

Research Center for Molecular-Scale Nanoscience

VIII-C Synthetic Approach Toward Molecular Scale Electronics

Electric properties of organic and in-organic nano structures are challenging field in material science. Those of aggregates, crystals, or polymers which are made from a large number of molecules or atoms have been well studied and established. In contrast, nano scale electronics is the forefront of science, and has been revealed gradually to have diverse phenomena such as quantum conductance, the Kondo effect, the Coulomb blockade, resonance tunneling and so on. In order to establish this field, we are synthesizing new organic and in-organic nano structures by using usual synthetic methods together with non-conventional lithographic technique, and measure their electric properties mainly.

VIII-C-1 Linear Functionalized Terthiophene Phenanthroline Polymer for Nanodevices

OGAWA, Takuji¹; ENDO, Hiroaki²; ARAKI, Koiti¹
(¹IMS, JST; ²IMS and Ehime Univ.)

The development of molecular electronic devices requires the preparation of new functional materials with suitable properties. Among them one have pursued the preparation of linear chain polymers constituted by porphyrins or ruthenium complexes that could be obtained in a controlled way. The redox and photo-physical properties of those compounds are well known, such that one were attracted by the possibility of generating nanodevices by connecting a bunch or even a single strand of those polymers to a couple of nanogap electrodes. In this communication we report the synthesis and characterization of the monomer as well as the properties of the a new linear hexathiophene-phenanthroline based charge transfer polymer functionalized with [Ru(bipy)₂(phen)] complexes, obtained by electropolymerization. The 1,10-phenanthroline with thiophene (tphen) and terthiophene (ttphen) radicals at the 3,8-positions were obtained by conventional Ni catalyzed coupling reactions and the complexes by reaction with [Ru(bipy)₂(OH₂)] in DMF. Both complexes exhibited four reversible waves in the -1 to -2 V range assigned to the reduction of each of the bipy, phen and thiophene groups to the corresponding radical anion. In the anodic side a quite different behavior was observed. While the tphen derivative exhibited a catalytic oxidation of tphen ligand around 1.3 V responsible for the electropolymerization, a reversible Ru(III/II) wave was observed for the tphen derivative. One found out that the polymeric complex can be easily grown in between the nanogap electrodes. The conduction and photoconduction properties are being investigated.

VIII-C-2 Synthesis of Self-Standing Molecular Jacks Bearing Long Anchoring Arms

OGAWA, Takuji¹; MIZUGUTI, Eisuke²
(¹IMS, JST; ²IMS and Ehime Univ.)

A series of porphyrin derivatives bearing more than four lipoic acyl groups have been synthesized. The

lipoic acyl group has disulfide moiety at the end of the acyl chain, and can be adsorbed to the gold surface. When rhodium metal is introduced in the center of the porphyrin, a variety of organic functional groups can be introduced as the axial group of the porphyrin plain. Thus, when the porphyrin plain is anchored to the gold surface by the lipoic acyl groups, the axial organic functional groups will stand perpendicularly to the gold surface. We call the porphyrin part of the molecule as a "molecular jack," because a variety of molecular wires can be connected to the electrode metal surface through the molecule.

One merit of the molecular jack is that the occupying area of the molecule on the electrode surface can be controlled by changing the length of the alkyl group connecting to the lipoic acyl group. We have synthesized a tetraarylporphyrin derivative whose aryl groups are substituted with (-O-(CH₂)₁₁-OCO-(CH₂)₄-C₃H₅(S-S)) at their 3,5-positions. The distance between one S-S group to that of the opposite side is about 6 nm. Consequently the molecule will occupy circular area of about 6 nm diameter on the adsorbed metal surface. Thus when the molecules are adsorbed to the metal electrodes with the size of 60 nm × 60 nm, only 100 molecules will be present on it at the most. By reducing the number of molecules present on the electrodes, it will become much easier to discuss about the electronic properties of the individual molecules.

VIII-C-3 Synthesis and Self-Assembly of Novel Porphyrin Molecular Wires

OGAWA, Takuji¹; KAWAO, Masahiro²
(¹IMS, JST; ²IMS and Ehime Univ.)

Long π -conjugated molecular-wires have been focused much attentions because they can be used for organic conducting material, nonlinear optical material and molecular wire. The recently reported meso-meso-linked porphyrin wires were soluble in organic solvent in spite of their high molecular weight. The high solubility can be explained by the vertically crossed porphyrin π -planes to each other: because of the sterical requirement, intermolecular π -stacking was prevented. However at the same time because of the configuration, π -electronic conjugation was not effective, and the absorption band do not shift to the longer wavelength

even for the long oligomers. Because tunnel resistance is generally less when the molecule has lower HOMO-LUMO gap, we need molecules of lower HOMO-LUMO gap for good molecular conductor.

We prepared sub-micrometer long oligo-diethynylporphyrins by usual copper catalyzed oxidative coupling of diethynylporphyrins. The products were purified by repeating gel permeation chromatography (GPC) and analyzed by analytical GPC, absorption spectroscopy, matrix assisted laser desorption time of flight mass spectroscopy (MALDI-TOFMS), and atomic force microscopy (AFM). Although with the MALDI-TOFMS no molecular peaks greater than ca. 100,000 could be detected, GPC and AFM data clearly indicated the presence of sub-micrometer long molecules.

These sub-micrometer π -conjugated molecules self-assembled on HOPG to make some kinds of ordered super structures as observed by AFM. When the length of the molecule is less than 100 nm and the concentration of the solution is relatively high, a regular network structure was formed in which the distance between each molecules is ca. 16 nm and the height is ca. 0.9 nm in average. In longer molecules with less concentrated solution, a rectangular sheet structure was observed with the distance of 4 nm and the height of 0.3 nm. Judging from the size, we postulate that in the regular network structure two or three molecular wires are stranded to make thicker molecular rope.

VIII-C-4 Synthesis and Characterization of Dendrimer Protected Sub-Micrometer Long Conjugated Porphyrin Wires

OGAWA, Takuji¹; OZAWA, Hiroaki²
(¹IMS, JST; ²IMS and Ehime Univ.)

Direct measurements of electronic properties of single molecule are still a challenging target of materials science, and have been reported in several papers by using scanning probe microscopic methods (SPM), or break junction methods. However, no one has ever succeeded in the electronic measurement with observing the molecules between the electrodes. One reason is that the roughness of electrodes surface, which was fabricated by usual electron beam lithographic methods, is larger than the diameter of the molecular wires, and it is difficult to observe the molecules clearly by SPM. In order to overcome the problem, we synthesized long (> 100 nm) and thick (3–5 nm) porphyrin wires surrounded by dendrimer moiety. Surrounding the wire with the dendrimer has several merits: (1) The diameter become enough large to observe them with AFM on the gapped electrodes, (2) solubility is increased, and (3) the wire may become rigid because of the steric hindrance between the adjacent moiety. Synthesized porphyrin wires were analyzed with gel permeation chromatography (GPC) and atomic force microscopy (AFM). The GPC analyses showed that the molecules have molecular weight greater than one million, which correspond to ca. 500 mer. The AFM images showed that the wires have the height of ca. 5 nm, and in some molecules the lengths were nearly 1 μm .

VIII-D Development of Organic Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on π -conjugated oligomers have been extensively studied as molecular thin-film devices. Organic semiconductors with low injection barriers and high mobilities are required for highly efficient OLEDs and OFETs. Radical cations or anions of an organic semiconductor have to be generated easily at the interface with an electrode (or a dielectric), and holes or electrons must move fast in the semiconducting layer. Compared with organic *p*-type semiconductors, organic *n*-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated oligomers are efficient electron-transport materials for OLEDs.

VIII-D-1 Oligo(2,6-Anthrylene)s: Acene-Oligomer Approach for Organic Field-Effect Transistors

ITO, Kaname; SUZUKI, Toshiyasu; SAKAMOTO, Youichi; KUBOTA, Daisuke¹; INOUE, Youji¹; SATO, Fumio¹; TOKITO, Shizuo¹
(¹NHK Sci. Technical Res. Labs.)

[*Angew. Chem., Int. Ed.* **42**, 1159–1162 (2003)]

Oligo(2,6-anthrylene)s (**2A** and **3A**) and their dihexyl derivatives (**DH-2A** and **DH-3A**) have been synthesized by the Suzuki coupling using palladium catalysts. Organic field-effect transistors (OFETs) of these anthracene oligomers were fabricated on SiO₂/Si substrates by high-vacuum evaporation. OFETs with **2A** exhibited FET activity, and the hole mobilities ranged from 0.0031 to 0.013 cm²V⁻¹s⁻¹. The oligomer **3A** showed even higher mobilities (0.064–0.072 cm²V⁻¹s⁻¹). Field-effect mobilities of **DH-2A** were greater than 0.1 cm²V⁻¹s⁻¹. The highest mobilities (0.18 cm²V⁻¹s⁻¹) were observed in **DH-3A** OFETs. X-ray diffraction studies on the films indicated a high degree of lamellar ordering and crystallinity.

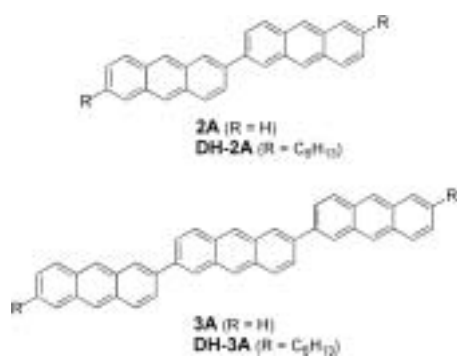


Figure 1. Structures of anthracene oligomers.

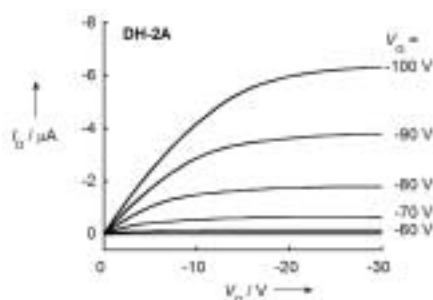


Figure 2. Drain current (I_D) vs drain voltage (V_D) as a function of gate voltage (V_G) for an OFET with **DH-2A** ($T_{\text{sub}} = 70$ °C). Channel length $L = 100$ μm and channel width $W = 1$ mm ($W/L = 10$).

VIII-D-2 Color Tunable Organic Light-Emitting Diodes Using Pentafluorophenyl-Substituted Iridium Complexes

TSUZUKI, Toshimitsu¹; SHIRASAWA, Nobuhiko; SUZUKI, Toshiyasu; TOKITO, Shizuo¹
(¹NHK Sci. Technical Res. Labs.)

[*Adv. Mater.* **15**, 1455–1458 (2003)]

Novel iridium complexes with perfluorophenyl-substituted phenylpyridine ligands have been developed. The figure shows the photoluminescence (PL) spectra of four complexes in the doped films. By changing the position of substitution, the peaks in the PL spectra are tuned in the wavelength region 513–578 nm. Light-emitting diodes using these complexes as the emitting material show an external quantum efficiency of 10–17%.

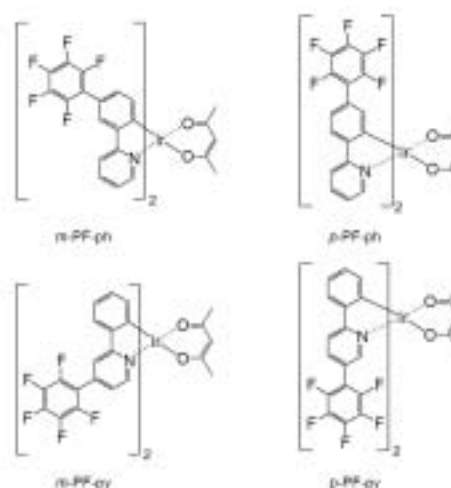


Figure 1. Structures of iridium complexes.

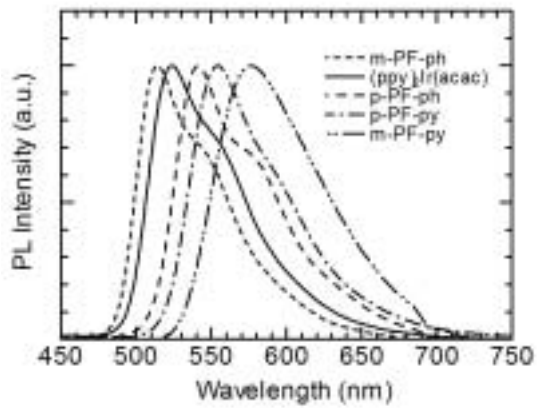


Figure 2. PL Spectra for films of the complexes (6%) doped in CPB.

VIII-E Field-Effect Transistors with Organic Semiconductors

Considerable attention has recently focused on organic field-effect transistors (OFET) because of their potential use in low-cost flexible electronic devices. In order to improve output characteristics, carrier transport in organic semiconductors is the most important subject to be elucidated.

VIII-E-1 Carrier Transport in Field-Effect Transistors Based on Single-Crystalline Wires of Bis-(1, 2, 5-thiadiazolo)-*p*-Quinobis(1, 3-dithiole) (BTQBT)

FUJIWARA, Eiichi; TAKADA, Masaki¹;
YAMASHITA, Yoshiro²; TADA, Hirokazu
(¹GUAS; ²Tokyo Inst. Tech.)

We prepared single-crystalline wires of bis(1, 2, 5-thiadiazolo)-*p*-quinobis(1, 3-dithiole), whose ends were anchored to the drain and source electrodes of bottom-contact-type field-effect transistors. Figure 1 shows the SEM image of BTQBT wires grown on the substrates at 360 K. Molecular crystalline wires bridge the gaps between electrodes. It is noted that wires are anchored selectively to the electrodes and no aggregates exist on SiO₂ surface under appropriate growth conditions. Figure 2 shows the temperature dependence of the field-effect mobilities of the devices composed of nanowires and small grains in the temperature range from 5 K to 300 K. The tunnel transport and thermally activated hopping were found to be dominant at $T < 30$ K and 30 K $< T < 150$ K, respectively, in both devices. While hopping behavior was still dominant in the device of small grains at $T > 150$ K, the mobility of wires varied as $T^{-1.3}$, indicating that phonon scattering governed carrier transport in single-crystalline wires.

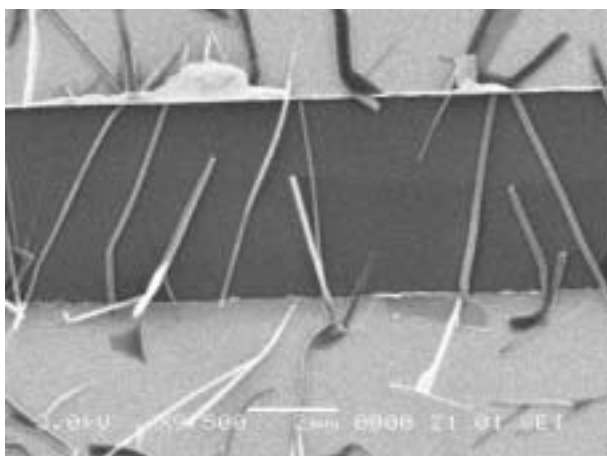


Figure 1. SEM image of BTQBT wires on FET electrodes with spacing of 5 μm .

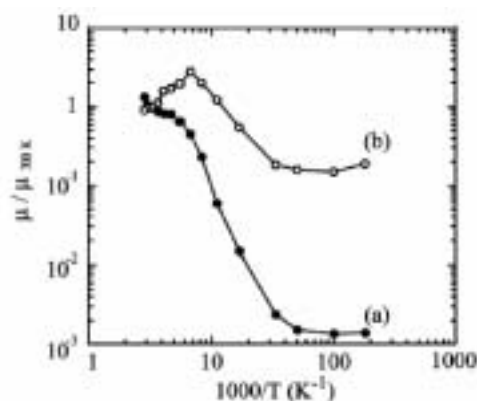


Figure 2. Temperature dependence of field-effect mobilities of small grains (a) and wires (b).

VIII-E-2 Field-Effect Transistors of F₁₆CuPc with Bottom- and Top-Contact Electrodes

MINARI, Takeo¹; FUJIWARA, Eiichi; TAKADA, Masaki²; TADA, Hirokazu; NEMOTO, Takeshi¹;
ISODA, Seiji¹
(¹Kyoto Univ.; ²GUAS)

Output characteristics of organic field-effect transistors depend strongly upon device structures. We have prepared bottom- and top-contact FET devices based on hexadecafluoro-copperphthalocyanine (F₁₆CuPc) films and studied electrical properties. It was found that electron mobilities of the top contact FETs were higher than those of the bottom contact FETs probably due to the difference in electric field distribution. Electron mobility of top contact FETs increased with increasing grain size of CuPcF₁₆ films, but large grains cause lower mobility owing to poor contact at the interface between the electrodes and the organic film in the bottom contact FETs. The FET with thick CuPcF₁₆ films resulted in the higher mobility in the bottom contact FETs because of less influence of air. In top contact FET, however, the thicker film gave rise to the less drain current because of the increase of resistance between source electrode and accumulation layer.

VIII-F Molecular Assemblies on Silicon Surfaces *via* Silicon-Carbon Covalent Bonds

Preparation of molecular assemblies on inorganic semiconductors such as silicon and germanium has received a growing interest because of their potential application to stable regist for nano-patterning. We have prepared organic monolayers on silicon by wet process and studied film structures with IR and AFM.

VIII-F-1 Molecular Conformation of *n*-Alkyl Monolayers Covalently Bonded to Si(111) Probed by Infrared-Visible Sum-Frequency Spectroscopy

ISHIBASHI, Taka-aki¹; ARA, Masato²; TADA, Hirokazu; ONISHI, Hiroshi¹
(¹KAST; ²GUAS)

[*Chem. Phys. Lett.* **367**, 376–381 (2003)]

Infrared-visible sum-frequency spectra of *n*-alkyl (C_nH_{2n+1} ; $n = 10-13, 18$) monolayers anchored on the Si(111) surface through a Si-C covalent bond were measured for the C-H stretch region. Spectral shapes exhibited azimuthorientation dependence compatible with the C_{3v} symmetry of the substrate as shown in Figure 1, indicating that the monolayers were epitaxially constructed on the substrate. Three methyl bands dominated each spectrum, and two-weak methylene bands were identified. Two distinct intensity patterns of the methyl bands were observed depending on n as shown in Figure 2. The observed spectra were interpreted with reference to reported molecular models of the monolayer that consist of alkyl chains with an all-trans head part and a twisted stem.

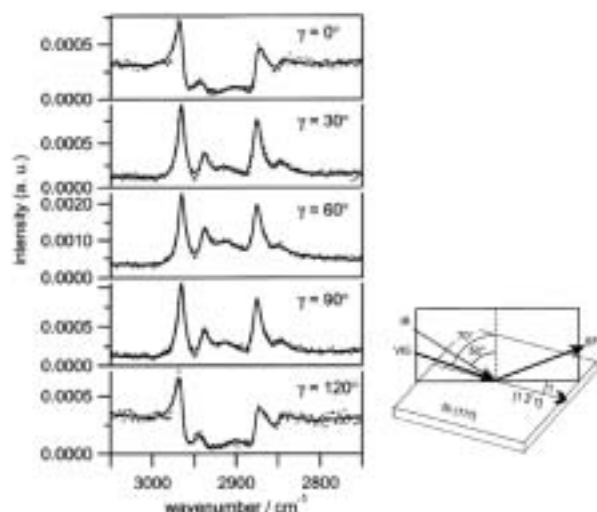


Figure 1. Azimuth dependence of SF spectra of tridecyl ($C_{13}H_{27}$) monolayer on Si(111). The spectra were measured at room temperature.

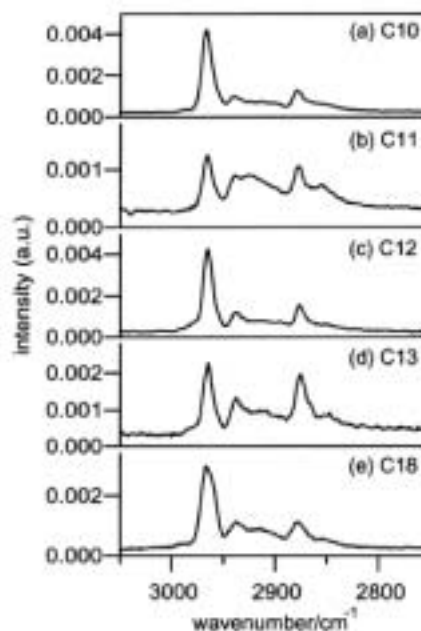


Figure 2. SF spectra of *n*-alkyl (C_nH_{2n+1} ; $n = 10-13, 18$) monolayers on Si(111) measured at the azimuth $\gamma = 60^\circ$.

VIII-F-2 Study on Phase Transition of Alkyl-Monolayers Anchored Covalently to Silicon by Temperature Dependent ATR-FT-IR

YAMADA, Ryo; ARA, Masato¹; TADA, Hirokazu
(¹GUAS)

The phase behavior of alkyl-monolayers formed on Si(111) surface was investigated by an attenuated total reflection Fourier transform infra-red spectroscopy from room temperature to 590 K (Figure 1). A continuous disordering process of the monolayer was indicated from the gradual peak shifts toward higher frequency in C-H stretching modes with small decrease in the peak intensities as temperature was increased to 440 K. The rapid decrease in peak intensity was observed above 440 K. The observed changes in the spectrum were reversible by 440 K while the peak intensity was decreased and peak position became higher when the substrate was cooled to room temperature after heated above 440 K, indicating the destruction of the monolayer above 440 K. The temperature limit for the reversible phase transition was much higher than that for alkanethiol monolayer on Au(111) surface (*ca.* 350K), showing that the monolayer formed by Si-C covalent bond was more stable than that of alkanethiols on Au(111) surface due to the stronger anchoring of the molecules to the substrate.

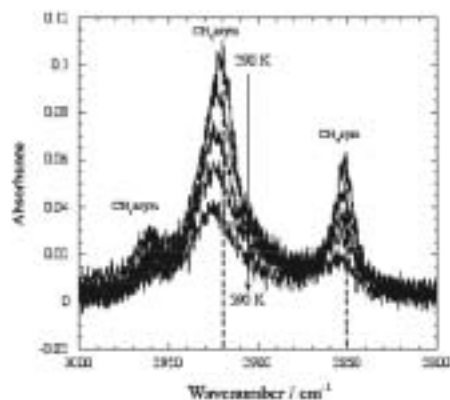


Figure 1. Temperature dependent ATR-FT-IR spectra in the C–H stretching region of octadecene-monolayer on Si(111) surface.

