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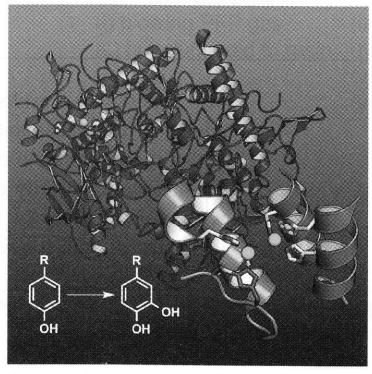
■ Award Accounts

The Chemical Society of Japan Award for Creative Work for 2014

Controlling Dicopper Protein Functions

Nobutaka Fujieda and Shinobu Itoh*



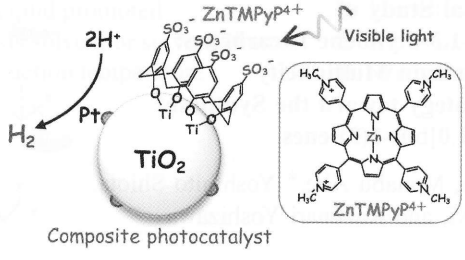
The activation process of the coupled dinuclear copper proteins such as tyrosinase remained to be clarified until lately. Thorough understanding of its molecular mechanism as well as the phenolase reaction mechanism is provided on the basis of the crystal structures.

Bull. Chem. Soc. Jpn. **2016**, *89*, 733–742

Design of Visible Light Sensitive Heterogeneous Photocatalyst by Utilization of Sulfocalixarene as a Linker of Zinc Porphyrin and Pt-TiO_2

Takashi Kamegawa,* Hiroki Imai, and Hiromi Yamashita*

Visible light sensitive heterogeneous photocatalyst for generation of H_2 was successfully designed by utilization of 4-sulfocalix[4]arene as a linker molecule for stable immobilization of 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)-porphyrinatozinc(II) ion on Pt-loaded TiO_2.

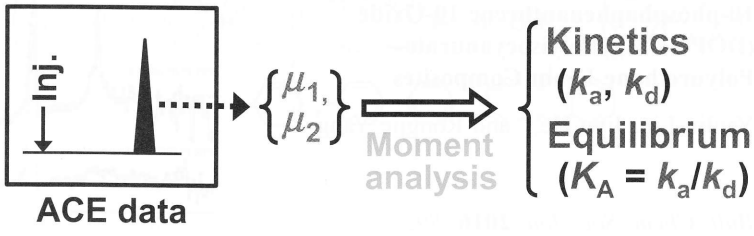


Bull. Chem. Soc. Jpn. **2016**, *89*, 743–745

Moment Analysis Theory for Kinetic Study of Intermolecular Interaction by Affinity Capillary Electrophoresis

Kanji Miyabe* and Nozomu Suzuki

The moment theory was developed to analytically determine association and dissociation rate constants from elution peaks measured by affinity capillary electrophoresis (ACE). Ample ACE data previously published can be used as a source for kinetic study of intermolecular interactions.



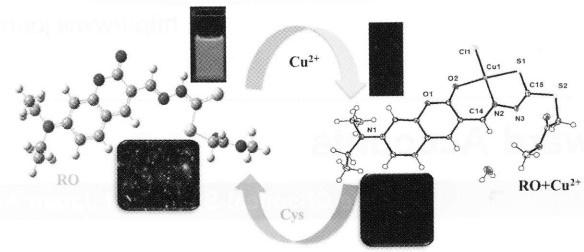
Bull. Chem. Soc. Jpn. **2016**, *89*, 746–753

Turn "Off–On" Fluorescent Recognition of Cu^{2+} and Cys in Aqueous Medium: Implementation of Molecular Logic Gate and Cell Imaging Studies

Virendra Kumar, Ajit Kumar, Uzra Diwan, Manish Kumar Singh, and K. K. Upadhyay*

Bull. Chem. Soc. Jpn. **2016**, *89*, 754–761

A fluorescent probe RO is fruitfully explored for the turn "off–on" recognition of Cu^{2+} and Cys in aqueous media with high sensitivity. The spectral observations were translated into an IMP molecular logic system. The RO also exhibited efficient bio-imaging of Cu^{2+} and Cys in *E. coli* cells.

