

# BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN

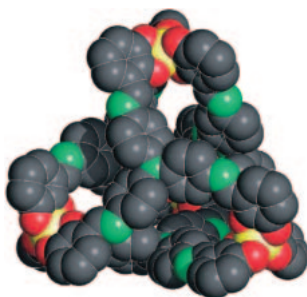
<http://www.csj.jp/journals/bcsj/>

Volume 80, Number 5, May 2007

## Vol. 80 Commemorative Accounts

### Symmetry Driven Self-Assembly of Metallo-Supramolecular Architectures

M. Albrecht\* and R. Fröhlich



The self-assembly leading to metallosupramolecular aggregates like helicates, *meso*-helicates or  $M_4L_4$  tetrahedra is controlled by the symmetry of the molecular building blocks: ligands as well as metal ions.

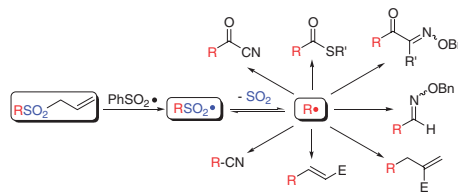
*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
797–808

## Vol. 80 Commemorative Accounts

### Tin-Free Radical Carbon–Carbon Bond-Forming Reactions Based on $\alpha$ -Scission of Alkylsulfonyl Radicals

S. Kim\* and S. Kim

Tin-free radical reactions based on  $\alpha$ -scission of alkylsulfonyl radicals are very useful for various carbon–carbon bond formations. Especially, alkyl allyl sulfone precursors are highly efficient and most reliable to generate primary alkyl radicals under tin-free conditions for the further formation of carbon–carbon bonds.



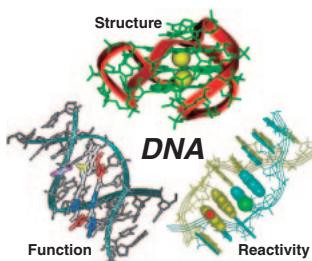
*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
809–822

## Award Accounts

### The Chemical Society of Japan Award for Creative Work for 2004

### Chemical Biology that Controls DNA Structure and Function: Lessons in Organic Chemistry from Nature

H. Sugiyama



Our long term efforts in understanding of DNA reactivity, structure, and function are reviewed. The prospective uses of the chemical biology of DNA are also discussed.

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
823–841

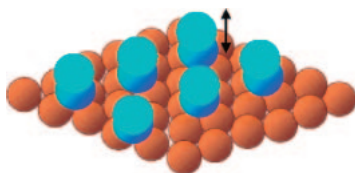
## Award Accounts

### The Chemical Society of Japan Award for Creative Work for 2005

#### Photochemistry and Photo-Induced Ultrafast Dynamics at Metal Surfaces

Y. Matsumoto

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 842–855



The stretching mode of alkali-metal adsorbates at a metal surface is coherently excited with femtosecond pump pulses and its decaying process is probed by using second harmonic generation in real time.

## Award Accounts

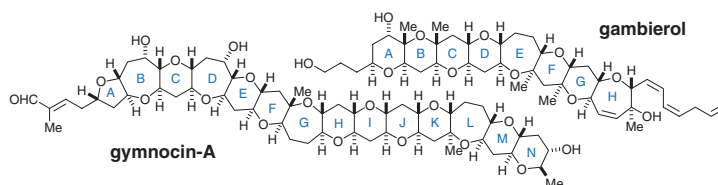
### The Chemical Society of Japan Award for Creative Work for 2005

#### Development and Application of a Convergent Strategy for the Total Synthesis of Polycyclic Ether Natural Products

M. Sasaki

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 856–871

The polycyclic ether class of marine natural products presents formidable and challenging synthetic targets due to their structural complexity and exceptionally potent biological activities. In this account, the development and application of a convergent strategy for the synthesis of natural polycyclic ethers are described.



