

# BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

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## Award Accounts

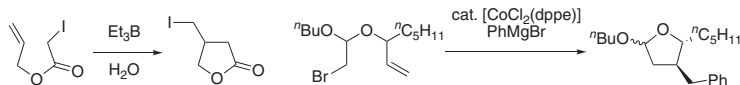
### The Chemical Society of Japan Award for 2006

#### Highly Selective Synthetic Reactions by the Combined Use of Organometallic Reagents and Radical Species

K. Oshima

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 1–24

Several new synthetic reactions have been developed: (1) Regio- and stereo-selective silylmethylation of acetylenes, (2) triethylborane induced radical reactions and radical cyclization of iodoacetate in water, and (3) organic synthesis with three organometallic ate complexes ( $R_3MnMgBr$ ,  $R_3MgLi$ , and  $R_3Co(L_2)-MgBr$ ).



## Award Accounts

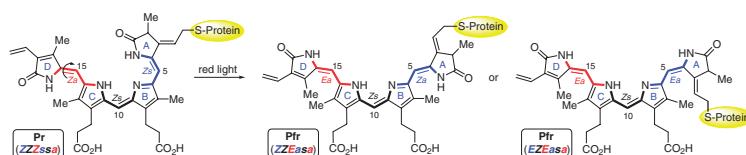
### The Chemical Society of Japan Award for Creative Work for 2006

#### Studies on the Structure and Function of Phytochromes as Photoreceptors Based on Synthetic Organic Chemistry

K. Inomata

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 25–59

An efficient and flexible synthetic method of phytochrome chromophores was developed. Assembly experiments of the synthetic chromophores with apo-phytochromes in vitro and in vivo provided us insights into the structure and function of phytochromes as photoreceptors.



## Award Accounts

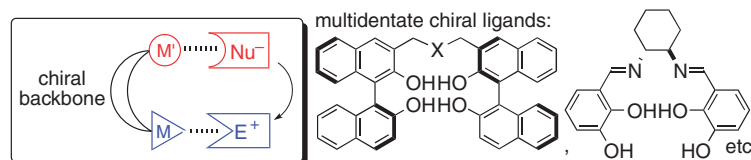
### The Chemical Society of Japan Award for Young Chemists for 2006

#### Multimetallic Bifunctional Asymmetric Catalysis Based on Proximity Effect Control

S. Matsunaga\* and M. Shibasaki\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 60–75

Design and applications of various homo- and hetero-multimetallic asymmetric catalysts based on the concept of proximity effect control are described. Strategies in designing suitable multidentate chiral ligands and selecting suitable metal combinations are introduced.

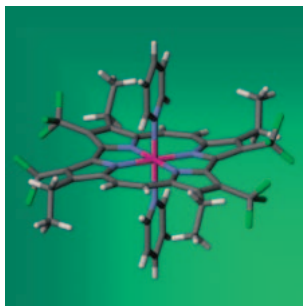


## BCSJ Award Article

### Isolable Iron(II)–Porphycene Derivative Stabilized by Introduction of Trifluoromethyl Groups on the Ligand Framework

K. Ito, T. Matsuo, I. Aritome,  
Y. Hisaeda, and T. Hayashi\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
76–83

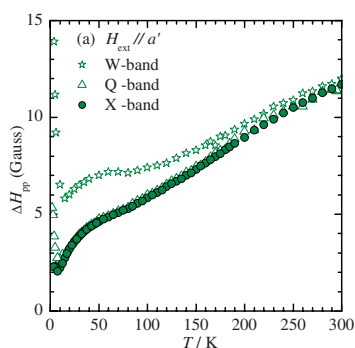


Trifluoromethylated iron porphycene  $\mu$ -oxo dimer was easily converted into the monomeric iron(II) species via the  $\text{Fe}^{\text{III}}\text{--O--Fe}^{\text{III}}$  bond cleavage upon dissolution in pyridine. The reduction product was quite stable and its structure was successively determined by X-ray crystallographic analysis.