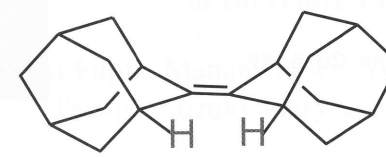


The Thermodynamic Stability of Adamantylideneadamantane and Its Proton- and Electron-Exchanges. Comparison with Simple Alkenes

José-Luis M. Abboud,* Ibon Alkorta,* Juan Z. Dávalos,* Ilmar A. Koppel, Ivar Koppel,* Dieter Lenoir,* Sonia Martínez, and Masaaki Mishima*

Bull. Chem. Soc. Jpn. **2016**, *89*, 762–769

We report the results of an experimental and computational study of adamantylideneadamantane (**1**). Calorimetric experiments provided the standard enthalpy of formation of **1**. FT-ICR spectroscopy allowed the determination of the gas phase basicity of **1**. These properties and the ionization potentials of **1** were computationally studied at the MP2/6-311+G(d,p) and/or G3 levels. Comparison with the reactivity of simple alkenes is given.

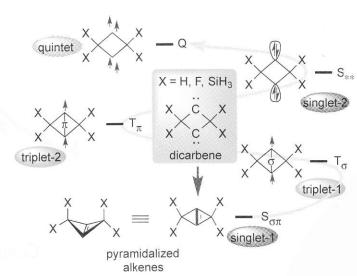


Selected Paper

Computational Study of Cyclobutane-1,3-diylidene Dicarbenes: Ground-State Spin Multiplicity and New Strategy toward the Synthesis of Bicyclo[1.1.0]but-1(3)-enes

Yoshiki Fujita, Manabu Abe,* Yoshihito Shiota, Tatsuya Suzuki, and Kazunari Yoshizawa

Bull. Chem. Soc. Jpn. **2016**, *89*, 770–778

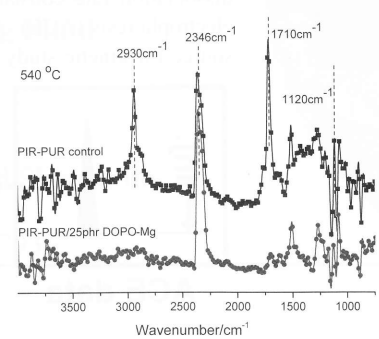


Coupled-cluster calculations were performed for cyclobutane-1,3-diylidene dicarbenes. The closed-shell singlet state with a bicyclo[1.1.0]but-1(3)-ene (BBE) structure found to be the ground-state was much lower in energy than other spin states.

The Thermal Properties and Flame Retardancy of 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (DOPO)–Mg/Polyisocyanurate–Polyurethane Foam Composites

Yanlin Liu, Jiyu He,* and Rongjie Yang

Bull. Chem. Soc. Jpn. **2016**, *89*, 779–785



DOPO–Mg changed the thermal degradation process of the PIR–PUR foam and prevented a kind of highly toxic flammable gas from being generated. DOPO–Mg can effectively produce spherical material covering the surface of the char to hinder flame and energy transmission in the condensed phase. The FTIR spectra of the pyrolytic gas products at 540 °C.

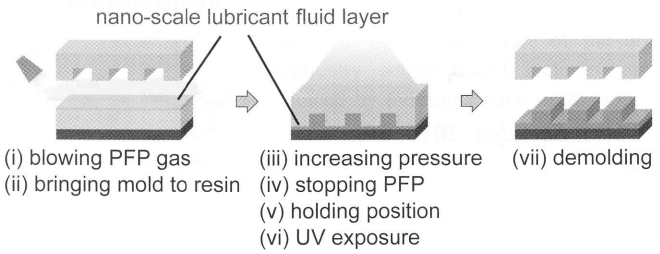
Selected Paper

Demolding in Ultraviolet Nanoimprinting Assisted by a Nanoscale Lubricating Fluid Layer of Condensed Alternative Chlorofluorocarbon