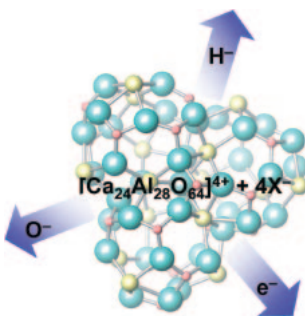
## Award Accounts

### The Chemical Society of Japan Award for Young Chemists for 2005

#### Functionalities of a Nanoporous Crystal $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ Originating from the Incorporation of Active Anions

K. Hayashi,\* M. Hirano, and H. Hosono

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 872–884



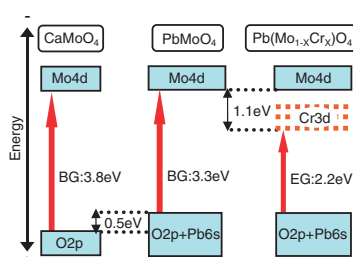
A cage structure in a positively charged lattice framework was utilized to incorporate and release chemically unstable anions. This approach imparted unique chemical and electronic activities to this material.

## BCSJ Award Article

#### Investigations of Electronic Structures and Photocatalytic Activities under Visible Light Irradiation of Lead Molybdate Replaced with Chromium(VI)

Y. Shimodaira, H. Kato, H. Kobayashi, and A. Kudo\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 885–893



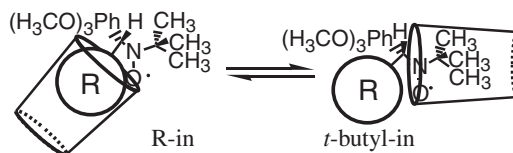
$\text{PbMo}_{1-x}\text{Cr}_x\text{O}_4$  exhibited visible light-driven photocatalytic activity for  $\text{O}_2$  evolution from an aqueous solution. On the basis of DFT calculations, the present study indicated that the formation of an electron-acceptor level is one strategy for developing new visible light driven photocatalysts.

### Group-Inclusion Complex and Its External High Pressure Effect in *O*-Methylated $\beta$ -Cyclodextrin as Compared with Unmodified $\beta$ -Cyclodextrin

Y. Sueishi,\* H. Tobisako, and Y. Kotake

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 894–898

High static pressure was applied to the inclusion complex of a modified  $\beta$ -cyclodextrin, heptakis(2,6-di-*O*-methyl)- $\beta$ -cyclodextrin (DM- $\beta$ -CD). We investigated group-inclusion equilibria in DM- $\beta$ -CD under high static pressure and compared with the data for unmodified  $\beta$ -CD.

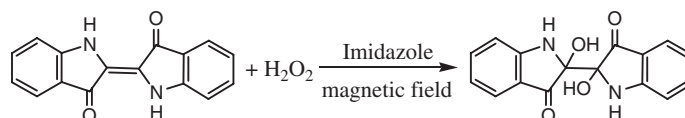


### The Effect of Magnetic Field on the Bleaching of Indigo Dyes with Hydrogen Peroxide Catalyzed by Imidazole

A. A. Rousan and A. M. Al-Ajlouni\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 899–901

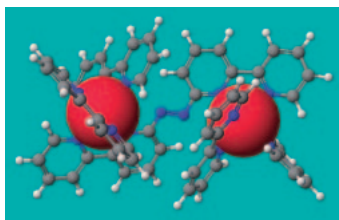
The effect of applying a magnetic field on the catalytic oxidation of indigo dyes by  $\text{H}_2\text{O}_2$ /imidazole was investigated. The rate of oxidation, in the presence of imidazole, was enhanced by applying an external magnetic field in the range of 0.035–0.12 T.



### 6,6''-Azobis(2,2'-bipyridine) and Its Dinuclear Ruthenium Complex: A Comparative Study with Positional Isomers

J. Otsuki,\* I. Kurihara, A. Imai, Y. Hamada, and N. Omokawa

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 902–909

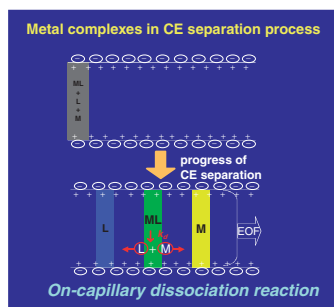


The ligand 6,6''-azobis(2,2'-bipyridine), a new member of the family of azo-bridged bis(bipyridine) ligands, was prepared. A dinuclear Ru complex bridged by this ligand was characterized, and it was shown that the bridge mediates a moderate, but the largest among the family, intermetallic interaction.