VIII-F-3 Friction Force Microscopy Using Silicon Cantilevers Covered with Organic Monolayers *via* Silicon-Carbon Covalent Bonds

ARA, Masato¹; TADA, Hirokazu
(¹GUAS)

[*Appl. Phys. Lett.* **83**, 578–580 (2003)]

Cantilevers covered with hydrocarbon (CH) and fluorocarbon (CF) monolayers *via* Si–C covalent bonds were prepared and used for adhesion force measurements and friction force microscopy of the surface patterned also with CH and CF areas. The adhesion and friction forces on CF areas were larger than those on CH areas, especially using CF cantilevers as shown in Figure 1. Large polarizabilities of CF molecules compared to CH molecules are found to enhance the contrast in adhesion and friction images. The cantilevers covered with organic monolayers *via* covalent bonds are useful for chemical force microscopy with contact and noncontact mode atomic force microscopy in various atmospheres since the interface between molecules and cantilevers is thermally and chemically stable.

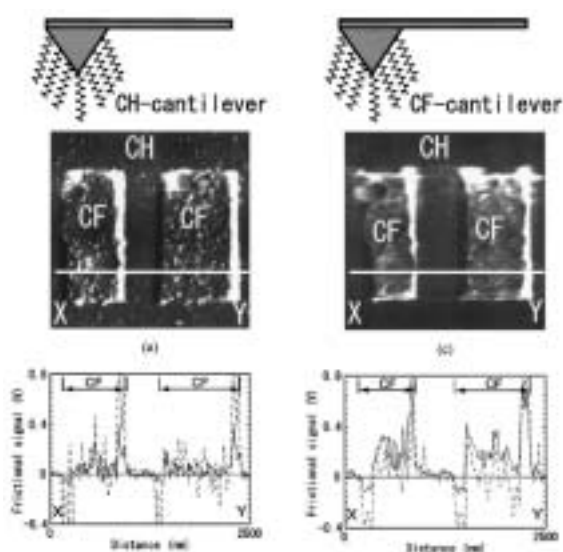


Figure 1. FFM images (a) and (c) (2.5 mm × 2.5 mm) and the friction profiles (b) and (d) of the patterned surface on Si(111) with a CH (a, b) and a CF cantilever (c, d). Spring constants of both cantilevers were 0.6 N/m. Typical loads applied were 30 nN. Solid curves and dashed curves were the profiles measured in air and *in vacuo*, respectively.

VIII-G Development of Precisely-Defined Macromolecules and Their Organization on Substrate Surfaces for Planar Molecular-Scale Electronics Circuits

The concept of molecular-scale electronics is now realized for individual components such as wire, diode, switch, and memory cell, but the fabrication of complete molecular-scale circuits remains challenging because of the difficulty of connecting molecular modules to one another. Molecular monolithic technology, which integrates the wiring, transistors and the required passive elements on a single macromolecule, has been proposed as a promising solution to this problem. In this project we have been trying to establish both the architecture of this novel class of macromolecules and the protocols for their purposive organization on metal/semiconductor substrate surfaces.

VIII-G-1 Characterization of Electronic Properties of Molecular Enamel Wires

TANAKA, Shoji

The precisely-defined “insulated molecular wire,” in which rigid insulators are placed around a π -conjugated backbone except the “electrical connections,” is one of the key modules for realizing ultra-dense molecular-scale electronic circuits. The well known approach to this special class of molecular wire is based on the supramolecular complex between π -conjugated oligomers and cyclodextrin molecules. As an alternative approach, we have proposed “molecular enamel wire” concept, in which the insulator mantle is covalently bonded to the backbone. The stability of insulator-attachment of molecular enamel wire will be superior to that of supramolecular wire due to the intrinsic toughness of a covalent bond. So far, we have established the synthetic approaches to molecular enamel wires based on building blocks **1** (Figure 1). Here we report the effects of the insulator mantles on electronic behaviors of these molecular enamel wires.

Figure 2 shows the absorption spectra of the vacuum-deposit thin films of oligomers **2–5** on quartz substrate as well as those in THF. Generally photophysical process of a π -conjugated molecule in solid state is complicated due to the intermolecular π - π interactions. The electronic spectra of the thin film of non-insulated oligothiophenes **2–3** are apparently dissimilar to those in the THF solution. In contrast, the thin film spectra of insulated oligothiophenes **4–5** are nearly identical to the THF solution spectra. These results indicate that the intermolecular π - π interactions are efficiently prevented by the insulator mantle of **4–5**. This conclusion is supported by the electrochemical data. Typical cyclic voltammograms of insulated and non-insulated α -12T derivatives **6–7** are shown in Figure 3. The voltammogram of non-insulated α -12T **6** is broad and ill-defined in contrast to that of insulated α -12T **7**, where three reversible waves are obtained. In general the ill-resolved cyclic voltammogram of long oligothiophenes has its origin in i) adsorption of charged species on the electrode surface and/or ii) π -complex formations such as “ π dimer” and “dimer radical ion.” Therefore the reversible electrochemical behavior of insulated α -12T **7** can be attributed to the steric inhibitions of adsorption and/or complex formation *via* π -system of the oligomers by the insulator mantle.

In conclusion these experimental data clearly demonstrate the availability of our “molecular enamel wire” concept in molecular-scale engineering.

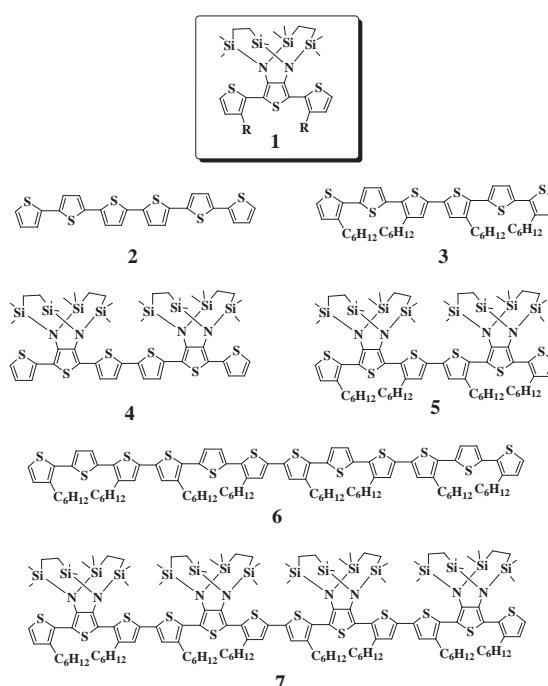


Figure 1. Molecular Structure of oligomers.

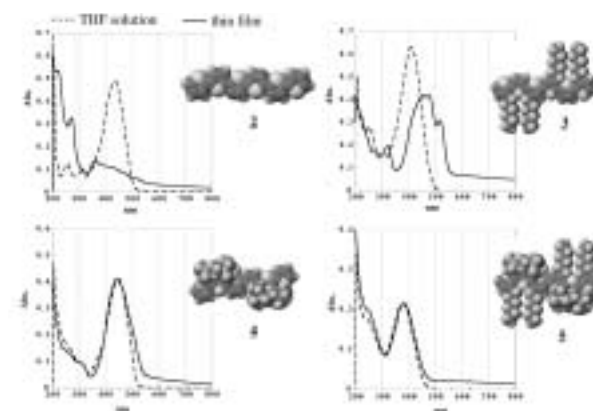


Figure 2. UV/Vis spectra of oligomers.

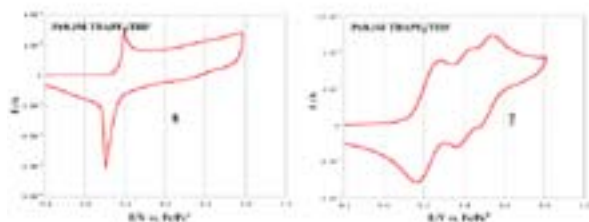


Figure 3. Cyclic voltammograms of oligomers.

VIII-G-2 Combined Spectroscopic and Theoretical Study of Narrow-Bandgap Heterocyclic Cooligomers Containing Alternating Aromatic-Donor and *o*-Quinoid-Acceptor Units

RUIZ DELGADO, Mari Carmen¹; HERNÁNDEZ, Víctor¹; LÓPEZ NAVARRETE, Juan T.¹; TANAKA, Shoji; YAMASHITA, Yoshiro²
(¹Univ. Málaga.; ²Tokyo Inst. Tech.)

In this paper we analyze, with the help of Density Functional Theory calculations, the relationship between the molecular structure and the optical and vibrational properties of two narrow-bandgap π -conjugated cooligomers containing an alternating

sequence of aromatic-donor and *o*-quinoid acceptor units. The optimized molecular geometries of these cooligomers reveal that short inter-ring S...N contacts occur in their minimum-energy structure between the two types of constituting units, and that the resulting rigid coplanar arrangement of the rings enhances the degree of π -conjugation and lowers the bandgap.

VIII-G-3 Electrochemical Synthesis and Properties of Poly[1,4-bis(*N*-pyrrolylalkoxy)benzene]s with a Three-Dimensional Crosslinked Structure

ONO, Katsuhiko¹; YAMADA, Satsuki¹; OHKITA, Masakazu¹; SAITO, Katsuhiko¹; TANAKA, Shoji; HANAICHI, Takamasa²
(¹Nagoya Inst. Tech.; ²Hanaichi UltraStruc. Res. Inst.)

[*Chem. Lett.* 516–517 (2003)]

The title polymers, which were composed of π -conjugated pyrroles and dialkoxybenzene crosslinkers, were prepared by electrochemical polymerization to afford amorphous thin films, which were characterized by cyclic voltammetry (CV), scanning electron microscope (SEM), and redox stability.

VIII-H Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

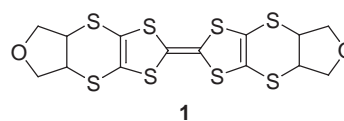
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π -conjugation decreases Coulombic repulsion. In addition intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies. In this project new electron acceptors, donors, and donor-acceptor compounds based on heterocycles such as 1,2,5-thiadiazole and 1,3-dithiole were synthesized and their properties including those of the charge-transfer complexes or ion-radical salts were investigated. Unique crystal structures were constructed by using weak intermolecular interactions such as hydrogen bonding or heteroatom contacts.

VIII-H-1 Non-Planar BEDT-TTF Derivatives Fused with Tetrahydrofuran Rings Affording Cation Radical Salts with Unusual Crystal Structures

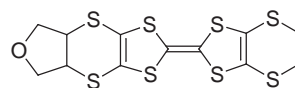
YAMASHITA, Yoshiro¹; TOMURA, Masaaki; IMAEDA, Kenichi²
(¹IMS and Tokyo Inst. Tech.; ²IMS and Chubu Univ.)

[*Mol. Cryst. Liq. Cryst.* **380**, 203–207 (2002)]

The title non-planar electron donors **1** and **2** were prepared by the several steps involving the addition reaction of oligo(1,3-dithiole-trithione) with 2,5-dihydrofuran. They afforded the cation radical salts as single crystals whose unusual crystal structures were revealed by X-ray analysis.



1



2

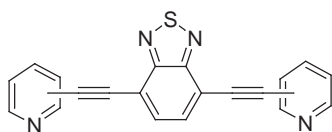
VIII-H-2 Synthesis and Characterization of New π -Conjugated Molecules Containing Bis(ethynylpyridine) Units with a Benzothiadiazole Spacer

AKHTARUZZAMAN, Md.¹; TOMURA, Masaaki; ZAMAN, Md. Badruz²; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro³
(¹Tokyo Inst. Tech.; ²IMS and Steacie Inst. Mol. Sci.;

³IMS and Tokyo Inst. Tech.)

[*J. Org. Chem.* **67**, 7813–7818 (2002)]

Three novel 4,7-bis(*n*-pyridylethynyl)-2,1,3-benzothiadiazoles (*n* = 2, 3 and 4) were synthesized by using the Sonogashira cross-coupling reaction of 4,7-dibromo-2,1,3-benzothiadiazole with the corresponding ethynylpyridines in the presence of a Pd(II) catalyst. The viologen analogues were also prepared by methylation of pyridyl nitrogen atoms. X-ray structure analysis of these compounds revealed the linear molecular structures with unusual columnar crystal structures. Insertion of a benzothiadiazole moiety into the acetylene-pyridine skeleton brings about a large increase in electron affinity and the bispyridyl compounds obtained here show high fluorescence quantum yields.



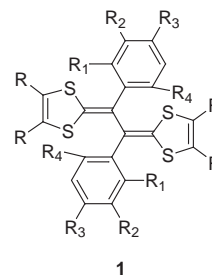
2,2'-dipyridyl, 3,3'-dipyridyl, 4,4'-dipyridyl

VIII-H-3 Preparation and Structures of Dication Salts of Phenyl Substituted TTF Vinyllogues

YAMASHITA, Yoshiro¹; TOMURA, Masaaki
(¹IMS and Tokyo Inst. Tech.)

[*J. Solid State Chem.* **168**, 427–432 (2002)]

Some TTF vinyllogues **1a–l** containing phenyl groups at the vinyl positions were synthesized. The redox properties were investigated by cyclic voltammograms, showing that they are strong electron donors and the Coulomb repulsion is decreased in the dication states. Some of the donors afforded their dication salts as single crystals by electrochemical oxidation or the reaction with CuCl₂. X-ray structure analysis has revealed that the dication molecules have structures with planar TTF vinyllogue units and twisted phenyl groups. The crystal structures are unusual to avoid the steric interactions of the phenyl groups.



	R,R	R ₁	R ₂	R ₃	R ₄
1a	(CH=CH) ₂	H	H	H	H
1b	(CH=CH) ₂	F	H	H	F
1c	(CH=CH) ₂	H	H	Cl	H
1d	(CH=CH) ₂	CN	H	H	H
1e	(CH=CH) ₂	H	H	CN	H
1f	(CH=CH) ₂	OCH ₂ O		H	H
1g	SCH ₂ CH ₂ S	F	H	H	F
1h	SCH ₂ CH ₂ S	Cl	H	H	H
1i	SCH ₂ CH ₂ S	CN	H	H	H
1j	SCH ₂ CH ₂ S	H	H	CN	H
1k	SCH ₂ CH ₂ S	OCH ₂ O		H	H
1l	H, H	F	H	H	F

VIII-H-4 Unsymmetrical Tetrathiafulvalene with a Fused 1,2,5-Thiadiazole Ring and an Ethylenedioxy Group

TOMURA, Masaaki; YAMASHITA, Yoshiro¹
(¹IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. E* **59**, o145–o147 (2003)]

In the crystal structure of the title compound, 4,5-ethylenedioxy[1,2,5]thiadiazolotetrathiafulvalene, C₈H₄N₂O₂S₅, a large number of short intermolecular S...S contacts are observed [3.519(5)–3.610(5) Å]. The molecules stack along the *c* axis in a face-to-face fashion.

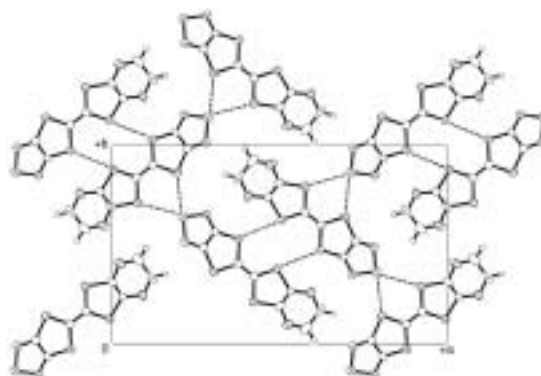


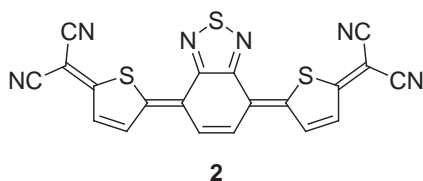
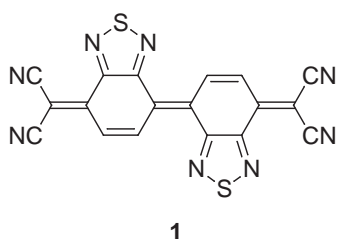
Figure 1. Packing diagram of the title compound viewed along the *c* axis. Dotted lines indicate the short intermolecular S...S contacts.

VIII-H-5 Novel Electron Acceptors Containing Nitrogen, Sulfur-Heterocyclic Units

YAMASHITA, Yoshiro¹; SUZUKI, Kazuharu²;
TOMURA, Masaaki
(¹IMS and Tokyo Inst. Tech.; ²IMS and Inst. Res.
Innov.)

[*Synth. Met.* **133-134**, 341–343 (2003)]

A tetracyanodiphenoquinodimethane (TCNDQ) analog **1** containing fused thiadiazole rings is a stronger electron acceptor than tetra-cyanoquinodimethane (TCNQ). The single crystals of this TCNDQ analog were found to exhibit semiconductive behaviors as a single component whose structures were revealed by X-ray structure analysis. The anion radical salts with Et₄N and Me₄P ions were obtained as single crystals by electrochemical reduction. They are 1:1 salts and showed semiconductive behaviors. The structures include tape-like networks formed by S...N contacts. Furthermore, one of the benzothiadiazole rings was replaced with a thiophene unit to give new π -extended quinonoid acceptors **2** which are highly polarized and exhibit their absorption maxima above 500 nm.

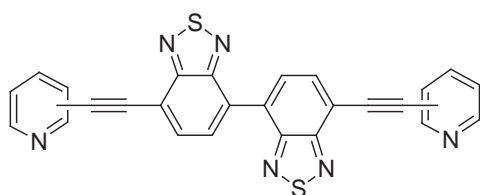


VIII-H-6 Linear Molecules with Ethynylpyridine and Bisbenzothiadiazole Units

AKHTARUZZAMAN, Md.¹; TOMURA, Masaaki; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro²
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[*Synth. Met.* **137**, 873–874 (2003)]

7,7'-Bis(pyridylethynyl)-4,4'-bis(2,1,3-benzothiadiazole) derivatives were synthesized using the Sonogashira reaction. X-ray crystallographic analysis of the 4,4'-dipyridyl derivative revealed the linear molecular structure with an unusual tape-like crystal structure. They show high electron affinity and fluorescence with large Stokes shifts. The viologen analogues were also prepared by methylation of the pyridyl nitrogen atoms.



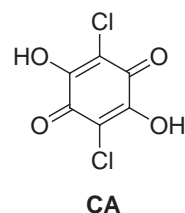
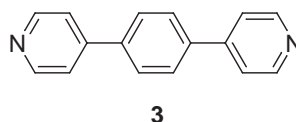
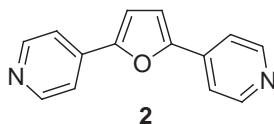
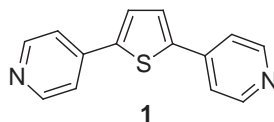
3,3'-dipyridyl, 4,4'-dipyridyl

VIII-H-7 Hydrogen Bonding Networks Consisted of Conjugation-Extended 4,4'-Bipyridines and Chloranilic Acid

AKHTARUZZAMAN, Md.¹; TOMURA, Masaaki; TAKAHASHI, Kazuko²; NISHIDA, Jun-ichi¹; YAMASHITA, Yoshiro³
(¹Tokyo Inst. Tech.; ²Tohoku Univ.; ³IMS and Tokyo Inst. Tech.)

[*Supramol. Chem.* **15**, 239–243 (2003)]

Hydrogen-bonding networks of π -extended 4,4'-bipyridines, 2,5-di(4-pyridyl)thiophene **1**, 2,5-di(4-pyridyl)furan **2** and 1,4-di(4-pyridyl)benzene **3** with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, **CA**) have been investigated. The dipyrindyl compounds afforded three complexes, (dication of **1**)·(monoanion of **CA**)₂, (dication of **2**)·(dianion of **CA**)·(MeOH) and **3**·(dication of **3**)·(dianion of **CA**)·(H₂O)₆ with **CA**. X-ray structure analyses revealed the formation of unusual molecular tape and sheet structures involving N–H...O, O–H...O, C–H...O and N–H...N hydrogen bonds, where the aromatic spacer groups play an important role in constructing the unique crystal structures.



VIII-I Green and Risk-Free Catalysis

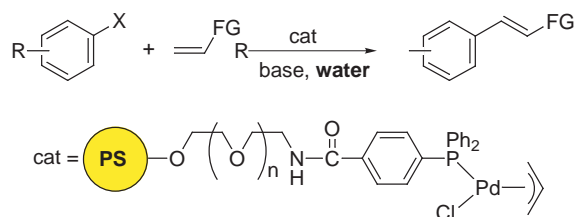
Catalytic organic transformations under mild, safe, and green conditions is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including π -allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. Rhodium-catalyzed hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids were also found to proceed smoothly in water. Here we wish to report that Heck reaction, Sonogashira reaction, Wacker reaction were successfully examined in water by use of PS-PEG resin-supported transition metal complexes.

VIII-I-1 Heck Reaction in Water with Amphiphilic Resin-Supported Palladium-Phosphine Complexes

UOZUMI, Yasuhiro; KIMURA, Tsutomu

[*Synlett* 2045–2048 (2002)]

The Heck reaction of various aryl halides and alkenes took place in water in the presence of an amphiphilic polystyrene-poly(ethylene glycol) resin-supported palladium-phosphine complex to give the corresponding styrene derivatives in quantitative yields.



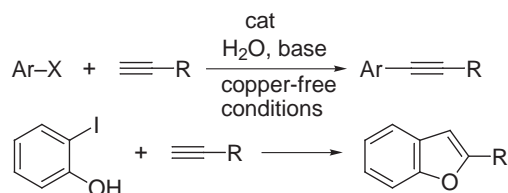
Scheme 1.

VIII-I-2 The Sonogashira Reaction in Water with an Amphiphilic Resin-Supported Palladium-Phosphine Complex under Copper-Free Conditions

UOZUMI, Yasuhiro; KOBAYASHI, Yukinari

[*Heterocycles* 59, 71–74 (2003)]

The Sonogashira reaction of aryl halides with terminal alkynes was catalyzed by an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported palladium-phosphine complex in water to give the corresponding aryl-substituted alkynes in high yields under copper-free conditions. Reaction of *o*-iodophenol with terminal alkynes under Sonogashira conditions gave benzofuran derivatives in one step.



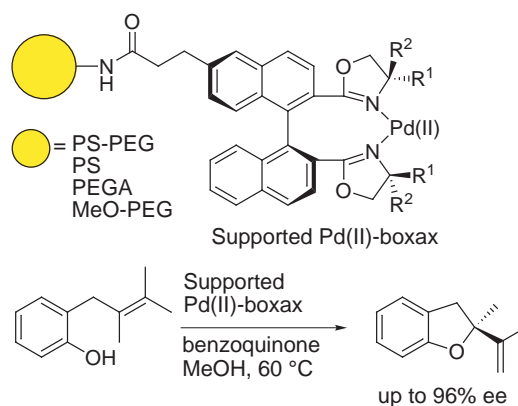
Scheme 1.

