

# BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

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

Volume 81, Number 6, June 2008

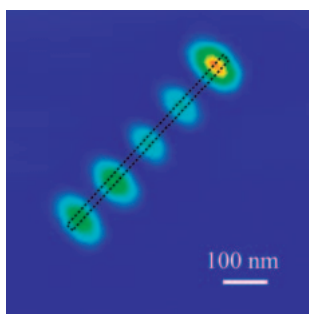
## Award Accounts

The Chemical Society of Japan Award for Young Chemists for 2006

### Development of Novel Near-Field Microspectroscopy and Imaging of Local Excitations and Wave Functions of Nanomaterials

K. Imura\* and H. Okamoto

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 659–675



We studied local excitations and wave functions of single noble metal nanoparticles by using newly developed methods of near-field microspectroscopy. We demonstrate that plasmon wave functions and optical fields in the neighbor of nanoparticles are visualized by the near-field methods.

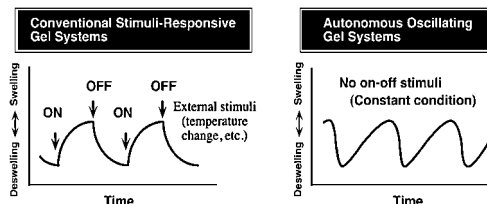
## Accounts

### Self-Oscillating Polymer and Gels as Novel Biomimetic Materials

R. Yoshida

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 676–688

As a novel biomimetic polymer, we have been studying a polymer with an autonomous self-oscillating function by utilizing oscillating chemical reactions. In this paper, our recent studies on the self-oscillating polymer and the design of functional material systems are summarized.



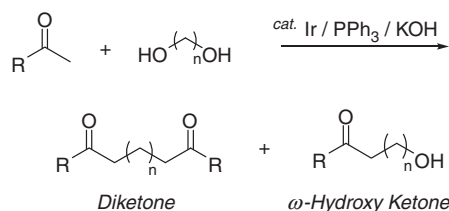
## BCSJ Award Article

### Synthesis of Diketones and $\omega$ -Hydroxy Ketones from Methyl Ketones and $\alpha,\omega$ -Diols by an $[\text{IrCl}(\text{cod})]_2/\text{PPh}_3/\text{KOH}$ System

K. Maeda, Y. Obora, S. Sakaguchi, and Y. Ishii\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 689–696

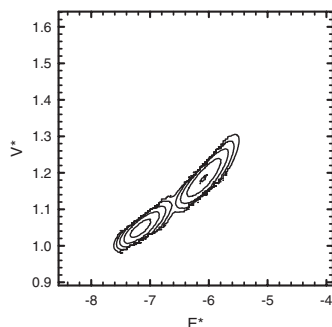
$\omega$ -Hydroxy ketones and diketones, which are important starting materials for the synthesis of cycloalkanones and heterocyclic compounds, were prepared by one-step reaction of methyl ketones with  $\alpha,\omega$ -diols under the influence of an iridium complex and a base.



### Monte Carlo Study of First-Order Phase Transitions of a Bulk Lennard-Jones Fluid System in the Isobaric-Multithermal Ensemble

C. Muguruma\* and Y. Okamoto

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 697–702

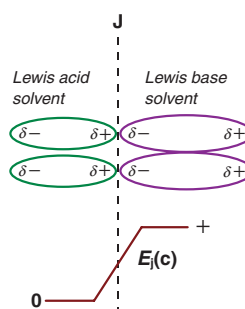


A Monte Carlo simulation in the isobaric-multithermal ensemble has been carried out for a bulk Lennard-Jones fluid system. The contour representation of the two-dimensional probability distribution of the potential energy  $E^*$  and the volume  $V^*$  at  $T_c^* = 0.726$  under  $P^* = 2.42 \times 10^{-3}$  indeed shows two phases.

### Liquid Junction Potential between Electrolyte Solutions in Different Solvents Studied by Use of Mixed Solvent/Pure Solvent Junctions

K. Izutsu

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 703–710



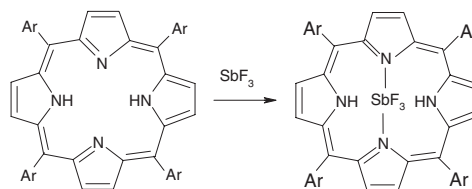
At mixed solvent/pure solvent junctions, the component of the liquid junction potential due to the interaction between different solvents (component (c)) primarily varies linearly with the volume fraction of the mixed solvent. However, there are cases of nonlinear variations.