### Dissociation Kinetics and Complexation Equilibrium Studies of a $\text{Zn}^{\text{II}}$ Complex with 1,5-Bis(2-hydroxy-5-sulphophenyl)-3-cyanoformazan during Capillary Electrophoretic Separation Process

T. Takahashi,\* Y. Takehara, and H. Hoshino

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 910–915

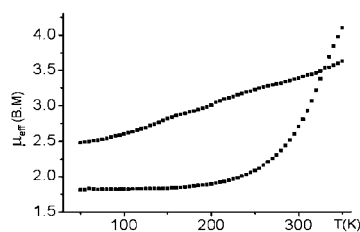


The dissociation reaction kinetics and the complexation equilibrium of a metal complex were studied to clarify whether the “stability” of the metal complex during capillary electrophoretic separation process is kinetic or thermodynamic.

### Dinuclear Valence Tautomeric 1,2-Semiquinonato/Catecholato-cobalt Complexes Containing 1,1,4,7,10,10-Hexamethyltriethylenetetramine

H. Liang, Y. M. Na, I. S. Chun, S. S. Kwon, Y.-A Lee, and O.-S. Jung\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 916–921



Intramolecular charge distribution between  $[\text{Co}^{\text{III}}]/[\text{Co}^{\text{II}}]$  valence tautomers of two dinuclear 1,2-semiquinonato/catecholato-cobalt complexes with 1,1,4,7,10,10-hexamethyltriethylenetetramine (hmteta) was investigated.  $[\text{Co}_2(\text{hmteta})(3,6\text{-dbbq})_4] \cdot 2\text{C}_6\text{H}_5\text{CH}_3$  was low spin  $[\text{Co}^{\text{III}}(3,6\text{-dbsq})(3,6\text{-dbcat})(\text{hmteta})\text{Co}^{\text{III}}(3,6\text{-dbsq})(3,6\text{-dbcat})]$  (3,6-dbsq = 3,6-di-*tert*-butyl-1,2-semiquinonato; 3,6-dbcat = 3,6-di-*tert*-butylcatecholato), while  $[\text{Co}_2(\text{hmteta})(3,5\text{-dbbq})_4] \cdot \text{C}_6\text{H}_5\text{CH}_3$  was close to  $[\text{Co}^{\text{II}}(3,5\text{-dbsq})_2(\text{hmteta})\text{Co}^{\text{II}}(3,6\text{-dbsq})_2]$  in the solid state at ambient temperature.

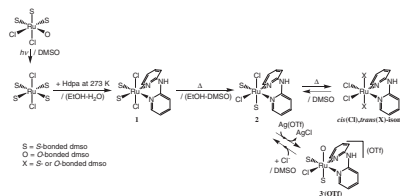
### Selected Paper

#### Syntheses and Crystal Structures of Mono(di-2-pyridylamine)chloro(dimethyl sulfoxide-*S*)ruthenium(II) Complexes [RuCl<sub>2</sub>(Hdpa)(dms-*S*)<sub>2</sub>] and [RuCl(Hdpa)(dms-*O*)(dms-*S*)<sub>2</sub>](OTf)

M. Toyama,\* R. Suganoya,  
D. Tsudaura, and N. Nagao\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
922–936

Two isomers of a mono(di-2-pyridylamine)ruthenium complex, *trans*(Cl),*cis*(*S*)- and *cis*(Cl),*cis*(*S*)-[RuCl<sub>2</sub>(Hdpa)(dms-*S*)<sub>2</sub>] (**1** and **2**, respectively), along with *cis*(Cl,*S*),*trans*(*O*,*S*)-[RuCl(Hdpa)(dms-*O*)(dms-*S*)<sub>2</sub>](OTf) (**3**•(OTf)), were selectively synthesized and characterized by X-ray crystallography. The crystal structures revealed that the conformation of the Hdpa ligand varies according to its interaction with the co-ligands (dms-*O* and Cl<sup>-</sup>) or counter-anion (OTf<sup>-</sup>).

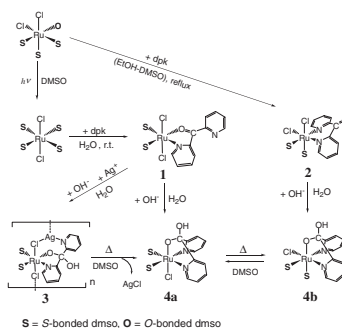


### Selected Paper

#### Syntheses, Crystal Structures, and Conversion of Three Linkage Isomers of Di-2-pyridyl Ketone in Dichlorobis(dimethyl sulfoxide-*S*)ruthenium(II) and Chlorobis(dimethyl sulfoxide-*S*)ruthenium(II) Complexes: [RuCl<sub>2</sub>(dpk-κ<sup>2</sup>*N*,*O*)(dms-*S*)<sub>2</sub>], [RuCl<sub>2</sub>(dpk-κ<sup>2</sup>*N*,*N'*)(dms-*S*)<sub>2</sub>], and [RuCl(dpk-OH-κ<sup>3</sup>*N*,*O*,*N'*)(dms-*S*)<sub>2</sub>]