### Multi-Frequency ESR Studies on Low-Dimensional Antiferromagnets, $\zeta$ -(BEDT-TTF) $_2$ PF $_6$ (THF) and $\gamma$ -(BEDT-TTF) $_2$ PF $_6$

K. Maeda,\* T. Hara,  
K. Furukawa, and T. Nakamura

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
84–90



Multi-frequency Electron Spin Resonance measurements were performed on  $\zeta$ -(BEDT-TTF) $_2$ PF $_6$ (THF) and  $\gamma$ -(BEDT-TTF) $_2$ PF $_6$ . Anomalous temperature and frequency dependence of the ESR linewidth was observed for  $\gamma$ -(BEDT-TTF) $_2$ PF $_6$ . The spin correlation in these salts is discussed in relation to the magnetic and structural dimensionality.

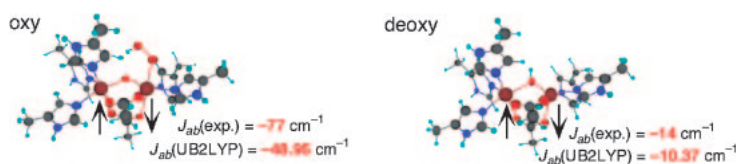
## Selected Paper

### Theoretical Studies on Electronic Structures and Chemical Indices of the Active Site of Oxygenated and Deoxygenated Hemerythrin

Y. Takano,\* H. Isobe, and K. Yamaguchi

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
91–102

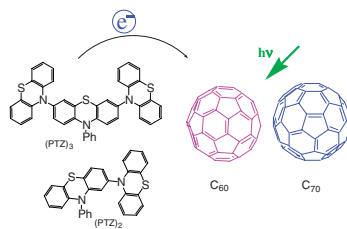
The origin of the magnetic couplings, the nature of the chemical bond, and the mechanism of the dioxygen binding of the active site of hemerythrin were examined with an appropriate theoretical method and realistic models.



### Photoinduced Electron-Transfer and Electron-Mediating Processes of Fullerenes and Phenothiazine Oligomers in a Polar Solvent

D.-M. S. Islam, Y. Sasaki, H. Kawauchi,  
M. Kozaki, Y. Araki,\* O. Ito, and K. Okada\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
103–109

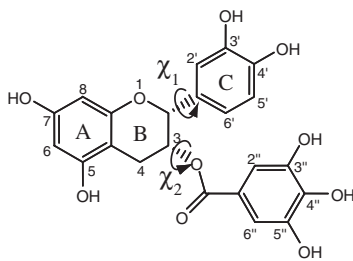


Photosensitizing electron-transfer/electron-mediating systems were established between  $\text{C}_{60}/\text{C}_{70}$  and  $(\text{PTZ})_n$  via  ${}^3\text{C}_{60}^*/{}^3\text{C}_{70}^*$  in the presence of viologen dication and an appropriate hole shifter. In addition, the structures of  $(\text{PTZ})_n^{\bullet+}$  generated through the photoinduced electron-transfer processes were elucidated.

### Ab Initio MO-MD Simulation Based on the Fragment MO Method. A Case of (-)-Epicatechin Gallate with STO-3G Basis Set

K. Tamura, T. Watanabe,  
T. Ishimoto, and U. Nagashima\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
110–112



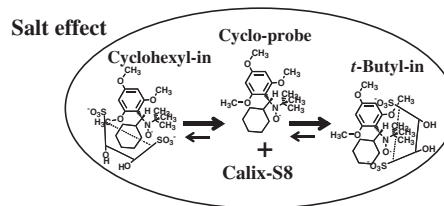
We performed ab initio MO-MD simulation based on the fragment MO method using the (-)-epicatechin gallate in order to examine the efficiency of fragmentation pattern in comparison with conventional MO-MD. We clearly demonstrated that the FMO-MD simulation is sufficient for determining the trajectory of the total energy and the geometry difference.

### Detection of Group-in Complexes with Water-Soluble *p*-Sulfonatocalix[8]arene on Addition of Alkali Salts by Using Electron Spin Resonance Spectroscopy

Y. Sueishi,\* K. Miyazono,  
M. Negi, and Y. Kotake

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
113–115

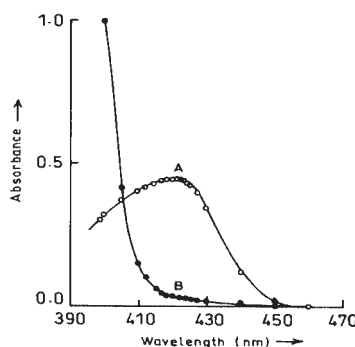
The change in ionic strength of the solution appeared to drive the functional group of the probe deep into the calixarene cavity, making it possible to detect group-in complexes by using ESR spectroscopy.