VIII-I-3 Polymer-Supported 2,2'-Bis(oxazolin-2-yl)-1,1'-Binaphthyls (boxax): Immobilized Chiral Ligands for Asymmetric Wacker-Type Cyclizations

HOCHE, Heiko; UOZUMI, Yasuhiro

[*Synlett* 2049–2053 (2003)]

Homochiral 2,2'-bis(oxazolin-2-yl)-1,1'-binaphthyl (boxax) ligands were anchored on various polymer supports including PS-PEG, PS, PEGA, and MeO-PEG via selective monofunctionalization at the 6-position of the binaphthyl backbone. Palladium(II) complexes of the supported boxax ligands catalyzed Wacker-type cyclization of 2-(2,3-dimethyl-2-butenyl)phenol to give 2-methyl-2-isopropenyl-2,3-dihydrobenzofuran with up to 96% ee.



Scheme 1.

VIII-J Designing Artificial Photosynthesis at Molecular Dimensions

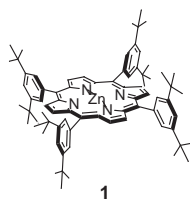
Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

VIII-J-1 Photooxidation of Alcohols by a Porphyrin/quinone/TEMPO System

NAGATA, Toshi; ITO, Hajime; NAGASAWA, Takayuki

Photoinduced electron transfers involving porphyrins are widely studied, but utilizing the high-energy radical ion pairs for driving chemical reactions remains to be a great challenge. We reported preliminary results on photooxidation of alcohols by a porphyrin/quinone/TEMPO system in AR2002. This year we report the mechanistic detail of this reaction system.

When a solution of porphyrin **1** (1 μmol), TEMPO (25 μmol), 2,5-di-*tert*-butyl-1,4-benzoquinone (100 μmol), benzyl alcohol (300 μmol) and *n*-dodecane (50 μmol ; an internal standard for the gas chromatography) in 0.5 ml of dry pyridine was irradiated with visible light ($\lambda > 500 \text{ nm}$), benzaldehyde was formed with concurrent formation of 2,5-di-*tert*-butyl-1,4-hydroquinone. The substrate dependence experiments revealed following order of reactivity: benzylic \approx allylic $>$ primary \gg secondary (no reaction). This is in accordance with other reported TEMPO-mediated oxidation.



With benzyl alcohol as a substrate, the initial rates of product formation were examined under various conditions (Figure 1). As shown in parts (a) and (b), the rate increases with increasing concentrations of PhCH_2OH and TEMPO. Particularly interesting is the dependence on the quinone concentration, shown in part (c). Here the initial rates decrease with increasing quinone concentration. The dependence on the porphyrin concentration (part (d)) also shows a similar trend.

The negative dependence on quinone concentration can be explained by considering the quantum yields of the triplet radical pairs. When the concentration of the triplet becomes higher, the quantum yield of the triplet radical pair is lowered because the singlet state is more likely to be quenched prior to intersystem crossing. On the other hand, the negative dependence on porphyrin concentration is ascribed to the electron-transfer equilibrium between the porphyrin cation

radical and TEMPO (Equation 1). As the concentration of porphyrin becomes higher, the equilibrium is pushed to the left and the steady-state concentration of the oxoammonium cation TEMPO^+ becomes lower. The proposed reaction mechanism is shown in Scheme 1.

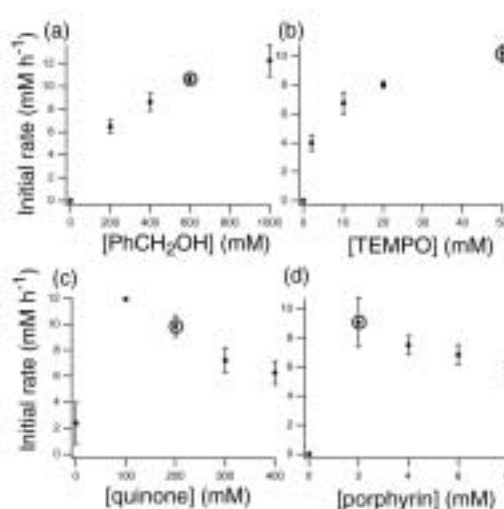
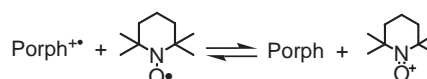
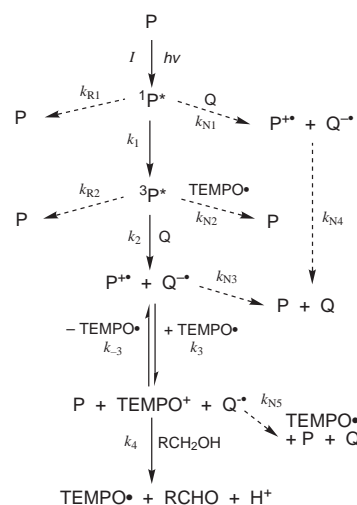


Figure 1. The initial rates of formation of PhCHO under various conditions.



Equation 1.



Scheme 1. Proposed reaction mechanism.

VIII-K Development of New Nanomaterials as Components in Advanced Molecular Systems

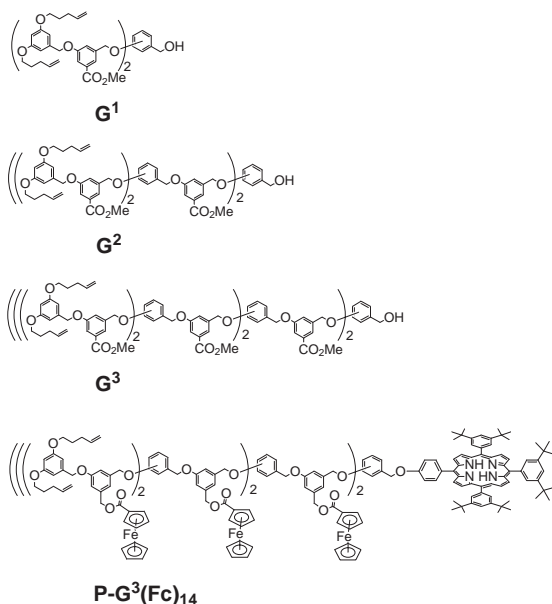
Nanometer-sized materials exhibit unique electronic behavior. In the quest of advanced redox catalysis, we are currently interested in combining nanometer-sized materials into molecular redox systems. Herein we report two attempts to develop new nanomaterials that potentially suit for combination with advanced molecular system.

VIII-K-1 Development of New Spatially-Relaxed Dendrimers and Their Application as Precursor to Redox Pool Molecules

KIKUZAWA, Yoshihiro; NAGATA, Toshi

We synthesized a series of new dendrimers with up to fourteen "internal" carboxyl groups. These dendrimers (G^1 – G^3) are made from a branching unit and a spacer unit with a carboxyl group. Introduction of the spacer groups makes the internal carboxyl groups more spatially relaxed than previously reported dendrimers.

This type of dendrimer was used as a building framework of new redox pool molecules. The dendrimer G^3 was connected to a porphyrin, the internal carboxyl groups were converted to alcohols, and ferrocene-carbonyl groups were introduced via ester linkages to give $P-G^3(Fc)_{14}$. This molecule will be useful for examination of photoinduced electron transfer between a porphyrin and multiple electron donor molecules.



VIII-K-2 Synthesis and Size Control of Gold Sub-Nanoparticles Stabilized by Tripod Organic Molecules

HOSOKAWA, Youichi; NAGATA, Toshi

Recently, gold nanoparticles have received much attention as potentially useful materials showing novel electronic, optical, optoelectronic, and magnetic properties derived from the quantum size effect. One promising application of these materials is utilization as

one of the functional "components" in molecular systems. To realize this idea we are developing techniques to treat metal nanoparticles as if they were "molecules."

We synthesized new tripod molecule 1 – 3 (Figure 1) and examined stabilization of gold sub-nanoparticles stabilized by them. These molecules are designed so that a single molecule can enclose a single metal nanoparticle to give a "molecular" nanoparticle complex (Figure 2). The multi-point interaction by arylthioether units will produce the stabilization, and the different "leg" length will also result in size-selection of metal nanoparticles. Figure 3 shows the TEM pictures and the observed diameter distribution of gold nanoparticles derived from 1 – 3 . The most frequent values of the diameter distribution became larger with increasing numbers of the benzyl thioether units.

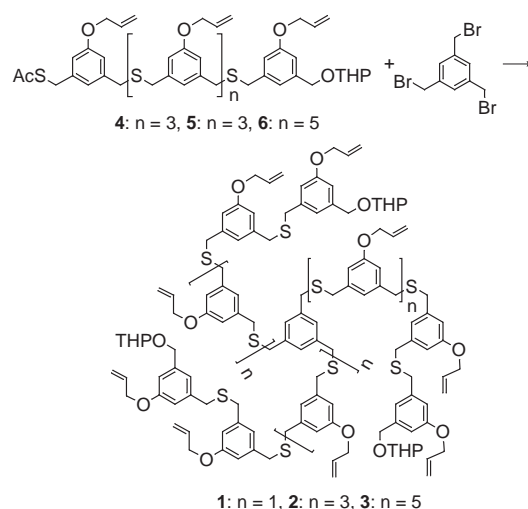


Figure 1. Preparation of the tripod molecules 1 – 3 .



Figure 2. A schematic representation of the complex between the tripod molecule and the metal nanoparticle.

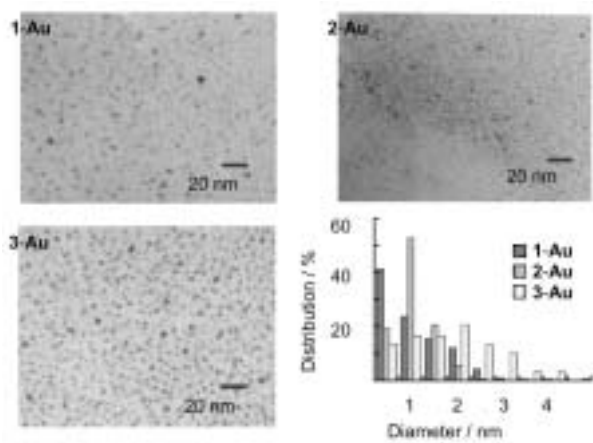


Figure 3. TEM images and the diameter distribution of 1-, 2-, and 3-Au.

VIII-L Photochemistry on Well-Defined Surfaces

Upon the irradiation of light in the wavelength range from visible to ultraviolet, a number of adsorbed molecules on metal surfaces reveal variety of photochemical processes, including photo-stimulated desorption, rearrangement of adsorbed states, photodissociation, and photo-initiated reactions with coadsorbates. A central and fundamental question in the surface photochemistry is to clarify how adsorbate-substrate systems are excited by photon irradiation. In addition, since photo-initiated reactions can be induced without any thermal activation of reactants, they may provide good opportunities for studying a new class of surface reactions that may not be induced thermally. We have studied photochemistry of various adsorption systems on well-defined metal and semiconductor surfaces mainly by temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), work function measurements, near edge x-ray absorption fine structure (NEXAFS) and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation.

VIII-L-1 Photo-Induced Oxygen Elimination on Silver Surfaces

NAKAGOE, Osamu¹; OHTA, Michiharu¹;
WATANABE, Kazuya¹; TAKAGI, Noriaki¹;
MATSUMOTO, Yoshiyasu
(¹GUAS)

[*Surf. Sci.* **528**, 144–150 (2003)]

We have investigated the structural changes in the added-rows of Ag–O chains at a Ag(110)(2×1)-O surface due to photo- and CO-induced elimination of O by using scanning tunneling microscopy. The photo-induced elimination occurs only on the surface contain-

ing carbidic carbon, resulting in the structural change of the added-rows from (2×1) to (4×1) according to the reduction of O coverage (θ_{O}). The structural change due to the CO-induced elimination depends on the carbon coverage: the (2×1) structure is retained in spite of the decrease of θ_{O} for the C-contained surface, while the structure changes sequentially from (2×1) to (4×1) and (6×1) for the carbon-free surface. Furthermore, the CO-induced elimination rate in the low θ_{O} on the carbon-free surface is much faster than that on the C-contained surface. These results indicate that the small amount of C atoms play an important role not only in the structural changes associated with the oxygen elimination reactions but also in the kinetics of the oxidation reaction of CO.

VIII-M Ultrafast Dynamics at Well-Defined Surfaces

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We demonstrate the real-time observations of substrate surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces.

VIII-M-1 Coherent Surface Phonon at a GaAs(100)-c(8×2) Surface

WATANABE, Kazuya¹; DIMITROV, Dimitre T.¹;
TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu
(¹GUAS)

[*Phys. Rev. B* **65**, 235328 (7 pages) (2002)]

Coherent surface phonon at a GaAs(100)-c(8×2)-Ga reconstructed surface has been investigated by time resolved TRSHG. The phonon mode is impulsively excited by an ultrashort laser pulse and subsequent coherent nuclear motion is monitored through the intensity modulation of the second harmonics of a probe pulse. Oscillatory traces are clearly observed in TRSHG signals and their Fourier transformation show two peaks

at 8.2–8.6 THz and 8.9 THz. Fitting these traces with two oscillatory components shows that the oscillatory signals are contributed by the bulk LO-phonon at 8.8 THz and the surface phonon at 6.0–8.6 THz. The relative amplitude of the surface phonon modes is sensitive to sputtering and annealing of the surface. Clear dips appear at 8.7 THz in the Fourier spectra, which is caused by the initial phase difference between the surface phonon and the bulk phonon modes. The frequency of the surface component shows red shifts as the pumping power increases. The shifts are indicative of a marked electron phonon interaction or anharmonicity of the surface phonon modes.

VIII-M-2 Impulsive Excitation of a Vibrational Mode of Cs on Pt(111)

WATANABE, Kazuya¹; TAKAGI, Noriaki¹;
MATSUMOTO, Yoshiyasu
(¹GUAS)

[*Chem. Phys. Lett.* **366**, 606–610 (2002)]

We have performed TRSHG measurements regarding a Cs–Pt stretching mode on a Cs-covered Pt(111) surface under an ultrahigh vacuum condition. The TRSHG trace obtained from the clean surface shows an instantaneous sharp rise right after the excitation. This is followed by a fast decaying component ($t < 1$ ps) and a slowly decaying one persistent to the longest delay ($t = 6$ ps) of the measurements. When the surface is covered

with Cs, SH signals are enhanced by about 70 times and strongly modulated waveforms are superimposed on the TRSHG traces. The power spectrum obtained from the Cs-covered Pt(111) surface shows a strong peak at 2.3 THz; this is assigned to the Cs–Pt stretching mode. The dephasing time of the coherent vibration was estimated to be 1.4 ps. The strong modulation is observed only the Cs-coverages larger than 0.24 ML. At these coverages alkali metal adsorbates are known to make metallic quantum wells. Thus, the resonant impulsive Raman process between quantum well states is responsible for the creation of the vibrating nuclear wavepacket motion in phase along the Cs–Pt stretching coordinate.

VIII-N Multiphoton Photoelectron Spectroscopy of Electronic States of Nano-Structured Materials on Surfaces

Electronic structure and excited state dynamics of nano-structured materials on surfaces are very important for exploring their properties, thermal reactivity and nonthermal processes including photochemistry and photo-induced charge transfer. For this purpose, we performed multiphoton photoelectron spectroscopy with fs lasers. This year we applied this method to a single-layered nano-graphite crystalline grown on a metal surface.

VIII-N-1 Anomalous Quenching of Electronic States of Nanographene on Pt(111) by Deuterium Edge Termination

KINOSHITA, Ikuo¹; INO, Daisuke²; NAGATA, Kaoru¹; WATANABE, Kazuya²; TAKAGI, Noriaki²; MATSUMOTO, Yoshiyasu
(¹Yokohama City Univ.; ²GUAS)

[*Phys. Rev. B* **65**, 241402R (4 pages) (2002)]

The electronically excited state and its decay dynamics of graphite nano-crystals on metal surfaces have been investigated by fs time-resolved multi-photon photoelectron spectroscopy. Single-layer graphite nano-

crystals are formed on a Pt(111) surface. The 3-photon photoelectron spectra taken from this surface reveal two peaks whose intensities are strongly correlated with the graphite coverage. By combining with the measurements of photoemission of adsorbed xenon used as another probe for local work functions, we can clearly identify for the first time that one of the peak is due to the electronically excited σ^* state of the graphite nano-crystal. Moreover, this state is extremely sensitive to hydrogen termination of the edge of the nano-crystal in contrast to the occupied π state. These findings clarify the properties of the electronic states of graphene and finally settle the controversy on the location of the interlayer band and its split-off state of bulk graphite.

VIII-O Chemistry of One-Dimensional Nano-Surface Compounds Studied by Scanning Tunneling Microscopy

The fluctuating configurations of low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, one-dimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics, *i.e.*, one chain does not make a crystal. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured compounds.

VIII-O-1 Role of Structural Fluctuation in a Surface Reaction Studied by Scanning Tunneling Microscopy: The $\text{CO} + \text{O} \rightarrow \text{CO}_2$ Clean-Off Reaction on $\text{Ag}(110)(2\times 1)\text{-O}$

NAKAGOE, Osamu¹; WATANABE, Kazuya¹; TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu (¹GUAS)

[*Phys. Rev. Lett.* **90**, 226105 (4 pages) (2003)]

It is well known that the adsorption of O on $\text{Ag}(110)$ results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms.

AgO chains arrange periodically to form $(n\times 1)$ ($n = 2 \sim 7$) depending on the fractional O coverage due to repulsive inter-chain interactions. While the chains appear as rigid straight lines in the (2×1) structure at room temperature, the structures fluctuate to appear as

segmented and sometimes “fizzy” chains in the $(n\times 1)$ ($n \geq 4$) structures. Energetically-equivalent structures of different configurations of segments exist, reflecting the 1D nature of the chains. Thus, chains fluctuate between configurations rather than freezing into a single configuration, and consequently segmented or fizzy chains are observed. Therefore, AgO chains on $\text{Ag}(110)$ is a good system for investigating the effects of structural fluctuation on reactivity.

The kinetics of the clean-off reaction of O adatoms by CO on $\text{Ag}(110)(2\times 1)\text{-O}$ is investigated by scanning tunneling microscopy. The reaction is accelerated in the lower O coverage range where AgO chains with $(n\times 1)$ ($n \geq 4$) configurations show significant structural fluctuation. Simulations based on the Ising model are used to provide a quantitative understanding of the acceleration, which originates from the dynamical formation of active O adatoms by fluctuation of AgO chains.

VIII-P Adsorbate Structure and Surface Chemistry on Well-Defined Surfaces

Surface reactions have been playing an important role in production of many useful compounds and also fabrication of electronic devices. In particular, investigations on the structures of adsorbates and their reactivity are the first step for understanding more complicated catalytic reactions. We investigate surface reactions and kinetics by means of various techniques including temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), work function measurements, Auger electron spectroscopy (AES), infrared reflection absorption spectroscopy (IRAS) and scanning tunneling microscopy (STM).

VIII-P-1 Thermal Decomposition of Acetylene on $\text{Pt}(111)$ Studied by Scanning Tunneling Microscopy

NAKAGOE, Osamu¹; TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu (¹GUAS)

[*Surf. Sci.* **514**, 414–419 (2002)]

The adsorption and the thermal decomposition processes of C_2H_2 on $\text{Pt}(111)$ have been investigated by the use of STM. For a high C_2H_2 coverage, a (2×2) structure is observed locally after the C_2H_2 -covered $\text{Pt}(111)$ surface is heated to 120 K. By heating to 220 K, the sample surface is covered with the (2×2) structure separated with brighter lines. After heating up to 370 K, (2×2) domains related to ethylidyne species appear with larger and brighter protrusions. For a low C_2H_2 coverage, adsorbates are located randomly and no ordered islands are observed after heating to 120 K. In contrast, heating to 220 K leads to the formation of (2×2) islands. This indicates that the adsorbate-adsorbate interaction in the (2×2) structure observed by 120 K heating is different from that in the (2×2) structure observed by 220 K heating; the former is repulsive, but the latter attractive. Therefore, it is suggested that different sur-

face species are formed by the decomposition of C_2H_2 at 220 K. The detail of the decomposition processes of C_2H_2 and the relation between the adsorbate-adsorbate interaction and the surface species are discussed. The results are also reported measured by heating up to higher temperatures above 400 K.

VIII-P-2 Reaction Intermediates in the Oxidation of Methanol on a $\text{Pt}(111)\text{-(}2\times 2\text{)O}$ Surface

LIU, Zhengxin¹; SAWADA, Takeshi¹; TAKAGI, Noriaki¹; WATANABE, Kazuya¹; MATSUMOTO, Yoshiyasu (¹GUAS)

[*J. Chem. Phys.* **119**, 4879–4886 (2003)]

The oxidation of methanol on a $\text{Pt}(111)\text{-(}2\times 2\text{)O}$ surface has been investigated by infrared reflection absorption spectroscopy and temperature-programmed desorption. Methanol is dehydrogenated to produce methoxy species in the annealing temperature range from 130 to 170 K. At above 170 K, the reaction proceeds differently, depending on methanol coverage. At the saturation coverage, methanol adsorbates partly desorb molecularly and partly react with precovered

oxygen atoms to produce CO, H₂ and H₂O. No detectable formaldehyde or formate is formed. In contrast, at submonolayer coverages, methoxy species is dehydrogenated to yield formaldehyde at ~ 180 K and further oxidized to formate at ~ 200 K. Formate is decomposed by 300 K. Defect sites such as steps are not relevant to the formation of the intermediates. When CO is coadsorbed on the surface, it destabilizes the reaction intermediates. The destabilization by coadsorbed CO makes the reaction intermediates short lived as not to be detectable at high initial coverages of methanol.

VIII-Q Structures and Photophysical Properties of Monolayer-Protected Metal Clusters

For the last decade, the monolayer-protected metal clusters (MPCs) have gained much attention both as prototype systems to study the size dependent evolution of the electronic properties of the metal clusters and as promising candidates for elementary units of nano-scale devices. The emergence of novel optical and electronic properties is expected for small-sized MPCs because their electronic energy levels become quantized due to the electron confinement into the small dimensions. For example, it is anticipated that the small MPCs exhibit photoluminescence since the radiative process of the photoexcited state can compete with the phonon-mediated nonradiative relaxation processes. Our interests are focused on the following issues on the MPCs: (1) preparation and characterization of the small MPCs with core diameters of ~ 1 nm range (~ 40 atoms/cluster) which may exhibit molecular-like electronic and charging properties, (2) determination of structural dimensions (core diameters and monolayer thickness), (3) development of size-selection method, and (4) clarification of the effects of the core size, core shape, and thiolate ligation on the optical and electronic properties.

VIII-Q-1 One-Pot Preparation of Subnanometer-Sized Gold Clusters via Reduction and Stabilization by *meso*-2,3-Dimercaptosuccinic Acid

NEGISHI, Yuichi; TSUKUDA, Tatsuya

[*J. Am. Chem. Soc.* **125**, 4046–4067 (2003)]

We report herein a simple method to prepare subnanometer-sized gold clusters by the reactions between hydrogen tetrachloroaurate (HAuCl_4) and *meso*-2,3-dimercaptosuccinic acid (DMSA; $\text{HO}_2\text{CCH}(\text{SH})\text{CH}(\text{SH})\text{CO}_2\text{H}$) in water. It is demonstrated that DMSA molecules efficiently reduce the Au(III) species and stabilize the resultant gold clusters. The Au:DMSA clusters, which tend to aggregate into assemblages in water, can be well-isolated each other by ion-pair formation between the carboxyl groups of DMSA and tetraoctylammonium (TOA) cations. This surface modification enables us to examine the core size distributions of the individual clusters by mass spectrometry and TEM. It is revealed that the gold clusters comprised of 10–13 atoms (*ca.* 0.8 nm) are the main products of the reactions.