M. Toyama,\* M. Nakahara, and N. Nagao\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
937–950

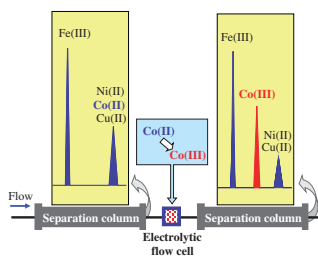


Ruthenium(II) complexes containing three linkage isomers of di-2-pyridyl ketone, *trans*(Cl),*cis*(*S*)-[RuCl<sub>2</sub>(dpk-κ<sup>2</sup>*N*,*O*)(dms-*S*)<sub>2</sub>] (**1**), *cis*(Cl),*cis*(*S*)-[RuCl<sub>2</sub>(dpk-κ<sup>2</sup>*N*,*N'*)(dms-*S*)<sub>2</sub>]•DMSO (**2**•DMSO), and *trans*(Cl,*O*),*cis*(*S*)-[RuCl(dpk-OH-κ<sup>3</sup>*N*,*O*,*N'*)(dms-*S*)<sub>2</sub>] (**4a**), as well as *trans*(Cl),*cis*(*S*)-[AgRuCl<sub>2</sub>(dpk-OH-κ<sup>3</sup>*N*,*O*,*N'*)(dms-*S*)<sub>2</sub>]<sub>n</sub> (**3**) were synthesized and characterized by X-ray crystallography. The reaction of **1** or **2** with OH<sup>-</sup> afforded **4a** or *cis*(Cl,*O*),*cis*(*S*)-[RuCl(dpk-OH-κ<sup>3</sup>*N*,*O*,*N'*)(dms-*S*)<sub>2</sub>] (**4b**), respectively.

#### On-Line Electrochemical Redox Derivatization for Enhancement of Separation Selectivity of Liquid Chromatography

K. Saitoh,\* S. Naitoh, M. Endo,  
M. Washiya, and M. Shibukawa

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
951–956



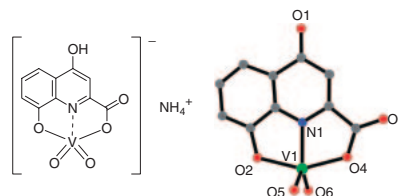
An on-line electrochemical redox derivatization HPLC system composed of two separation flow cell columns and a small electrolytic flow cell placed between them is presented. Selective separation of an analyte compound was achieved by controlling the redox reactions specific for the analyte through alteration of the potential applied to the cell.

#### Structural Characterization of a Dioxovanadium(V) Complex with 4,8-Dihydroxyquinoline-2-carboxylic Acid

T. Moriuchi, M. Nishiyama, T. Beppu,  
T. Hirao,\* and D. Rehder\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
957–959

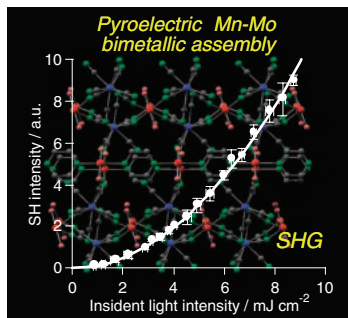
A *cis*-dioxovanadium(V) complex with 4,8-dihydroxyquinoline-2-carboxylic acid was synthesized and found to be packed in a hexagonal molecular arrangement through  $\pi$ - $\pi$  interaction, creating a channel cavity for a one-dimensional water chain.



