

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

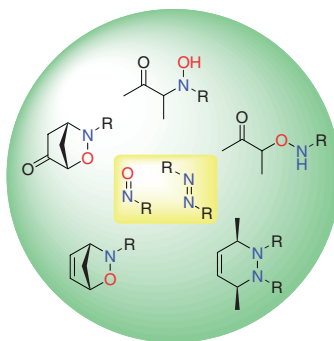
<http://www.csj.jp/journals/bcsj/>

Volume 80, Number 4, April 2007

Vol. 80 Commemorative Accounts

Nitroso and Azo Compounds in Modern Organic Synthesis: Late Blooming but Very Rich

H. Yamamoto* and M. Kawasaki



Although nitroso and azo compounds are attractive tools for hydroxylation and amination of organic compounds, no reports on a catalytic asymmetric version of these reactions had been reported until recently. The recent advances in this area are summarized in this review.

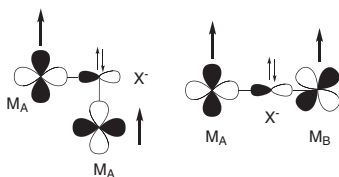
Bull. Chem. Soc. Jpn. **2007**, *80*,
595–607

Award Accounts

The Chemical Society of Japan Award for Creative Work for 2005

Rational Syntheses of Multinuclear High-Spin Complexes

H. Oshio* and M. Nihei



Ferromagnetic interactions in homo- and hetero-metal systems.

Magnetic interactions within or between molecules are typically antiferromagnetic, and in preparing metal complexes with high-spin ground states careful molecular designs that take into consideration magnetic orbital symmetry and bridging structures are necessary. In this article, the rational synthesis of high-spin molecules and its applications to single-molecule magnets are presented.

Bull. Chem. Soc. Jpn. **2007**, *80*,
608–620

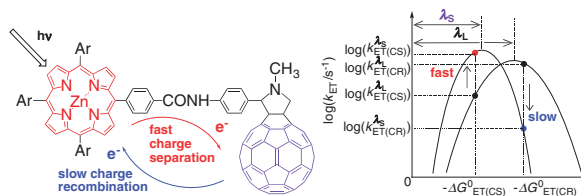
Award Accounts

The Chemical Society of Japan Award for Creative Work for 2005

Creation of Fullerene-Based Artificial Photosynthetic Systems

H. Imahori

We demonstrated small reorganization energies of fullerenes, which make it possible to produce a long-lived charge-separated state with a high quantum yield. The finding provides us scientific basis for the advantages of fullerenes as electron acceptors in artificial photosynthesis.



Bull. Chem. Soc. Jpn. **2007**, *80*,
621–636

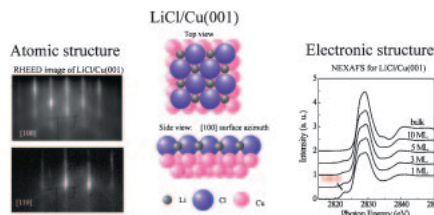
Award Accounts

The Chemical Society of Japan Award for Young Chemists for 2005

Atomic and Electronic Structures and Properties of Nanomaterials on Metal Substrates

M. Kiguchi

Atomic and electronic structures and chemical/physical properties were investigated for well-defined nanostructures on metal substrates. The formation of metal induced gap states at the well-defined LiCl/Cu(001) interface was shown using near edge X-ray absorption fine structure.

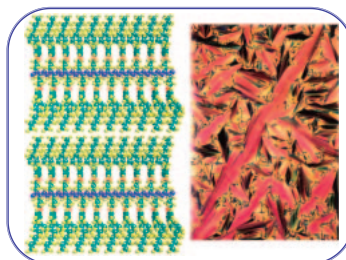


Bull. Chem. Soc. Jpn. **2007**, *80*, 637–648

Accounts

Synthesis and Properties of Liquid-Crystalline-Conjugated Polymers

K. Akagi



Liquid-crystalline polyacetylene derivatives with mesogenic groups in the side chains were synthesized. The polymers showed smectic phases due to layered structures. Macroscopic alignment of the polymers using external force afforded an enhancement by two orders in electrical conductivity.