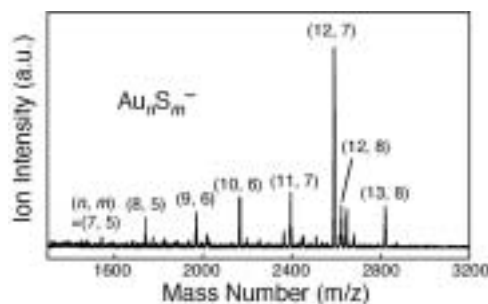


Figure 1. Laser desorption ionization mass spectrum of Au:DMSA-TOA clusters.

VIII-Q-2 Photoluminescence from Nearly Monodispersed Au_{12} Clusters Protected by *meso*-2,3-Dimercaptosuccinic Acid

NEGISHI, Yuichi; TSUKUDA, Tatsuya

[*Chem. Phys. Lett.* **383**, 161–165 (2004)]

Nearly monodispersed gold clusters (Au_{12}) protected by *meso*-2,3-dimercaptosuccinic acid (DMSA) exhibit luminescence at 630 nm with a quantum yield of 1×10^{-6} upon the photoexcitation at 390 nm into the lowest electronic excited state. The large Stokes shift (1.2 eV) suggests that the visible PL is assigned to phosphorescence originating from a triplet-like excited state. The PL quantum yield was enhanced up to 0.9%, greater by 8 orders of magnitude than that of bulk gold, by thickening the protecting layer and freezing of the solvent at 77 K. The emission peak energy is discussed within the context of core-size dependent electronic structures by comparing with those of other gold MPCs reported in literatures.

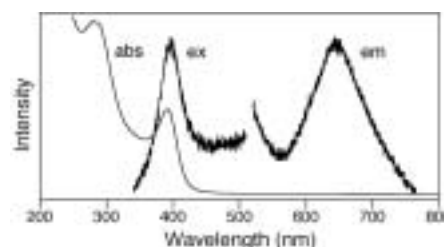


Figure 1. Optical absorption, emission and excitation spectra of Au:DMSA clusters at 298 K; $\lambda_{\text{ex}} = 400$ nm, $\lambda_{\text{em}} = 630$ nm.

VIII-Q-3 Isolation and Characterization of Subnanometer-Sized Gold Clusters

NEGISHI, Yuichi; SATO, Seiichi¹; TAKASUGI, Yoshimitsu¹; YAO, Hiroshi¹; KIMURA, Keisaku¹; SCHAAFF, T. Gregory²; WHETTEN, Robert L.³; TSUKUDA, Tatsuya

(¹Himeji Inst. Tech.; ²Oak Ridge Natl. Lab.; ³Georgia Inst. Tech.)

The Au:SG clusters with the core diameters of 0.8–1.0 nm were synthesized in Kimura group by reducing AuCl_4^- with NaBH_4 in the presence of glutathione GSH molecules ($\text{AuCl}_4^-:\text{GSH} = 1:2$).¹ The Au:SG clusters thus prepared were further fractionated into five distinct components by using polyacrylamide gel electrophoresis (PAGE).^{2,3} In order to characterize the chemi-

cal composition of these components, the electrospray ionization (ESI) mass spectra were recorded by using an apparatus constructed at IMS. The negative-ion mode ESI mass spectra of these fractions are comprised of series of multiply charged ions of $\text{Au}_{21}(\text{SG})_{12}$, $\text{Au}_{25}(\text{SG})_{14}$, $\text{Au}_{28}(\text{SG})_{16}$, $\text{Au}_{32}(\text{SG})_{20}$, $\text{Au}_{38}(\text{SG})_{23}$, respectively, demonstrating the isolation of nearly singly-sized clusters. It is found that these isolated clusters exhibit visible photoluminescence with quantum yields in the order of 10^{-3} .

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- 1) S. H. Chen and K. Kimura, *Langmuir* **15**, 1075–1082 (1999).
- 2) T. G. Schaaff, G. Knight, M. N. Shafiqullin, R. F. Borkman and R. L. Whetten, *J. Phys. Chem. B* **102**, 10643–10646 (1998).
- 3) T. G. Schaaff and R. L. Whetten, *J. Phys. Chem. B* **104**, 2630–2641 (2000).

VIII-Q-4 Construction of Apparatus for Photoelectron and Photodissociation Studies of Mass-selected Organometallic Clusters

NEGISHI, Yuichi; NARUSHIMA, Takashi¹; TSUKUDA, Tatsuya
(¹GUAS)

The electronic structures of the MPCs, especially in the subnanometer-sized regime, are significantly influenced by the thiolate (RS) coordination against the metallic cores as well as their core sizes. In order to study such effects, it is necessary to prepare and isolate the mass selected $\text{M}_n(\text{SR})_m$ clusters ($m \geq 0$) in the gas phase, since the clusters with small m are unstable against the aggregation in liquid dispersion. To this end, we have developed a new apparatus, which consists of a cluster ion source, a tandem time-of-flight mass spectrometer, and a photoelectron spectrometer. In the cluster source, the bare metal clusters produced by laser vaporization of the metal target are allowed to react with the thiol molecules, RSH, to form organometallic clusters. The anionic clusters, $\text{M}_n(\text{SR})_m^-$, are mass-selected by the first TOF mass spectrometer and then irradiated by pulsed laser light. The photoelectrons and photofragments are detected by the magnetic-bottle type photoelectron spectrometer and the secondary TOF mass spectrometer, respectively.

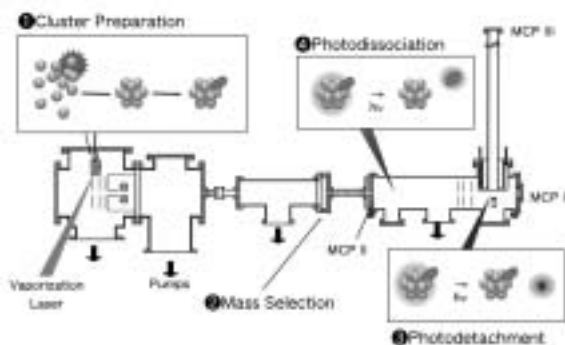


Figure 1. Schematic diagram of the experimental setup.

VIII-Q-5 EXAFS Study on Interfacial Structure between Pd Cluster and *n*-Octadecanethiolate Monolayer: Formation of Mixed Pd–S Interlayer

MURAYAMA, Haruno; ICHIKUNI, Nobuyuki¹; NEGISHI, Yuichi; NAGATA, Takashi²; TSUKUDA, Tatsuya
(¹Chiba Univ.; ²Univ. Tokyo)

[*Chem. Phys. Lett.* **376**, 26–32 (2003)]

The geometrical structure of a Pd cluster (diameter of ≈ 3.1 nm) protected by *n*-octadecanethiolate monolayer has been investigated by high-resolution TEM (HRTEM), XRD, and EXAFS spectroscopy. The HRTEM and XRD measurements have revealed that the cluster core is comprised of an *fcc* single crystal of Pd. The mean coordination numbers of the Pd–Pd and Pd–S shells determined by the Pd *K*-edge EXAFS analysis suggest that the surface of the Pd core is sulfurized to form a mixed Pd–S layer underneath the thiolate monolayer.

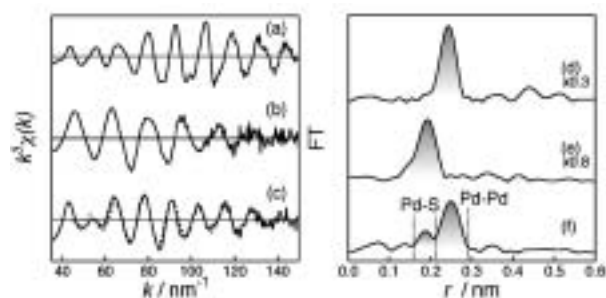


Figure 1. k^3 -weighted Pd *K*-edge EXAFS spectra after background subtraction; (a) Pd foil, (b) PdS pellet, (c) Pd:SC₁₈ clusters. The broken line in panel (c) represents the best-fit result. Fourier-transforms of the EXAFS spectra; (d) Pd foil, (e) PdS pellet, (f) Pd:SC₁₈ clusters.

VIII-Q-6 Structures and Stabilities of Alkanethiolate Monolayers on Palladium Clusters as Studied by Gel Permeation Chromatography

MURAYAMA, Haruno; NARUSHIMA, Takashi¹; NEGISHI, Yuichi; TSUKUDA, Tatsuya
(¹GUAS)

[*J. Phys. Chem. B* submitted]

Palladium clusters protected by a series of *n*-alkane-thiolates, Pd:SC_{*n*} (SC_{*n*} = *n*-C_{*n*}H_{2*n*+1}S, *n* = 10, 12, 14, 16, and 18), were prepared by a ligand exchange approach: Pd clusters protected by poly (*N*-vinyl-2-pyrrolidone) (PVP) were transferred from aqueous phase to the toluene phase containing the thiols. The structures and stabilities of the thiolate monolayers of the Pd:SC_{*n*} clusters were investigated by gel permeation chromatography (GPC) together with TEM, XPS, and FT-IR. The thicknesses of the thiolate layers formed on the Pd clusters were evaluated from the differences between the hydrodynamic diameters and core diameters of the Pd:SC_{*n*} clusters, determined by GPC and TEM, respec-

tively. The thicknesses thus obtained are in good agreement with the lengths of the corresponding thiols in the all-*trans* conformations, illustrating that the alkanethiolates in nearly straight configurations are aligned almost perpendicularly to the core surfaces. Fractionation of the Pd:SC₁₈ clusters by GPC yielded a series of the purified samples: the clusters in each fraction are different in their core sizes. The GPC

measurements on the Pd:SC_{*n*} clusters with small *n* revealed the decomposition of the monolayers through spontaneous etching and their reconstruction by heat treatment in the presence of the free thiols. The mechanism of these processes is discussed. The present study demonstrates that the GPC provides an elemental and versatile means to characterize and purify the monolayer-protected clusters.

VIII-R Mass Spectroscopic Studies on Nanoscale Materials

Information on the size, shape, and dispersity is of fundamental importance in understanding natures and functions of nanoscale materials. Traditionally, transmission electron microscope (TEM) and powder X-ray diffraction have been employed to measure size, shape and size distributions of the nanoscale materials. We have applied an alternative technique, mass spectrometry, to provide more detailed insight into the structures of these fascinating materials.

VIII-R-1 Self-Assembly of Si Clusters into Single Crystal Arrangements: Formation of Si₁₀ Cluster Crystals

SATO, Seiichi¹; YAMAMOTO, Naoaki¹;
NAKANISHI, Kentaro¹; YAO, Hiroshi¹; KIMURA,
Keisaku¹; NARUSHIMA, Takashi²; NEGISHI,
Yuichi; TSUKUDA, Tatsuya
(¹Himeji Inst. Tech.; ²GUAS)

[*Jpn. J. Appl. Phys.* **42**, L616–L618 (2003)]

Single crystals at an air/solution interface or a solution/hydrogen-terminated Si substrate interface were created using a self-assembly process, which originated from the hydrophobic nature of Si clusters. Mass analysis indicated that the components of the cluster crystals were partially oxidized hydrogenated Si₁₀ clusters. At either interface the nearest-neighbor distances between lattice points in the Si cluster crystals were 0.53 nm or 0.60 nm, which is consistent with the diameters of the Si₁₀ clusters. The slight difference in these values seems to be due to variations in the surface passivation of the component Si₁₀ clusters.

VIII-R-2 Highly Oxygenated Fullerene C₆₀O_{*n*} formed by Corona Discharge Ionization in the Gas Phase

TANAKA, Hideki¹; TAKEUCHI, Kazuo¹;
NEGISHI, Yuichi; TSUKUDA, Tatsuya
(¹RIKEN)

[*Chem. Phys. Lett.* in press]

Oxygenated fullerenes were produced by a vaporization source equipped with a corona discharge ionizer in the presence of a trace amount of oxygen. *In situ* mass analysis revealed that the species formulated as C₆₀O_{*n*} (*n* ≤ 30) are formed in the source and that the degree of oxygenation can be altered through the discharge current. Formation of the epoxidized structure in the C₆₀O_{*n*} was confirmed by XPS measurements of the thin films of C₆₀O_{*n*} and semi-empirical PM3 calculations for C₆₀O₃₀. The structures and formation processes for higher analogues (C₆₀)_{*m*}O_{*n*} (*m* = 2, 3) are briefly discussed.

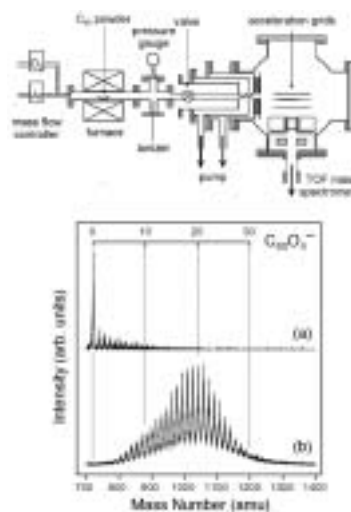


Figure 1. Schematic diagram of experimental setup (top) and typical mass spectra of the negative ions produced by the corona discharge ionizer (bottom) operated at 100 mA under Ar gas flow (a) without oxygen and (b) with 1% oxygen.

VIII-S Structures and Reactions of Molecular Cluster Ions

Molecular clusters, intermediate states of matter between the bulk and the molecule, provide us unique opportunities to study how the chemical and physical properties evolve with a degree of aggregation. We have studied reactions of hydrated anions with a simple molecule by using mass spectrometry, photoelectron and photodissociation spectroscopies and *ab initio* calculations.

VIII-S-1 Gas-Phase Reaction of Hydrated $\text{CO}_2^{\cdot-}$ Anion Radicals with CH_3I

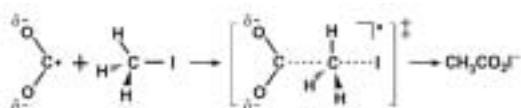
TSUKUDA, Tatsuya; NAGATA, Takashi¹
(¹Univ. Tokyo)

[*J. Phys. Chem. A* **107**, 8476–8483 (2003)]

Hydrated $\text{CO}_2^{\cdot-}$ anion radicals, $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n$, are selectively prepared in an electron-impact free jet of $\text{CO}_2^{\cdot-}$ containing H_2O . Mass spectrometric measurement reveals that $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n$ reacts with CH_3I to form an anion with $[(\text{CO}_2)(\text{H}_2\text{O})]^-$ stoichiometry. The product $[(\text{CO}_2)(\text{H}_2\text{O})]^-$ is further identified as the anion of acetyloxy iodide, $\text{CH}_3\text{CO}_2\text{I}^-$, based on the observation that $[(\text{CO}_2)(\text{H}_2\text{O})]^-$ photodissociates at 532 nm into $\text{CH}_3\text{CO}_2^- + \text{I}$ or $\text{CH}_3\text{CO}_2 + \text{I}^-$ channels. The $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n + \text{CH}_3\text{I}$ reaction thus presents a sharp contrast to the corresponding reaction in solution: the gas-phase $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n$ behaves as a carboxylation reagent for alkyl halide (RX), whereas in aqueous solutions the reaction proceeds as $\text{CO}_2^{\cdot-} + \text{RX} \rightarrow \text{CO}_2 + \text{R} + \text{X}^-$. *Ab initio* calculations suggest that $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n$ can take on structures preferable for radical reactions: the hydraion occurs on the O atoms of $\text{CO}_2^{\cdot-}$ and the unpaired electron on the C atom remains uncovered with H_2O solvents. The reaction mechanism of the $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n + \text{CH}_3\text{I}$ process is discussed in conjunction with previous results of $(\text{CO}_2)_n^{\cdot-} + \text{CH}_3\text{I}$.¹⁾

Reference

1) T. Tsukuda, M. Saeki, S. Iwata and T. Nagata, *J. Phys. Chem. A* **101**, 5103–5110 (1997).



Scheme 1.

VIII-T Nanoscale Characterization of Heterogeneous Catalyst Surfaces

Heterogeneous catalysis occurs on a surface of a solid catalyst. Active centers for heterogeneous catalysis commonly consist of clusters of several surface atoms, and thus a long-range order of surface atoms is not normally required. Therefore, when using precious metals as catalysts, nanometer-scale superfine particles are commonly employed in order to increase its surface area and to decrease the amount of catalysts. This introduces difficulties in characterizing the catalyst surfaces and their active centers, because characterization techniques of solid surfaces at nanometer-scale are not well established. Here we mainly used scanning probe microscopes, in conjunction with other surface characterization techniques, to characterize catalytically active centers as well as the nature of catalyst-support interactions.

VIII-T-1 Monte Carlo Simulation of Pyridine Base Adsorption on Heulandite (010)

YOKOI, Yasuto¹; YELKEN, Gulnihal²; OUMI, Yasunori³; KOBAYASHI, Yasunori¹; KUBO, Momoji¹; MIYAMOTO, Akira¹; KOMIYAMA, Masaharu⁴

(¹Tohoku Univ.; ²Izmir Inst. Tech.; ³Japan Inst. Sci. Tech.; ⁴IMS and Yamanashi Univ.)

[*Appl. Surf. Sci.* **188**, 377–380 (2002)]

Adsorption of pyridine base molecules (pyridine and α -, β - and γ -picolines) on a surface of a natural zeolite, heulandite (010), was examined by Monte Carlo simulations. Two types of adsorption areas were identified on heulandite (010) bound by surface OH arrays, and each area showed different influence on the adsorption and orientation for pyridine base molecules. The presence of methyl group and its position within the adsorbed molecule also influenced its adsorption characteristics. For pyridine adsorption, molecular dynamics simulation was also performed. The results were compared with existing experimental data obtained through atomic force microscopy.

VIII-T-2 Apparent Local Structural Change Caused by Ultraviolet Light on a TiO₂ Surface Observed by Scanning Tunneling Microscopy

KOMIYAMA, Masaharu¹; LI, Yanjun; YIN, Donghong²

(¹IMS and Yamanashi Univ.; ²Funan Normal Univ.)

[*Jpn. J. Appl. Phys.* **41**, 4936–4938 (2002)]

An apparent local surface structural change at nanoscale was observed by scanning tunneling microscopy on a TiO₂ surface upon irradiation with ultraviolet (UV) light. This phenomenon was reversible with UV light irradiation, and was interpreted to be due to the local accumulation of photoexcited states. This is the first real-space observation of inhomogeneous local charge distribution under UV light irradiation at nanoscale on a semiconductive photocatalyst surface, which may help identify the photocatalytic active sites and elucidate their reaction mechanisms.

VIII-T-3 Electronic Structure Change on TiO₂ Surface due to UV Light Irradiation

KOMIYAMA, Masaharu¹; YIN, Donghong²; LI, Yanjun

(¹IMS and Yamanashi Univ.; ²Funan Normal Univ.)

[*Stud. Surf. Sci. Catal.* **145**, 153–156 (2003)]

Photocatalysts have been paid extensive attentions for their environmental as well as energy applications. Although each photocatalytic processes may be different in terms of their kinetics and surface reactions involved, they are all initiated with the photoexcitation of TiO₂ electrons, the process commonly understood and explained by the so-called band model which assumes an infinite array of crystallographic lattice points. In contrast, catalytic reactions involved in photocatalysis are highly local in nature: some reactant may need particular local arrangements of atoms that are present on the catalyst surface, and others may need particular local electronic states of the surface atoms to provide unique adsorption or reaction sites. Despite this gap that exist in between the two descriptions involved in heterogeneous photocatalysis (band model and local catalysis), no efforts to address and bridge this gap are known to the authors. The present report is the first of such attempts, and examines the local electronic characters of TiO₂ surface upon UV-light illumination by means of scanning tunneling microscopy (STM).

VIII-T-4 In Situ Observations of Tetraamineplatinum (II) Hydroxide Adsorption from Its Aqueous Solution on Heulandite (010) Surface by Atomic Force Microscopy

KOMIYAMA, Masaharu¹; LI, Yanjun; GU, Ning²

(¹IMS and Yamanashi Univ.; ²Southeast Univ.)

Adsorption of tetraamineplatinum (II) hydroxide, a Pt catalyst precursor, from its aqueous solution on a (010) surface of a natural zeolite heulandite was observed, in situ, by atomic force microscopy (AFM). The Pt complex exhibited certain adsorption habits on the surface, frequently forming a short chain along the zeolite *a* axis, separated by three times the *c* unit cell length in the *c* direction. Possible adsorption sites on the surface were identified and discussed. The present work constitutes the first in situ atomic-level observation of a

liquid-phase preparation process of supported metal catalysts.

VIII-T-5 Defect Creation on Rutile TiO₂ (110)-(1×1) Surface due to Light Irradiation Observed by Scanning Tunneling Microscopy

**LI, Yanjun; MATSUMOTO, Taki; GU, Ning¹;
KOMIYAMA, Masaharu²**

(¹*Southeast Univ.*; ²*IMS and Yamanashi Univ.*)

Laser light irradiation created atomic-scale structures on rutile TiO₂ (110)-(1×1) surface, the number of which increased with irradiation time. The created bright structures appear to be cross-shaped, each bridging two titanium [001] rows, and having dark areas in the front and in the back. The structure is interpreted as an oxygen deficiency on the (1×1) surface, and the one of the dark spots around the structure as the oxygen atom displaced from its original position. The structure often appears as a pair aligned along [1-10] direction, which could be viewed as a local (2×3) structure.

VIII-T-6 Crater Structures on a Molybdenite Basal Plane Observed by Ultra-High Vacuum Scanning Tunneling Microscopy

**KOMIYAMA, Masaharu¹; KIYOHARA,
Kohei²; LI, Yanjun; KUBOTA, Takeshi²;
OKAMOTO, Yasuaki²**

(¹*IMS and Yamanashi Univ.*; ²*Shimane Univ.*)

Atomic structure of a natural molybdenite (MoS₂) single crystal basal plane was examined by ultra-high vacuum scanning tunneling microscopy (UHV-STM). After high-temperature (473 K) resulfidation, numbers of crater structures with diameters ranging from 6 to 8 nm were observed. Atomic structures within these craters were continuous from the surrounding terrace, with no step structures at the rims of the craters. Atoms in the bottom of the craters showed higher corrugations compared to the terrace atoms, indicating perturbed electronic states in the craters. Its implication in hydrodesulfurization activity over MoS₂ basal plane is discussed.

