Molecular electronics is a fairly new and fascinating area of research that is firing the imagination of scientists. However, most single organic molecules are not conductive in a classical sense, long range electronic transport through single molecules can not be so effective to realize practical electronic circuits. Our group is interested in (1) construction of nano-structures made from conductive materials such as carbon nanotubes, metal particles or rods, with functional organic molecules, (2) measurements of electric or photonic properties of individual nano-structures while observing their nanometric images, and (3) conductance change of single molecules by external stimulation such as electric field, photon irradiation or chemical species.

IX-A-1 Synthesis and Self-Assembly of Novel Porphyrin Molecular Wires

KAWAO, Masahiro1; OZAWA, Hiroaki2; TANAKA, Hirofumi2; OGAWA, Takuji3
(1JST and Ehime Univ.; 2JST and SOKENDAI; 3IMS and JST)

[Thin Solid Films 499, 23–28 (2005)]

Sub-micrometer long butadiyne-linked porphyrin wires were synthesized by oxidative coupling of diethynylporphyrin. The porphyrin wires were analyzed by analytical gel permeation chromatography, absorption spectroscopy and matrix-assisted laser desorption/ionization time of flight mass spectroscopy. Observations of the wire were performed by atomic force microscopy. Self-assembled structures of the wires were observed on highly oriented pyrolytic graphite. Self-assembling features of the porphyrin wires depended on the length of the porphyrin wires and the concentration of the depositing solution.

IX-A-2 Molecular Junctions Composed of Oligothiophene Dithiol Bridged Gold Nanoparticles Exhibiting Photoresponsive Properties

HUANG, Wei1; MASUDA, Gou2; MAEDA, Seisuke2; TANAKA, Hirofumi3; OGAWA, Takuji3
(1Nanjin Univ.; 2Ehime Univ.; 3IMS and JST)


Three oligothiophene dithiols with different number of thiophene rings (3, 6 or 9) were synthesized and characterized. X-ray single crystal structures of compounds 3’,4’-dibutyl-5’,5’'-dithiocyanato-2’,2’’:5’,2’’’-terthiophene (2) and 5,5’’’’-dithiocyanato-tetrabutyl-2’,2’’:5’,2’’’’-hexathiophene (5) were involved herein to show the exact molecular lengths as well as the difference between their UV-vis spectra arising from the different packing modes. These dithiols with different chain lengths were then treated with tert-dodecanethiol protected active gold nano-particles (Au-NPs) via in situ thiol-to-thiol ligand exchange in the presence of 1 µm gap Au-electrodes. Thus the molecular junctions composed of self-assembled films were prepared, where oligothiophene dithiol bridged Au-NPs were attached to two electrodes by means of Au–S bonded contacts. The morphologies and I-V characteristics of these films were studied by SEM and AFM approaches, which suggest the thickness of the films varied within the size of one isolated Au-NPs and typical distance dependent semiconductor properties could be observed. Current-voltage (I-V) measurements for these devices were performed where the films served as active elements in the temperature range 6 ~ 300 K and classical Arrhenius plots and their linear fittings were carried out to give the activation energies (ΔE). Furthermore, preliminary studies on the photoresponsive properties of these junctions were explored at 80, 160 and 300 K, respectively. Physical and photochemical mechanisms were used to explain the possible processes. To the best of our knowledge, this is the first report where oligothiophene dithiols act as bridging units to link Au-NPs, and also the first report about functionalized Au-NPs exhibiting photo response properties in the solid state.

IX-A-3 Simple Preparation Method for Supramolecular Porphyrin Arrays on Mica Using Air/Water Interface

SATO, Hirokazu1; TSUTSUMI, Osamu1; TAKEDA, Kazuyoshi1; TANAKA, Hirofumi2; OGAWA, Takuji3
(1Ebara Research Co.; 2IMS and JST)


The fabrication of supramolecular porphyrin arrays on the surface of a mica substrate is demonstrated. The supramolecular structures are prepared at the air–water interface from a dilute solution of porphyrin dimer and bidentate ligand and then transferred to mica by using the conventional Langmuir-Blodgett method. Isolated wire-like structures and networks of structures are observed by atomic force microscopy. From the analysis of the height histogram and average width, these structures are considered to be side-by-side arrangements of supramolecular chains of porphyrin dimer and bidentate
IX-A-4 Porphyrin Molecular Nanodevices Wired Using Single-Walled Carbon Nanotubes

TANAKA, Hirofumi1; YAJIMA, Takashi; MATSUMOTO, Takuya2; OTSUKA, Yoichi2; OGAWA, Takaji1
(1IMS and JST; 2Osaka Univ. and JST)

[Adv. Mater. 18, 1411–1415 (2006)]

For the future development of molecular electronics, we should construct nanosized molecular devices placed on nanowiring. To obtain high-quality devices composed of a few molecules, the wiring and the device should be connected well to maintain a constant interface. For this purpose, a single-walled carbon nanotube (SWNT)/porphyrin complex was prepared and then its electronic property was investigated while observing a topographic image using point-contact current imaging atomic force microscopy (PCI-AFM). Using PCI-AFM, we can measure the current along the long axis of the wiring by which the quality of the device in the circuit can be determined. The I-V curves were asymmetric with respect to the origin where an aggregate of several porphyrin molecules was absorbed, while they were symmetric without them. This means the porphyrin aggregation works as a rectification device on SWNT wiring. This is the first study which proves the electron property of a few porphyrin molecules absorbed on SWNT.


TANAKA, Hirofumi1; YAJIMA, Takashi2; KAWAO, Masahiro2; OGAWA, Takaji1
(1IMS and JST; 2SOKENDAI)


The electronic properties of a porphyrin polymer wire absorbed on a single-walled carbon nanotube (SWNT) were investigated. Current-voltage (I-V) curves were measured simultaneously along with topographic observations using point-contact current imaging atomic force microscopy (PCI-AFM). I-V curves taken at the location of porphyrin polymer wire absorption were asymmetric with respect to the origin, while they were symmetric in the absence of a porphyrin polymer wire. The electron conduction mechanism of the porphyrin on the SWNT was similar to the case of SWNT/ 5,15-Bispentylporphyrinato zinc(II) complex in our recent work.

IX-A-6 Preparation of Very Reactive Thiol-Protected Gold Nanoparticles: Revisiting the Brust-Schiffrin Method

ARAKI, Koiti1; MIZUGUCHI, Eisuke2; TANAKA, Hirofumi3; OGAWA, Takaji3
(1SaoPaulo Univ.; 2Ehime Univ.; 3IMS and JST)


Metal nanoparticles have attracted great interest in nanoscience and nanotechnology because of the many possibilities envisaged by the bottom-up approach since they possess unique optical, electrical, bonding and catalytic properties. Among them, the gold clusters are the most stable and extensively studied materials, and have been proposed for applications such as in photo-electrochemical devices, drug delivery systems and chemical and immunosensors. In all these cases, the properties of the materials should be adjusted by anchoring molecular species with suitable properties on the surface. In this sense, the availability of easily functionalizable and stable starting materials is an important aspect since there is a myriad of molecular species and other materials that can be combined with for the development of new inorganic-organic hybrid nanomaterials and applications.

The higher stability and possibility to isolate a solid that can be repeatedly isolated and redissolved in common organic solvents without decomposition and the possibility to treat them just as another organic molecular species is very convenient. However, there is a drawback for the widespread use of such a thiol protected materials: the sluggishness of the functionalization reaction by substitution of the protecting species, which can take more than a day to proceed until completion. The use of conventional organic chemistry on ω-functionalized protecting molecules is also tedious and hampers the preparation of organic-inorganic hybrid nanomaterials, for example by coordinative layer-by-layer assembly. Accordingly, we revisited the Brust-Schiffrin method envisaging the preparation of substitutionally reactive but stable enough thiol protected gold nanoparticles to isolate them as a solid.

IX-A-7 Spontaneous Resolution of Delta and Gamma Enantiomeric Pair of [Ru(phen)(bpy)2](PF6)2 (phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine) by Racemic Conglomerate Crystallization

HUANG, Wei1; OGAWA, Takaji
(1Nanjin Univ.)

[Polyhedron 25, 1379–1385 (2006)]

Spontaneous resolution study is realized for a Δ and Λ enantiomeric pair of ruthenium(II) complexes obtained by racemic conglomeration from solution, crystallizing in P4_1 and P4_3 space groups. A ligand exchange reaction between phen and bpy ligands is found for these Ru(II) complexes, but racemization is accompanied which has been proved by the single-crystal structure of the product. To extend our research, counter-ion (BF_4^-)
IX-A-8 Structural and Spectroscopic Characterizations of Low-Spin [Fe(4,4-dimethyl-2,2’-bipyridine)]3 (NCS)2/H2O Prepared from High-Spin Iron(II) Dithiocyanate Tetrapyridine

Hirofumi OZAWA, Hiroaki; OGA W A, Takuji; TANAKA, Hirofumi
(1SOKENDAI; 2IMS and JST)

Redetermination of the crystal structure of high-spin iron(II) dithiocyanate tetrapyridine [Fe(dmbpy)3] (NCS)2 (I) (pyZpyridine) at 85 and 291 K exhibits different unit cells when compared with that reported in 1967. An elongation in the compressed octahedron coordination environment around central ferrous ion is observed at low temperature, which can be verified by the DFT calculations of energy and dipole moments. I was then used as the Fe(II) source to synthesize [Fe(dmbpy)3] (NCS)2·3H2O (2) (dmbpyZ4,40-dimethyl-2,20-bipyridine). The X-ray diffraction studies of 2 reveal that six Fe–N bond distances are in the range 1.959(3)–1.971(3) Å suggesting the formation of the low-spin Fe(II) complex.

IX-A-9 Morphology and Electric Properties of Nonathiophene/Au Nano-Composite Thin Films Formed between 1 μm Gapped Electrodes

OGAWA, Takuji1; HUANG, Wei2; TANAKA, Hirofumi1
(1IMS and JST; 2Nanjin Univ.)


A nano-composite conductive film is formed between gold electrodes by immersion of the electrode pair in a chloroform solution of nonathiophenedithiol and gold nanoparticles. The homogeneous thin film is formed over an area of 3 mm × 3 mm surrounding the 1μm-gapped electrodes. The thickness of the film (20 nm) corresponds to 2–3 layers of the dithiol-bridged Au nanoparticles. Temperature-dependent I–V curves reveal that a thermionic mechanism dominates in the high-temperature region (>80 K), while molecular tunneling is the main transport process at lower temperatures.

IX-A-10 Synthesis of End-Functionalized π-Conjugated Porphyrin Oligomers

OZAWA, Hiroaki1; OGAWA, Takuji2; TANAKA, Hirofumi2
(1SOKENDAI; 2IMS and JST)

[Annual Review 2006 143]

4-(S-acetylthiomethyl)phenyl- and pyrenyl-functionalized π-conjugated porphyrin oligomers were synthesized. The distribution of the length of the oligomers could be controlled by changing the ratio of the starting porphyrin to the capping molecules. Oligomers from dimers to heptamers were isolated using size exclusion chromatography. The spectroscopic properties of these oligomers were measured to determine the influences of the number of porphyrin units and capping molecules on the absorption and emission spectra.

IX-A-11 Fabrication of Nanoscale Gaps Using a Combination of Self-Assembled Monomolecular and Electron Beam Lithographic Techniques

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(1ICORP , JST; 2NIMS)

[Appl. Phys. Lett. 88, 223111 (2006)]

We describe a new method of fabricating nanogaps using a combination of the self-assembled molecular lithographic and the electron beam lithographic techniques. The method enables us to control the size of a gap with an accuracy of ~2 nm, and design the positions, where the nanogap should be formed, in the high-resolution patterning by employing an electron beam lithography. The utility of the fabricated nanogap is demonstrated by measurement of a single electron tunneling phenomenon through the dodecanethiol-coated Au nanoparticles placed in the fabricated nanogap.