### Extractive Spectrophotometric Determination of Tungsten(VI) as Its 6-Chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran Complex

R. Agnihotri, N. Agnihotri, and J. R. Mehta\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
116–119

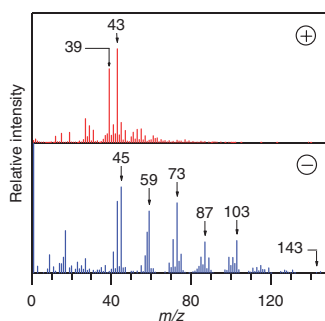


6-Chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran [CHTB] formed a yellow-colored (1:3) complex with tungsten(VI), which was extracted into chloroform from 0.16–0.32 mol dm<sup>-3</sup> HCl solutions. The complex showed an absorption maximum at 417–423 nm (figure curve A: W<sup>VI</sup> complex (2 μg cm<sup>-3</sup>) studied against reagent blank, curve B: reagent blank against pure chloroform). The absorbance followed Beer's law in the range of 0–3.0 μg of W cm<sup>-3</sup>, and a molar absorptivity of 4.05 × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> and a stability constant of 7.34 × 10<sup>11</sup> were obtained.

### Single Particle Analysis of Secondary Organic Aerosols Formed from 1,4-Cyclohexadiene Ozonolysis Using a Laser-Ionization Single-Particle Aerosol Mass Spectrometer

M. Narukawa, Y. Matsumi,\* J. Matsumoto,  
K. Takahashi, A. Yabushita, K. Sato,  
and T. Imamura

*Bull. Chem. Soc. Jpn.* **2008**, *81*,  
120–126

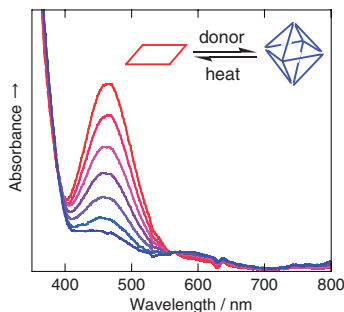


Real-time analysis of secondary organic aerosol (SOA) particles formed from 1,4-cyclohexadiene ozonolysis was performed using a laser-ionization single-particle aerosol mass spectrometer. Intense peaks in negative-ion mass spectra suggest that chemical compositions of the SOA particles vary with the particle size.

### Synthesis, Crystal Structure, and Chromotropic Properties of Mixed-Ligand Nickel(II) Complexes with 1,3-Diketone and P–N Bidentate Ligands

M. Arakawa, N. Suzuki, S. Kishi, M. Hasegawa, K. Satoh, E. Horn, and Y. Fukuda\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 127–135

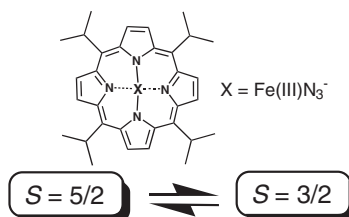


Solvatochromic and thermochromic behaviors of nickel(II) complexes containing P–N bidentate ligand were investigated by spectroscopic analysis in solvents with different donor number at varying temperature.

### Electronic Properties in a Five-Coordinate Azido Complex of Nonplanar Iron(III) Porphyrin: Revisiting to Quantum Mechanical Spin Admixing

S. Neya,\* A. Takahashi, H. Ode, T. Hoshino, A. Ikezaki, Y. Ohgo, M. Takahashi, Y. Furutani, V. A. Lórenz-Fonfría, H. Kandori, H. Hiramatsu, T. Kitagawa, J. Teraoka, N. Funasaki, and M. Nakamura

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 136–141



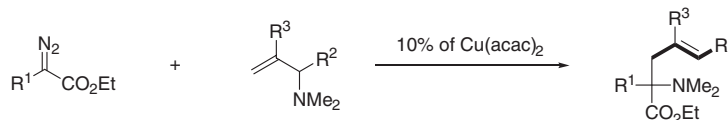
An iron-bound azido ligand in a ruffled iron(III) porphyrin complex was found to exhibit two IR bands, suggesting that the  $S = 5/2$  and  $3/2$  spin-isomers are in thermal equilibrium with a minimum lifetime of 0.4 ps.