Bull. Chem. Soc. Jpn. **2007**, *80*, 649–661

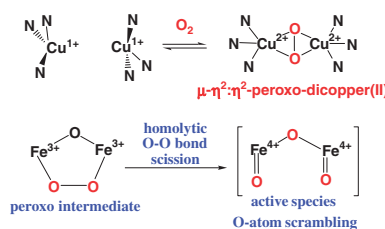
Accounts

Reversible O₂-Binding and Activation with Dicopper and Diiron Complexes Stabilized by Various Hexapyridine Ligands. Stability, Modulation, and Flexibility of the Dinuclear Structure as Key Aspects for the Dimetal/O₂ Chemistry

M. Kodera* and K. Kano

Bull. Chem. Soc. Jpn. **2007**, *80*, 662–676

Reversible O₂-binding and activation have been studied using dicopper and diiron complexes of various hexapyridine ligands as functional models of hemocyanin (Hc) and soluble methane monooxygenase (sMMO), respectively.

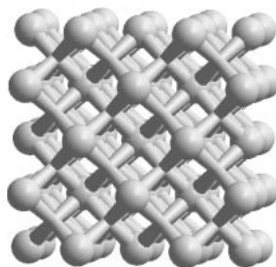


BCSJ Award Article

Three-Dimensionally Ordered Macroporous (3DOM) Materials of Spinel-Type Mixed Iron Oxides. Synthesis, Structural Characterization, and Formation Mechanism of Inverse Opals with a Skeleton Structure

M. Sadakane,* C. Takahashi, N. Kato, H. Ogihara, Y. Nodasaka, Y. Doi, Y. Hinatsu, and W. Ueda*

Bull. Chem. Soc. Jpn. **2007**, *80*, 677–685



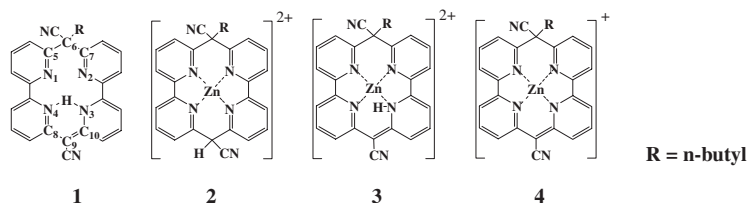
Three-dimensionally ordered macroporous (3DOM) polycrystalline spinel-type mixed iron oxide with skeleton structure was obtained in high yield. The synthesis, structural characterization, and formation mechanism are described.

Theoretical Study of Geometries and Electronic Transition of Color-Switching Molecules: Tetra-Aza Macrocycle and Its Zinc Complexes

Z. Zhu, K. Takano,* A. Furuhashi, S. Ogawa, and S. Tsuchiya

Bull. Chem. Soc. Jpn. **2007**, *80*, 686–693

Geometries and spectroscopic features of the tetra-aza macrocycles containing 2,2'-bipyridine moieties, which undergo color-switching as well as its zinc complexes were studied from the viewpoints of DFT and TDDFT calculations combined with the PCM method.

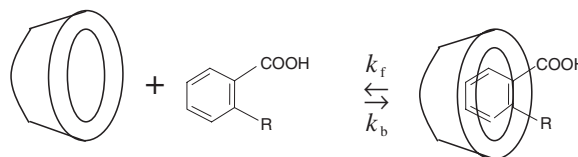


Ultrasonic Relaxation Associated with Inclusion Complex of Drugs and β -Cyclodextrin

S. Nishikawa,* M. Kondo, E. Kamimura, and S. Xing

Bull. Chem. Soc. Jpn. **2007**, *80*, 694–698

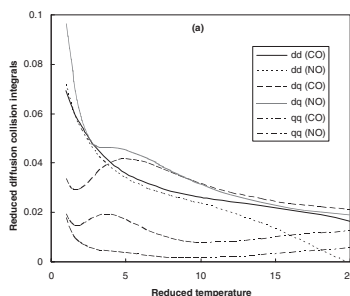
Ultrasonic relaxation associated with a dynamic interaction between β -cyclodextrin (β -CD) and salicylic acid and between β -CD and benzoic acid was investigated in a frequency range from 0.8 to 95 MHz. The rate and thermodynamic constants were evaluated and the benzene group was found to be included in the cavity of β -CD.