IX-A-12 Synthesis and Photochemical Behavior of Metalloporphyrin Complexes Containing a Photochromic Axial Ligand

TSUTSUMI, Osamu1; SATO, Hirokazu1; TAKEDA, Kazuyoshi2; OGAWA, Takuji
(1Ebara Research Co.)


Metalloporphyrin complexes with a photochromic axial ligand were synthesized and photoisomerization behavior of those complexes was investigated. In this study, 3,3V-azopyridine (AZP) was used as the axial ligand. We found that the structure of the axial-coordinated complexes depended on the center metal of the porphyrin. When magnesium was employed as the center metal, a 1:1 coordinated complex was obtained. On the other hand, zinc or rhodium porphyrins formed the sandwich-bonded complexes. The photoisomerization behavior also depended on the center metal of the porphyrins, and the cis-to-trans "one-way" photoisomerization of the AZP axial ligand took place in the complexes of zinc and rhodium porphyrins. The one-way isomerization may be interpreted as the results of the photoinduced electron transfer from porphyrin to AZP.
IX-B Development of Organic Semiconductors for Molecular Thin-Film Devices

Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on \( \pi \)-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 aromatic compounds are efficient n-type semiconductors for OLEDs and OFETs.

IX-B-1 Synthesis and Characterization of Three Novel Perfluoro-Oligothiophenes Ranging in Length from the Trimer to the Pentamer

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(1Univ. Málaga)


In this article, we report on the synthesis and full characterization of three perfluorinated oligothiophenes, ranging in length from the trimer to the pentamer (PF-\( n \)T, with \( n = 3, 4, \) or 5). The differential pulse voltammetry (DPV) analysis of the compounds showed that they can be both oxidized and reduced (i.e., they display a dual or amphoteric electrochemical behavior), with the reduction peaks positively shifted relative to those of the corresponding unsubstituted oligothiophenes. The electrochemically determined energy gaps are in agreement with those measured from the UV-vis-NIR absorption spectra in solution. The conjugational properties have been investigated by means of FT-Raman spectroscopy, both as pure solids and as dilute solutes in \( \text{CH}_2\text{Cl}_2 \), revealing that: (i) \( \pi \)-conjugation does not still reach saturation with chain length for the longest oligomer, and (ii) conformational distortions from a nearly coplanar arrangement of the successive thiophene units upon solution are not too large. DFT and TDDFT quantum chemical calculations have been performed, at the B3LYP/6-31G** level, to assess information about the optimized molecular structure, equilibrium atomic charges distribution, energies and topologies of the frontier molecular orbitals (MO) around the gap, vibrational normal modes associated with the most outstanding Raman scatterings, and vertical one-electron excitations that give rise to the main optical absorptions.

Figure 1. Structures and syntheses of perfluoro-oligothiophenes.
IX-C Development of Multi-Function Integrated 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.

IX-C-1 Stepwise Synthesis of Molecular Wire with a Double-Tunnel Junction
TANAKA, Shoji

We have developed a synthetic protocol for precisely-defined linear macromolecules with a double-tunnel junction as shown in Figure 1. The nature of intramolecular charge transport in a π-conjugated macromolecule with tunnel junctions is of fundamental importance for single electron/hole device applications. In the field of applied physics metal–molecule–metal double junction systems have been intensively studied so far. In contrast, little attention has been paid to an intramolecular tunnel junction system because of the problem of precise fabrication of tunnel junction structures in a macromolecule. Based on our synthetic approach, a series of intramolecular junction systems will be prepared from various types of non-conjugated molecular blocks and the 1–10 nm long π-conjugated molecular blocks that we have already developed.

![Synthetic scheme of 25 nm long molecular wire with a double-tunnel junction.](image)

IX-C-2 Direct Identification of Conformational Isomers of Adsorbed Oligothiophene on Cu(100)
YOKOYAMA, Takashi1; KURATA, Saki1; TANAKA, Shoji
(1Yokohama City Univ.)

A direct conformational analysis using scanning tunneling microscopy (STM) has been performed for individual adsorbed α-octithiophene molecules 8T-Si on Cu(100). s-Cis and s-trans conformational isomers are induced by the rotational flexibility of individual thiophene rings. By adding bulky N-silyl substituents to octithiophene, we successfully identify the s-cis and s-trans conformational isomers using STM. The obtained relative abundances of the s-cis and s-trans conformations are analyzed using ab initio molecular orbital calculations.

**Figure 1.** Synthetic scheme of 25 nm long molecular wire with a double-tunnel junction.
IX-D Nano- and Complex-Catalysis

Objectives of this research group is development of nano- and complex-catalysts which exhibit novel catalytic functions, in particular, to promote efficient organic molecular transformations. Three major subjects are (1) preparation and properties of novel pincer complexes, (2) development of polymeric complex-catalysis in water, and (3) development of polymer-supported nano-metal catalysts. Representative results are shown below.

IX-D-1 NCN Pincer Palladium Complexes: Their Preparation via a Ligand Introduction Route and Their Catalytic Properties

UOZUMI, Yasuhiro; TAKENAKA, Kazuhiro; MINAKA W A, Maki


A wide range of NCN pincer palladium complexes, [4-tert-2,6-bis(N-alkylimino)phenyl]chloropalladium (alkyl = n-butyl, benzyl, cyclohexyl, t-butyl, adamantyl, phenyl, 4-methylphenyl), were readily prepared from trans-(4-tert-butyl-2,6-diformyl-phenyl)chlorobis(triphenylphosphine)palladium via dehydrative introduction of the corresponding alkylimino ligand groups (ligand introduction route) in excellent yields (71–98%). NMR studies on this route for forming pincer complexes revealed the intermediacy of [4-tert-2,6-bis(N-alkylimino)phenyl]chlorobis(triphenylphosphine)palladium which is in equilibrium with the corresponding NCN pincer complexes via coordination/dissociation of the intramolecular imino groups and triphenylphosphine ligands. A series of chiral NCN pincer complexes bearing pyrroloimidazolone units as the trans-chelating donor groups, [4-tert-butyl-2,6-bis{(3R,7aS)-2-phenylhexahydro-1H-pyrrolo[1,2-c]imidazol-1-on-3-yl}phenyl]chloropalladium, were also prepared from the same precursor via condensation with proline anilides in high yields. The catalytic properties of the NCN imino and the NCN pyrroloimidazolone palladium pincer complexes were examined in the Heck reaction and the asymmetric Michael reaction to demonstrate their high catalytic activity and high enantioselectivity.

IX-D-2 Asymmetric P-allylic Etherification of Cycloalkenyl Esters with Phenols in Water Using a Resin-Supported Chiral Palladium Complex

UOZUMI, Yasuhiro; KIMURA, Masahiro

[Catalytic asymmetric allylic amination of cycloalkenyl carbonates (methyl cyclohexen-2-yl carbonate, methyl cyclohexen-2-yl carbonate, methyl 5-methoxyacyrlylcyclohexen-2-yl carbonate, methyl cyclohexenyl carbonate, t-butyl 5-methoxyacyrlylcyclohexen-1,2,5,6-tetrahydropyridinedicarboxylate) with phenolic nucleophiles was achieved in water under heterogeneous conditions by use of a palladium complex of (3R,9aS)-3-[2-(diphenylyphosphino)phenyl]-2-phenyltetrahydro-1H-imidazo[1,5-a]indole-1-one anchored on polystyrene-poly(ethylene glycol) copolymer resin (2 mol % Pd) to give the corresponding cycloalkenylamines with high enantiomeric selectivity (up to 94% ee).

IX-D-3 A Solid-Phase Self-Organized Catalyst of Nanopalladium with Main-Chain Viologen Polymers: α-Alkylation of Ketones with Primary Alcohols

YAMADA, Yoichi; UOZUMI, Yasuhiro

[Org. Lett. 8, 1375–1378 (2006)]

A novel solid-phase self-organized catalyst of palladium nanoparticles was prepared from PdCl2 with main-chain viologen polymers via complexation and reduction. This insoluble nanocatalyst nano-Pd-V efficiently promoted α-alkylation of ketones with primary alcohols in the presence of Ba(OH)2·H2O under atmospheric conditions without organic solvents. The nano-Pd-V catalyst was reused without loss of catalytic activity.
IX-E  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. As a basic architecture, composites of organic molecules and gold nanoparticles were synthesized and molecular dynamic simulations were carried out to predict the solution structures.

IX-E-1  Automated Design of Protecting Molecules for Metal Nanoparticles by Combinatorial Molecular Simulations

NAGATA, Toshi

[J. Organomet. Chem. in press]

New tripod oligo(dibenzyl sulfide) molecules were designed by computer modeling calculations so that they would form 1:1 complexes with an Au147 nanoparticle. Twelve aromatic molecules containing two methylthiomethyl groups were used as construction units (“residues”). Combinations of the residues (“sequences”) were examined by molecular dynamic simulations, and those sequences giving the largest interaction energies with the gold nanoparticle were sought through either full search or genetic algorithm. Best-fit sequences were found for \( N = 5 \) and 6 (\( N \) is the number of “residues” in one leg of the tripod molecule).

![Figure 1. (a) The base structure of the protecting molecule. (b) The “residues” used in this study.](image)

Figure 2. The surface covering schemes for the two lowest energy structures for \( N = 6 \). The atoms in the three “legs” are drawn in white, gray, and black, respectively.

IX-F  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. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.
In order to estimate the average structures of our ferrocene-dendrimer-porphyrins (Figure 1), we carried molecular-dynamic (MD) simulations of these molecules in CHCl₃ solutions. Figure 2 shows the spatial distribution of the iron atoms of all the ferrocenyl groups, in relative to the porphyrin ring at the core. Figure 3 shows the radial distribution functions of the iron atoms in the first, second, and third layers from the center of the porphyrin ring. These figures clearly show that only the ferrocenyl groups in the second layer have significant probability to approach the porphyrin ring closer than 10 Å. This observation is consistent with the results of ¹H NMR and fluorescence quenching, namely the second layer had a larger interaction with the porphyrin ring than the first and third layers.

It is also interesting to note that such layered distribution was more distinct in G₃(Fc)₁₄-ZnP than in G₂(Fc)₆-ZnP, the generation 2 compound with the similar architecture. The spatial distribution and radial distribution functions of the iron atoms in G₂(Fc)₆-ZnP also showed similar trends as G₃(Fc)₁₄-ZnP, although the distribution of the first layer Fe atoms was somewhat broader in G₂(Fc)₆-ZnP than in G₃(Fc)₁₄-ZnP. These results suggest that, even in the case of these “spatially relaxed” dendritic frameworks, the presence of the higher-generation branches restricts the movements of the inner layer.
Reconstitution of the Mn-depleted Photosystem II (PSII) particles with synthetic binuclear Mn complexes (two Mn(II) complexes and one Mn(IV) complex) was examined. The reconstituted PSII particles showed lower restored activities than our previous studies in photo-induced electron transfer and oxygen evolution. These results were ascribed to the “robustness” of the Mn complexes used in this study. The ESI-MS spectra of the Mn(II) complexes showed that the macrocyclic ligand remained intact even after release of the Mn(II) ions, so it was proposed that the macrocyclic ligand remained in the vicinity of the PSII proteins and caused distortion of the protein structures. On the other hand, the lower activity of the Mn(IV) complex was ascribed to the robustness of the bis-μ-oxo structure which caused transfer of the Mn ions to the PSII protein less efficient than the previously examined Mn complexes with mono-nuclear or mono-μ-oxo binuclear structures. These results implies that subtle balance between the stability and lability of the complexes are important in successful reconstitution of PSII.