### Spectrophotometric Studies of the Thermodynamics of Molecular Interaction between Some Free Base *meso*-Tetraarylporphyrins and $\text{SbF}_3$

H. Dehghani,\* M. Bordbar, S. Rezakhani, and M. R. Mansournia

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 711–715

$\text{SbF}_3$  and para-, meta-, and ortho-substituted *meso*-tetraarylporphyrins ( $\text{H}_2\text{t}(\text{Xp})\text{p}$ ; X: H,  $\text{OCH}_3$ ,  $\text{CH}_3$ , and Cl) produced 1:1 molecular complexes,  $[(\text{SbF}_3)\text{H}_2\text{t}(\text{Xp})\text{p}]$ , in chloroform solution.  $K_f$  for the molecular complexation is increased with the enhancement of electron donation and the steric hindrance diminution of the aryl rings in the porphyrins.

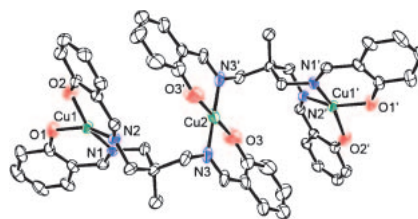


### Mono- and Trinuclear $\text{Cu}^{\text{II}}$ Complexes with Tripodal Ligands

Y. Sunatsuki, T. Kobayashi, K. Harada, T. Yamaguchi, M. Nonoyama, and M. Kojima\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 716–725

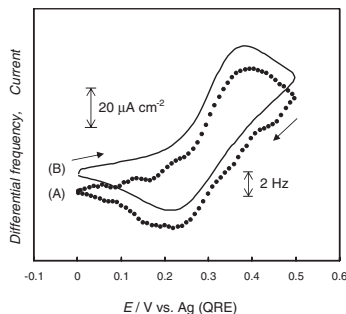
Mononuclear  $[\text{Cu}(\text{HL})]$  and trinuclear  $[\text{Cu}_3(\text{L})_2]$  complexes were synthesized, where  $\text{H}_3\text{L}$  is a tripodal ligand obtained by condensation of 1,1,1-tris(amino-methyl)ethane and salicylaldehyde (1:3). In  $[\text{Cu}_3(\text{L})_2]$ , an imine nitrogen atom and a phenolate oxygen atom of one arm of each terminal unit coordinate to the central  $\text{Cu}^{\text{II}}$  ion to form a linear trinuclear complex.



### In Situ Electrochemical Quartz Crystal Microbalance Measurement of Au Deposition and Dissolution in Room-Temperature Ionic Liquid Containing Chloride Ion

T. Oyama, T. Okajima, T. Ohsaka,\*  
S. Yamaguchi, and N. Oyama\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
726–732



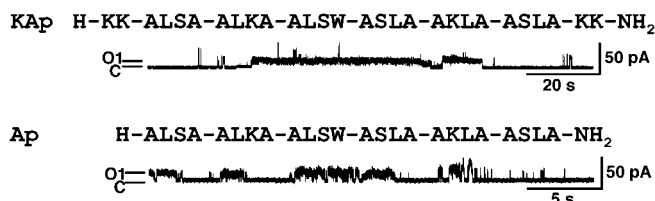
(A) Differential frequency and (B) cyclic voltammetric current responses, which were simultaneously obtained with Au film-coated quartz crystal electrode in EMIBF<sub>4</sub> containing 8.40 mM EMICl at 10 mV s<sup>-1</sup>, demonstrate that the observed CV response is directly correlated with the mass change of the Au electrode surface.

### Modifications of Hydrophobic Value and Hydrophobic Moment Value of Cationic Model Peptides for Conversion of Peptide–Membrane Interactions

J. Taira, S. Furukawa, T. Hatakeyama,  
H. Aoyagi, and H. Kodama\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
733–739

The hydrophobic and amphiphilic characteristics of cationic helical peptide 4<sub>6</sub> reported previously were modified to elucidate biological activities including antimicrobial activities, hemolytic activities, and ion channel activities. The modification caused drastic change of the biological activities.

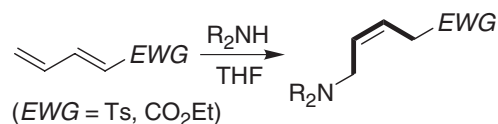


### “Syn Effect” in Nucleophilic Addition of Amines to 1,3-Dienyl Sulfone and Ethyl (E)-2,4-Pentadienoate

M. Yamazaki, S. K. Guha,  
Y. Ukaji,\* and K. Inomata\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
740–753

Nucleophilic addition of amines to (*E*)-1-tosyl-1,3-butadiene and ethyl (*E*)-2,4-pentadienoate in low concentration of amines at high temperature, afforded the corresponding sterically unfavorable (*Z*)-allylic amines preferentially. As the origin of the predominant formation of *Z* isomers was proposed a “syn effect.”