Transport Properties of Non-Spherical Gases

A. Maghari* and A. H. Jalili

Bull. Chem. Soc. Jpn. **2007**, *80*, 699–706

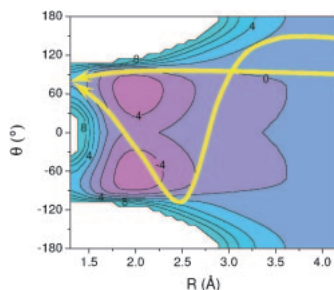


The transport properties of dilute gases consisting of non-spherical molecules are described in this work on the basis of permanent and induced electric multipole moments. We obtained the general expressions for non-central contributions to the collision integrals.

Stereoselectivity as a Probe of Unexpected Reaction Pathways

L. Bonnet,* P. Larrégaray, B. Duguay, J.-C. Rayez, D.-C. Che, and T. Kasai

Bull. Chem. Soc. Jpn. **2007**, *80*, 707–710

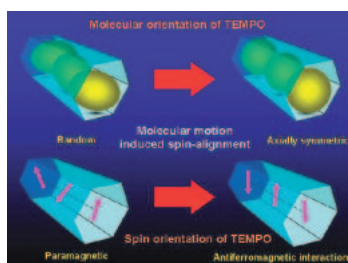


For gas-phase chemical reactions like $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$, which involves a relatively deep pre-barrier van der Waals well, quasi-classical trajectory calculations showed that unexpected reaction pathways involving strong reorientation of the reagents may be clearly evidenced by controlling the spatial orientation of both reagent molecules. In such a case, the venerable notion of cone of acceptance does not suffice, on its own, to rationalize steric effects.

Spin-Spin Interaction of TEMPO Molecular Chains Formed in an Organic One-Dimensional Nanochannel as Studied by Electron Spin Resonance (ESR)

H. Kobayashi, T. Ueda,* K. Miyakubo, T. Eguchi, and A. Tani

Bull. Chem. Soc. Jpn. **2007**, *80*, 711–720

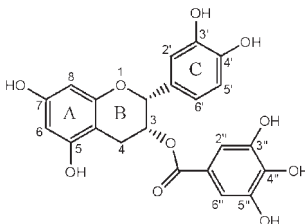


The magnitude and dimensionality of spin-spin interactions among 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) molecules in a 1D nanochannel consisting of tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP) were examined using electron spin resonance (ESR) spectroscopy. The host channel topology implied 1D exchange narrowing.

Fragmentation Position Dependency of the Total Energy and Atomic Charge Difference between the Fragment MO Method and Conventional Ab Initio SCF-MO Method. A Case of (–)-Epicatechin Gallate with STO-3G Basis Set

K. Tamura, Y. Inadomi, and U. Nagashima*

Bull. Chem. Soc. Jpn. **2007**, *80*, 721–723



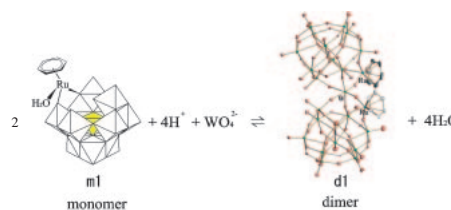
The fragmentation pattern dependence of total energy and atomic charge difference between the fragment MO method and conventional ab initio Hartree-Fock SCF-MO method (HFMO) was investigated using 44 patterns of (–)-Epicatechin gallate.