Reactions of ClCo(PPh₃)₃ with sodium salts of cyclopentadienyl derivatives NaCp R (R = H, COOMe, CH₂CH₂SMe) gave five-coordinate Co(I) complexes Cp²Co(PPh₃)₂ (R = H, 2; COOME, 3; CH₂CH₂SMe, 4) in 60–80% yields as crystals. The structures of 2–4 were determined by X-ray crystallography (Figure 1). On the other hand, the reaction of LiCp*(Cp* = C₅Me₅) with ClCo(PPh₃)₃ resulted in a formation of a diamagnetic dimer complex [Cp*Co(μ-Ph)(μ-PPh₂)CoCp*]₂, 5, which has bridging phenyl and diphenyl-phosphide groups. This compound was isolated from hexane solution as black crystals in 64% yield. The structure was confirmed by X-ray crystallography (Figure 2). We propose that the bridging phenyl and phosphide ligands were generated by a C–P bond cleavage caused by the action of the strongly nucleophilic Cp*Co fragment.
Figure 1. The ORTEP drawing of 3.

Figure 2. The ORTEP drawing of 5.
IX-H Synthesis of Buckybowls and Heterobuckybowls

Bowl-shaped π-conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Heteroatom-containing buckybowls (heterobuckybowls) have also been expected to exhibit unique physical characters. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiralbowl has appeared. In addition, most of thus-reported procedures are performed under severe reaction conditions, limiting the sort of the introducible atoms/functional groups.

In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls using the organic synthesis approach.

IX-H-1 Regio- and Stereo-Selective Synthesis of Multi-Substituted Benzene Derivatives by Cyclotrimerization of Haloalkene Derivatives

SAKURAI, Hidehiro; HIGASHIBAYASHI, Shuhei

Bridged multi-substituted benzene derivatives have been of interest because of the bond alternation of benzene ring and the utility for syntheses of cup-shaped molecules or buckybowls. The regio- and stereo-selective syntheses are important for the synthetic utility. Chiral multi-substituted benzene derivatives were synthesized from chiral halononorbornene derivatives through the regio- and stereo-selective cyclotrimerization catalyzed by palladium nanocluster. Thus prepared chiral benzene derivatives are expected to serve as the synthetic intermediates for chiral buckybowls.
IX-I  Spectroscopy and Chemistry of Metal Nanoclusters on Surfaces

The structure and reactivity of metal nanoclusters are important issues because of their relevance to heterogeneous catalysis. In particular, Au nanoclusters on titanium oxide surfaces has attracted a lot of interest since the discovery of its catalytic activity on CO oxidation. We apply various surface science techniques to clarify correlations between structures and reactivity of metal nanoclusters deposited on surfaces. In this year, we use alkanethiolate-coated gold nanoclusters as a primary target in collaboration with Tsukuda (IMS) and Al-Shamery (U. Oldenburg) groups.

IX-I-1  STM Observation and Fabrication of Films of Gold Nanoclusters with and without Alkanethiolate Ligands on TiO₂(110)

MATSUMOTO, Taketoshi; NICKUT, Patricia¹; SAWADA, Takeshi; TSUNOYAMA, Hironori; WATANABE, Kazuya; TSUKUDA, Tatsuya; AL-SHAMERY, Katharina¹; MATSUMOTO, Yoshiyasu (¹Carl v. Ossietzky U. Oldenburg)

Films of Au nanoclusters protected with alkanethiolate ligands fabricated before and after etching on the TiO₂(110) surface were investigated by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The Au nanoclusters were produced by reducing HAuCl₄ in micelles and fractionalized by size with gel permeation chromatography. Au nanoclusters with hexanethiolate formed single layers and were coated on TiO₂(110). Replacing the ligands with n-octadecanethiolate resulted in forming three layers. Au nanoclusters with ligands are mobile on TiO₂ at room temperature and it is possible to manipulate their positions by a STM tip. XPS spectra showed that O-atom etching removes ligands effectively and produces gold oxide on nanocluster surfaces. The oxide was reduced effectively by H atom etching. These etching procedures causes aggregation of Au nanoclusters, increasing apparent height from ~1.5 nm to 3–6 nm. Adding hexanethiol and decane to the films of Au nanocluster with hexanethiolate did not show significant changes before and after etching. No diffusion was induced by STM tips after O atom etching.

IX-J  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), infrared reflection absorption spectroscopy (IRAS), x-ray photoelectron spectroscopy (XPS), work function measurements, and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation. In this year, the photochemistry of cyclic alkane on Pt(111) and Cu(111) surfaces was studied mainly by TPD, XPS, and IRAS.

IX-J-1  Photochemistry of Cyclohexane on Cu(111)

YAMAGUCHI, Dai; MATSUMOTO, Taketoshi; WATANABE, Kazuya; TAKAGI, Noriaki¹; MATSUMOTO, Yoshiyasu (¹SOKENDAI and Univ. Tokyo)


The photochemistry of cyclohexane on Cu(111) and its excitation mechanism have been studied by temperature-programmed desorption, ultraviolet and X-ray photoelectron spectroscopy. Cyclohexane weakly adsorbed on Cu(111) has been known to show a broadened and redshifted CH stretching band, i.e., CH vibrational mode softening. Although no dehydrogenation takes place thermally on this surface and by the irradiation of photons at 5.0 eV, adsorbed cyclohexane is dissociated to cyclohexyl and hydrogen by the irradiation of photons at 6.4 eV. This is a marked contrast to cyclohexane in the gas phase where the onset of absorption is located at 7 eV. When the surface irradiated by 6.4-eV photons is further annealed, cyclohexyl is dehydrogenated to form cyclohexene that desorbs at 230 K. The systematic measurements of photochemical cross sections at 6.4 eV with linearly polarized light as a function of incident angle indicate that the electronic transition from the highest occupied band of cyclohexane to a partially occupied hybridized band near the Fermi level is respon-
sible for the photochemistry. The hybridized band is formed by the interactions between the electronic states of cyclohexane and the metal substrate. The role of the hybridized band in the photochemistry and the CH vibrational mode softening is discussed.

**IX-J-2 Photochemistry and Post-Irradiation Chemistry of Cyclohexane on Pt(111)**

YAMAGUCHI, Dai; MATSUMOTO, Taketoshi; WATANABE, Kazuya; TAKAGI, Noriaki1; MATSUMOTO, Yoshiyasu

(1SOKENDAI and Univ. Tokyo)

Photochemistry and post-irradiation thermal chemistry of cyclohexane on Pt(111) were investigated by TPD, XPS and IRAS. From TPD results, photo-dehydrogenation of cyclohexane was confirmed on Pt(111). IRAS spectra after photo-irradiation indicate that the primary photoproduct is cyclohexyl. The photoexcitation cross sections of cyclohexane on Pt(111) at 6.4 and 5.0 eV are $(3.1\pm0.2)\times10^{-21}$ and $(1.1\pm0.6)\times10^{-21}$ cm$^2$, respectively. The appreciable cross section at 5.0 eV suggests the larger adsorbate interactions on Pt(111) compared with those on Cu(111). The excitation mechanism was investigated by the same procedure for Cu(111). The cross sections with p-polarized light again deviate from the absorbance of the substrate. This indicates clearly that the excitation mechanism is the same on Cu(111). On Pt(111), it has been known that cyclohexane is thermally dehydrogenated to benzene via $\text{C}_7\text{H}_8$. Benzene converted from the monolayer of cyclohexane does not desorb molecularly because benzene is further dehydrogenated to atomic C. In contrast, after photo-irradiation at 6.4 eV, the desorption of benzene in post-irradiation TPD was clearly observed. Then, the thermal reactions of the primary photoproduct, cyclohexyl, were investigated by IRAS. Absorption bands attributable to cyclohexene appeared at 200 K. This species has not been identified in the studies on thermal reactions of cyclohexane on Pt(111). UV photons can produce a larger amount of cyclohexyl than that induced thermally. In this case, the adsorption sites are largely occupied by produced cyclohexyl and hydrogen, which may increase the activation barriers for dehydrogenation of cyclohexene and benzene in the post-irradiation thermal chemistry.

**IX-K 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 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. This year, in particular, we have focused on K on Pt(111) and Na on Cu(111) adsorption systems.

**IX-K-1 Coherent Surface Phonon Dynamics at K-Covered Pt(111) Surfaces Investigated by Time-Resolved Second Harmonic Generation**

FUYUKI, Masanori1; WATANABE, Kazuya; MATSUMOTO, Yoshiyasu

(1SOKENDAI)

[Phys. Rev. B submitted]

We have investigated coherently excited surface phonons at K-covered Pt(111) surfaces by using femtosecond time-resolved second harmonic generation spectroscopy. The frequency of the K–Pt stretching phonon mode depends on the superstructure of K: 5.0–5.3 and 4.5–4.8 THz for $(2\times2)$ and $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructures, respectively. In addition to the stretching mode, a couple of Pt surface phonon modes are simultaneously observed when the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure is formed. The dephasing time of the K–Pt stretching mode becomes shorter and its frequency redshifts as the absorbed fluence of a pump pulse increases. This is in stark contrast to the Pt surface phonon modes whose frequencies are independent of fluence. The fluence dependence of the K–Pt stretching mode is interpreted to be due to anharmonic coupling between the K–Pt stretching and lateral modes.

**IX-K-2 Excitation Mechanism of Coherent Surface Phonons on Na-Covered Cu(111)**

FUYUKI, Masanori1; WATANABE, Kazuya; INO, Daisuke1; MATSUMOTO, Yoshiyasu

(1SOKENDAI)

We observed time-resolved second harmonic signals from the Cu(111) surface with a full monolayer of Na in ultra-high vacuum and investigated the excitation-wavelength dependence of the wave packet dynamics of the coherently excited Na–Cu stretching mode. Changing the photon energy of the pump pulse (25 fs) from 2.0 to 2.5 eV, the oscillation amplitude derived from the Na–Cu stretching motion is enhanced. The careful measurements of photon-energy dependence indicates that the
excitation efficiency mimics the absorbance of bulk Cu. Holes created in the d-bands by the optical transitions could be filled by electrons in the adsorbate-induced occupied state of the metallic quantum well by an Auger-type transition. Hence, holes can be created in the adsorbate-induced occupied state. Moreover, since this Auger decay can occur significantly faster than the oscillation period of the Na–Cu stretching mode, the substrate excitation may be a possible excitation mechanism for the coherent oscillation.

**IX-L  Vibrational Dynamics at Surfaces and Interfaces Studied by Time-Resolved Sum Frequency Spectroscopy**

In addition to time-resolved second harmonic generation and two-photon photoemission spectroscopy, we have developed fs time-resolved sum frequency generation (SFG) spectroscopy to study ultrafast surface dynamics. Time-resolved SFG is a versatile tool for investigating vibrational dynamics at surfaces and interfaces. In this year, we applied this technique to probe vibrational energy transfer at the interface between Pt(111) and ice layers where CO monolayer is inserted.

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### IX-L-1 Vibrational Energy Relaxation at the Interface of Ice/CO/Pt(111) Studied by fs Time-Resolved Sum Frequency Generation

**NAGAO, Masashi; WATANABE, Kazuya; MATSUMOTO, Yoshiyasu**

We studied the vibrational excitation and relaxation dynamics of surface adsorbate for D_2O/CO/Pt(111) by the femtosecond time resolved vibrational SFG spectroscopy (VIS: 800 nm, 3 ps; IR: 3–5 mm, 130 fs; pump: 400 nm, 130 fs) under ultra vacuum condition. D_2O/CO/Pt(111) was prepared by dosing D_2O molecules on the CO covered Pt(111) surface at 140 K. Two peaks were observed in CO stretching region at 2068 and 2095 cm$^{-1}$ when 10 ML D_2O layer was formed on the surface, because D_2O crystals exhibit island growth on this surface. The former peak ($\nu^*(\text{CO})$) is assigned to the adsorbed CO intact with D_2O and the latter ($\nu(\text{CO})$) is assigned to the CO free from D_2O. Both peaks were redshifted and broadened by the irradiation of a pump pulse, because the frustrated translation and rotation modes of CO coupled to Pt hot electrons generated by the excitation pulse. We found the following features in the transient SFG spectra. The maximum peak shift of $\nu^*(\text{CO})$ was larger than that of $\nu(\text{CO})$ and the peak shift of $\nu^*(\text{CO})$ shows much faster recovery than that of $\nu(\text{CO})$ within 3 ps after the excitation. We analyze the spectra by the numerical simulation of SFG polarization based on the Bloch equations, which describe the time-dependent evolution of the density matrix for the CO stretching mode. The transient response of time-resolved SFG spectra can be characterized by the time-dependent evolution of the density matrix for the CO stretching mode. The transient SFG spectra can be characterized by the time-dependent evolution of the density matrix for the CO stretching mode. The transient SFG spectra can be characterized by the time-dependent evolution of the density matrix for the CO stretching mode. The transient SFG spectra can be characterized by the time-dependent evolution of the density matrix for the CO stretching mode.
IX-M 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.