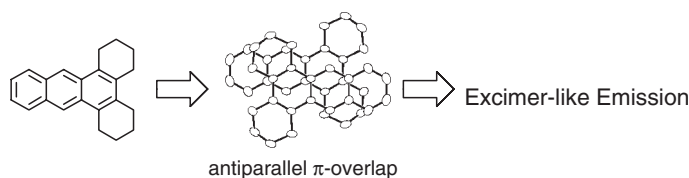


### Study on Facile Synthesis, Crystal Structure, and Solid-State Fluorescence of Dicyclohexane-Annulated Anthracene

C. Kitamura,\* C. Matsumoto,  
N. Kawatsuki, A. Yoneda, K. Asada,  
T. Kobayashi, and H. Naito

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
754–756

Dicyclohexane-annulated anthracene was synthesized using a new facile method. The first step involved a Diels–Alder reaction between in situ-generated 2,3-dehydronaphthalene and dicyclohexane-fused furan. X-ray analysis revealed that the molecule adopted an antiparallel face-to-face slipped  $\pi$ -overlap in the crystal structure, which induced an excimer-like emission in the solid state.



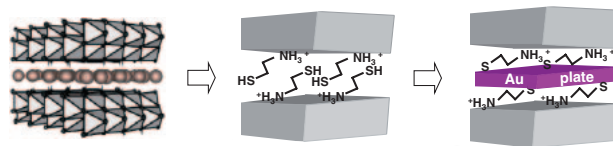
### Selected Paper

#### Synthesis of Au Nanoparticles in the Interlayer Space of a Layered Titanate Intercalated with 2-Aminoethanethiol

Y. Ide, Y. Nakasato, and M. Ogawa\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 757–760

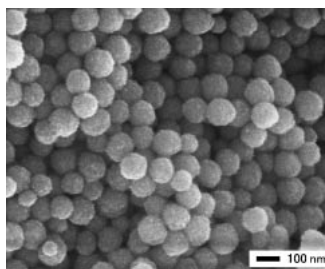
Platy Au nanoparticles formed in the interlayer space of a 2-aminoethanethiol-intercalated layered titanate.



#### Controlled Synthesis of Monodispersed Cerium Oxide Nanoparticle Sols Applicable to Preparing Ordered Self-Assemblies

N. Izu,\* I. Matsubara, T. Itoh, W. Shin, and M. Nishibori

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 761–766

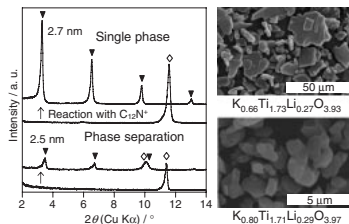


Sols of spherical cerium oxide nanoparticles with size of 50–120 nm are prepared by a reflux method adding polymer. The nanoparticle size can be controlled by adjustment of the molecular weight of the polymer. Colloidal crystals are also obtained.

#### Composition-Dependent Ion-Exchange Reactivity of Potassium Lithium Titanates

Y. Fuse, Y. Ide, and M. Ogawa\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 767–772

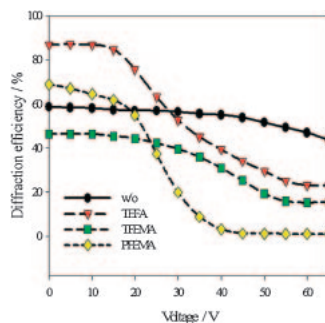


The reactivity of potassium lithium titanates toward an alkylammonium ion varied depending on the composition and was successfully tuned by controlling the composition.

#### Holographic PDLC Containing Fluorine Segments

E. H. Kim, J. Y. Woo, Y. H. Cho, and B. K. Kim\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 773–777



Fluorine segments added to conventional HPDLC induced low driving voltage ( $<4 \text{ V } \mu\text{m}^{-1}$ ) and fast rise time ( $<8 \text{ ms}$ ) caused by low anchoring strength between polymer and LC, in addition to high diffraction efficiency with maximum of about 80% at 5% fluorine monomer.

#### Volume Effect of Alkyl Chains on Organization of Ionic Self-Assemblies toward Hexagonal Columnar Mesophases

T. Noguchi, K. Kishikawa, and S. Kohmoto\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 778–783

Upon ionic complexation of triamine and mono-acids, hexagonal columnar mesophases were generated. The most stable columnar mesophase of the ionic complexes is attained with appropriate amine–acid ratios specific to the alkyl substituents of the acids.