VIII-U Fundamental Study on Electrostatic Manipulation of Biomolecules and its Application to Gene Analysis

Since conventional DNA sequencing method can determine up to 1000 base pairs at one time, longer DNA must be cut into small fragments. However, order information among these fragments is inevitably lost resulting in tremendous post sequencing process to do a puzzle. To cope with the problem, we have studied DNA sequencing method based on one-by-one DNA handling. The method includes (1) electrostatic manipulation of genomic DNA, (2) fixation in a stretched form, (3) cut from the terminus, (4) recovery and amplification of the fragments.

VIII-U-1 Manipulation of Single Coiled DNA Molecules by Laser Clustering of Microparticles

HIRANO, Ken¹; BABA, Yoshinobu¹;
MATSUZAWA, Yukiko²; KATSURA, Shinji²;
MIZUNO, Akira
(¹Tokushima Univ.; ²Toyoashi Univ. Tech.)

A method of manipulating single DNA molecules for application in single-molecule analysis was developed. Manipulation of laser clustered beads allowed manipulation of a single DNA molecule without modification. Figure 1 shows sequential photographs of a DNA molecule anchored at both end to a glass surface. The DNA molecule was tweezed at one point and successfully stretched (figure1(b)–(d)). The stretched DNA molecule returned to its original form after releasing by turning off the laser beam (figure1(e)).

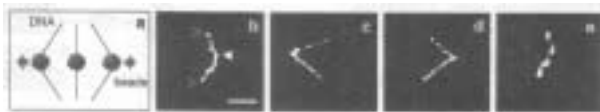


Figure 1. Sequential images of the manipulation of a single DNA molecule using laser clustering of 0.2 μm latex beads.

VIII-U-2 One-End Immobilization of Individual DNA Molecules on a Functional Hydrophobic Glass Surface

MATSUURA, Shun-ichi¹; KURITA, Hirofumi¹;
NAKANO, Michihiko¹; KOMATSU, Jun¹;
TAKASHIMA, Kazunori¹; KATSURA, Shinji¹;
MIZUNO, Akira
(¹Toyoashi Univ. Tech.)

An extremely simple technique of DNA immobilization on a hydrophobic glass surface was developed. The technique includes hydrophobic processing of a cover slip with dichlorodimethylsilane and modification of the terminus of DNA with sulfhydryl group. Dichlorodimethylsilane reacts with silanol groups on a cover slip surface (figure1(a)) and forms hydrophobic monolayer of dichlorodimethylsilane (figure1(b)). Sulfhydryl group of DNA molecule modified at one terminus reacts on the dichlorodimethylsilane layer resulting in anchoring of a single DNA molecule to the cover slip (figure1(c))

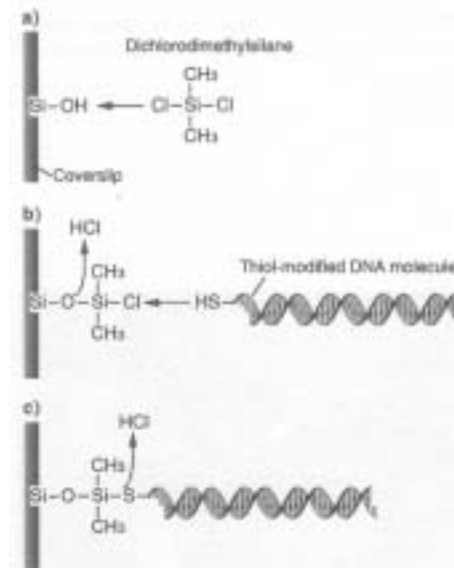


Figure 1. Schematic diagram of reaction mechanism of DNA immobilization on a dichlorodimethylsilane-coated surface.

VIII-U-3 Single-Molecule PCR using Water-in-Oil Emulsion

NAKANO, Michihiko¹; KOMATSU, Jun¹;
MATSUURA, Shun-ichi¹; TAKASHIMA,
Kazunori¹; KATSURA, Shinji¹; MIZUNO, Akira
(¹Toyoashi Univ. Tech.)

[*J. Biotechnology* **102**, 117–124 (2003)]

A simple PCR method utilizing a water-in-oil (W/O) emulsion was developed. Numerous numbers of droplets serving as reaction mixture are included in bulk oil phase in this system. The method allows amplification of very low concentration DNA samples because such droplets increase effective concentration of template DNA. In this method, PCR was started with emulsified samples, in which template DNA was amplified to sufficient amount applicable to conventional PCR next step. After the first PCR in emulsified state was completed, W/O emulsion was broken by centrifuging to start the conventional PCR. By using this method consisting of 13 and 25 cycles in the first and the second step, target DNA of which concentration is 1 molecule/tube was successfully amplified.

VIII-U-4 FIM Observation of DNA Molecules

FURUMAKI, Takuya¹; TSUJI, Yuuta¹; NAKANO,

Michihiko¹; TAKASHIMA, Kazunori¹; UCHIDA, Hironaga¹; KATSURA, Shinji¹; MIZUNO, Akira
(¹*Toyohashi Univ. Tech.*)

An application of field ion microscope (FIM) to DNA sequencing has been experimentally studied. By applying a DC voltage to a FIM tip on which a DNA molecule is attached, the bases may be released and carried along the electric field. Ultra high-speed genome analysis will be feasible by detecting the digested bases. We constructed a DNA sequencing system based on a field ion microscope. An electro-polished gold was used as a substrate. DNA molecules modified with sulfhydryl (-SH) group prepared by PCR (polymerase chain reaction) were attached on the needle tip. High voltage up to 7 kV was applied to DNA-bound tip to observe the FIM images. It was found that binding of DNA on samples decreased on-set voltage of FIM images suggesting the existence of an atomically rough surface.

VIII-U-5 Micro Reactor System Based on Water-in-Oil Emulsion

NAKANO, Michihiko¹; NAKAI, Naohito¹; TAKASHIMA, Kazunori¹; KATSURA, Shinji¹; MIZUNO, Akira
(¹*Toyohashi Univ. Tech.*)

A method called as “combinatory chemistry” has been proposed to create useful enzymes higher active and stable. Since the combinatory chemistry is based on multiple mutations of enzymes and evaluation of those mutants, high through-put production and analysis of enzymes is required to promote this method. For this purpose, miniaturization of reactors has been developed by using micro fabrication techniques. However, the miniaturization accompanies with difficulty of liquid handling, therefore size of reactors was limited by liquid handling technique.

To overcome this problem, we have been engaged in development of reaction system based on water-in-oil emulsion. W/O emulsion contains large amount of water droplets in continuous oil phase. Because many biological molecules are hydrophilic, those can be enclosed in the droplets. This indicates that the droplets play a role of small reactors, however reaction control of the droplets has not been established. We are developing unit operations such as transport, fusion to achieve reaction control of the droplets. In this term, we have developed transport methods based on electro-osmosis and charge injection. We have succeeded to drive the droplets by both methods. Now, we are engaged in improving controllability of droplet transport.

VIII-V Studies of Electronic Structure of Organic Thin Films

Electronic structures of organic film surface and organic/inorganic interface are expected to play an important role in organic-device properties. It is important to clarify the characteristics of not only occupied states but also unoccupied states for organic thin films, since the device properties such as the efficiency of the electron and/or the hole injection depend on the position and/or the distribution of these electronic states. We have investigated the electronic structure of organic film surface and organic/inorganic interface using surface sensitive spectroscopies such as photoelectron spectroscopy and near-edge x-ray absorption fine structure (NEXAFS). To help the assignment of NEXAFS spectra, we use the photon energy dependence of photon-stimulated ion desorption, since the chemical bond scission by inner-shell excitation depends on the electronic configuration of the excited state.

VIII-V-1 Photodegradation of Poly(Tetrafluoroethylene) and Poly(Vinylidene Fluoride) Thin Films by Inner Shell Excitation

OKUDAIRA, K. Koji; YAMANE, Hiroyuki¹; ITO, Kazuyuki¹; IMAMURA, Motoyasu²; HASEGAWA, Shinji; UENO, Nobuo¹
(¹Chiba Univ.; ²AIST)

[*Surf. Rev. Lett.* **9**, 335–340 (2002)]

Ion time-of-flight (TOF) mass spectra of poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) thin films near fluorine and carbon *K*-edges were observed. For PTFE thin films peaks corresponding to F^+ , CF^+ , and CF_3^+ appeared, while for PVDF F^+ and H^+ were mainly observed. They indicate that for PTFE the polymer chain (C–C bonds) as well as C–F bonds are broken by irradiation of photons near fluorine and carbon *K*-edges, while for PVDF the bond scission occurs mainly at the C–F and C–H bond. In Figures 1 (a), (b), and (c) partial ion yield (PIY) spectra of F^+ , CF^+ and CF_3^+ for PTFE thin films are compared with total electron yield (TEY) near the fluorine *K* absorption edge. PIY spectra of F^+ , CF^+ and CF_3^+ are different from the TEY spectrum. The intense PIY feature of F^+ appears at $h\nu = 689$ eV corresponding to the transition from $F1s$ to $\sigma(C-F)^*$. The PIY intensity of F^+ at $h\nu = 689$ eV is much stronger than at $h\nu = 693$ eV corresponding to the transition from $F1s$ to $\sigma(C-C)^*$, while the TEY intensity at $h\nu = 689$ eV is slightly stronger than that at $h\nu = 693$ eV. That is, the C–F bond scission by irradiation of photons at $h\nu = 689$ eV ($F1s \rightarrow \sigma(C-F)^*$) is expected to occur more effectively than at $h\nu = 693$ eV ($F1s \rightarrow \sigma(C-C)^*$). For the case of PVDF, the intense PIY feature of F^+ appears at the transition from $F1s$ to $\sigma(C-F)^*$. The excitation from fluorine $1s$ to $\sigma(C-F)^*$ is specially efficient for F^+ ion production for both PTFE and PVDF.

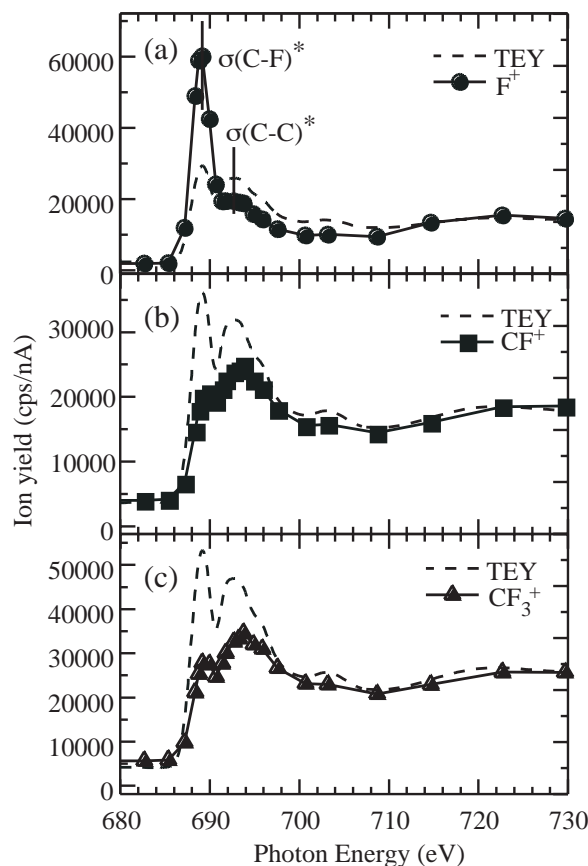


Figure 1. PIY spectra of (a) F^+ , (b) CF^+ and (c) CF_3^+ for PTFE thin film near the fluorine *K* absorption edge. TEY spectra (broken curve) are also shown for comparison. TEY spectra are renormalized at $h\nu = 682.5$ eV and at $h\nu = 730$ eV to fit PIY intensities.

VIII-V-2 Excited States of Perfluorinated Oligo(p-phenylene) by Inner-Shell Excitation

OKUDAIRA, K. Koji; OHARA, Kosuke¹; SETOYAMA, Hiroyuki¹; SUZUKI, Toshiyasu; SAKAMOTO, Youichi¹; IMAMURA, Motoyasu²; HASEGAWA, Shinji; MASE, Kazuhiko³; UENO, Nobuo¹
(¹Chiba Univ.; ²AIST; ³IMSS)

[*Nucl. Instrum. Methods Phys. Res., Sect. B* **199**, 265–269 (2003)]

Ion time-of-flight (TOF) mass spectra and near edge x-ray absorption fine structure (NEXAFS) spectra of

perfluorinated oligo(*p*-phenylene) (PF-8P) films near fluorine (F) and carbon (C) *K*-edges were observed. In ion TOF mass spectra near F and C *K*-edges, F^+ , CF^+ , and CF_3^+ were intensely observed. It indicates that C–C bonds of phenyl ring as well as C–F bonds are broken by irradiation of photons near F and C *K*-edges. Partial ion yield (PIY) spectra of PF-8P show clear $h\nu$ dependence near F and C *K*-edges. Especially, near F *K*-edge, the PIY spectra of F^+ increases remarkably at $h\nu = 689.2$ eV, which corresponds to the lowest peak in NEXAFS. The lowest peak in the NEXAFS near fluorine *K*-edge is assigned to the transition from $F1s$ to $\sigma(C-F)^*$. Furthermore, from the analysis of PIY spectra of PF-8P near carbon *K*-edge, the peak at $h\nu = 289.5$ eV is ascribed to the transition from $C1s$ to $\sigma(C-F)^*$.

VIII-W Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Electron Impact near the Bethe Ridge

Binary ($e,2e$) or electron momentum spectroscopy (EMS), based on the so-called electron Compton scattering, is a high-energy electron-impact ionization experiment in which kinematics of all the electrons are fully determined by coincident detection of the two outgoing electrons. The ability to measure electron momentum distribution for each molecular orbital, square modulus of the momentum-space wavefunction, is a remarkable feature of this technique. Since momentum-space and position-space are uniquely related to each other by Fourier transformation, electron momentum distribution is highly sensitive to diffuse parts of the position-space wavefunction that are important in chemical reaction and molecular recognition. However, the potential of EMS has not been fully achieved as yet, due mainly to the extremely small cross sections involved. For these reasons, together with various improvements to spectrometers we are aiming at developing next-generation EMS for chemistry, which would give quite unique and versatile information on electronic structure of molecules.

VIII-W-1 A High Sensitivity Electron Momentum Spectrometer with Simultaneous Detection in Energy and Momentum

TAKAHASHI, Masahiko; SAITO, Taku¹; MATSUO, Motoaki¹; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

[*Rev. Sci. Instrum.* **73**, 2242 (2002)]

A new apparatus for electron-electron coincidence experiments has been developed to examine molecular orbital patterns quantitatively by electron momentum spectroscopy. Using a spherical analyzer and position-sensitive detectors, it enables one to measure energy and angular correlations between the two outgoing electrons simultaneously. The design and performance of the apparatus is reported together with results on Ar to show extensive improvements in coincidence count rates and statistical precision, covering a wide range of binding energies and momenta.

VIII-W-2 The Impact Energy Dependence of Momentum Profiles of Glyoxal and Biacetyl and Comparison with Theory at Their High-Energy Limits

TAKAHASHI, Masahiko; SAITO, Taku¹; HIRAKA, Jyunya¹; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

[*J. Phys. B: At., Mol. Opt. Phys.* **36**, 2539 (2003)]

We report an electron momentum spectroscopy study of the two outermost orbitals of dicarbonyls, glyoxal and biacetyl. The experiments were performed at impact energies of 800, 1200 and 1600 eV by using a recently developed multichannel ($e,2e$) spectrometer. The experimental momentum profiles clearly show remarkable variations in the low momentum region with increase in impact energy. Furthermore, it has been found that the two molecules reach their high-energy limits at different impact energies, indicating that the range of the validity of the plane-wave impulse approximation (PWIA) largely depends on the target in

question. The results at 1600 eV are employed for comparisons with PWIA calculations using Hartree-Fock and density functional theory (DFT). While the DFT calculations reproduce well the observations for glyoxal, considerable discrepancies between experiment and theory exist in biacetyl.

VIII-W-3 ($e,2e$) Ionization-Excitation of H₂

TAKAHASHI, Masahiko; KHAJURIA, Yugal; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

[*Phys. Rev. A* in press]

Binary ($e,2e$) measurements are reported for simultaneous ionization-excitation processes of H₂. The experiments were performed at impact energies of 1200, 1600 and 2000 eV using an energy- and momentum-dispersive spectrometer. Momentum profiles for transitions to the $2s\sigma_g$ and $2p\sigma_u$ excited final ion states are presented as normalized intensities relative to the cross section of the primary ionization to the $1s\sigma_g$ ground ion state. The results are compared with theoretical calculations of Lermer *et al.* [*Phys. Rev. A* **56**, 1393 (1997)] using the first-order plane-wave impulse approximation. Certain features of the discrepancies between experiment and theory can be explained by incorporating contributions from the second-order two-step mechanisms into the ($e,2e$) cross sections. Furthermore, the present results suggest that $2s\sigma_g$ and $2p\sigma_u$ cross sections approach their high-energy limits in different ways.

VIII-W-4 Electron Momentum Spectroscopy of N₂O

KHAJURIA, Yugal; TAKAHASHI, Masahiko; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

[*J. Electron Spectrosc.* in press]

An electron momentum spectroscopy study of the outer valence orbitals of N₂O is reported. The experi-

ments were performed at impact energies of 1000, 1200, 1600 and 1800 eV by using a recently developed multichannel ($e,2e$) spectrometer. The experimental momentum profiles are compared with each other to examine their impact energy dependence. The results are used for comparisons with Hartree-Fock (HF) and density functional theory (DFT) calculations using various basis sets. The DFT and HF calculations with large basis sets are in good agreement with the measured electron momentum profiles, with the exception of that of the 6σ orbital for which the HF method underestimates the cross sections in the low momentum region.

VIII-W-5 A High Sensitivity Electron Momentum Spectrometer with Two-Dimensional Detectors and Electron Momentum Distributions of Several Simple Molecules

TAKAHASHI, Masahiko; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

[*J. Electron Spectrosc.* submitted]

Electron momentum spectroscopy (EMS) makes it possible to examine orbital patterns of individual molecular orbitals in momentum space. A new spectrometer for electron-electron coincidence experiments for EMS has been developed to obtain orbital patterns quantitatively. Using a spherical analyzer and position-sensitive two-dimensional detectors combined with fast electronics, simultaneous measurements of energy and angular correlations between the two outgoing electrons can be made. This spectrometer features high sensitivity and an ease of changing impact energies. Details of the apparatus are described and impact energy dependence of electron momentum distributions of the HOMO of H₂ and biacetyl are compared.

VIII-W-6 Electron-Impact Double Ionization Mechanisms in the Impulsive Regime

VAN BOEYEN, Roger W.¹; WATANABE, Noboru;
DOERING, John P.¹; MOORE, John H.²; COPLAN,
Michael A.²; COOPER, John W.²
(¹Johns Hopkins Univ., USA; ²Univ. Maryland, USA)

[*Phys. Rev. Lett.* submitted]

Five-fold differential cross sections (5DCS) for the electron-impact double ionization of the $3s$ electrons of magnesium have been measured in a high-impact-energy, high-momentum-transfer regime within the ionization mechanisms can be accurately described by simple models in which the ionization processes and the initial-state atomic properties can be separated. In the unique experimental geometry, the form of the measured cross sections provides strong evidence for impulsive two-collision ionization mechanisms. Second Born calculations are in agreement with the experimental data providing further evidence for the mechanisms. The implications for the measurement of two-electron densities are discussed.

VIII-W-7 Second Born Approximation Calculations of Double Ionization of Mg

WATANABE, Noboru; COOPER, John W.¹; VAN
BOEYEN, Roger W.²; MOORE, John H.¹
(¹Univ. Maryland, USA; ²Johns Hopkins Univ., USA)

Electron impact double ionization, also called the ($e,3e$) reaction, can provide direct information on correlated motion of atomic electrons, provided that the collision mechanism is known. Possible mechanisms for the ($e,3e$) reaction include shake-off (SO), two-step 1 (TS1), and two-step 2 (TS2). The SO and TS1 are of the first order in the projectile-target interaction, while the TS2 is a second-order process. In this study we theoretically examine contributions from TS2 in the scattering geometry chosen for the ($e,3e$) experiments of the Maryland group, which investigate correlated motion of the $3s$ electrons in the magnesium atom. It has been found that dominant contribution from the Second Born term is involved in the observed ($e,3e$) cross sections of Mg. Electron correlation effects in the initial target state are also studied using a configuration interaction wave function.

VIII-W-8 Orbital Momentum Profiles and Binding Energy Spectra for the Complete Valence Shell of CO

SAITO, Taku¹; TAKAHASHI, Masahiko;
UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

Electron momentum profiles and binding energy spectra for the complete valence shell of CO have been measured using an energy- and momentum-dispersive ($e,2e$) spectrometer at an impact energy of 1600 eV. It has been found that shapes of the orbital momentum profiles are well reproduced by Hartree-Fock calculations. Binding energy spectra and momentum profiles in the satellite region beyond 22 eV binding energy of CO are studied in detail, determining pole strength distributions of the molecule. Comparisons are made for the pole strength distributions with theoretical predictions of Ehara and Nakatsuji using the SAC-CI general-R method. The agreement between experiment and theory is generally good, but some discrepancies remain for ionization transitions with small pole strength lower than about 0.1.

VIII-W-9 ($e,2e$) Study on Ionization-Excitation and Double Ionization of He

TAKAHASHI, Masahiko; UDAGAWA, Yasuo¹
(¹Tohoku Univ.)

A binary ($e,2e$) study has been carried out for He at an impact energy of 2000 eV using a recently developed energy- and momentum-dispersive spectrometer. Binding energy and momentum ranges up to about 100 eV and 4 au were then covered. Momentum distributions of the individual ionization-excitation transitions, converging to the double ionization threshold, have been compared with first-order plane-wave impulse

calculations of Mitroy *et al.* [*J. Phys. B* **18**, 4149 (1985)]. For the primary ionization that leaves the residual He^+ ion in the $n = 1$ ground state, agreement between experiment and theory is satisfactory. On the other hand, for ionization-excitation that leads to change of state of both the two target electrons the experiments always exhibit larger intensity than theory, suggesting noticeable contributions from the second-order two step mechanisms.

VIII-W-10 Development of a Triple Coincidence Spectrometer for a Complete Three-Dimensional Mapping of Electron Momentum Densities in Gaseous Molecules

TAKAHASHI, Masahiko; WATANABE, Noboru; UDAGAWA, Yasuo¹; ELAND, John H. D.²
(¹Tohoku Univ.; ²Oxford Univ., England)

Electron momentum spectroscopy has been developed as a powerful means for the investigation of electronic structure and electron correlation. In particular, the ability to measure electron momentum distribution for each molecular orbital, square modulus of the momentum-space wavefunction, is a remarkable feature of this technique. It is unfortunate, however, that experimentally observable electron momentum distribution is spherically averaged due to random orientation of gaseous targets, smearing out details of electronic structure inherently involved in the experiments.