IX-M-1 Direct Observation of a Propagating Chemical Wave in Disproportionation Reactions of Water on Oxidized Ag(110) Surface by Scanning Tunneling Microscopy

NAKAGOE, Osamu1; TAKAGI, Noriaki2; WATANABE, Kazuya; MATSUMOTO, Yoshiyasu (1SOKENDAI; 2Univ. Tokyo)


It is well known that the adsorption of O on 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 \((n\times1)\) \((n = 2 \sim 7)\) depending on the fractional O coverage due to repulsive inter-chain interactions. On the added-row reconstructed Ag(110)\((n\times1)\)-O surfaces, one-dimensional –Ag–O–Ag–O– chains arrange periodically. Scanning tunneling microscopy was used for studying spatio-temporal evolution of the disproportionation reaction of H\(_2\)O with O adatoms on oxidized Ag(110) surfaces where quasi-one dimensional AgO chains form ordered structures. Initially the reaction takes place slowly on Ag(110)-(5\(\times\)1)-O at the end of AgO chain, whereas the reaction accelerates explosively upon the appearance of a chemical wave that propagates along the direction perpendicular to the chain. The surface morphology of the region swept over by the chemical wave completely changes from (5\(\times\)1)-O to that with many rectangular islands, indicating the formation of H\(_2\)O(OH)_2. The induction time and explosive acceleration with the propagating chemical wave imply that the reaction is autocatalytic. Water clusters hydrating OH produced likely play a central role in serving as a reservoir of H\(_2\)O to feed to the reaction and enhancing the reactivity of H\(_2\)O with O adatoms in AgO chains.
IX-N  Structures, Stabilities and Physicochemical Properties of Organometallic Hybrid Clusters

Recently, metal clusters have gained much attention because they exhibit novel physicochemical properties that are beyond the prediction made by a dimensional scaling of those of the corresponding bulk. In this regard, metal clusters protected by thiolates or stabilized by polymers are promising candidates for elementary units of nano-scale devices. Our interests are focused on the following issues on the organometallic hybrid clusters: (1) a large-scale preparation of the subnanometer-sized clusters, (2) development of size-selection method, (3) determination of chemical compositions of size-selected clusters (i.e. the numbers of metal atoms and organic molecules), and (4) elucidation of effect of the core size, core shape, and interaction with organic molecules on stabilities, electronic structures, and chemical properties.

IX-N-1 Aerobic Oxidation Catalyzed by Gold Nanoclusters as quasi-Homogeneous Catalysts: Generation of Hydrogen Peroxide Using Ammonium Formate

SAKURAI, Hidehiro; TSUNOYAMA, Hironori; TSUKUDA, Tatsuya


Gold(0) nanocluster with $d_{av} = 1.3\pm0.3$ nm stabilized by poly(N-vinyl-2-pyrrolidone) (Au:PVP-1) showed high catalytic activity toward the generation of hydrogen peroxide in water under ambient conditions using ammonium formate as a reductant. Generation of hydrogen peroxide was monitored by tracking the conversion of o-tolylboronic acid to o-cresol. In the presence of excess ammonium formate, o-cresol was obtained from o-tolylboronic acid with ~60% yield within 24 hours at 300 K. In order to investigate the dependence of the reactivity on cluster size, monodisperse gold nano-clusters (Au:PVP-$n$; $n=2–4$) with average diameters up to ~5 nm were prepared by the seed-mediated growth method using Na$_2$SO$_3$ as a reductant. Smaller cluster showed superior catalytic activity compared to larger clusters, suggesting that molecular oxygen species preferentially adsorbed on small Au clusters played an essential role in the formation of hydrogen peroxide.

IX-N-2 Spectroscopic Investigation of Dendrimer-Encapsulated Gold Clusters

IMAMURA, Masaki$^1$; MIYASHITA, Takeho$^1$; TANAKA, Akinori$^1$; YASUDA, Hidehiro$^1$; YANAGIMOTO, Yasushi; NEGISHI, Yuichi; TSUKUDA, Tatsuya

(1Kobe Univ.)


We have carried out the spectroscopic studies of dendrimer-encapsulated Au nanoclusters smaller than 2.4 nm. In this study, a 1.5th generation sodium carboxylate-terminated polyamidamine dendrimer was used as a template to control the size and stability of Au nanoclusters. The dendrimer-encapsulated Au nanoclusters were prepared by the chemical reduction of Au ions loaded within the dendrimer templates. The synthesized smallest nanocluster used in this work shows the strong blue photoluminescence at 2.8 eV photon energy, while larger nanocluster shows no photoluminescence. Furthermore, we carried out the X-ray photoemission study in the valence-band region of dendrimer-encapsulated Au nanocluster. From these results, we will discuss the size dependent properties of Au nanoclusters encapsulated within the dendrimer templates.

IX-N-3 Chromatographic Isolation of “Missing” Au$_{55}$ Clusters Protected by Alkanethiolates

TSUNOYAMA, Hironori; NEGISHI, Yuichi; TSUKUDA, Tatsuya


We report on the first synthesis of alkanethiolate-protected Au$_{55}$ (11 kDa), which has been a “missing” counterpart of Schmid’s Au$_{55}$(PR$_3$)$_{12}$Cl$_6$. Au:SC$_x$ clusters ($x=12, 18$) were prepared by the reaction of alkanethiol (C$_x$SH) with polymer-stabilized Au clusters (~1.3 nm) and subsequently incubated in neat C$_x$SH. The resulting clusters were successfully fractionated by recycling gel permeation chromatography into Au$_{38}$:SC$_x$ and Au$_{55}$:SC$_x$, and identified by laser-desorption ionization mass spectrometry. The Au$_{55}$:SC$_x$ clusters exhibited structured optical spectra, suggesting molecular-like properties. The thiolate monolayers were found to be liquid-like on the basis of the IR spectrum and the monolayer thickness estimated from the hydrodynamic diameter.

Figure 1. Isolation and characterization of Au$_{55}$:SC$_{18}$.


IX-N-4 Chiroptical Activity of BINAP-Stabilized Undecagold Clusters

YANAGIMOTO, Yasushi; NEGISHI, Yuichi;
**FUJIHARA, Hisashi**; TSUKUDA, Tatsuya
(1Kinki Univ.)


Undecagold cluster compounds \([Au_{11}(BINAP)_{4}X_{2}]^{+}\) (X = Cl and Br) were synthesized by chemical reduction of the corresponding precursor complexes, \(Au_{2}X_{2}\) (BINAP), where BINAP represents the bidentate phosphine ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. The circular dichroism spectra of \(Au_{11}\) stabilized by the enantiomers \(Au_{11}(R\text{-}BINAP)_{4}X_{3}\) and \(Au_{11}(S\text{-}BINAP)_{4}X_{3}\) exhibited intense and mirror-image Cotton effect, whereas those of \(Au_{11}^{3+}\) clusters stabilized by achiral monodentate phosphine ligands did not. The origin of the chiroptical activity of \([Au_{11}(BINAP)_{4}X_{2}]^{+}\) is discussed in the context of the structural deformation of the \(Au_{11}^{3+}\) core.

**Figure 1.** CD spectra of \([Au_{11}(BINAP)_{4}X_{2}]^{+}\).


**IX-N-5 Kinetic Stabilization of Growing Gold Clusters by Passivation with Thiolates**

NEGISHI, Yuichi; TAKASUGI, Yoshimitsu1; SATO, Seiichi1; YAO, Hiroshi1; KIMURA, Keisaku1; TSUKUDA, Tatsuya
(1Univ. Hyogo)


Small gold clusters (<1 nm), protected by monolayers of glutathione, \(N\text{-}(2\text{-mercaptobiotropionyl})\text{glycine or mercaptosuccinic acid, were prepared by reducing the corresponding Au(I)–thiolate polymers, and were fractionated by size using polyacrylamide gel electrophoresis (PAGE). Mass analysis of the fractionated clusters revealed that their core sizes varied with the molecular structures of the thiolates. This finding indicates that the reduction of the Au(I)–thiolate polymers yields small clusters whose growth is kinetically hindered by passivation with thiolates. Optical spectra of the clusters with identical compositions exhibited different profiles depending on the thiolate molecular structures, implying that deformation of the underlying gold cores is induced by inter-ligand interactions.

**Figure 1.** Kinetic stabilization of growing gold clusters by passivation with thiolates.


**IX-N-6 Size Effect on the Catalysis of Gold Clusters Dispersed in Water for Aerobic Oxidation of Alcohol**

TSUNOYAMA, Hironori; SAKURAI, Hidehiro; TSUKUDA, Tatsuya


We prepared a set of nearly monodisperse gold clusters ranging from 1.3 to 10 nm by a seed-mediated growth in the presence of poly(N-vinyl-2-pyrrolidone) (PVP). The seed clusters with a diameter of 1.3±0.3 nm were prepared by reducing \(AuCl_{4}^{-}\) with \(NaBH_{4}\) in a low-temperature aqueous solution of PVP. Subsequent reduction of more \(AuCl_{4}^{-}\) by \(Na_{2}SO_{3}\) in the presence of the seed clusters yielded a series of larger Au:PVP clusters. Catalytic activities of the Au:PVP clusters for aerobic oxidation of \(p\)-hydroxybenzyl alcohol increased with decrease in the core size. The size dependence is discussed in light of the electronic structures of the cores probed by optical spectroscopy.

**Figure 1.** Catalytic activities of the Au:PVP clusters for aerobic oxidation of \(p\)-hydroxybenzyl alcohol increased with decrease in the core size.


**IX-N-7 X-Ray Magnetic Circular Dichroism of Size-Selected, Thiolated Gold Clusters**

NEGISHI, Yuichi; TSUNOYAMA, Hironori; SUZUKI, Motohiro1; KAWAMURA, Naomi1; MATSUSHITA, M. Michio2; MARUYAMA, Koichi; SUGAWARA, Tadashi2; YOKOYAMA, Toshihiko; TSUKUDA, Tatsuya
(1JASRI/SPring-8; 2Univ. Tokyo)

We report herein the X-ray magnetic circular dichroism (XMCD) at the Au L\textsubscript{2,3} edges of a series of Au clusters protected by glutathione (GSH). The samples used here included Au\textsubscript{N} (SG)\textsubscript{M} with (N, M) = (10, 10), (15, 13), (18, 14), (22, 16), (25, 18), (29, 20), (39, 24) and a sodium gold(I) thiomalate (SGT) as a reference. Magnetic moments per cluster were found to be increased with size, whereas those per Au–S bond were nearly constant. This finding suggests that a localized hole created by Au–S bonding at the gold/glutathione interface, rather than the quantum size effect, is responsible for the spin polarization of gold clusters.