### Copper-Catalyzed Intermolecular Generation of Ammonium Ylides with Subsequent [2,3]Sigmatropic Rearrangement. Efficient Synthesis of Bifunctional Homoallylamines

K. Honda,\* H. Shibuya, H. Yasui, Y. Hoshino, and S. Inoue

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 142–147

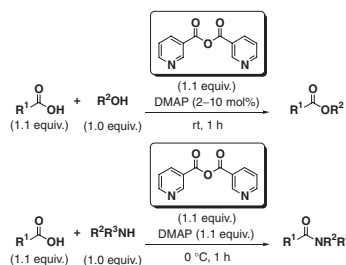
The copper-catalyzed [2,3]sigmatropic rearrangement of allylic ammonium ylides, which were generated by the reaction of *N,N*-dimethyl-1-alkyl-2-methylallylamines, derived from terpene alcohols, with diazo compounds, gave tri-substituted *E*-olefins in one-pot. In addition, the substituent effect at the 2-position of *N,N*-dimethylallylamine was investigated.



### A Versatile, Practical, and Inexpensive Reagent, Pyridine-3-carboxylic Anhydride (3-PCA), for Condensation Reactions

S. Funasaka and T. Mukaiyama\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 148–159



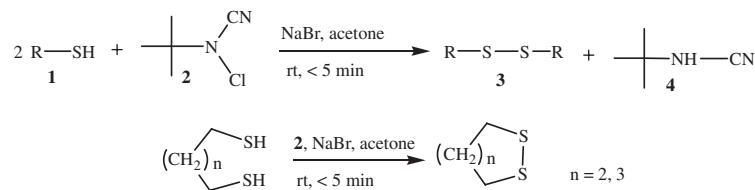
A highly useful method for the preparation of carboxylic esters and carboxamides from various carboxylic acids was established by using pyridine-3-carboxylic anhydride (3-PCA) in the presence of 4-(dimethylamino)pyridine. These reactions proceeded smoothly under mild conditions by using simple experimental procedure.

### Efficient Oxidative Coupling of Thiols into Disulfides Using *N*-*tert*-Butyl-*N*-chlorocyanamide

V. Kumar and M. P. Kaushik\*

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 160–162

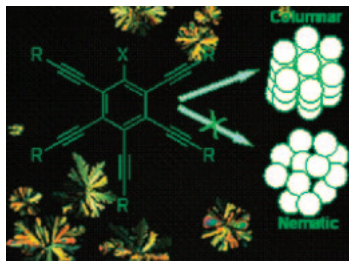
Reaction of aliphatic/aromatic/heterocyclic thiols with *N*-*tert*-butyl-*N*-chlorocyanamide in presence of sodium bromide is described. The reaction was very rapid and resulted in the formation of disulfides in excellent yields under mild conditions.



### Discotic Liquid Crystals: Synthesis and Characterization of Radial Polyalkynylbenzene Derivatives

S. K. Varshney,\* H. Takezoe, and D. S. S. Rao

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 163–167



New radial polyalkynylbenzene derivatives, which consist of 4-phenylacetylene unit connected with a central phenyl, phenoxy, or tolyl linking moiety, are presented. The hexaalkynylbenzene derivatives in a pure form showed a columnar mesophase, and the pentaalkynylbenzene and pentaalkynyltoluene derivatives remained in the highly viscous liquid state even at room temperature, whereas the D–A complexes showed a columnar hexagonal mesophase.

### Hydrosilanes as Reducing Reagents of Copper Salts into Copper Metal Particles under Remarkably Mild Conditions

M. Takahashi, J. Kamada,\* K. Iwata, K. Goto, H. Watanabe, and S. Tamai

*Bull. Chem. Soc. Jpn.* **2008**, *81*, 168–170

Copper nanoparticles were synthesized using hydrosilanes as the reducing agent. The reaction smoothly occurred under remarkably mild conditions, i.e., room temperature. The reaction depended on the counter anions of the copper salts and the structure of the hydrosilanes.