To overcome the experimental difficulty a new apparatus has been developed for a complete three-dimensional mapping of electron momentum densities in gaseous molecules. Based on the axial recoil, measurements of vector correlations among the two outgoing electrons and fragment ion correspond to $(e,2e)$ experiments with oriented molecules. Dissociation of molecular ions perpendicular to the incident electron momentum vector are detected with seven independent channeltrons, while the two outgoing electrons are detected with a pair of position-sensitive detectors. A schematic diagram of the kinematics of our experiments is shown in Figure 1.

Although there are substantial backgrounds due to a huge number of fragment ions produced by forward scattering of electron projectile, we have successfully measured genuine triple coincidence signals for the first time. Figure 2 shows an example of the results, which plots directional electron momentum densities obtained

for the $2\sigma_g$ ionization of O_2 . While the statistics of the data is not satisfactory, we can clearly see anisotropy of electron momentum densities. For establishing this method developments in detection of the outgoing electrons in the momentum dispersive plane around full 2π azimuth are now in progress to increase sensitivity of two additional orders of magnitude.

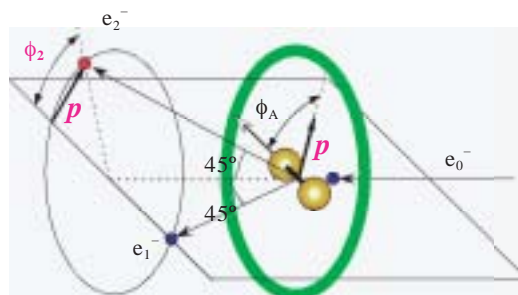


Figure 1. Schematic diagram of the kinematics of the $(e,2e)$ directional momentum density experiment. The spectrometer records only the component of momentum perpendicular to the scattering plane. When dissociation takes place in the perpendicular plane, the channeltron detectors will record the arrival of the dissociation products.

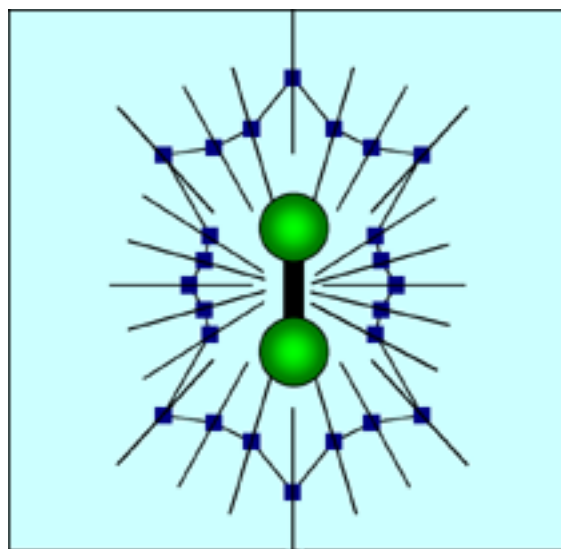


Figure 2. Directional electron momentum densities for the $2\sigma_g$ orbital ionization of O_2 .

VIII-X Electronic Structure and Collision Dynamics of Atoms and Molecules Studied by Photon Impact

The group takes another, photon-impact, approach to issues of electronic structure and collision dynamics, since photon-impact and electron-impact or photoelectric effects and Compton scattering are complementary to each other.

VIII-X-1 Multilayer Polarizers for the Use of He-I and He-II Resonance Lines

HATANO, Tadashi¹; KONDO, Yuzi¹; SAITO, Katsuhiko¹; EJIMA, Takeo¹; WATANABE, Makoto¹; TAKAHASHI, Masahiko
(¹Tohoku Univ.)

[*Surf. Rev. Lett.* **9**, 587 (2002)]

Multilayer polarizers for the use of He resonance lines have been developed. Si/Mg and SiC/Mg multilayers were designed and fabricated for the He-I and He-II resonance lines, respectively. The performance was checked by the use of synchrotron radiation. The polarizance and *s*-reflectance of the He-II polarizer measured at an angle of incidence of 40° were 0.98 and 41%, respectively. The polarizance of the He-I polarizer measured at an angle of incidence of 31.5° was 0.96.

VIII-X-2 Polarization Measurements of Laboratory VUV Light: A First Comparison between Multilayer Polarizers and Photoelectron Angular Distributions

TAKAHASHI, Masahiko; HATANO, Tadashi¹; EJIMA, Takeo¹; KONDO, Yuzi¹; SAITO, Katsuhiko¹; WATANABE, Makoto¹; KINUGAWA, Tohru²; ELAND, John H. D.²
(¹Tohoku Univ.; ²Oxford Univ., England)

[*J. Electron Spectrosc.* **130**, 79 (2003)]

The use of photoelectron angular distributions to determine the linear polarization of VUV light over a wide range of photon energies is demonstrated. Light at wavelengths from 25.6 to 73.6 nm, partially polarized by large angle reflections in a toroidal grating monochromator and at a refocus mirror, has been analyzed. The results are validated by comparison measurements at spot wavelengths using multilayer polarizers.

VIII-X-3 Carbon K-Shell Photoelectron Angular Distribution from Fixed-in-Space CO₂ Molecules

SAITO, Norio¹; FANIS, Albert De²; KUBOZUKA, Kenichiro³; MACHIDA, Masatake³; TAKAHASHI, Masahiko; YOSHIDA, Hiroaki⁴; SUZUKI, Isao H.¹; CASSIMI, Amine⁵; CZASCH, Achim⁶; DÖRNER, Reinhard⁶; WANG, Kwanghsi⁷; ZIMMERMANN, Björn⁷; MCKOY, Vincent⁷; KOYANO, Inosuke³; UEDA, Kiyoshi²
(¹Natl. Metrology Inst.; ²Tohoku Univ.; ³Himeji Inst. Tech.; ⁴Hiroshima Univ.; ⁵Univ. Caen, France; ⁶Univ. Frankfurt, Germany; ⁷California Inst. Tech., USA)

[*J. Phys. B: At., Mol. Opt. Phys.* **36**, L25 (2003)]

Measurements of photoelectron angular distributions for carbon *K*-shell ionization of fixed-in-space CO₂ molecules with the molecular axis oriented along, perpendicular and at 45° to the electric vector of the light are reported. The major features of these measured

spectra are fairly well reproduced by calculations employing a relaxed-core Hartree-Fock approach. In contrast to the angular distribution for *K*-shell ionization of N₂, which exhibits a rich structure dominated by the *f*-wave (*l* = 3) at the shape resonance, the angular distribution for carbon *K*-shell photoionization of CO₂ is quite unstructured over the entire observed range across the shape resonance.

VIII-X-4 N 1s Photoionization Cross Sections of the NO Molecules in the Shape Resonance Region

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2}; TAKAHASHI, Masahiko; YAGISHITA, Akira^{1,2}
(¹Tokyo Univ.; ²KEK-PF)

[*J. Phys. B: At., Mol. Opt. Phys.* in press]

The N 1s partial photoionization cross sections of NO leading for the ³Π and ¹Π ionic states have been measured in the shape resonance region for the first time. The twin local maxima in the cross sections have been tentatively assigned, based on the simple models for the photoabsorption intensities and for the branching ratio of the ³Π and ¹Π ionic states from the σ* shape resonance state.

VIII-X-5 Multiplet-Specific N 1s Photoelectron Angular Distributions from the Fixed-in-Space NO Molecules

HOSAKA, Kouichi¹; ADACHI, Junichi^{1,2}; TAKAHASHI, Masahiko; YAGISHITA, Akira^{1,2}; LIN, Ping³; LUCCHESI, Robert R.³
(¹Tokyo Univ.; ²KEK-PF; ³Texas A&M Univ., USA)

[*Phys. Rev. Lett.* submitted]

Angular distributions of multiplet-specific N 1s photoelectrons from the fixed-in-space NO molecules have been measured for the first time. The dynamics of the σ* shape resonance appeared in the channel leading to the ³Π and ¹Π ionic states has been made clear from the analyses of the angular distributions. Multiplet-specific multichannel calculations have reproduced the observed angular distributions fairly well.

VIII-X-6 Shape-Resonance-Enhanced Vibrational Effects in the Angular Distributions of C 1s Photoelectrons from Fixed-in-Space CO Molecules

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹; FURUYA, Shuusaku³; SOEJIMA, Kouich³; TAKAHASHI, Masahiko; YAGISHITA, Akira^{1,2}; SEMENOV, Sergei K.⁴; CHEREPKOV, Nikolai A.⁴
(¹Tokyo Univ.; ²KEK-PF; ³Niigata Univ.; ⁴State Univ. Aerospace Instrum., Russia)

[*Phys. Rev. Lett.* in press]

Angular distributions of C1s photoelectrons from fixed-in-space CO molecules have been measured with

vibrational resolution. A strong dependence of the angular distributions on the vibrational states of the residual molecular ion has been found for the first time in the region of the shape resonance. Calculations in the relaxed core Hartree-Fock approximation have reproduced the angular distributions fairly well in the general shapes of the angular distributions due to the correct description of nuclear motion as an average of the internuclear-distance-dependent dipole amplitudes.

VIII-X-7 Angular Distributions of Vibrationally Resolved C 1s Photoelectrons from Fixed-in-Space CO Molecules: Vibrational Effect in the Shape-Resonant C 1s Photoionization of CO

ADACHI, Junichi^{1,2}; HOSAKA, Kouichi¹;
FURUYA, Shuusaku³; SOEJIMA, Kouich³;
TAKAHASHI, Masahiko; YAGISHITA, Akira^{1,2};
SEMENOV, Sergei K.⁴; CHEREPKOV, Nikolai A.⁴
(¹Tokyo Univ.; ²KEK-PF; ³Niigata Univ.; ⁴State Univ.
Aerospace Instrum., Russia)

[*J. Electron Spectrosc.* submitted]

We have measured molecular-frame photoelectron angular distributions (MF-PAD) for the vibrationally resolved C1s photoelectron from CO molecule in the s shape resonance region. The MF-PAD's for the $v_f = 0, 1$, and 2 levels in the C1s $\rightarrow \epsilon l \sigma$ channel are apparently different each other at each incident photon energy. These MF-PAD's agree with the present theoretical results from the averaging the nuclear distance dependent dipole matrix elements with the relaxed core Hartree-Fock calculations. The present results show that the internuclear distance dependences of the phase and of the magnitude of the dipole matrix element play a crucial role in the C1s photoionization of CO.

VIII-X-8 Coulomb Hole in N₂, CO and O₂ Deduced from X-Ray Scattering Cross Sections

WATANABE, Noboru; KAMATA, Yohei¹;
YAMAUCHI, Kota¹; UDAGAWA, Yasuo¹;
MÜLLER, Thomas²
(¹Tohoku Univ.; ²Res. Cent. Jülich, Germany)

Total (elastic + inelastic) x-ray scattering cross sections $\sigma_{ee}(q)$ are very sensitive to electron correlation effects, since they are related to the Fourier transform of the radial electron-electron pair distribution function $P(r_{12})$.¹⁾ X-ray scattering experiments can hence provide a crucial check of whether or not a theoretical wave function takes electron correlation properly into consideration.

In this study, accurate $\sigma_{ee}(q)$ of N₂, CO and O₂ were measured by the use of the energy dispersive method up to a momentum transfer of $q = 12$ a.u. $P(r_{12})$ was extracted from the cross sections. The Coulomb hole, defined as the difference between the exact $P(r_{12})$ and the corresponding function evaluated at Hartree-Fock limit, has been derived from experimental data. Comparison with configuration interaction calculations shows small but systematic differences between the theoretical and experimental results.

Reference

1) N. Watanabe *et al.*, *Review of Modern Quantum Chemistry*, K. D. Sen, Ed., World Scientific; Singapore, 553 (2002).

VIII-X-9 Absolute Surface Coverage Measurement Using a Vibrational Overtone

PIPINO, Andrew C. W.¹; HOEFNAGELS, Johan P. M.²; WATANABE, Noboru
(¹Natl. Inst. Standards Tech., USA; ²Eindhoven Univ. Tech., Netherland)

Sub-monolayer absolute surface number densities are obtained by cavity ring-down spectroscopy (CRDS) for trichloroethylene, cis-dichloroethylene, and trans-dichloroethylene adsorbed on silica using the first C-H stretching overtones, which are probed with the idler of a seeded optical parametric amplifier having a 0.075 cm⁻¹ line width. The absolute surface number densities are found by invoking conservation of the integrated band intensity with adsorption together with knowledge of the transition moment orientation as derived from the adsorbate polarization anisotropy. The evanescent wave CRDS (EW-CRDS) measurements employ a fused-silica monolithic folded resonator with a peak finesse of $\approx 28,500$ at 1650 nm. The absolute coverage of trichloroethylene on SiO₂ is also obtained by a mass-spectrometer-based surface-uptake technique, which is briefly contrasted with the EW-CRDS method. The sensitivity of EW-CRDS for trichloroethylene detection with an unclad resonator is found to be comparable to that obtained with a long-effective-path-length waveguide having a trichloroethylene-enriching polysiloxane coating.

VIII-Y Study on Compact X-Ray Sources

Electron storage rings are useful devices as x-ray sources. However, these synchrotron radiation facilities usually occupy large area and cost much. So that there have been many works to investigate compact x-ray sources using small electron accelerators. It is also useful to use laser undulator radiation or backward Compton scattering caused by the interactions of electron beams with laser photons, if we provide enough electrons to produce practical intensity of x-rays. RF-photocathode would produce high peak intensity electron beam so that it is a useful candidate of a electron source. It is necessary to search good materials as the photocathode for construction of a practical compact x-ray source. Cesium telluride has reported to have a good quantum efficiency, so that we have studied about it.

In order to generate high brilliant x-rays using small electron accelerators, we propose metal multi-foils as the target irradiated by the electron beam. We have studied x-ray intensity generated from the multi-foil target using Monte Carlo simulation code.

VIII-Y-1 Feasibility Study of X-Ray Generation by Using Metal Multi-Foil Target Irradiated by High Energy Electron Beam

TAKASHIMA, Yoshifumi; KOBAYAKAWA, Hisashi¹; MATSUBARA, Masahide¹
(¹Nagoya Univ.)

We performed feasibility study of x-ray source using metal multi-foil target irradiated by high energy electrons. Figure 1 shows the sketch of the setup. High energy electron beams extracted from small accelerators are incident on metal multi-foil targets with small angles. X-rays generated in the foils by bremsstrahlung are reflected on the surface of the next foils if the incident angle is small enough to satisfy the total reflection condition.

We calculate the spectrum and angular spread of the x-rays radiated from the multi-foil targets by using EGS4¹⁾ simulation code. Figure 2 shows the geometry used in the EGS4 calculation. We use stacks of copper foils as the target. The thickness, width and length of a foil are 0.1 μm , 100 mm and 500 mm, respectively. We stack 100 foils as the target for EGS4 calculation. Incident electron energy was 150 MeV and the incident angle of the electron on the surface of the target was 1 mrad.

Figure 3 shows the angular spread of 5keV x-rays using multi-foil and bulk targets. The total thickness of the multi-foil is 10 μm which is the same thickness of the bulk target. The yield of the x-rays from multi-foil target is larger than that from the bulk target because of the reflection of x-rays between the foils.

The energy spectra of x-rays from the multi-foil and bulk targets are shown in Figure 4. X-ray intensity radiated from multi-foil is larger than bulk target in the low energy region, because low energy x-rays have large total reflection angles so that it is not absorbed in the target material but extracted by reflection between foils.

We calculated the spectrum and angular distribution of x-rays generated from metal multi-foils irradiated by high energy electrons using EGS4 simulation code. For further study, we should include the effect of transition radiation in the calculation in order to estimate x-ray intensity more precisely.

Reference

1) W. R. Nelson, H. Hirayama and D. W. O. Rogers, SLAC-Report-256, (1985).

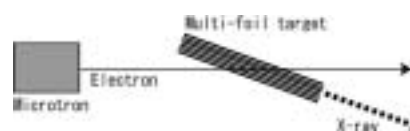


Figure 1. Sketch of experimental setup using multi-foil target.

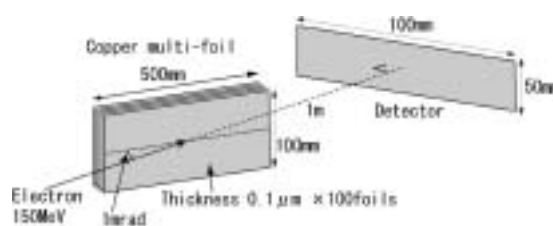


Figure 2. Geometry used in EGS4 simulation.

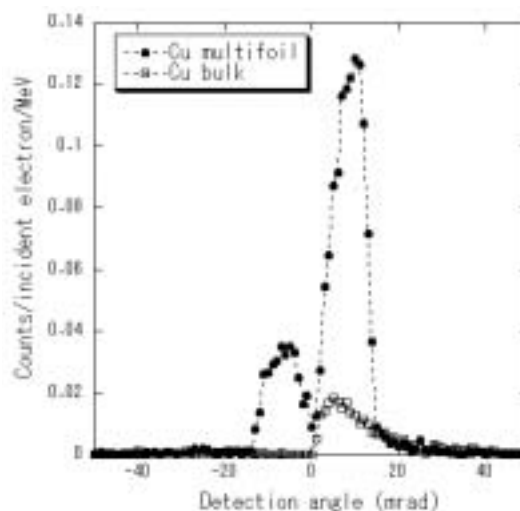


Figure 3. Angular distribution of x-rays generated from multi-foil and bulk targets.

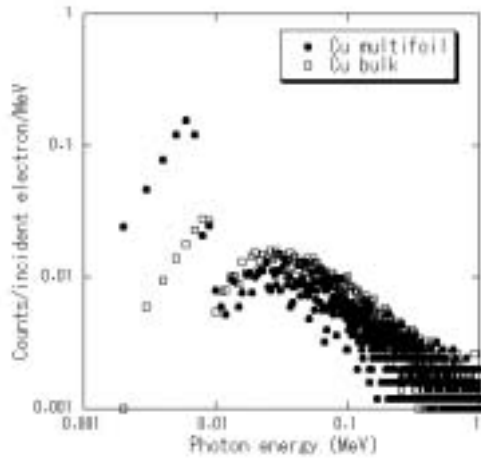


Figure 4. Energy spectrum of x-rays generated from multi-foil and bulk targets.

VIII-Z Syntheses of Fullerene-Based New Materials with Novel Physical Properties and Their Application toward New-Generation Electronic Devices

Fullerene-based new materials are synthesized and their structures and electronic properties are studied in solid, thin film and nanometer scale. The crystal structures of metallofullerene solids are determined by Rietveld refinements for X-ray diffraction patterns with synchrotron radiation. The resistivity and field effect transistor (FET) characteristics are studied with thin films of metallofullerenes and higher-fullerenes. Furthermore, the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of metallofullerenes deposited onto the well-defined semiconducting surfaces are studied under ultrahigh vacuum.

VIII-Z-1 Crystal Structure and Electronic Transport of Dy@C₈₂

KUBOZONO, Yoshihiro; **TAKABAYASHI, Yasuhiro**¹; **SHIBATA, Kana**²; **KANBARA, Takayoshi**²; **FUJIKI, Satoshi**; **KASHINO, Setsuo**²; **FUJIWARA, Akihiko**³; **EMURA, Shuichi**⁴
(¹IMS and Okayama Univ.; ²Okayama Univ.; ³JAIST; ⁴Osaka Univ.)

[*Phys. Rev. B* **67**, 115410 (2003)]

The crystal structure of Dy@C₈₂ isomer I at 298 K has been determined by Rietveld refinement for x-ray powder diffraction with synchrotron radiation. Isomer I shows a simple cubic structure (sc: $Pa\bar{3}$) with a lattice constant a of 15.78(1) Å. The C₂ axis of a C_{2v}-C₈₂ cage aligns along the [111] direction of this crystal lattice. The C₈₂ cage is orientationally disordered to satisfy a $\bar{3}$ symmetry along [111], which is requested in this space group. The large thermal parameter for the Dy atom estimated from the x-ray diffraction probably reflects a large disorder caused by a floating motion of the Dy atom inside the C₈₂ cage as well as a ratchet-type motion of the Dy@C₈₂ molecule. The electronic transport of thin film of Dy@C₈₂ shows a semiconducting behavior. The energy gap E_g is estimated to be 0.2 eV. Further, the variation of valence from Dy³⁺ to Dy²⁺ is found by metal doping into the Dy@C₈₂ crystals.

VIII-Z-2 Synthesis, Structure, and Magnetic Properties of the Fullerene-Based Ferromagnets, Eu₃C₇₀ and Eu₉C₇₀

TAKENOBU, Taishi¹; **CHI, Dam Hieu**²; **MARGADONNA, Serena**³; **PRASSIDES, Kosmas**⁴; **KUBOZONO, Yoshihiro**; **FITCH, Andrew N.**⁵; **KATO, Ken-ichi**⁶; **IWASA, Yoshihiro**¹
(¹Tohoku Univ.; ²JAIST; ³Univ. Cambridge; ⁴Univ. Sussex; ⁵European Synchrotron Radiation Facility; ⁶JASRI)

[*J. Am. Chem. Soc.* **125**, 1897 (2003)]

Intercalation of C₇₀ with europium affords two kinds of magnetic compounds, a canted antiferromagnet Eu _{x} C₇₀ ($x \approx 3$) and a ferromagnet Eu _{x} C₇₀ ($x \approx 9$) with transition temperatures (T_c) of 5 and 38 K, respectively. The Curie constants in the paramagnetic phase and the

saturation moment in the ferromagnetic phase are both understood by the full moment of Eu²⁺ for both systems. The structure of Eu_{3- δ} C₇₀ ($\delta \approx 0.27$) is pseudo-monoclinic, derived by a simple deformation of the parent face-centered cubic (*fcc*) structure. Eu_{9- δ} C₇₀ ($\delta \approx 0.2$) forms an *fcc* structure, in which cuboctahedral clustering of Eu²⁺ ions is observed in the enhanced size octahedral holes. The observed T_c of the Eu_{9- δ} C₇₀ ferromagnet is comparable to or larger than those of simple binary Eu-based ferromagnets, such as Eu chalcogenides or carbides, despite the low atomic ratio of Eu in the chemical formulas. This can be understood by the short Eu²⁺-Eu²⁺ distances and high coordination numbers permitted by the multiple occupation by Eu²⁺ ions of the expanded octahedral interstitial sites in higher fullerene-based solids.