Masaru Nakagawa,* Shu Kaneko, and Shunya Ito

Bull. Chem. Soc. Jpn. **2016**, *89*, 786–793

We demonstrated that demolding in ultraviolet (UV) nanoimprinting was assisted by a nanoscale lubricating fluid layer of a liquefied 1,1,1,3,3-pentafluoropropane (PFP) gas. UV-curable *Resin A* composed of glycerol 1,3-diglycerolate diacrylate with low PFP absorption showed low surface roughness of 22-nm line-and-space imprint patterns with the smallest line edge roughness (LER) value of $3\sigma = 1.8$ nm.

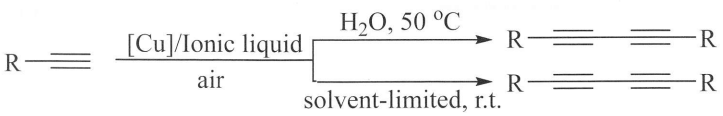


Ionic Liquid-Promoted Copper(II)-Catalyzed Homocoupling of Terminal Alkynes in Aqueous Phase or under Solvent-Limited Conditions

Shiguang Li, Xi Chen, Jinping Chen, and Hang Gong*

Bull. Chem. Soc. Jpn. **2016**, *89*, 794–797

A reusable ionic liquid 1-butyl-3-methylimidazolium bromide/Cu(II) system was proven to be a reusable catalyst for the homocoupling of terminal alkynes at mild temperature using air as oxidant in aqueous phase or under solvent-limited conditions. In most cases, good to excellent yields can be achieved. Furthermore, this reaction can be easily scaled up to gram level.



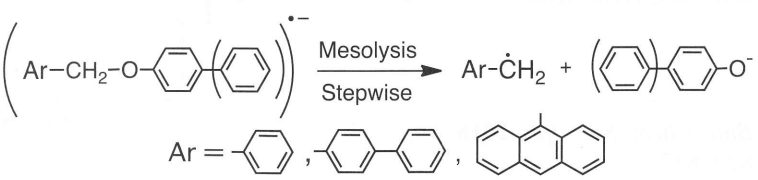
- Ionic liquid promoted
- Water as solvent or solvent-limited
- Low reaction temperature
- Directly recyclable
- Air as oxidant
- Gram reaction

Mesolysis Processes with Benzylic Carbon–Oxygen Bond Cleavage in Radical Anions of Aryl Benzyl Ethers Studied by Electron Pulse Radiolysis in DMF

Minoru Yamaji,* Sachiko Tojo, Mamoru Fujitsuka, Akira Sugimoto, and Tetsuro Majima*

Bull. Chem. Soc. Jpn. **2016**, *89*, 798–803

Mesolysis profiles due to the C–O bond cleavage in benzyl phenyl ether radical anions generated during electron pulse radiolysis in DMF were investigated based on transient absorption measurements at various temperatures and DFT calculations. The Arrhenius parameters for the mesolysis were determined. The mesolysis was shown to proceed via a stepwise mechanism.

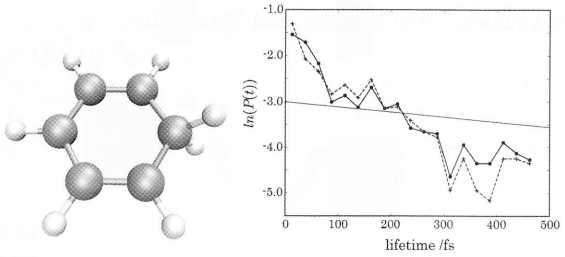


Proton-Transfer Dynamics in Protonated Benzene

Ayaka Kuroki, Hiroshi Ushiyama,* and Koichi Yamashita*

Bull. Chem. Soc. Jpn. **2016**, *89*, 804–809

The dynamically calculated lifetime distributeon contains a large number of short lifetime trajectories at $t < 50$ fs. By analyzing the nature of these short lifetime trajectories, we found that a transferred proton can be trapped between two carbon atoms. Based on these analysis, the concept of "dynamically stable trapped state" is proposed.