![Figure 1. Magnetic moments per cluster as a function of core size.](image1)


**IX-N-8 Mechanism of Selective Formation of Thiolated Au\textsubscript{25} Clusters in Ligand Exchange of Phosphine-Stabilized Gold Clusters: Size Focusing via Core Etching**

SHICHIHUBI, Yukatsu; NEGISHI, Yuichi; TSUNOYAMA, Hironori; KANEHARA, Masayuki\textsuperscript{1}; TERANISHI, Toshiharu\textsuperscript{1}; TSUKUDA, Tatsuya (\textsuperscript{1}Univ. Tsukuba)

Recently, we have succeeded in large-scale selective synthesis of Au\textsubscript{25}:SG clusters via ligand exchange reactions of triphenylphosphine-stabilized Au\textsubscript{11} clusters with glutathione (GSH) under optimized conditions (Shichibu, Y. et al. J. Am. Chem. Soc. 127, 13464 (2005)). The mechanism of the selective formation of Au\textsubscript{25}:SG was studied by monitoring the size distribution of the ligand exchange products using electrophoresis and optical absorption spectroscopy. It was found that the core size distributions of the Au\textsubscript{n}:SG clusters extracted at the initial stage are polydisperse and are subsequently focused into Au\textsubscript{25}:SG in the presence of free GSH molecules. The reaction of a series of the size-selected Au\textsubscript{n}:SG clusters (n = 10, 15, 18, 22, 25, 29, 33, 39) with free GSH under aerobic conditions revealed that two different reaction modes are operative depending on the core size. The Au\textsubscript{n}:SG (n < 25) clusters are completely oxidized to Au(I):SG complexes while Au\textsubscript{n}:SG (n ≥ 25) clusters are etched into Au\textsubscript{25}:SG by free GSH molecules. This indicates that the “ligand exchange reaction” we referred to in our previous paper, consists of two processes, i.e., a ligand exchange accompanying rapid agglomeration of Au cores and subsequent etching of the cores. We conclude that the extremely high stability of Au\textsubscript{25}:SG clusters against etching is the main cause for the selective formation.

Other gold clusters stabilized by polymer (ϕ = 1.3±0.3 nm) or triphenylphosphine (ϕ = 1.5±0.4 nm) were also converted selectively to Au\textsubscript{25}:SG by treatment with excess GSH, supporting the proposed mechanism.

![Figure 1. Mechanism of size focusing in the ligand exchange.](image2)
IX-O  Structural Analyses of Biological Macromolecules by Ultra-High Field NMR Spectroscopy

Our research seeks the underlying molecular basis for the function of biological macromolecules. In particular, we are interested in the function of molecular machines that work in the cellular processes involving protein folding, transport and degradation, and of glycoproteins playing important roles in the humoral and cellular immune systems. By use of ultra-high field NMR spectroscopy, we aim to elucidate the three-dimensional structure, dynamics, and interactions of proteins and glycoconjugates at the atomic level. Here we report stable-isotope-assisted NMR studies of Ufm1, a ubiquitin-like modifier, and IgG-Fc glycoprotein.

IX-O-1  Solution Structure and Dynamics of Ufm1, a Ubiquitin-Fold Modifier 1

SASAKAWA, Hiroaki¹; SAKATA, Eri²; YAMAGUCHI, Yoshiki³; KOMATSU, Masaaki³; TATSUMI, Kanako⁴; KOMINAMI, Eiki²; TANAKA, Keiji²; KATO, Koichi¹

(¹IMS and Nagoya City Univ.; ²Nagoya City Univ.; ³Tokyo Metropolitan Inst. Medical Sci. and Juntendo Univ.; ⁴Tokyo Metropolitan Inst. Medical Sci.; ⁵Juntendo Univ.)


The ubiquitin-fold modifier 1 (Ufm1) is one of various ubiquitin-like modifiers and conjugates to target proteins in cells through Uba5 (E1) and Ufc1 (E2). The Ufm1-system is conserved in metazoa and plants, suggesting its potential roles in various multicellular organisms. Herein, we analyzed the solution structure and dynamics of human Ufm1 (hsUfm1) by nuclear magnetic resonance spectroscopy. Although the global fold of hsUfm1 is similar to those of ubiquitin (Ub) and NEDD8, the cluster of acidic residues conserved in Ub and NEDD8 does not exist on the Ufm1 surface. ¹⁵N spin relaxation data revealed that the amino acid residues of hsUfm1 exhibiting conformational fluctuations form a cluster at the C-terminal segment and its spatial proximity, which correspond to the versatile ligand-binding sites of Ub and other ubiquitin-like proteins (Ubls). We suggest that Ub and other Ubl-modifiers share a common feature of potential conformational multiplicity, which might be associated with the broad ligand specificities of these proteins.

Figure 1. Backbone atom superposition of the final 10 structures (left) and ribbon representation of the lowest energy structure (right) of human Ufm1.

IX-O-2  Glycoform-Dependent Conformational Alteration of the Fc Region of Human Immunoglobulin G1 as Revealed by NMR Spectroscopy

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(¹IMS and Nagoya City Univ.; ²Nagoya City Univ; ³Kyowa Hakko Kogyo Co., Ltd.)


The Fc portion of immunoglobulin G (IgG) expresses the biantennary complex type oligosaccharides at Asn297 of the CH2 domain of each heavy chain with microheterogeneities depending on physiological and pathological states. These N-glycans are known to be essential for promotion of proper effector functions of IgG such as complement activation and Fcγ receptor (FcγR)-mediated activities. To gain a better understanding of the role of Fc glycosylation, we prepared a series of truncated glycoforms of human IgG1-Fc and analyzed their interactions with human soluble FcγRIIIa (sFcγRIIIa) and with staphylococcal protein A by surface plasmon resonance and nuclear magnetic resonance (NMR) methods. Progressive but less pronounced reductions in the affinity for sFcγRIIIa were observed as a result of the galactosidase and subsequent N-acetylhexosaminidase treatments of IgG1-Fc. The following endoglycosidase D treatment, giving rise to a disaccharide structure composed of a fucosylated GlcNAc, abrogated the affinity of IgG1-Fc for sFcγRIIIa. On the other hand, those glycosidase treatments did not significantly affect the affinity of IgG1-Fc for protein A. Inspection of stable-isotope-assisted NMR data of a series of Fc glycoforms indicates that the stepwise trimming out of the carbohydrate residues results in concomitant increase in the number of amino acid residues perturbed thereby in the CH2 domains. Furthermore, the cleavage at the GlcNAcβ1-4GlcNAc glycosidic linkage induced the conformational alterations of part of the lower hinge region, which makes no direct contact with the carbohydrate moieties and forms the major FcγR-binding site, while the conformation of the CH2/CH3 interface was barely perturbed that is the protein A-binding site. These results indicate that the carbohydrate moieties are required for maintaining the structural integrity of the FcγR-binding site.
Figure 1. Mapping on the crystal structure of IgG1-Fc of the amino acid residues perturbed upon deglycosylation of carbohydrate chains attached onto Fc.
IX-P-1 Design and Construction of Variably Polarized Undulator

KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; HAYASHI, Kenji; HARU, Toru

(1RIKEN/SPring-8)

A new undulator was designed and constructed, which will provide bright VUV radiation to a beam-line BL7U at UVSOR-II. The period length and number of periods are 76 mm and 40, respectively. Permanent magnet blocks made of Nd-Fe-B are arranged in Apple-II configuration. The undulator has capability of producing linear polarized light in both planes (horizontal and vertical) and circular polarized light in both directions (right handed and left handed).

A new beam duct for this undulator was also designed and constructed. The vertical aperture is 18 mm, which is narrowest in the UVSOR-II storage ring. The inner wall was covered by a Cu layer of 100 micron thick to reduce resistive wall impedance. The duct is pumped by two sputtering ion pumps and three NEG pumps.

The duct was successfully installed in the ring. Soon after finishing the field measurement, the undulator will be installed in the ring.

IX-P-2 Upgrade of Booster Synchrotron Magnet Power Supplies

KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; HAYASHI, Kenji

Top-up operation is a new technology to keep the intensity of electron beam circulating in a storage ring approximately constant by replenishing electrons frequently, typically with an interval of several minutes. The constant intensity of synchrotron radiation (SR) realized by this scheme will enable more accurate experiments.

Preparing for the top up injection, energy upgrade of the booster synchrotron is in progress at UVSOR-II. The maximum energy of the booster synchrotron had been limited at 600 MeV by the capacity of the magnet power supply, which is lower than the operation energy of the storage ring, 750 MeV. New power supplies compatible with the full energy injection were designed and constructed. In July, 2006, the power supplies were replaced. The acceleration to 600 MeV was successfully tested. Soon, full energy acceleration will be tested.

IX-P-3 One Watt Lazing in Deep UV Region of UVSOR-II Free Electron Laser

HOSAKA, Masahito; KATOH, Masahiro;

MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; SHIMADA, Miho; TAKASHIMA, Yoshifumi; HARU, Toru

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The shortest wavelength of the UVSOR free electron laser (FEL) had been at 239 nm for many years. However, the low emittance owing to the new magnetic lattice introduced in 2003 and the higher peak current owing to the new RF cavity installed in 2005 have drastically increased the gain of FEL. The higher gain have made the FEL oscillate in deep UV region with high output power. The shortest wavelength is now 215 nm with output power of several milli-watt level. Lasing at shorter wavelength around 230 nm was tried in near future. Average output power exceeding one watt was recorded at the wavelength of 230 nm. Some users experiments using this high power deep UV laser have started and a few others are under planning.

IX-P-4 Production of Coherent Terahertz Radiation by Laser Bunch Slicing Method

KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; YAMAZAKI, Jun-ichiro; SHIMADA, Miho; KIMURA, Shin-ichi; TAKASHIMA, Yoshifumi; TAKAHASHI, Toshiharu; HARU, Toru

(1Nagoya Univ.; 2Kyoto Univ.; 3RIKEN/SPring-8)

Laser bunch slicing is a technology to slice out a part of an electron bunch moving with relativistic velocity in particle accelerators. At UVSOR-II, an Ti:Sa laser which can be synchronized with the RF acceleration of the electron storage ring was installed in 2005. By using the existing optical system and the optical klystron for the free electron laser experiment, we have started a laser bunch slicing experiment, aiming to produce intense terahertz radiation. As a result of the interaction between the laser pulse and the electron bunch, a dip is created on the longitudinal density structure of the electron bunch. The width of the dip is basically same as the laser pulse width; sub-pico-second in our case. An electron bunch which has such structure emits intense coherent terahertz radiation. The terahertz radiation synchronized with the laser injection was successfully observed at an existing beam-line BL6B, which is one of the most powerful infrared beam-line in the world. The observed intensity of the terahertz pulses is \(10^{4-5}\) times higher than that of normal synchrotron radiation. The intensity was observed to be proportional to the square of the electron intensity. This clearly indicates that the observed terahertz pulses are produced by coherent radiation.
IX-P-5 Coherent Harmonic Generation by Using Ultra-Short Pulse Laser

LABAT, Marie1; COUPRIE, Marie, Emmanuelle1; LAMBERT, Guillaume1; HARA, Toru2; KATOH, Masahiro; HOSAKA, Masahito; MOCHIHASHI, Akira; TAKASHIMA, Yoshifumi3

(1CEA; 2IMS and RIKEN/SPring-8; 3Nagoya Univ.)

Coherent harmonic generation was successfully demonstrated at UVSOR-II. In the experiment, ultra-short laser pulses are injected to the storage ring. The laser pulses and the electron pulses interact in an optical klystron type undulator. The electrons are either accelerated or decelerated depending on the phase of the laser field. As the result, a periodic energy modulation is created on the electron pulse, whose period is exactly same as the laser wavelength. This energy modulation is converted to a density modulation, which has a periodicity of laser wavelength and its higher harmonics. Electron bunches which have such a longitudinal density structure emit coherent radiation at the laser wavelength and also at its higher harmonics. Intense radiation at the third harmonic (267 nm) synchronized with the laser injection was successfully observed. The intensity of the coherent harmonics was proportional to the square of the intensity of the electron pulses. This clearly indicates that the observed radiation is a coherent harmonic radiation.