Organometallic Complexes Supported on a Metal-Oxide Cluster. pH-Dependent Interconversion between the Monomeric and Dimeric Species of the Polyoxoanion-Supported [(arene)Ru]²⁺ Complex

K. Nomiya,* K. Hayashi, Y. Kasahara, T. Iida, Y. Nagaoka, H. Yamamoto, T. Ueno, and Y. Sakai

Bull. Chem. Soc. Jpn. **2007**, *80*, 724–731

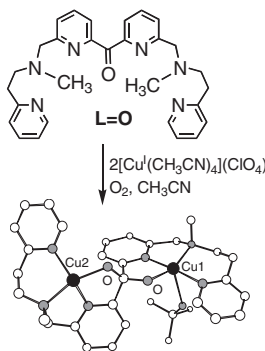
The proportion of the monomer to the dimer in solution, for the mono-lacunary Keggin polyoxometalate (POM)-based (arene)Ru²⁺ complexes (arene = benzene, *p*-cymene, and hexamethylbenzene) was carefully examined with pH-varied ³¹P NMR spectroscopy. The key factors for the formation of the dimeric species were clarified.



Copper–Dioxygen Reactivity Using Dinucleating Ligands with Activated Methylene or Ketone Function

D.-H. Lee,* N. N. Murthy, and K. D. Karlin*

Bull. Chem. Soc. Jpn. **2007**, *80*, 732–742



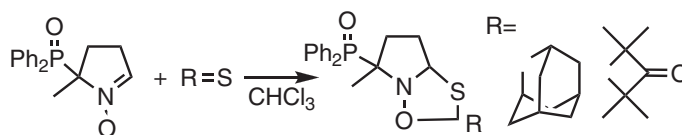
New dinucleating ligands containing an active methylene group spacer between tridentate or tetradentate pyridylalkylamine donor groups underwent catalytic oxygenation with copper salts and O₂, giving ketonic products. One of these, **L=O**, formed a dicopper(I) complex that reacted with O₂ to give the dialkoxide complex [Cu^{II}₂{L-(O⁻)₂}⁻(ClO₃)⁻]⁺.

Cycloadditions of 3,4-Dihydro-2H-pyrrole N-Oxide with Thioketones and a Selenoketone

K. Shioji,* A. Matsumoto, M. Takao, Y. Kurauchi, T. Shigetomi, Y. Yokomori, and K. Okuma

Bull. Chem. Soc. Jpn. **2007**, *80*, 743–746

Cycloadditions of 3,4-dihydro-2H-pyrrole *N*-oxide possessing diphenylphosphoryl group at C5 position, with thioketones afforded the corresponding oxathiazolidines.



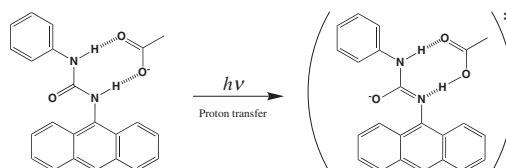
Selected Paper

Photochemical Behavior of an Anthracene–Urea Derivative Interacting with Anions

I. Ohshiro, M. Ikegami, Y. Shinohara, Y. Nishimura, and T. Arai*

Bull. Chem. Soc. Jpn. **2007**, *80*, 747–751

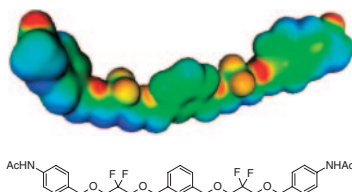
A new anthracene derivative with a phenylurea group at the 9-position of the anthracene, 1-anthracen-9-yl-3-phenylurea (9PUA), showed a monomer emission maximum at 450 nm, and the monomer emission was quenched by adding acetate, upon which a new emission with a maximum at 580 nm was observed. The emission at 580 nm was assigned to the tautomer form of 9PUA generated by intermolecular hydrogen atom transfer as a result of the association with an acetate anion in the excited state.