### Crystal Structure, Magnetic Properties, and Second Harmonic Generation of a Three-Dimensional Pyroelectric Cyano-Bridged Mn–Mo Complex

W. Kosaka, T. Nuida,  
K. Hashimoto, and S. Ohkoshi\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
960–962

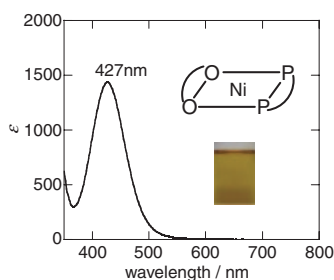


A paramagnetic pyroelectric 3-dimensional cyano-bridged bimetal assembly,  $[\{Mn^{II}(H_2O)_2\}\{Mn^{II}(pyrazine)(H_2O)_2\}\{Mo^{IV}(C-N)_8\}]\cdot 4H_2O$  ( $P2_1$ ) was synthesized. This compound displayed second harmonic generation with a value of  $6.0 \times 10^{-11}$  esu.

### Synthesis, Structures, and Properties of Nickel(II) Mixed-Ligand Complexes Containing Various $\beta$ -Diketonates and a Phosphorus Donor Bidentate Ligand

M. Arakawa, H. Miyamae, and Y. Fukuda\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
963–965



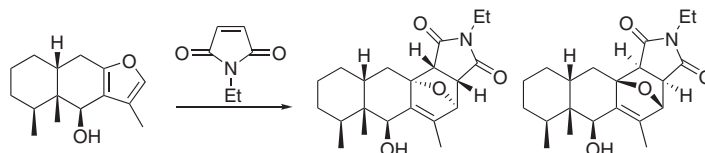
The ternary complexes,  $[Ni(dike)(dppe)]X$  keep their square-planar structures both in solid state and in donor solvents due to the strong ligand field strength of dppe. The peak positions of these complexes are not so much different between substituent groups of  $\beta$ -diketonates.

### Fixation of Natural Furanoremorphilane by Diels–Alder Reaction

K. Iida, M. Mitani, and C. Kuroda\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
966–971

Unstable natural furanoeremophilanes were fixed as stable Diels–Alder adducts with maleimide.

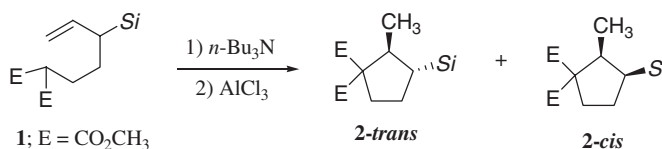


### Carbocyclization Reaction of Malonate Derivatives with Allylsilane Moiety Mediated by $AlCl_3$ - $n$ - $Bu_3N$

S. Imazeki,\* R. Kinoshita, and T. Akiyama

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
972–978

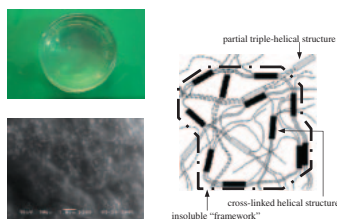
Allylsilane bearing active methine compounds underwent intramolecular carbocyclization reaction by means of  $AlCl_3$ - $n$ - $Bu_3N$  to give silyl-substituted cyclopentanes with good yields.



### Radiation-Induced Cross-Linking of Gelatin by Using $\gamma$ -Rays: Insoluble Gelatin Hydrogel Formation

M. Bessho,\* T. Kojima,  
S. Okuda, and M. Hara

*Bull. Chem. Soc. Jpn.* **2007**, *80*,  
979–985

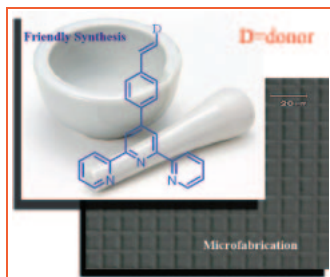


Hydrogels of Type-A gelatin were cross-linked by  $\gamma$ -ray irradiation, and then, their physical properties were investigated. From these results, we propose a model for the formation of insoluble gelatin hydrogels induced by  $\gamma$ -ray irradiation.

### Synthesis, Structures, and Optical Properties of Two Novel Two-Photon Initiators Derived from 2,2':6',2''-Terpyridine

Z.-J. Hu, J.-X. Yang,\* Y.-P. Tian,\* X.-T. Tao, L. Tian, H.-P. Zhou, G.-B. Xu, W.-T. Yu, Y.-X. Yan, Y.-H. Sun, C.-K. Wang, X.-Q. Yu, and M.-H. Jiang

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 986–993

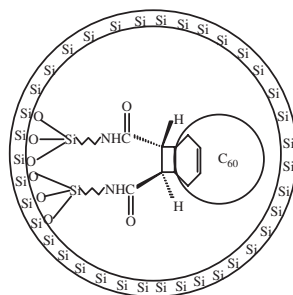


Efficient aqueous-phase aldol condensation, Michael addition, and solvent-free Wittig reactions were employed to synthesize two D- $\pi$ -A-type two-photon initiators derived from 2,2':6',2''-terpyridine. The title initiators, which have good one and two-photon activities, were successfully utilized as initiators to realize microfabrication by TPIP.