IX-Q Researches by the Use of UVSOR

IX-Q-1 Experimental Investigation of Core-Valence Double Photoionization

HIKOSAKA, Yasumasa; AOTO, Tomohiro1; LABLANQUIE, Pascal2; PENENT, Francis2; SHIGEMASA, Eiji; ITO, Kenji1

(1KEK-PF; 2LCP-MR)


Core-valence double photoionization has been observed in Ne atoms and N2 molecules using a magnetic bottle time of flight spectrometer. The multi-electron coincidence datasets give complete information on the energy correlations between all emitted electrons, which supports a detailed description of the core-valence double photoionization process including direct spectroscopy of the core-valence doubly ionized states, the final states populated by their Auger decay and details of the dynamics of core-valence double photoionization for selected states.

IX-Q-2 Efficient Production of Metastable Fragments around the 1s Ionization Threshold in N2

HIKOSAKA, Yasumasa; LABLANQUIE, Pascal1; SHIGEMASA, Eiji

(1LCP-MR)


Metastable formation has been investigated in the inner-shell region of N2. Enhanced N* formation has been observed around the 1s threshold, and is shown to result from dissociation of high N2+ Rydberg states. These N2+ states are populated by spectator Auger decay from the core-excited states, as well as by the recapture of slow photoelectrons into the Rydberg orbitals. The present measurement demonstrates that the metastable observation is a new and sensitive tool to study the decay dynamics of core-excited states and the photoelectron recapture due to post-collision interaction.

IX-Q-3 Anisotropic Fragment Emission on Valence Photoionization of CF4

HIKOSAKA, Yasumasa; SHIGEMASA, Eiji

[J. Electron Spectrosc. Relat. Phenom. 152, 29 (2006)]

Photoion images from photoionization of CF4 with an isotropic geometry have been measured in the photon energy range of 17–60 eV. Fragment ion emissions below 40 eV are found to be anisotropic with respect to the electric vector of the linearly polarized light. This observation directly implies that the Td symmetry is broken on the dissociative photoionization process. The excited states associated with the transitions to the unoccupied orbitals are subject to symmetry lowering, which promotes the anisotropic fragment emissions from the highly-symmetrical molecule.

IX-Q-4 Auger Decay of Ne 1s Photoionization Satellites Studied by a Multi-Electron Coincidence Method

HIKOSAKA, Yasumasa; AOTO, Tomohiro1; LABLANQUIE, Pascal2; PENENT, Francis2; SHIGEMASA, Eiji; ITO, Kenji1

(1KEK-PF; 2LCP-MR)


The Auger decay of Ne 1s photoionization satellite states is studied with a magnetic-bottle multi-electron coincidence method. The energy correlations among the multi-electrons associated with the double Auger decay from the Ne* satellite states are extracted from the accumulated coincidence dataset. It is concluded that the Ne2+ states populated through the initial Auger decays from the Ne* satellite states can be excited states that lie
above the Ne\(^{3+}\) threshold. Their subsequent decay produces slow electrons in the 0–25 eV kinetic energy range. Possible assignments of the intermediate Ne\(^{2+}\) and the final Ne\(^{3+}\) states are given.

**IX-Q-5 Inner-Valence States of N\(^{2+}\) and the Dissociation Dynamics Studied by Threshold Photoelectron Spectroscopy and Configuration Interaction Calculation**

AOTO, Tomohiro\(^1\); ITO, Kenji\(^1\); HIKOSAKA, Yasumasa; SHIBASAKI, Akihiro\(^2\); HIRAYAMA, Ryo\(^2\); YAMAMOTO, Norifumi\(^2\); MIYOSHI, Eisaku\(^2\)

\(^1\)KEK-PF; \(^2\)Kyushu Univ.; \(^3\)PTCL; \(^4\)KEK-PF

The N\(^{2+}\) states lying in the ionization region of 26–45 eV and the dissociation dynamics are investigated by high-resolution threshold photoelectron spectroscopy and threshold photoelectron-photoion coincidence spectroscopy. The threshold photoelectron spectrum exhibits several broad bands as well as sharp peaks. The band features are assigned to the N\(^{2+}\) states associated with the removal of an inner-valence electron, by a comparison with a configuration interaction calculation. In contrast, most of the sharp peaks on the threshold photoelectron spectrum are allocated to ionic Rydberg states converging to N\(^{2+}\). Dissociation products formed from the inner-valence N\(^{2+}\) states are determined by threshold photoelectron-photoion coincidence spectroscopy. The dissociation dynamics of the inner-valence ionic states is discussed with reference to the potential energy curves calculated.

**IX-Q-6 Electron Correlation in Xe 4d Auger Decay Studied by Slow Photoelectron–Auger Electron Coincidence Spectroscopy**

SHEINERMAN, Sergei\(^1,2\); LABLANQUE, Pascal\(^1\); PENENT, Francis\(^1\); PALAUDOUX, Jerome\(^1\); ELAND, John\(^2\); AOTO, Tomohiro\(^3\); HIKOSAKA, Yasumasa; ITO, Kenji\(^4\)

\(^1\)Kyoto Univ.; \(^2\)NSRRC; \(^3\)St. Petersburg Univ.; \(^4\)PTCL; \(^5\)KEK-PF

Two different experimental methods, namely threshold electron–Auger electron coincidences and slow photoelectron–Auger electron coincidences are applied to investigate the Xe 4d Auger decay in the near-threshold region and reveal the essential role of electron correlation. The coincidences allow us to select the different channels for the Xe 4d Auger decay which lead to different final states of the Xe\(^{2+}\) ion: 5s\(^{-2}\)(1S\(_0\)), 5s\(^{-1}\)5p\(^{-1}\)(1P\(_1\)), 5p\(^{-2}\)(1S\(_0\)), 5p\(^{-2}\)(2P\(_2\)), 5p\(^{-1}\)5p\(^{-1}\)(1P\(_1\)), 5p\(^{-2}\)(1D\(_2\)), 5p\(^{-2}\)(P\(_{0,1}\)) and 5p\(^{-3}\)(P\(_2\)). Measurements of the threshold electrons with the first method reveal strong PCI distortion of electron spectra in all channels. Comparison with calculations carried out in the framework of the quantum-mechanical PCI model allows us to clarify the dynamics of threshold electron production. In the 5p\(^{-2}\)(1S\(_0\)) channel, the main contribution comes from the PCI retardation of slow photoelectrons. In the 5p\(^{-2}\)(1D\(_2\)) and 5p\(^{-2}\)(P\(_1\)) final state channels, additional processes of PCI recapture followed by valence multiplet decays play a role at and below the N\(_4\) and N\(_5\) thresholds. The slow photoelectron spectra measured by the second method reveal also a strong PCI distortion. Analysis within the framework of the eikonal model shows the influence of the Auger electron on the PCI distorted line shapes.

**IX-Q-7 Development of Symmetry-Resolved Zero-Kinetic-Energy Photoelectron Spectroscopy for Probing Multielectron Processes**

GEJO, Tatsuo\(^1\); NAKAMURA, Eiken; SHIGEMASA, Eiji

\(^1\)Univ. Hyogo

A new experimental setup for probing multielectron processes in molecular inner-shell ionization regions has been developed. Symmetry-resolved zero-kinetic-energy (ZEKE) spectra have been measured by scanning the photon energy along with monitoring the intensity of the coincidence signals between ZEKE electrons and fragment ions detected at 0° and 90° relative to the electric vector of the light. The actual performance of the method is illustrated by using it to reveal the symmetry decomposition of the multielectron processes, such as double excitations and shake-up satellites, in the K-shell ionization region of nitrogen.

**IX-Q-8 Iron-Based Heavy Quasiparticles in SrFe\(_4\)Sb\(_{12}\): An Infrared Spectroscopic Study**

KIMURA, Shin-ichi; MIZUNO, Takafuli\(^1\); IM, Hojun\(^1\); HAYASHI, Katsuyuki\(^2\); MATSUOKA, Eiichi\(^2\); TAKABATAKE, Toshiro\(^2\)

\(^1\)SOKENDAI; \(^2\)Hirosima Univ.

Temperature-dependent infrared reflectivity spectra of SrFe\(_4\)Sb\(_{12}\) have been measured. A renormalized Drude peak with a heavy effective mass and a pronounced pseudogap of 10 meV develops in the optical conductivity spectra at low temperatures. As the temperature decreases below 100 K, the effective mass (m\(^*\)) rapidly increases, and the scattering rate (1/\(\tau\)) is quenched. The temperature dependence of m\(^*\) and 1/\(\tau\) indicates that the hybridization between the Fe 3d spins and the charge carriers plays an important role in determining the physical properties of SrFe\(_4\)Sb\(_{12}\) at low temperatures. This result is the clear evidence of the iron-based heavy quasiparticles.

**IX-Q-9 Optical Pseudogap from Iron States in Filled Skutterudites AFe\(_4\)Sb\(_{12}\): An Infrared Spectroscopic Study**

SICHELSCHMIDT, J.\(^1\); VOEVODIN, V.\(^1\); IM, Hojun\(^2\); KIMURA, Shin-ichi; ROSNER, H.\(^1\); LEITHE-JASPER, A.\(^1\); SCHINELLE, W.\(^1\); BURKHARDT, U.\(^1\); MYDOSH, J. A.\(^1\); GRIN, Yu.\(^1\);
Optical investigations are presented of the filled skutterudites A$\text{Fe}_4\text{Sb}_{12}$ with divalent cations $A = \text{Yb, Ca, Ba}$. For each of these compounds a very similar pseudo-gap structure in the optical conductivity develops in the far-infrared spectral region at temperatures below 90 K. Highly accurate local-density approximation electronic band structure calculations can consistently explain the origin of the pseudogap structure generated largely by transition metal 3d states. In particular, a 4f-conduction electron hybridization or strong correlations can be ruled out as origin for the pseudogap.

IX-Q-10 Continuity of Ce 4f Electronic Structure across the Quantum Critical Point: A Resonant Photoemission Study on CeNi$_{1-x}$Co$_x$Ge$_2$

IM, Hojun$^1$; ITO, Takahiro; HONG, J. B.$^2$; KIMURA, Shin-ichi; KWON, Yong-seung$^2$

(1SOKENDAI; 2Sungkyunkwan Univ., Korea)

[Phys. Rev. B 72, 220405(R) (4 pages) (2005)]

Ce 3d–4f and 4d–4f resonant photoemission spectroscopies have been performed on the heavy-fermion compound CeNi$_{1-x}$Co$_x$Ge$_2$, where the ground-state properties systematically change from the magnetic (0 $<$ x $<$ 0.3) to nonmagnetic (0.3 $<$ x $<$ 1.0) regime via the quantum critical point (QCP, x = 0.3). Co-substitution dependence of the bulk Ce 4f electronic structure shows gradual evolution of Kondo resonance at the Fermi level together with the reduction of the Ce 4f$^0$ ground state in agreement with the single impurity Anderson model (SIAM). The SIAM analysis shows that the Kondo temperature and specific-heat coefficient change continuously from the weakly hybridized CeNiGe$_2$ to strongly hybridized CeCoGe$_2$. These indicate that the Ce 4f electronic structure of CeNi$_{1-x}$Co$_x$Ge$_2$ changes continuously through the QCP.

IX-Q-11 Optical Study on Clathrates Sr$_3$Ga$_{16}$Ge$_{30}$ and $\beta$-Eu$_5$Ga$_{16}$Ge$_{30}$

SAKURAL, Yoko; NISHI, Tatsuhiko$^1$; KIMURA, Shin-ichi; KWON, Yong-seung$^2$; AVILA, M. A.$^3$; TAKABATAKE, Toshiro$^4$

(1SOKENDAI; 2Sungkyunkwan Univ., Korea; 3Kobe Univ.; 4Hiroshima Univ.)