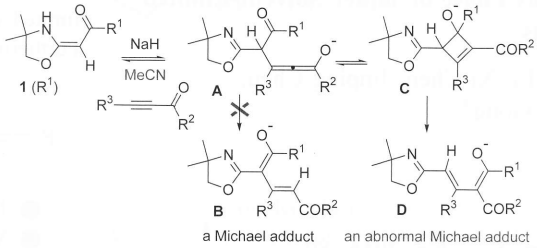


A Novel Abnormal Michael Reaction of 2-Acylmethyl-4,4-dimethyl-2-oxazolines with Acetylenic Ketones and Esters

Yasuo Tohda,* Takeshi Yanagidani, and Noriko Asaka

Bull. Chem. Soc. Jpn. **2016**, *89*, 810–822

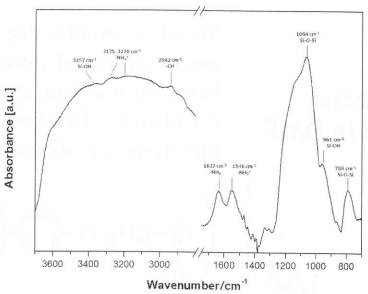
The first example of abnormal Michael reaction of an active methylene compound, 2-acylmethyl-4,4-dimethyl-2-oxazoline, with acetylenic ketone in acetonitrile is reported. Selectivity of the reaction depends on bulkiness of all the substituents of both the substrate and the reagent.



Effect of Surfactant on CO_2 Adsorption of APS-Grafted Silica Gel by One-Pot Process

Chang Hun Lee, Hyunchul Jung, Dong Hyun Jo, Sunbin Jeon, and Sung Hyun Kim*

Bull. Chem. Soc. Jpn. **2016**, *89*, 823–832



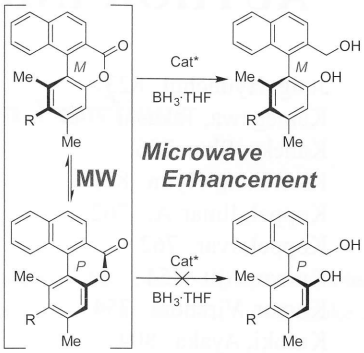
(3-Aminopropyl)trimethoxysilane (APS)-silica gels were prepared by a one-pot process using sodium silicate as a low-cost source of silica. After introducing several surfactants, the adsorption properties of gels were improved. By comparison of the pore and CO_2 uptake properties, we confirmed that P123 was a suitable surfactant for the preparation of APS-silica gel by a one-pot process using sodium silicate as the silica source.

■ BCSJ Award Article

Microwave Specific Effect on Catalytic *atropo*-Enantioselective Ring-Opening Reaction of Biaryl Lactones

Shigeki Tashima, Kazuya Nushiro, Kodai Saito, and Tohru Yamada*

Bull. Chem. Soc. Jpn. **2016**, *89*, 833–835



The microwave specific effect on the catalytic *atropo*-enantioselective ring-opening reaction of biaryl lactones was investigated. Under strictly controlled temperature conditions, the reaction was accelerated by microwave irradiation without any loss of the enantioselectivity. Also, it was revealed that the racemization rate of the *atropo*-optically active biaryl lactone was enhanced by the microwave irradiation.

Solvent Effects for Spectroscopic Properties of Near-Infrared Absorbing Nickel–Dithiolene Complex [Ni(*i*Pr$_2$timdt)$_2$] (*i*Pr$_2$timdt: Monoanion of 1,3-Diisopropylimidazolidine-2,4,5-trithione)

Tomoyuki Warashina* and Hitoshi Hoshino

Bull. Chem. Soc. Jpn. **2016**, *89*, 836–841

We have found out that the near-IR spectroscopic behavior of [Ni(*i*Pr$_2$timdt)$_2$] depends on the properties (coordination property, relative permittivity) of organic solvents.