Molecular Design and Synthesis of Fluorinated Polyethers toward Organic Materials with High Dielectric Constants and Ferroelectricity

T. Okano,* M. Hiraishi, and T. Mizutani

Bull. Chem. Soc. Jpn. **2007**, *80*, 752–757



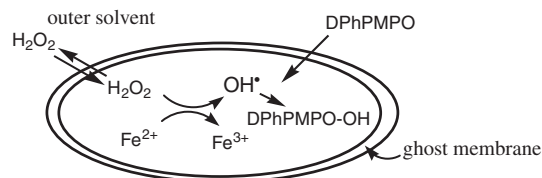
Several fluorinated polyethers with high dielectric constants based on the 2,2-difluoropropane-1,3-dioxy group structure were prepared. Although most of these products were not ferroelectric, a bisacetamide molecule with intermolecular hydrogen bonding showed ferroelectricity.

ESR Measurement Using 2-Diphenylphosphinoyl-2-methyl-3,4-dihydro-2H-pyrrole *N*-Oxide (DPhPMPO) in Human Erythrocyte Ghosts

K. Shioji,* H. Iwashita, T. Shimomura, T. Yamaguchi, and K. Okuma

Bull. Chem. Soc. Jpn. **2007**, *80*, 758–762

The trapping of hydroxyl radicals generated in human erythrocyte ghosts was accomplished using DPhPMPO.

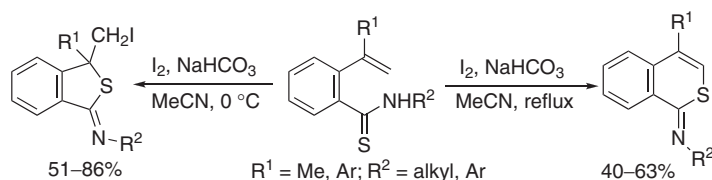


Synthesis of 1(3*H*)-Imino-2-benzothiophene and 1-Imino-1*H*-2-benzothiopyran Derivatives by Reactions of Secondary *o*-(Vinyl)thiobenzamide Derivatives with Iodine

K. Kobayashi,* S. Fujita, M. Hase, O. Morikawa, and H. Konishi

Bull. Chem. Soc. Jpn. **2007**, *80*, 763–767

1(3*H*)-Imino-2-benzothiophene derivatives were prepared by treating secondary *o*-(vinyl)thiobenzamide derivatives with iodine in the presence of sodium hydrogencarbonate in acetonitrile at 0 °C. Similar treatment at reflux afforded 1-imino-1*H*-2-benzothiopyran derivatives.

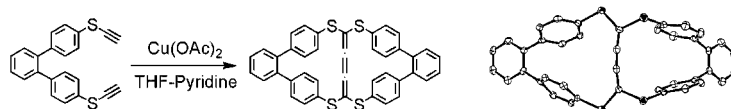


Macrocyclic Compounds Having Sulfide Moieties Derived from *o*-Terphenyl

R. Sato,* G. Hamasaka, T. Yamamoto, H. Muraoka, S. Nakajo, and S. Ogawa

Bull. Chem. Soc. Jpn. **2007**, *80*, 768–776

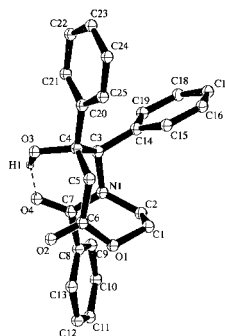
Eight macrocycles having sulfide moieties were synthesized from 4,4''-dimercapto-*o*-terphenyl. The thioethynyl compound derived from 4,4''-dimercapto-*o*-terphenyl gave a novel cumulene upon treatment with cupric acetate in THF/pyridine. The structures of these products were determined by using X-ray crystallographic analysis. UV–vis, emission spectra and cyclic voltammograms were also obtained.