VIII-Z-3 Pressure-Induced Structural Phase Transition in Fullerides Doped with Rare Earth Metals

CHI, Dam Hieu¹; **IWASA, Yoshihiro**^{1,2}; **UEHARA, Katsuyuki**¹; **TAKENOBU, Taishi**²; **ITO, Takayoshi**¹; **MITANI, Tadaoki**¹; **NISHIBORI, Eiji**³; **TAKATA, Masaki**^{3,4}; **SAKATA, Makoto**³; **OHISHI, Y.**⁴; **KATO, Ken-ichi**⁴; **KUBOZONO, Yoshihiro**
(¹JAIST; ²Tohoku Univ.; ³Nagoya Univ.; ⁴JASRI)

[*Phys. Rev. B* **67**, 94101 (2003)]

Rare-earth-metal-doped fullerides with nominal composition of R₃C₇₀ ($R = \text{Sm, Eu}$) adopt a pseudo-monoclinic structure in which C₇₀ dimers glued with rare-earth ions are involved. High-pressure powder x-ray diffraction experiments revealed that these compounds undergo a reversible first-order structural phase transition at 1.5 GPa, associated with 2.7%–2.9% reduction of the unit cell volume. Structural analyses showed that the rare-earth ions, which are located close to the edge of tetrahedral sites at ambient pressure, move back to the center of the tetrahedral sites. Simultaneously, C₇₀ molecules are realigned so that the fivefold (long) axes are perpendicular to the (10 $\bar{1}$) or (11 $\bar{1}$)_{*fcc*} plane at high pressure. The derived charge density map indicates that the transition is regarded as a structural change from dimers to three-dimensional polymers of fullerenes. These features are ascribed to the unique bonding nature in rare-earth C₇₀ compounds.

VIII-Z-4 Molecular- and Atomic-Like Photoionization of C₆₀ in the Extreme Ultraviolet

KOU, Junkei; MORI, Takanori; ONO, Masaki; HARUYAMA, Yusuke¹; KUBOZONO, Yoshihiro²; MITSUKE, Koichiro

(¹Okayama Univ.; ²IMS and Okayama Univ.)

[*Chem. Phys. Lett.* **374**, 1 (2003)]

Photoion yield spectra of C₆₀ in the gas phase were measured from 23 to 180 eV by synchrotron radiation. Two peaks at 26 and 34 eV and a flat area ranging 40–50 eV are newly observed in the high-energy side of the giant resonance at ~ 20 eV. These features are assigned to the shape resonance on photoionization of the valence electrons of C₆₀; the ionized electron is temporarily trapped inside a centrifugal barrier. Above ~ 50 eV the yield curve shows a steady decrease with increasing photon energy like the photoabsorption cross section of atomic carbon. Thus, the spectrum is interpreted as essentially determined by photoionization of the 2s orbitals of carbon atoms.

VIII-Z-5 A Complex Fulleride Superstructure-Decoupling Cation Vacancy and Anion Orientational Ordering in Ca_{3+x}C₆₀ with Maximum Entropy Methods

CLARIDGE, J. B.¹; KUBOZONO, Yoshihiro; ROSSEINSKY, M. J.¹

(¹Univ. Liverpool)

[*Chem. Mater.* **15**, 1830 (2003)]

The structure of the alkaline-earth fulleride Ca_{3.01}C₆₀ is refined using maximum entropy data analysis of synchrotron powder diffraction data. Despite the size and complexity of the structural problem, the fulleride anion orientations and the details of multiple occupancy of the octahedral interstitial sites in the fcc anion array are determined. The power of the maximum entropy technique in solving underdetermined problems in powder crystallography is thus demonstrated.

VIII-Z-6 Development of a Photoionization Spectrometer for Gaseous Fullerenes in the Extreme Ultraviolet

MORI, Takanori; ONO, Masaki; KOU, Junkei; HARUYAMA, Yusuke¹; KUBOZONO, Yoshihiro; MITSUKE, Koichiro

(¹Okayama Univ.)

[*Rev. Sci. Instrum.* **74**, 3769 (2003)]

A photoionization spectrometer has been developed for measuring the ion yields for fullerenes in the photon energy range of 23–200 eV. Gaseous fullerenes were supplied from a high-temperature oven, ionized by irradiation of monochromatized synchrotron radiation, and detected after analysis with a time-of-flight mass spectrometer. The fluxes of the synchrotron radiation and fullerene beams were monitored concurrently with

the acquisition of the ion signal counts in order to obtain reliable photoionization efficiency curves. The performance of the apparatus was examined by measuring the efficiency curve of C₆₀⁺ produced from C₆₀. The spectrum demonstrated better statistics than the previous results in the same photon energy region. Three distinct features were newly observed in the higher-energy side of the prominent resonance at ~ 20 eV.

VIII-Z-7 Structural and Electronic Properties of Ce@C₈₂

SHIBATA, Kana¹; RIKIISHI, Yoshie¹; HOSOKAWA, Tomoko¹; HARUYAMA, Yusuke¹; KUBOZONO, Yoshihiro²; KASHINO, Setsuo¹; URUGA, Tomoya³; FUJIWARA, Akihiko⁴; KITAGAWA, Hiroshi^{5,6}; TAKANO, Takumi⁷; IWASA, Yoshihiro⁷

(¹Okayama Univ.; ²IMS, JST and Okayama Univ.;

³JASRI; ⁴JAIST; ⁵Univ. Tsukuba; ⁶PRESTO/JST;

⁷Tohoku Univ.)

[*Phys. Rev. B* **68**, 94104 (2003)]

X-ray diffraction patterns for a solid sample of Ce@C₈₂ that contains a mixture of two isomers, I and II, can be indexed in a face-centered cubic lattice with a lattice constant of 15.88(5) Å, while x-ray diffraction patterns for Ce@C₈₂ isomer I alone indicate a simple cubic lattice with a lattice constant of 15.78(1) Å. Rietveld refinement for the x-ray diffraction pattern of the latter, Ce@C₈₂ isomer I, has been carried out with a space group of *Pa* $\bar{3}$. Thin films of Ce@C₈₂ were first prepared by thermal deposition under ~ 10⁻⁷ Torr. The Raman spectra for these thin films show a peak ascribable to a Ce-C₈₂ cage-stretching mode at ~ 160 cm⁻¹, implying that the valence of Ce in this structure is +3. This valence of +3 is supported by Ce L_{III}-edge XANES for a thin film of Ce@C₈₂. Furthermore, the local structure around the Ce ion could be determined by Ce L_{III}-edge EXAFS for a thin-film. Transport properties of a thin film of Ce@C₈₂ have been studied by a four-probe method, and these demonstrate a semiconducting behavior with a small gap of 0.4 eV.

VIII-Z-8 N-Channel Field Effect Transistors with Fullerene Thin Films and Their Application to a Logic Gate Circuit

KANBARA, Takayoshi¹; SHIBATA, Kana¹; FUJIKI, Satoshi; KUBOZONO, Yoshihiro²; KASHINO, Setsuo¹; URISU, Tsuneo; SAKAI, Masahiro; FUJIWARA, Akihiko³; KUMASHIRO, Ryotaro⁴; TANIGAKI, Katsumi⁴

(¹Okayama Univ.; ²IMS and Okayama Univ.; ³JAIST;

⁴Osaka Univ.)

[*Chem. Phys. Lett.* **379**, 223 (2003)]

N-channel field effect transistors (FETs) were fabricated with thin films of C₆₀ and Dy@C₈₂. A typical enhancement-type FET property was observed in C₆₀ FET above 220 K. The mobility of C₆₀ FET increased with increasing temperature. This fact suggests hopping

transport as the conduction mechanism, with the activation energy of 0.29 eV. The Dy@C₈₂ FET was found to be a normally-on type FET, which has a property different from that for C₆₀ and C₇₀ FETs. A complementary metal oxide semiconductor (CMOS) logic gate circuit was first fabricated with C₆₀ and pentacene thin-film FETs.

VIII-Z-9 Scanning Tunneling Microscopy of Dy@C₈₂ and Dy@C₆₀ Adsorbed on Si(111)-(7×7) Surfaces

FUJIKI, Satoshi¹; KUBOZONO, Yoshihiro¹; HOSOKAWA, Tomoko²; KANBARA, Takayoshi³; FUJIWARA, Akihiko⁴; NONOGAKI, Youichi; URISU, Tsuneo
(¹IMS and Okayama Univ.; ²Okayama Univ.; ³Tohoku Univ.; ⁴JAIST)

[Phys. Rev. B in press]

Dy@C₈₂ and Dy@C₆₀ adsorbed on Si(111)-(7×7) surface are investigated by scanning tunneling microscopy (STM) at 295 K. The Dy@C₈₂ molecules in the first layer are adsorbed on Si(111)-(7×7) surface without formation of islands and nucleation, and the internal structure of the Dy@C₈₂ molecule is first observed on the surface at 295 K. The average heights of the Dy@C₈₂ molecule in the first and second layers are estimated to be 7.2 and 10.8 Å, respectively, by STM. These results suggest strong interactions between the Si atoms and the Dy@C₈₂ molecules in the first layer. The STM image reveals that Dy@C₆₀ molecule is nearly spherical, showing that the metal endohedral C₆₀ possesses a cage-form structure.

VIII-Z-10 Preferred Locations of Metal Ions in Two M@C₈₂ Isomers

TAKABAYASHI, Yasuhiro¹; HARUYAMA, Yusuke¹; RIKIISHI, Yoshie¹; HOSOKAWA, Tomoko¹; SHIBATA, Kana¹; KUBOZONO, Yoshihiro²
(¹Okayama Univ.; ²IMS and Okayama Univ.)

[submitted]

Location of metal ion in the minor isomer of M@C₈₂ (M: metal ion with valence of +3) was determined for the first time by Dy L_{III}-edge EXAFS of Dy@C₈₂. The Dy ion lied near the fused bond between two hexagon rings. On the other hand, the EXAFS showed that the Dy ion in the major isomer of Dy@C₈₂ lied near the center of a hexagon ring. The locations found in the minor and major isomers were consistent with those predicted theoretically for the respective isomers.

VIII-Z-11 Fabrication and Characterization of a New Type of Carbon Cluster Field Effect Transistor

SHIBATA, Kana¹; KUBOZONO, Yoshihiro²; KANBARA, Takayoshi¹; HOSOKAWA, Tomoko¹; FUJIWARA, Akihiko³; SHINOHARA, Hisanori⁴

ITO, Yasuhiro⁴
(¹Okayama Univ.; ²IMS and Okayama Univ.; ³JAIST; ⁴Nagoya Univ.)

[submitted]

A new type of carbon cluster field effect transistor (FET) was fabricated with thin film of C₈₄, and *n*-channel normally-on depletion-type FET characteristics were found in this FET device. The C₈₄ FET device exhibited the highest mobility, μ , of $1.3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ among normally-on carbon cluster FETs. The carrier transport of this FET device suggested a thermally-activated hopping transport. Carrier type (*n*-channel) and transport mechanism (hopping) reflect the electronic properties of the C₈₄ molecule. This is the first report of the FET with higher-fullerene thin-film.

VIII-Z-12 Structural and Electronic Characterizations of Two Ce@C₈₂ Isomers

RIKIISHI, Yoshie¹; HOSOKAWA, Tomoko¹; SHIBATA, Kana¹; HARUYAMA, Yusuke¹; TAKABAYASHI, Yasuhiro¹; KUBOZONO, Yoshihiro²
(¹Okayama Univ.; ²IMS and Okayama Univ.)

[submitted]

X-ray diffraction patterns for the Ce@C₈₂ isomers I and II, which refer to major and minor isomers, respectively, are studied in a wide temperature region. The diffraction patterns observed at 295 K can be indexed based on a simple cubic (sc) structures with the lattice constants, *a*'s of 15.78(1) Å for the isomer I and 15.74(4) Å for the isomer II. Rietveld analyses are achieved for these X-ray diffraction patterns with a space group of *Pa* $\bar{3}$. Temperature dependence of *a* for the isomer I shows a drastic change around 150 K which implies an existence of structural phase transition. The structural phase transition above 300 K cannot be detected for the Ce@C₈₂ isomer I in contrast with the fact that the phase transition at 400 K was previously reported for La@C₈₂ isomer I by a differential scanning calorimetry and dielectric constant measurements. Temperature dependence of *a* for the isomer II indicates no structural phase transition from 100 to 300 K. Pressure dependence of *a* for the isomer I exhibits a monotonous decrease with an increase in pressure. This result implies no pressure-induced structural phase transition for the isomer I.

VIII-AA Study of Electronic Structure of Organic Thin film and Organic/Inorganic Interface

Organic semiconductors have gained increasing interest because of their potential use in various optoelectronic devices. In order to understand electronic processes at interface in the organic devices, many surface sensitive techniques such as high-resolution ultraviolet photoemission spectroscopy (UPS) have been performed for organic thin films, because origins of the energy position and the bandwidth of ultraviolet photoelectron spectra are keys to understand interface properties, such as the energy level alignment at the interface and molecule-molecule and/or molecule-substrate interaction. The energy-band structure is a fundamental basis for the understanding of electronic and optical properties of solids. The intermolecular band dispersion for the organic thin film is observed using angle-resolved UPS using synchrotron radiation, since the width of band dispersion depends the intermolecular interaction.

VIII-AA-1 Intermolecular Energy-Band Dispersion in PTCDA Multilayers

YAMANE, Hiroyuki¹; KERA, Satoshi;
YOSHIMURA, Daisuke; OKUDAIRA, K. Koji;
SEKI, Kazuhiko²; UENO, Nobuo¹
(¹Chiba Univ.; ²Nagoya Univ.)

[*Phys. Rev. B* **68**, 033102 (4 pages) 2003]

The electronic structure of a well-oriented perylene-3,4,9,10-tetracarboxylic acid-dianhydride multilayer prepared on MoS₂ single crystal surface were studied by angle-resolved ultraviolet photoemission spectroscopy using synchrotron radiation. From the photon energy dependence of normal emission spectra, we observed an intermolecular energy-band dispersion of about 0.2 eV for the highest occupied molecular orbital (HOMO) band of single π character. The observed energy-band dispersion showed a cosine curve, which originates from the intermolecular π - π interaction. Analyses using the tight-binding model gave that the transfer integral of about 0.05 eV for the π - π interaction, the effective mass of HOMO hole $m_h^* = 5.28m_0$, and the hole mobility $\mu_h > 3.8 \text{ cm}^2/\text{V s}$. This is the first observation of the intermolecular energy-band dispersion of a conventional single-component organic semiconductor only with the weak intermolecular van der Waals interaction.

VIII-AA-2 Very Narrow Photoemission Bandwidth of the Highest Occupied State in a Copper-Phthalocyanine Monolayer

KERA, Satoshi; YAMANE, Hiroyuki¹; SAKURAGI, Isamu¹; OKUDAIRA, K. Koji; UENO, Nobuo¹
(¹Chiba Univ.)

[*Chem. Phys. Lett.* **364**, 93–98 (2002)]

We observed a very narrow bandwidth of the highest occupied molecular orbital (HOMO) state in ultraviolet photoemission spectra (UPS) of copper-phthalocyanine monolayer deposited on graphite. The HOMO band in UPS consists of three components which may originate from the vibrational coupling. The full width at half maximum of each component was found to be $\sim 150 \text{ meV}$ at 295 K. This HOMO-bandwidth leads to an estimation that the lifetime of the HOMO hole should be at least longer than 2.2 fs, which may be dominated by the electron transfer rate from the substrate to the molecule.

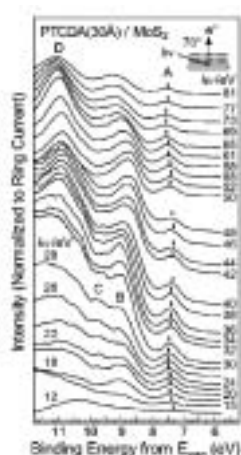


Figure 1. Photon energy ($h\nu$) dependence of SR-ARUPS spectra along the surface normal for the 30-Å-thick PTCDA multilayer ($\sim 8 \text{ ML}$) prepared on the MoS₂ surface. The binding energy (E_B) scale refers to the vacuum level (E_{vac}).

VIII-BB Effects of High Magnetic Field on Chemical and Physical Processes

We have studied the effects of high magnetic field on chemical reaction and physical processes of diamagnetic and paramagnetic materials to unravel the mechanisms of the interaction of matter and magnetic field and to develop unique methods controlling chemical and physical processes and improving chemical and physical properties of functional materials. Currently we are using a vertical superconducting magnet which can generate high magnetic fields (15 T, 1500 T²/m) in a 40 φ bore tube. Magnetic levitation of a water droplet and others is capable using the magnet. It is shown that many chemical reactions and physical processes are significantly affected by the magnetic field. For example, we have succeeded, for the first time, to induce 3D-morphological chirality in zinc silicate membrane tube using a high magnetic field. The results are interpreted in terms of the Lorentz force on ions thermally moving in an aqueous solution. In NaCl:Eu crystals, dislocation mobility is affected by a magnetic field.

VIII-BB-1 3D-Morphological Chirality Induction in Zinc Silicate Membrane Tube Using a Magnetic Field

UECHI, Ichiro¹; KATSUKI, Akio², DUNIN-BARKOVSKIY, Lev R.; TANIMOTO, Yoshifumi
(¹IMS and Hiroshima Univ.; ²Shinshu Univ.)

[J. Phys. Chem. in press]

We report *three-dimensional morphological chirality* induction using a vertical magnetic field. Right-handed *circular* helix of zinc silicate membrane tube was *selectively* induced by application of a magnetic field (5–15 T), whereas the tube grew straightly upward at zero field as shown in Figure 1. Left-handed circular helix was also selectively obtained by changing experimental condition. *Square* and *triangular* helices were also prepared. The results are interpreted in terms of the boundary-assisted magnetohydrodynamics mechanism in which cyclotron motion of ions in solution results in one-way convection of the solution near the boundary.



Figure 1. Magnetic field effects on the growth of zinc silicate membrane. (a) 0 T, (b) 6 T, (c) 13.5 T.

VIII-BB-2 Effects of a High Magnetic Field on the Growth of 3-Dimensional Silver Dendrites

KATSUKI, Akio¹; UECHI, Ichiro²; TANIMOTO, Yoshifumi
(¹Shinshu Univ.; ²IMS and Hiroshima Univ.)

[Bull. Chem. Soc. Jpn. in press]

A liquid/solid redox reaction between silver ion and copper metal was investigated under a *vertical* and *inhomogeneous* high magnetic field (maximum field strength: 15 T). 3-Dimensional silver dendrites produced *via* the reaction were affected drastically by the magnetic field. Black and round dendrites were obtained in the magnetic field, whereas metallic silver crystals were grown under the gray dendrites at zero field. The yields of silver dendrite and copper ion increased significantly in the magnetic fields. The results are interpreted in terms of magnetic convection of the solution which is induced by the magnetic force on paramagnetic copper ions generated in the reaction as well as the Lorentz force on ions.

VIII-BB-3 Magnetic Field Effects on TiO₂ Photocatalytic Reaction

KAMOCHI, Masataka¹; FUJIWARA, Yoshihisa¹; TANIMOTO, Yoshifumi
(¹Hiroshima Univ.)

We attempted to examine whether a magnetic field could affect photo-catalytic reaction of titanium oxide, as little was known about the magnetic field effect (MFE) on catalytic reaction. The reaction studied here is as follows,



A methanol-water (1:1) solution containing titanium oxide powder and chloroplatinic (IV) acid hexahydrate was irradiated with light from a xenon lamp in the absence and presence of a magnetic field and the volume of the photo-generated gas was determined. The yield of the gas decreased gradually with increasing a magnetic field from zero to 4 T (*ca.* -10% at 4 T). Similar MFE was observed on the photocurrent of the photo-galvanic cell, TiO₂(s)|NaOH(aq)||H₂SO₄(aq)|Pt(s).

The present MFE is tentatively explained in terms of

a radical pair model (Δg mechanism). Upon photo-excitation of TiO_2 , excited singlet TiO_2 , $^1\text{TiO}_2^*$, is generated. While $^1\text{TiO}_2^*$ undergoes intersystem crossing (ISC) to $^3\text{TiO}_2^*$, singlet electron-hole pair is generated from $^1\text{TiO}_2^*$. The free electron and hole will be formed by the dissociation of the singlet pair. In a magnetic field, the singlet-to-triplet ISC in the pair is accelerated due to the difference in g -values of electron and hole, leading the depression in the yield of free electron and hole by which the succeeding redox reaction is initiated.

VIII-BB-4 On the Movement of Paramagnetic Ions in an Inhomogeneous Magnetic Field

FUJIWARA, Masao; CHIE, Kenjiro¹; SAWAI, Jun¹; SHIMIZU, Daisuke¹; TANIMOTO, Yoshifumi
(¹Hiroshima Univ.)

[*J. Phys. Chem.* submitted]

The movement of transition metal ions was observed in an inhomogeneous magnetic field. The solution containing Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} ions was spotted on a silica gel support, and exposed to magnetic fields up to $410 \text{ kOe}^2\text{cm}^{-1}$. The distribution of the metal ions was measured, and the frictional coefficient of the movement was analyzed in relation to the susceptibility and concentration of the metal ions as well as to the size of the silica gel particles. When the concentration is higher, the metal ions move to a larger the distance. It is shown that a large group composed of the metal ions and water molecules moves in a magnetic field.

VIII-BB-5 Magnetic Separation of Metal Ions

CHIE, Kenjiro¹; FUJIWARA, Masao; FUJIWARA, Yoshihisa¹; TANIMOTO, Yoshifumi
(¹Hiroshima Univ.)

[*J. Phys. Chem.* in press]

The magnetic separation was investigated for Co^{2+} ($9500 \times 10^{-6} \text{ cm}^3\text{mol}^{-1}$) and Fe^{3+} ($14600 \times 10^{-6} \text{ cm}^3\text{mol}^{-1}$) ions and for Cr^{3+} ($6200 \times 10^{-6} \text{ cm}^3\text{mol}^{-1}$) and Al^{3+} ($-2 \times 10^{-6} \text{ cm}^3\text{mol}^{-1}$) ions. The metal ion solutions were spotted on a silica gel support and exposed to a magnetic field of $410 \text{ kOe}^2\text{cm}^{-1}$ intensity \times gradient. The Co^{2+} ions move to a larger distance toward the maximum field than the Fe^{3+} ions. The result is explained by the fact that the Fe^{2+} ions are adsorbed more strongly on the silica gel support than the Co^{2+} ions. The Cr^{3+} ions move farther toward the field center than the Al^{3+} ions. This occurs because the Cr^{3+} ions are attracted more strongly by the magnetic force than the Al^{3+} ions. It is demonstrated that the separation makes effective use of the adsorption activities as well as the magnetic susceptibilities.

VIII-BB-6 Influence of Magnetic Field up to 15 T on Luminescence of NaCl:Eu Crystals

BASKAKOV, A. A.¹; DUNIN-BARKOVSKIY, Lev

R.²; MORGUNOV, Roman B.²; TANIMOTO, Yoshifumi
(¹ISSP, Chernogolovka; ²IMS and ISSP, Chernogolovka)

Variations of Eu^{2+} luminescent spectra during Eu aggregation in NaCl crystal lattice has been found. These variations caused by extremely high sensitivity of electronic levels splitting to intracrystalline electrical field and Eu^{2+} environment continuously changing during aggregation process. Influence of magnetic field on luminescent excitation spectra in nonequilibrium quenched crystals during the aggregation acted was found (Figure 1). Redistribution of luminescent bands intensity in the excitation spectra gradually increases with the sample exposure in magnetic field (Figure 1). It is unreasonable to suppose that Eu^{2+} ions being paramagnetic can take part in a spin-dependent solid state reaction controlled by magnetic field.