### Monodispersed Fullerene Derivatives Introduced into the Channels of Mesoporous Silica via Chemical Bond Interactions

H. Wu, Y. Lin,\* J. Tang, D. Gao, R. Cai, and D. Zhao\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 994–998



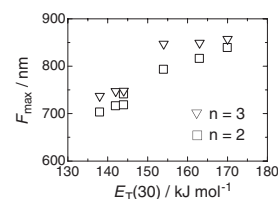
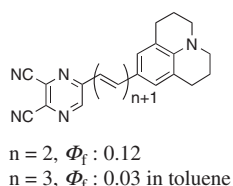
The fullerene derivative  $C_{60}(CHCOOH)_2$  was chemically grafted to the backbone of mesoporous silica SBA-15, and SBA-15 was shown to be an effective carrier for fullerene derivatives.

### Near-Infrared Fluorescent 2,3-Dicyanopyrazines

M. Matsui,\* T. Maehashi, and K. Funabiki

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 999–1003

Novel non-ionic NIR fluorescent 2,3-dicyanopyrazines with clear positive solvatochromism were prepared.

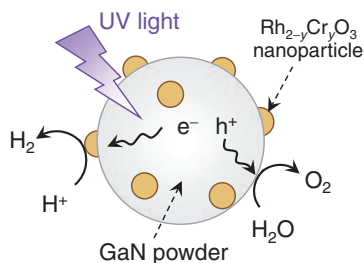


### Selected Paper

#### Photocatalytic Overall Water Splitting on Gallium Nitride Powder

K. Maeda, K. Teramura, N. Saito, Y. Inoue, and K. Domen\*

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 1004–1010



GaN powder modified with  $Rh_{2-y}Cr_yO_3$  nanoparticles as a cocatalyst for  $H_2$  evolution were found to be an active and stable photocatalyst for overall water splitting under UV irradiation ( $\lambda > 300$  nm).

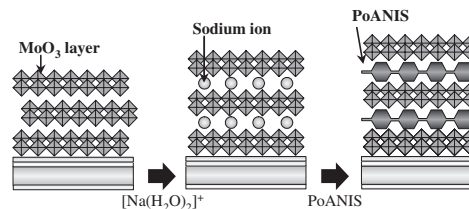
### Selected Paper

#### Preparation and Characterization of a Layered Molybdenum Trioxide with Poly(*o*-anisidine) Hybrid Thin Film and Its Aldehydic Gases Sensing Properties

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

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 1011–1016

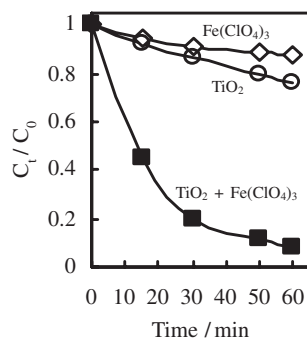
Layered molybdenum trioxide with PoANIS ((PoANIS)<sub>x</sub>MoO<sub>3</sub>) hybrid thin film was formed by CVD and an intercalation process, in which sodium ions were exchanged for PoANIS into MoO<sub>3</sub>. The (PoANIS)<sub>x</sub>MoO<sub>3</sub> hybrid thin film was investigated by gas-sensing properties analysis.



#### Degradation of Phenol under Visible Light Irradiation Using TiO<sub>2</sub> with Fe<sup>III</sup> and Easy Sedimentation of TiO<sub>2</sub> Particles

M. S. Nahar, K. Hasegawa,\*  
S. Kagaya, and S. Kuroda

*Bull. Chem. Soc. Jpn.* **2007**, *80*, 1017–1019



The combined photocatalytic system (P25 TiO<sub>2</sub> + Fe(ClO<sub>4</sub>)<sub>3</sub>) was visible light active, and phenol degradation was significantly increased. The reason is discussed based on the catalytic cycle of Fe<sup>III</sup>/Fe<sup>II</sup>. The suspended TiO<sub>2</sub> particles were easily sedimented by neutralizing the suspension.