Photocyclization of 2-(*N*-Benzoyl-*N*-benzylamino)ethyl Benzoylacetate via Remote Hydrogen Abstraction. Enhancing Effect on Biradical Cyclization by the *N*-Benzoyl Group

T. Hasegawa,* T. Anma, S. Suzuki, Y. Maeda, and E. Horn

Bull. Chem. Soc. Jpn. **2007**, *80*, 777–779



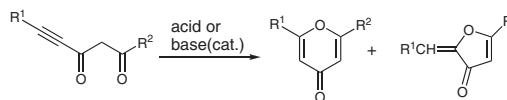
Upon irradiation, 2-(*N*-benzoyl-*N*-benzylamino)ethyl benzoylacetate underwent photocyclization facilitated by hydrogen bonding between the hydroxy and benzoyl carbonyl group in a 1,8-biradical intermediate.

Synthesis and Acid- or Base-Catalyzed Cyclization of Various 4-Pentyne-1,3-dione Derivatives

H. Kuroda* and H. Izawa

Bull. Chem. Soc. Jpn. **2007**, *80*, 780–782

4-Pentyne-1,3-dione derivatives having various substituents were conveniently synthesized from ynals and silyl enol ethers in two steps. The cyclization behaviors of the obtained 4-pentyne-1,3-diones were studied.

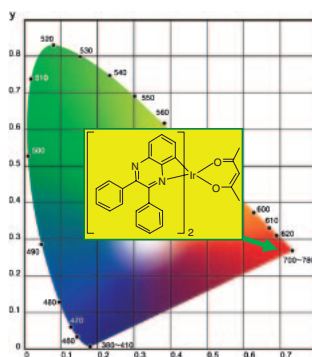


R ¹	R ²	R ¹	R ²
<i>n</i> -Bu	Ph	<i>t</i> -Bu	Ph
Ph	Ph	<i>n</i> -Bu	<i>t</i> -Bu

Iridium(III) Complexes Bearing Quinoxaline Ligands with Efficient Red Luminescence Properties

K. Tani, H. Fujii, L. Mao, H. Sakurai, and T. Hirao*

Bull. Chem. Soc. Jpn. **2007**, *80*, 783–788

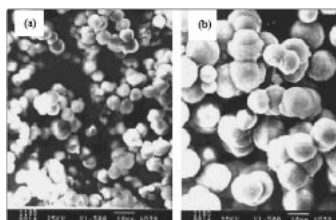


Newly designed cyclometalated iridium complexes bearing 2,3-diphenylquinoxalines, which were shown to be highly efficient and vivid-red emitting materials for electrophosphorescent organic light-emitting diodes, were synthesized and characterized.

Synthesis and Characterization of Zeolites by Conventional and Microwave-Assisted Methods Using (2-Hydroxyethyl)trimethylammonium Hydroxide as a Template

A. Samadi-Maybodi* and N. Goudarzi

Bull. Chem. Soc. Jpn. **2007**, *80*, 789–793



SEM micrographs of the zeolites synthesized (a) without and (b) with template (2-HETMA).

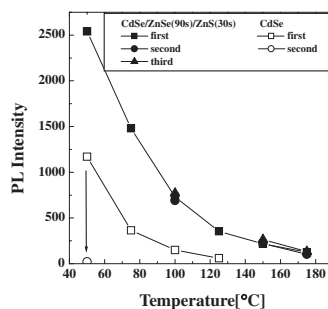
Different zeolites were synthesized by conventional hydrothermal and microwave-radiation-assisted methods using (2-hydroxyethyl)trimethylammonium hydroxide (2-HETMAOH) as a template. In the presence of template, large particle sizes were obtained, samples without template have small size.

Selected Paper

Micro-Space Synthesis of Core-Shell-Type Semiconductor Nanocrystals for Thermosensing

C.-G. Lee, M. Uehara, Y. Yamaguchi, H. Nakamura, and H. Maeda*

Bull. Chem. Soc. Jpn. **2007**, *80*, 794–796



CdSe and its composite particles were prepared by using a microreactor and the temperature dependence of their optical properties was examined. The luminescence of CdSe/ZnSe/ZnS nanocrystals was reversibly dependent on temperature, whereas CdSe was not reversible, indicating the suitability of composite nanocrystals for temperature measurement.