The optical reflectivity spectra of clathrates Sr$_3$Ga$_{16}$Ge$_{30}$ and $\beta$-Eu$_5$Ga$_{16}$Ge$_{30}$ have been measured to investigate their electronic structure. A clear Drude shape was observed in the spectrum of Sr$_3$Ga$_{16}$Ge$_{30}$. On the other hand, a broad Drude shape due to magnetic scattering by Eu 4f electrons and a peak originated from Eu 4f states were observed in the spectrum of $\beta$-Eu$_5$Ga$_{16}$Ge$_{30}$. No clear change of optical conductivity due to the magnetic order was observed in $\beta$-Eu$_5$Ga$_{16}$Ge$_{30}$ and no evidence of the rattling in Sr$_3$Ga$_{16}$Ge$_{30}$ observed in contrast to $\alpha$-Eu$_5$Ga$_{16}$Ge$_{30}$. These results essentially originated from the large carrier density of these materials.

IX-Q-12 Infrared Study on Electronic Structure of Sr$T_4$Sb$_{12}$ ($T$ = Fe, Ru)

KIMURA, Shin-ichi; IM, Hojun$^1$; SAKURAL, Yoko; MIZUNO, Takafumi$^1$; TAKAGAHARA, Katsuhiko$^2$; HARIMA, Hisatomo$^3$; HAYASHI, Katsuyuki$^4$; MATSUOKA, Eiichi$^5$; TAKABATAKE, Toshiro$^4$

(1SOKENDAI; 2Hiroasaki Univ.; 3Kobe Univ.; 4Hiroshima Univ.)

[Physica B 383, 137–139 (2006)]

The temperature dependent optical conductivity spectrum of strontium filled skutterudites Sr$T_4$Sb$_{12}$ ($T$ = Fe, Ru) has been measured to investigate the origin of the heavy-fermion-like physical properties and the enhancement of the thermopower at around 50 K. The optical conductivity spectra of $T$ = Fe and Ru at the temperature of 7 K have peak structures at the photon energies of 24 and 190 meV, respectively. From the band structure calculation, the peaks correspond to the density of states (DOS) mainly originating from the Fe 3d and Ru 4d characters locating in the unoccupied states, i.e., SrFe$_4$Sb$_{12}$ has a very narrow band near the Fermi level ($E_F$) than SrRu$_4$Sb$_{12}$. The shape of DOS near $E_F$ is concluded to be the origin of the unconventional physical properties.

IX-Q-13 Angle-Resolved Photoemission Study on CeTe$_2$

ITO, Takahiro; IM, Hojun$^1$; KIMURA, Shin-ichi; KWON, Yong-seung$^2$

(1SOKENDAI; 2Sungkyunkwan Univ., Korea)


We have used angle-resolved photoemission spectroscopy as a function of excitation energy to elucidate the three dimensionality at the electronic structure of quasi-two-dimensional strongly correlated Ce 4f electron compound CeTe$_2$. We observed that there are two types of Te 5p bands along IZ symmetry line at the valence band, one is non-dispersive bands and the other is dispersive one. While the former is ascribed to the Te quasi-two-dimensional strongly correlated CeTe$_2$. We observed that there are two types of Te 5p bands along IZ symmetry line at the valence band, one is non-dispersive bands and the other is dispersive one. While the former is ascribed to the Te double layers relating to the CDW formation, the latter to one at CeTe double layers.

IX-Q-14 High-Resolution Photoemission Spectroscopy of CeNiGe$_2$ and CeCoGe$_2$

IM, Hojun$^1$; ITO, Takahiro; KIMURA, Shin-ichi; HONG, J. B.$^2$; KWON, Yong-seung$^2$

(1SOKENDAI; 2Sungkyunkwan Univ., Korea)


We have performed the high-resolution photoemis-
sition spectroscopy on the isostructural heavy fermion compounds, CeCoGe$_2$ and CeNiGe$_2$, as the representative samples of CeNi$_{1-x}$Co$_x$Ge$_2$ to investigate the origin of the wide Ce 4f characters from the magnetic ($x = 0$) to non-magnetic regime ($x = 1$) via the quantum critical point ($x = 0.3$). We directly observed a Kondo peak, whose width corresponds to the Kondo temperature, in both materials but the crystal field splitting only in CeNiGe$_2$. Both the Kondo temperature and the crystal field splitting are concluded to be affected by the hybridization between Ce 4f and Ni/Co 3d states.

**IX-Q-15 Infrared Absorption in Heavy Fermion System CeNi$_{1-x}$Co$_x$Ge$_2$**

KWON, Yong-seung$^1$; HONG, J. B.$^1$; IM, Hojun$^2$; NISHI, Tatsuhiko$^2$; KIMURA, Shin-ichi

($^1$Sungkyunkwan Univ.; Korea; $^2$SOKENDAI)


We have measured optical conductivity spectra $\sigma(\omega)$ of CeNi$_{1-x}$Co$_x$Ge$_2$ at several temperatures. The $\sigma(\omega)$ spectra exhibit two peaks in middle infrared regions at low temperatures. The peaks show a strong temperature dependence and disappear above a characteristic temperature ($T^*$) at last. We suggest that the middle infrared peaks arise from transitions between d-states below $E_F$ and c–f hybridization states just above $E_F$. 
Although development of lasers is remarkable, there are no lasers which lase in ultraviolet and far infrared regions. However, it is expected that these kinds of lasers break out a great revolution in not only the molecular science but also in the industrial world.

In this project we research characters of new materials for ultraviolet and far infrared lasers, and develop new lasers by using these laser materials.

IX-R-1 Photonic-Crystal-Fiber Pigtail Device Integrated with Lens-Duct Optics for Terahertz Radiation Coupling

DIWA, Girbert; QUEMA, Alex; ESTACIO, Elmer; POBRE, Romeric1; MURAKAMI, Hidetoshi; ONO, Shingo; SARUKURA, Nobuhiko (1De La Salle Univ.)

[Appl. Phys. Lett. 87, 151114 (2005)]

An integrated optics called terahertz (THz) pigtail, which is comprised of an emitter, an optically transparent launching media, and a waveguide, is devised and fabricated. The InAs emitter under a 1 T magnetic field is coupled to the launching media using silicone grease, an index matching liquid. The launching media, a lens duct made from a polymer based on poly 4-methyl pentene-1 (commonly known as TPX), is designed based on the concept of guiding THz radiation into Teflon photonic crystal fiber (PCF) waveguide by means of total internal reflection. It is found that the constructed THz lens duct is able to channel and couple the THz radiation into the PCF waveguide with a loss of < 1 dB. The results here show that the idea of using the THz pigtail can be a potential means of effectively directing THz radiation.

IX-R-2 Band-Structure Design of Fluoride Complex Materials for Deep-Ultraviolet Light-Emitting Diodes

ONO, Shingo; EL OUENZERFI, Riadh; QUEMA, Alex; MURAKAMI, Hidetoshi; SARUKURA, Nobuhiko; NISHIMATSU, Takeshi1; TERAKUBO, Noriaki1; MIZUSEKI, Hiroshi1; KAWAZOE, Yoshiyuki1; YOSHIKAWA, Akira1; FUKUDA, Tsugo1 (1Inst. Phys. Elect.)

[Jpn. J. Appl. Phys. 44, 7984 (2005)]

Nonlinear absorption properties of Ce3+-doped LiCaAlF6 (Ce:LiCAF) crystals at wavelength of 266 nm are studied using open-aperture Z-scan method and a Q-switch Nd:YAG laser. Saturable absorption of solid-state materials in ultraviolet region is demonstrated for the first time.

IX-R-3 Ce3+-Doped LiCaAlF6 Crystals as a Solid-State Ultraviolet Saturable Absorber and Role of Excited State Absorption

HAI, Le Hoang1; HUNG, Nguyen Dai1; QUEMA, Alex; DIWA, Girbert; MURAKAMI, Hidetoshi; ONO, Shingo; SARUKURA, Nobuhiko (1De La Salle Univ.)

[Appl. Phys. Lett. 87, 261112 (2005)]

Terahertz (THz) radiation generated from photoconductive antenna fabricated on a single crystal zinc oxide (ZnO) is presented. The THz-radiation power is saturated at bias voltages above 800 V/cm and the obtained spectrum extends up to 1 THz. Moreover, ZnO is found to be highly transparent in the visible, near-infrared, mid-infrared and THz frequency regions. The results depicted here will categorically unravel the prospects of using ZnO as a material for integrated active optics.

IX-R-4 Generation of Terahertz Radiation Using Zinc Oxide as Photoconductive Material Excited by Ultraviolet Pulses

ONO, Shingo; MURAKAMI, Hidetoshi; QUEMA, Alex; DIWA, Girbert; SARUKURA, Nobuhiko; NAGASAKA, Ryujiro1; ICHIKAWA, Yo1; OGINO, Hiraku2; OISHIMA, Eriko2; YOSHIKAWA, Akira2; FUKUDA, Tsugo2 (1Inst. Phys. Elect.; 2Tohoku Univ.)

IX-R-5 Ultraviolet Irradiation Effect of Ce3+-Doped BaMgF4 Crystals

HAYASHI, Eiji1; ITO, Kiyotaka1; YABASHI, Satoshi1; YAMAGA, Miisu1; KODAMA, Nobuhiro2; ONO, Shingo; SARUKURA, Nobuhiko

The design principle for fluoride-containing optical devices for applications in the deep ultraviolet range is discussed. Variations in band gap energy, band structure and lattice constant of LiBa2CaSr(1-x-y)F6 and LiBa(1-x)K1Ba(1-y)MgF3 have been studied. The band structure and transition type of these fluorides are predicted by ab initio band calculations based on the local density approximation. The lattice-matched double-hetero structure of direct-band-gap compounds LiBa2CaSr(1-x-y)F6 on LiSrF3 and LiBa2CaSr(1-x-y)F6 on either LiBaF3 or KMgF3 is sufficiently feasible to fabricate.
Ce³⁺-doped BaMgF₄ (BMF) crystals have the absorption and luminescence spectra in the vacuum ultraviolet (VUV) and ultraviolet (UV) ranges. Strong excitation of the fourth harmonic (266 nm) of a pulsed Nd:YAG laser colours the BMF crystal brown and produces a new luminescence spectrum with double peaks at 445 and 500 nm and a lifetime of less than 10 ns. When the sample temperature is elevated up to 200 degrees C, the crystal colour is changed from brown to green. The colouration is due to localized electrons and holes created by the strong UV excitation, which are identified by the electron spin-resonance (ESR) technique. This new luminescence may be due to Ce³⁺ perturbed by the colour centres.

IX-R-6 Vacuum Ultraviolet and Ultraviolet Spectroscopy of BaMgF₄ Codoped with Ce³⁺ and Na⁺

HAYASHI, Eiji¹; ITO, Kiyotaka¹; YABASHI, Satoshi¹; YAMAGA, Mitsuo¹; KODAMA, Nobuhiro²; ONO, Shingo; SARUKURA, Nobuhiko

(J. Lumin. 119, 69 (2006))

Ce³⁺/Na⁺-doped BaMgF₄ (BMF) crystals with a nonlinear property show strong absorption in the vacuum ultraviolet (VUV) and ultraviolet (UV) ranges. Three different fluorescence bands (A, B, C) at 300, 340, and 430 nm were observed when pumped at different wavelengths. Under excitation of the fourth harmonic (266 nm) from a pulsed Nd:YAG laser the BMF crystal changed its colour from transparent to brown due to formation of colour centres. The A, B and C bands are assigned to three different sites of Ce³⁺: site A is Ce³⁺ substituting for perfect Ba²⁺ sites; site B is Ce³⁺ (Ba²⁺) perturbed by Na⁺ as a charge compensator; and site C is a complex composed of Ce³⁺ and F⁻ vacancies, which trapped one or two electrons.