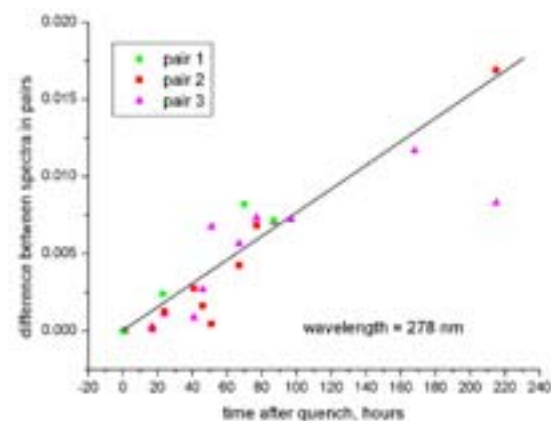


Figure 1. Dependencies of difference between luminescence intensity in reference sample and identical crystal stored in magnetic field after quenching on storage duration for 3 pairs of the identical NaCl:Eu crystals.

VIII-BB-7 Magnetic Field Effect on Dislocation Mobility in NaCl:Eu Crystals

BASKAKOV, A. A.¹; DUNIN-BARKOVSKIY, Lev R.²; MORGUNOV, Roman B.²; TANIMOTO, Yoshifumi
(¹ISSP, Chernogolovka; ²IMS and ISSIP, Chernogolovka)

Recent investigation shown that mobility of dislocations (elementary carriers of plastic deformation) could be considered as an electron spin-dependent process. Magnetic field and its influence on dislocation displacements can serve as a facilities to distinguish spin-dependent part of dislocation interaction with the obstacles. All experiments in this area were carried out early in magnetic fields up to 2 T or in pulsed fields. In this work comparatively strong static magnetic field 15 T was used. It is important because identification of concrete mechanism of spin state mixing in magnetic field as a rule based on correct field dependencies of the magnetic effects.

Displacements of individual dislocation and movement of dislocation in slip bands after exposure of

diamagnetic NaCl:Eu crystals in magnetic field with an induction 15 T were found (Figure 1). Since there was no an external loading of crystals during experiments, the internal stress were the main reason of dislocation displacements. Magnetic field initiates unpinning of dislocations from local obstacles that are Eu aggregates. After magnetic field was switched off increased mobility of the dislocations takes place during 1–2 days. Obtained results open a new possibilities to reliable comparison of theory predictions with the experimental data.

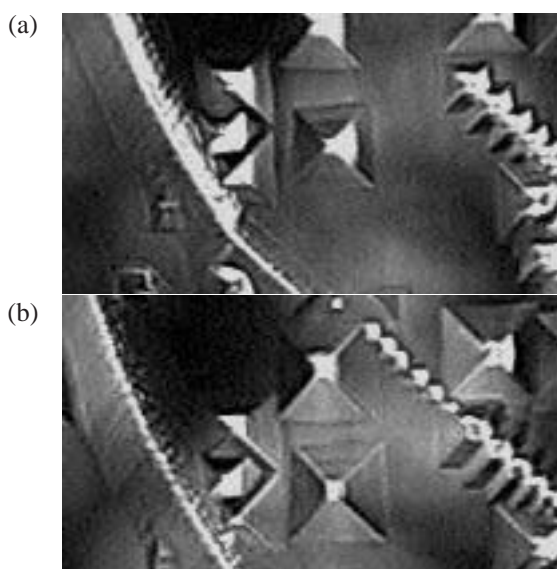


Figure 1. Surface of NaCl crystal a) before, b) after exposure in MF. Big pyramidal pits are initial position of dislocation lines entering on the surface. Small pits are new dislocation line positions after displacement.

VIII-BB-8 Imprinting Magnetic Memory Cells in Molecular Based $\text{NiL}_2(\text{C}_2\text{H}_5\text{OH})_2$ Heterospin Crystals

**BASKAKOV, A. A.¹; FOKIN, S. V.²;
GUDOSHNIKOV, S. A.³; MORGUNOV, Roman
B.⁴; OSSIPYAN, YU. A.¹; OVCHARENKO, V. I.²;
SAGDEEV, R. Z.²; SKOMARVSKII, V. S.³;
TANIMOTO, Yoshifumi**

(¹ISSP, Chernogolovka; ²Intl. Tomography Cent.,
Novosibirsk; ³Inst. Terrestrial Magnetism, Troitsk;
⁴IMS and ISSP, Chernogolovka)

Magnetic studies of molecular based crystals have stirred great interest in the magnetic properties of structural defects induced by plastic deformation. In our experiments local deformation of molecular based magnet was carried out by diamond indenter. Local magnetic field around indentation pit was measured by scanning SQUID magnetometer. It has been found that local deformation causes ferromagnetic exchange interaction in $\text{NiL}_2(\text{C}_2\text{H}_5\text{OH})_2$ heterospin single crystals at unusually high temperatures (≥ 77 K). These magnetization temperatures are much higher than the temperature observed for the same, but undeformed crystals (~ 5 K). Ferro- and antiferromagnetic ordering around dislocation cores arise from lattice distortions

and changes in distances between the magnetic atoms. Near structural defects high pressure will strongly affect exchange interactions in many spin paramagnetic crystals. Thus, in spite of usual aspiration for perfect crystals grows our experiment shown that disordering can give fruitful results. Local plastic deformation should be considered as a method of control over the magnetic properties of molecular based crystals and as a technique for improving their magnetic characteristics. It offers a nice possibility to imprint the magnetic structure and to distribute magnetic memory cells on the surface premeditatedly. Nanoindentation technologies will probably allow the imprinting of separate magnetic cells ~ 1 –10 nm in size.

VIII-BB-9 Localization of Conduction-Band Electrons in β'' -(BEDT-TTF) $_4\text{NH}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{DMF}$ Single Crystals

**MORGUNOV, Roman B.¹; BASKAKOV, A. A.²;
DUNIN-BARKOVSKIY, Lev R.¹; KHASANOV, S.
S.¹; SHIBAEVA, R. P.²; PROKHOROVA, T. G.³;
YAGUBSKIY, E. B.³; KATO, Tatsuhisa;
TANIMOTO, Yoshifumi**

(¹IMS and ISSP, Chernogolovka; ²ISSP,
Chernogolovka; ³Inst. Problems Chem. Phys.,
Chernogolovka)

Temperature dependence of EPR spectrum of β'' -(BEDT-TTF) $_4\text{NH}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot\text{DMF}$ single crystals, which consists of two separate lines characterizing magnetic features of BEDT-TTF and Cr^{3+} ions, was studied within the range 1.5–300 K. It was found that reconstruction of the EPR spectrum occurs under decrease of the temperature down to $T \approx 20$ K. The reconstruction consists in change of Lorentzian shape of the BEDT-TTF line to Gaussian one and in decrease of the effective magnetic moment of Cr^{3+} ions. Analysis of temperature and orientation dependencies of parameters of the EPR spectra allows one to suppose that localization of conduction electrons within regions with dimensions close to the size of individual BEDT-TTF molecules occurs at $T \approx 20$ K. Exchange interactions between Cr^{3+} ions change towards antiferromagnetic spin correlations as well.

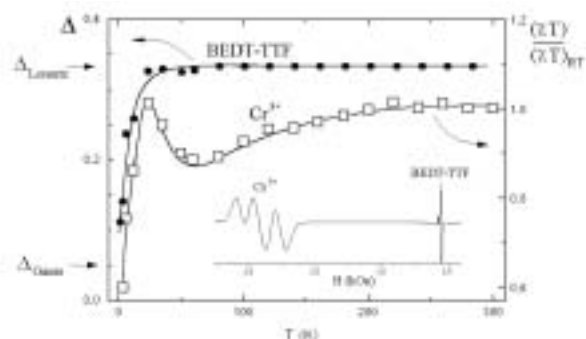


Figure 1. Dependencies of χT and line-shape parameter Δ ($\Delta = 0.05$ for pure Lorentz line and $\Delta = 0.33$ for pure Gauss one) on temperature T . ESR spectrum of the salt at room temperature is shown on the insert.

VIII-CC Theoretical and Computational Study on Gas Phase Reactions and Chromic Molecules

1. Quantum chemical calculations are used to produce potential energy surface (PES) to do reaction dynamics simulations. We develop the methodology to generate PES efficiently and automatically using quantum chemical calculation results. The method does not need any derivative information in quantum chemical calculations.
2. Another interest of our group is theoretical explanation and prediction of structural and spectral changes of photochromic and electrochromic substances.
3. We also search a reasonable pathway to form H₂ from H atoms *via* PAH related catalysts to solve why H₂ is abundant in interstellar space.

VIII-CC-1 Theoretical Study on Photoinduced Color Change and Charge Transfer of Methylviologen

ISHIDA, Toshimasa; MURAKAMI, Makoto¹; WATANABE, Go¹; YOSHIKAWA, Hirofumi²; NISHIKIORI, Shin-ichi²
(¹Shizuoka Univ.; ²Univ. Tokyo)

[*Internet Electronic J. Mol. Design* **2**, 14–23 (2003)]

Methylviologen dication is easily reduced to a monocation radical, and turned to be blue, forming a charge-transfer complex with a donor molecule. Yoshikawa *et al.* recently reported photo-induced reduction and charge transfer complexes in polycyano-polycadmamate host clathrates. We study this reduction using quantum chemical calculations. The energy changes with the torsion angle of the two cations and the spectral change, solvent effect and the charge transfer between the dication and other guest molecules in the clathrates are investigated. The Hartree-Fock, DFT, CI singles, time dependent DFT calculations are carried out for the ground state and excited states of the two cations. Solvation effect is treated with the polarizable continuum model, and the charge transfer in the clathrates is modeled based on crystal structures determined experimentally. The optimized geometry of the monocation radical was found to be planar while that of the dication is twisted. These results are consistent with recent calculations for related compounds. The color change upon the photoreduction was reproduced by the calculation. The solvent effect of acetonitrile was found to be small. Charge transfer absorption was reproduced for the mesitylene-methylviologen dication complex in the clathrate host using a small model. The geometry modification and the color change were reproduced satisfactorily. The TDDFT scheme reproduces the observed spectra better than the CIS scheme, but the latter scheme is still valuable to evaluate qualitative feature of spectra.

VIII-CC-2 Crystal Structure and Spectroscopic Properties of the CT Complex of Methyl Viologen Dication and *o*-Dimethoxybenzene Included in a Polycyano-Polycadmamate Host, and Theoretical Study on Its Red Shifted CT Absorption

YOSHIKAWA, Hirofumi¹; NISHIKIORI, Shin-

ichi¹; ISHIDA, Toshimasa
(¹Univ. Tokyo)

[*J. Phys. Chem. B* **107**, 9261–9267 (2003)]

Using the polycyano-polycadmamate host that is a negative charged Cd cyanide complex with a framework structure built with Cd²⁺ ions and bridging cyanide ligands, we synthesized a clathrate including methyl viologen dication (MV²⁺) and *o*-dimethoxybenzene (ODMB) as guests. The color of the clathrate was red and its origin was considered to be charge transfer (CT) interaction of a CT complex formed with MV²⁺ as an acceptor and ODMB as a donor in the host. The wavelength at the CT absorption maximum was largely red shifted compared with that of the CT complex in an acetonitrile solution. The single crystal X-ray diffraction analysis revealed a π - π stacking structure of the CT complex and a 1D arrangement of the CT complexes in a channel-like cavity of the framework host. In the array of the CT complexes, MV²⁺ ions are adjacent to each other and their separation is short. The direction of the transition moment of the CT absorption determined from the structural information and the spectrum measured on a crystalline sample agreed with that derived from *ab initio* calculations at the CIS/6-31+G* level. Our calculations also showed that the red shift of the CT absorption is mainly due to electrostatic effects between the CT complexes, not due to the shortening of the distance between MV²⁺ and ODMB, which is generally believed to be the reason. The negative charged host stabilizes the ground state of the CT complex, but the electrostatic interaction between the CT complexes heightens the ground state and lowers the excited state. In this clathrate, due to the CT complex array with the short separation the effect from the guests overcomes that from the host and the red shift appears.

VIII-CC-3 A Local Interpolation Scheme Using No Derivatives in Potential Sampling: Application to O(¹D) +H₂ System

ISHIDA, Toshimasa; SCHATZ, George C.¹
(¹Northwestern Univ.)

[*J. Comput. Chem.* **24**, 1077–1086 (2003)]

We recently proposed a local interpolation scheme, in which interpolant moving least squares (IMLS) and Shepard interpolation are employed to describe potential

energy surfaces. This IMLS/Shepard scheme is applicable to do potential interpolation with quantum chemical results for which analytical derivatives are not available. In this study, we apply the scheme to the highly exothermic $O(^1D) + H_2 \rightarrow H + OH$ reaction and compare it with results based on Shepard interpolation using second order Taylor expansions. An analytical surface is used to define the potential function so that errors in the interpolation function may accurately be determined. We found that the present scheme reproduces the correct reactive cross sections more accurately than the Shepard scheme, and with rms errors for energy and gradients that are significantly smaller than those from Shepard interpolation. This occurs even though the present scheme does not utilize derivative and hessian information whereas the Shepard interpolation does. The Bayesian approach proposed by Bettens and Collins does not improve the IMLS/Shepard results significantly although it does the Shepard-only approach. The accuracy in the IMLS/Shepard scheme is surprising, but can be explained by the more global nature of the interpolation.

VIII-CC-4 Possible Molecular Hydrogen Formation Mediated by the Radical Cations of Anthracene and Pyrene

HIRAMA, Mutsumi¹; ISHIDA, Toshimasa;
AIHARA, Jun-ichi¹
(¹Shizuoka Univ.)

[*J. Comput. Chem.* **24**, 1378–1382 (2003)]

Hydrogen molecules cannot be formed readily by the association of gaseous hydrogen atoms. Possible H₂ formation mediated by the radical cations of typical polycyclic aromatic hydrocarbons (PAHs), anthracene and pyrene, was studied at the B3LYP/6-31G** level of theory. We presumed that H₂ is formed by way of two elementary reactions, the addition of an H atom to a PAH molecular cation and the H abstraction from the resulting monohydro-PAH cation (*i.e.*, arenium ion) by a second H atom to yield H₂. The first reaction takes place without any activation energy. The second reaction is also predicted to proceed along almost barrierless pathways although it is far from being a typical ion-molecule reaction. There is a possibility that these reactions might constitute one of the mechanisms for H₂ formation in extremely cold interstellar space. Deuterium enrichment in PAH cations is possibly accompanied by such H₂ formation since deuteration lowers the energies of polyatomic PAH cations appreciably.

VIII-CC-5 Molecular Hydrogen Formation Mediated by a Naphthalene Radical Cation

TOKOSUMI, Takaaki¹; HIRAMA, Mutsumi¹;
TERADA, Yoshihiro¹; HAGIWARA, Noriko¹;
ISHIDA, Toshimasa; AIHARA, Jun-ichi¹
(¹Shizuoka Univ.)

[*Phys. Chem. Chem. Phys.* submitted]

Hydrogen molecules cannot be formed readily by

the association of gaseous hydrogen atoms. Bauschlicher and we independently proposed a possible molecular hydrogen formation mediated by polycyclic aromatic hydrocarbon (PAH) radical cations in space. We studied such a reaction process at the B3LYP/6-31G** level of theory and for the first time succeeded in determining the entire reaction pathway for the H₂ formation mediated by the naphthalene radical cation. We presumed that H₂ is formed by way of two elementary reactions, the addition of an H atom to a naphthalene cation and the H abstraction from the resulting naphthalenium ion by a second H atom to yield H₂. The first reaction takes place without any activation energy. The second reaction is predicted to proceed *via* a van der Waals complex but with little activation energy. These reactions are supposed to enhance the deuteration of the naphthalene cation. Neutral naphthalene also mediates the H₂ formation but needs some activation energy.

VIII-CC-6 Possible Molecular Hydrogen Formation Mediated by the Inner Carbon Atoms of PAH Radical Cations

HIRAMA, Mutsumi¹; ISHIDA, Toshimasa;
AIHARA, Jun-ichi¹
(¹Shizuoka Univ.)

[in preparation]

Molecular hydrogen in space is believed to form from atomic hydrogen. During the past few years, we have been performing density functional theory (DFT) calculations to explore the possibility of H₂ formation mediated by the radical cations of gaseous polycyclic aromatic hydrocarbons (PAHs). As a continuation of this study, we explored the catalytic ability of inner carbon atoms of some typical PAH cations at the B3LYP/6-31G** level of theory. We presumed as before that H₂ is formed by way of two elementary reactions, the addition of an H atom to a PAH cation and the H abstraction from the resulting arenium ion by another H atom to yield H₂. We found that both reactions proceed without any activation energy. It follows that almost all carbon atoms of a PAH cation give sites for molecular hydrogen formation. Since there are large compact PAHs abundantly in space, the H₂ formation at the inner carbon atoms of such PAH cations can never be overlooked. Even if inner carbon atoms might be less reactive than peripheral ones, there are many inner carbon atoms in large compact PAH cations.

VIII-DD Macromolecular Self-Assembly Opens the Way for Development of Novel Materials that Have Characteristics of Cellular Systems

Self-assembly is a principle to integrate molecular devices into a cellular supramolecular system. Exchangeability of the components, characteristic of assembled structures, allows the system to be repairable, reusable and modifiable on demand, and enables metabolism, adaptation, and evolution of the system. This insight may open new perspective for artificial photoelectronic apparatuses at the nano scale. Development and integration of molecular devices have been focuses for downsizing and energy-saving in the field of photoelectronics. For global, sustainable development, in our opinion, the future materials should also be “entropy-saving” (reusable, repairable, and bio-degradable) that has not been considered to date. We thus aimed at development of an artificial photosynthetic system that allows on-demand reuse (Figure 1); for their basis, we also study on molecular mechanisms of photosynthesis. Our study should serve a new design concept for nano- and molecular-scale intelligent materials (see also Special Research Project (c)).

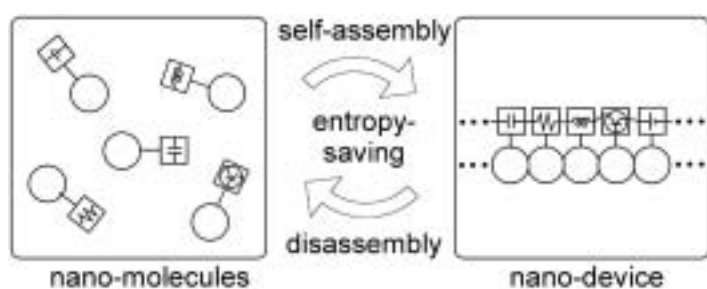


Figure 1. A concept of the “entropy-saving” nano-devices. The device does not function until on-demand self-assembly of nano functional blocks, and the device can easily be decomposed into the reusable components on demand.

VIII-DD-1 Engineering of Tobacco Mosaic Virus

OBA, Toru; TAKATOYA, Haruki¹; MINABE, Masahiro¹
(¹Utsunomiya Univ.)

Green photosynthetic bacteria possess rod-shaped nano-elements ($4 \sim 5 \text{ nm}\phi \times 200 \sim 300 \text{ nm}$) as cores of light-harvesting antenna function. The rod-element is thought to be a self-assembled chlorophylls whose details remain yet unclear. Such a supramolecule may be useful as unique devices for future photoelectronics and biotechnology, but (1) it is impossible to obtain intact rod-elements from the cell and (2) it is quite difficult to build artificial tubule supramolecules by self-assembly of chlorophylls. We aimed at construction of nano-tubule of self-assembled chlorophylls by using tobacco mosaic virus (TMV) as a template. TMV possesses a tubule structure with an outer diameter of 15 nm, inner diameter of 4 nm, and length of 300 nm: the size of the channel matches that of the chlorosomal rod-element. We synthesized novel hydrophilic chlorophyll derivatives, and examined their affinities for the inner surface of TMV and their self-assemblies in the channel.

VIII-DD-2 Synthesis and Properties of Novel Biotin Derivatives

OBA, Toru; TOBITA, Hiromi¹; MINABE, Masahiro¹
(¹Utsunomiya Univ.)

Arrangement and connection of functional

molecules in desired sequences and shapes are basic techniques for future fabrication of elaborate molecular systems including nano-devices and nano-computers. We aimed at development of a new method to arrange functional molecules sequentially in a desired order by utilizing specific interaction between avidin and biotin. Avidin is a 6.8 kDa protein (*ca.* $5 \times 5 \times 6 \text{ nm}$ in size) that can bind four biotin molecules. The topology of the biotin binding sites is appropriate to link avidin molecules linearly when using a linear molecule that possesses two biotin moieties at both ends. Syntheses of novel bitoin derivatives and examination of their abilities to control the assembly of avidin molecules are now under way.

VIII-DD-3 Physicochemical Studies on the Molecular Mechanism of Photosynthesis

OBA, Toru; TAMIYAKI, Hitoshi¹
(¹Ritsumeikan Univ.)

[*Photosynth. Res.* **74**, 1–10 (2002)]

Since chlorophylls (Chls) and bacteriochlorophylls (BChls) are highly asymmetric molecules, an external ligand can coordinate to the central Mg atom of (B)Chls either from the chlorin macrocycle side where the C13²-methoxycarbonyl moiety protrudes (denoting as the “back” side) or from the other side (the “face” side, Figure 2). We found that the “back” side is favored for the ligand coordination, by survey of the highly resolved crystal structures of photosynthetic proteins and by theoretical calculations of model molecules. The calculations reveal that stability of the (B)Chl-ligand

complex is sensitive to distortion of the macrocycle, and the distortion is affected by steric repulsion between particular peripheral substituents as well as flexibility of the macrocycle. We note that not only the static pigment-protein (pigment-pigment) interactions but also dynamics of the pigment-protein (pigment-pigment) assembly should be clarified for better understanding of the role of the planar chirality of (B)Chls *in vivo*.

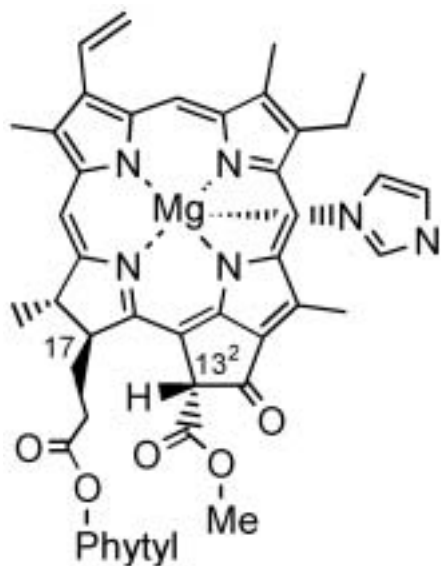


Figure 1. Molecular structure of the “back” type chlorophyll *a*-imidazole complex.