-phenoxycarbonylglycinate with various aldehydes afforded the corresponding *cis*-4,5-oxazolidinone derivatives, which were effectively converted to (*E*)-α,β-didehydroamino acids by means of base.



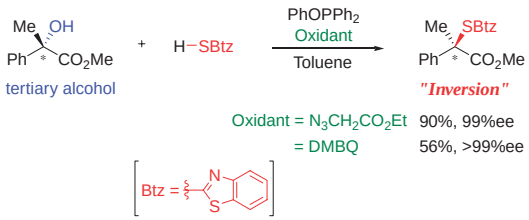
Selected Paper

Conversion of Alcohols to Alkyl Aryl Sulfides by a New Type of Oxidation–Reduction Condensation Using Phenyl Diphenylphosphinite

K. Kuroda, Y. Maruyama, Y. Hayashi,* and T. Mukaiyama*

Bull. Chem. Soc. Jpn. **2009**, *82*, 381–392

A new type of oxidation–reduction condensation of alcohols with arenethiols by the combined use of $PhOPPh_2$ and oxidant is described. In this reaction, chiral secondary and tertiary alcohols are converted into the corresponding sulfides with inversion of configuration.

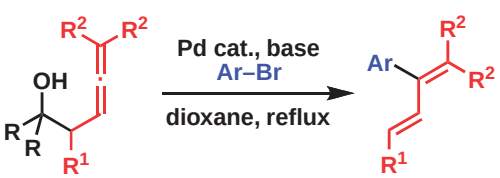


Palladium-Catalyzed 1-Methylene-2-propenylation Reactions of Aryl Bromides with 3,4-Alkadien-1-ols via Carbon–Carbon Bond Cleavage for the Synthesis of 2-Aryl-1,3-butadiene Derivatives

J. Imoto, S. Hayashi, K. Hirano, H. Yorimitsu,* and K. Oshima*

Bull. Chem. Soc. Jpn. **2009**, *82*, 393–400

Treatment of aryl bromides with 3,4-alkadien-1-ols in the presence of a palladium catalyst results in 1-methylene-2-propenyl group transfer to aryl bromides by taking advantage of palladium-catalyzed retro-allylation as an sp^3C–sp^3C bond cleavage reaction.

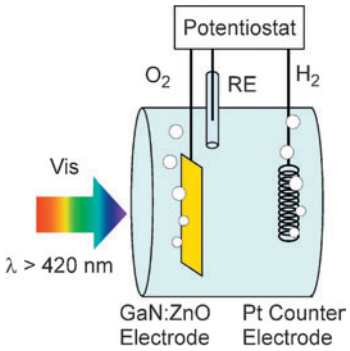


Selected Paper

Photoresponse of GaN:ZnO Electrode on FTO under Visible Light Irradiation

H. Hashiguchi, K. Maeda, R. Abe, A. Ishikawa, J. Kubota, and K. Domen*

Bull. Chem. Soc. Jpn. **2009**, *82*, 401–407



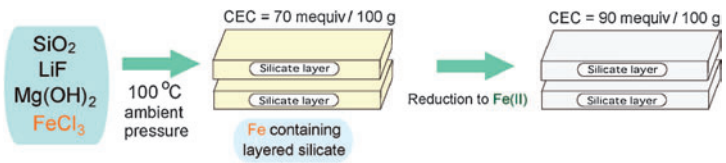
The photoelectrochemical properties of a GaN:ZnO solid solution coated on conductive glass are investigated. The electrode exhibits anodic photocurrent under visible light, indicating functionality as an n-type semiconductor electrode. The evolution of H_2 and O_2 is confirmed during photoelectrolysis.

Preparation of Iron-Containing Hectorite-Like Swelling Silicate

M. Ogawa,* T. Matsutomo, and T. Okada

Bull. Chem. Soc. Jpn. **2009**, *82*, 408–412

Iron-containing hectorite-like layered silicate was synthesized from LiF, $Mg(OH)_2$, colloidal silica, and $FeCl_3$. The increase of the cation-exchange capacity from 70 to 90 mequiv (100 g clay)$^{-1}$ was observed by the reduction of incorporated iron.

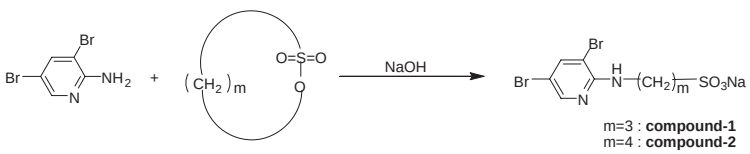


Synthesis of 3,5-Dibromopyridines with –NH(CH$_2$)$_m$SO$_3$Na ($m = 3$ and 4) Groups at the 2-Position of Pyridine and Use of the Dibromo Compound for Polymer Synthesis

K. Shiramizu, Y. Harada, and T. Yamamoto*

Bull. Chem. Soc. Jpn. **2009**, *82*, 413–415

Reactions of 2-amino-3,5-dibromopyridine with sultones gave 3,5-dibromopyridines with –NH(CH$_2$)$_m$SO$_3$Na ($m = 3$ and 4) groups at the 2-position of pyridine. The obtained compound served as a starting material for polypyridine with –NH(CH$_2$)$_m$SO$_3$H side chain.



Selected Paper

Nanogel–Calcium Phosphate Hybrid Nanoparticles with Negative or Positive Charges for Potential Biomedical Applications

S. Yamane, A. Sugawara, Y. Sasaki, and K. Akiyoshi*

Bull. Chem. Soc. Jpn. **2009**, *82*, 416–418

Self-assembled polysaccharide nanogels with negative or positive charge were used as templates for mineralization of calcium phosphate for potential biomedical application. Nanogel–calcium phosphate hybrid nanoparticles with negative or positive charge were prepared.