IX-R-7 Vacuum Ultraviolet Spectroscopy of Ce³⁺-Doped SrMgF₄ with Superlattice Structure

YAMAGA, Mitsuo¹; HAYASHI, Eiji¹; KODAMA, Nobuhiro²; ITO, Kiyotaka¹; YABASHI, Satoshi¹; MASUI, Yuki¹; ONO, Shingo; SARUKURA, Nobuhiko; HAN, T. P. J.³; GALLAGHER, H. G.³

(J. Phys.: Condens. Matter 18, 6033 (2006))

X-ray diffraction of Ce³⁺-doped SrMgF₄ (SMF:Ce) crystals shows a superlattice structure, reflecting the distribution of Ce³⁺ polyhedra centres observed in optical experiments. Optical absorption bands and fluorescence bands from the Ce³⁺ polyhedra centres overlap in the vacuum ultraviolet (VUV) and ultraviolet (UV) regions, respectively, so that wide pumping and tuning ranges are expected for laser operation. The SMF: Ce crystals, as well as the isomorphous BaMgF₄, are candidates for a tunable laser gain material with nonlinear properties. The optical absorption, excitation, and fluorescence bands observed in the SMF: Ce crystals at low temperatures are ascribed to five distinct fluorescent centres. Three centres have well-known Ce³⁺ optical characters, for example, fluorescence with double peaks separated by 2000 cm⁻¹ and five resolved absorption/excitation bands. These centres are assigned to Ce³⁺-polyhedra classified by weak and strong crystal fields as a consequence of the superlattice structure. The other two fluorescence bands observed in the visible region have 1.5–2 times larger linewidths than those of the former three bands. These bands are interpreted as optical transitions from complexes consisting of Ce³⁺ and one or two electrons trapped at a vacancy of the nearest neighbour F⁻-ligand ions.
IX-S Development and Research of Advanced Tunable Solid State Lasers

Diode-pumped solid-state lasers can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Additionally, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. These kinds of advanced tunable solid-state light sources, so to speak “Chroma Chip Lasers,” will assist the research of molecular science.

In this projects we are developing Chroma Chip Lasers based on diode-pumped-microchip-solid-state lasers and advanced nonlinear frequency conversion technique.

IX-S-1 300W Continuous-Wave Operation of Diode Edge-Pumped, Hybrid Composite Yb:YAG Microchip Laser

TSUNEKANE, Masaki; TAIKA, Takunori


300 W continuous-wave operation of a diode edge-pumped, hybrid (single-crystal/ceramic) composite, Yb3+ :YAG microchip laser with a 5-mm-diameter and 300-μm thickness, single-crystal core uniformly bonded to a water-cooled heat-sink by the new Au–Sn soldering system has been demonstrated. The beam quality factor, $M^2$ follows the mode-mismatch between the core and the fundamental mode, and was improved to 17 with the maximum output power of 230 W. The thermally induced convex mirror with a spherical radius of curvature ranging from –2.5 to –1.5 m, which decreases as the pump power increases by thermal deformation of a microchip, was observed.

Figure 1. CW output power and the beam quality characteristics ($M^2$ factor) with four different cavity configurations as a function of input pump power.


SATO, Yoichi; TAIKA, Takunori; IKESUE, Akio1 (1JFCC)

[OSA Topical Meeting of Advanced Solid State Photonics TuB3 (2006)]

We have fabricated the all-ceramic layered composite device with Nd:YAG and Nd:YSAG, which can perform efficient laser oscillation. From its spectroscopic properties, this layer-by-layer composite device will offer new function of laser oscillation by pump wavelength tuning. For example when pumped from YSAG side at 810.5 nm, it can oscillate at 1064 nm. On the other hand, it will oscillate at 1061 nm when pumped at 808.5 nm.

Due to the difference in the dependence on the wavelength of the portion of the pumped power absorbed in Nd:YAG-layer and in Nd:YSAG-layer depends on the pumping wavelength. This resulted in the tuning of the component ratio of the Nd:YAG and Nd:YSAG in the fluorescence. The dependence of fluorescence profiles in this composite on the pump wavelength is shown in Figure 1.

Figure 1. Measured fluorescent spectral profiles by changing pumping wavelength.

IX-S-3 Thermal Properties of Y3Al5O12, GdVO4, and YVO4

SATO, Yoichi; TAIKA, Takunori
We have measured thermal conductivity of Y₃Al₅O₁₂, GdVO₄, and YVO₄. In order to avoid the misleading from three-dimensional (3D) thermal diffusion, we developed the quasi-one-dimensional (q1D) flash method. By taking in account the heat radiation effect in transparent materials for this measurement, YVO₄ was found to have larger thermal conductivity than GdVO₄. The measured thermal conductivities were 12.1, 10.5, 10.1, 8.9, and 8.5 W/mK for c-cut YVO₄, c-cut GdVO₄, YAG, a-cut YVO₄, and a-cut GdVO₄, respectively. The measured value in the range from room temperature to 200 °C is shown in Figure 1. The dependence of Nd conductivity coefficient (dNd/dT) for convenient evaluation of the doping effect in thermal conductivity is also discussed.

**Figure 1.** Thermal conductivities of undoped YAG, GdVO₄, and YVO₄.

**IX-S-4 Spectroscopic Properties and Laser Operation of RE³⁺-Ion Doped Garnet Materials**

TAIRA, Takunori; SATO, Yoichi; SAIKAWA, Jiro; IKESUE, Akio¹

¹JFCC

[Proc. SPIE 6216, 62160J (2006)]

Lately developed RE³⁺-ion-doped disordered laser ceramic materials, Y₃Sc₃Al₅₋ₓO₁₂, which are a solid solution of YAG and Y₃Sc₂Al₃O₁₂ (YSAG), have been interested in because of its compositional tuning of parameter x. The disordered Y₃Sc₃Al₅₋ₓO₁₂ (YAG/YSAG) ceramics exhibit relatively low minimum pump intensity (Iₘᵟᵣ₉) and broad emission bandwidth. The value of Iₘᵟᵣ₉ in the Yb:Y₃Sc₃Al₅₋ₓO₁₂ ceramics was found to be 2/3 compared with the Yb:YAG single crystal under 970nm zero-line pumping. Efficient laser oscillation of 72% slope efficiency was obtained for input power. Next, we have demonstrated passively mode-locked Yb:Y₃Sc₃Al₅₋ₓO₁₂ disordered ceramic laser by using a semiconductor saturable-absorber mirror. Pulses as short as 280 fs having an average power of 62 mW at 1035.8 nm was obtained as shown in Figure 1. As a conclusion, the possibility of tailored fluorescence spectral profile in layer-by-layer type ceramic composite is also discussed.

**Figure 1.** Flow-chart of the Hybrid process in this work.

**IX-S-6 High-Energy, Narrow-Bandwidth 2-µm Optical Parametric Oscillator/Power Amplifier Based on Periodically Poled MgO:LiNbO₃**

SAIKAWA, Jiro; FUJII, Masaaki¹; ISHIZUKI, Hideki; TAIRA, Takunori

[IEEE J. Sel. Top. Quantum Electron. 11, 613 (2005)]

We have proposed the hybrid procedure of determining spectroscopic parameters for uniaxial solid-state laser crystals. Figure 1 shows the procedure of this process. By using our procedure the spectroscopic properties of Nd:GdVO₄ were evaluated and compared to those of Nd:YVO₄. The product of stimulated emission cross section and fluorescence lifetime (τₛτᵣ) of Nd:GdVO₄ was smaller than that of Nd:YVO₄ under 1.0-at.% of Nd³⁺-doping concentration. Because of the low value of radiative quantum efficiency of Nd:GdVO₄ (50%), careful cavity design is required for creating a well performing solid-state laser with Nd:GdVO₄, based on the larger τₛτᵣ product than τₛτᵣ product of Nd:YAG.

**Figure 1.** Second-harmonic autocorrelation trace and spectrum (inset) for the shortest-pulse generation with a 0.5% output coupler. The solid-line indicates ideal sech² shape.
We demonstrated a high-energy, high-efficiency quasi-phase-matched optical parametric oscillator/power amplifier system based on $5 \times 5 \text{mm}^2$ large aperture periodically poled MgO:LiNbO$_3$. Maximum pulse energy of 52 mJ (optical conversion efficiency of 60\%) with resolution limit spectral bandwidth of $< 2 \text{ nm}$ at 2.128 $\mu\text{m}$ degeneracy point was obtained. These experimental result shows that large aperture PPMgLN device is useful for the development of the high-energy, efficient, narrowband 2$\mu\text{m}$ light source.

**IX-S-7 High-Energy Quasi-Phase Matched Optical-Parametric Oscillation in Periodically Poled MgO:LiNbO$_3$ Device with 5 mm x 5 mm Aperture**

ISHIZUKI, Hideki; TAIRA, Takunori


Fabrication of 5mm-thick periodically poled MgO-doped LiNbO$_3$ device with 32.1$\mu\text{m}$ period for mid-infrared generation was demonstrated. The periodic structure was evaluated by measurement of second-harmonic generation with $d_{31}$-coefficient. Optical-parametric oscillation using the device with uncoated 5 mm $\times$ 5 mm aperture and 36mm effective length realized a high-energy output of 77 mJ for both signal (wavelength: 1.83 $\mu\text{m}$) and idler (2.54 $\mu\text{m}$) waves with 72\% slope efficiency at 110mJ pumping of Q-switched Nd:YAG laser with 12ns pulse duration.
Equipment Development Center

IX-T  Development of New Instruments and Experimental Devices

The technical staff of the Equipment Development Center is partly engaged in planning, researching, designing and constructing high technology experimental instruments in collaboration with the scientific staff. And these experimental instruments are incorporated with new manufacturing technology and new mechanical ideas.

IX-T-1  Manufacture of a Mold for a Microchip Using a Surface Impression Agent

AOYAMA, Masaki; SUZUI, Mitsukazu; SHINTANI, Takafumi1; NODA, Masaharu1
(1NIBB)

Figure 1 shows an external photograph and an SEM photograph of a produced mold. A microchip is produced by injecting PDMS into the mold. The mold has first projections of 0.5 mm in width and 3 mm in height on both sides which form liquid sump sections, and second projections extending between the first projections each having a width of 90 \( \mu \)m and a height 60 \( \mu \)m which form passages.

The mold cannot be produced by machinery because of tool interference. Therefore, a master die is produced first by machinery, and the produced master die is transferred to make an inverse shape. In general, the transferring step is performed using an electrocasting method. However, because the electrocasting method is expensive, the master die is transferred to the inverse shape using a surface impression agent (Heraeus Kulzer GmbH & Co. Technovit 3040), which is an easier method. With the method, the mold for a PDMS microchip is produced in a short time at low cost. A produced PDMS microchip is used for making protein stripes on plastic dishes or glass coverslips as substrates for neural cell culture.

Figure 1. The externals and the SEM photographs of the mold.

IX-T-2  A Compact Mechanical Velocity Selector to Analyze Molecular Alignment

YANO, Takayuki; SUZUI, Mitsukazu; OKADA, Michio1; KASAI, Toshio1
(1Osaka Univ.)

We received a request on the production of disks from Professor Kasai (Department of Chemistry Graduate School of Science, Osaka University). As a new attempt, we expand our service to the outside researchers of universities and research institutes since October 2005. We suggested the application of the wire-cut electrical discharge machining (WEDM) to manufacturing the fine disks. However, it was difficult to apply the conventional method as it is. Therefore, we devised and made supporting tools. And we examined a routine of the production process. Selector dimensions and technical data are shown in table 1. Schematical drawing of a disk of the mechanical velocity selector is shown in Figure 1. Magnified view of fine slits on the disk is also shown in Figure 2. We used a wire of 70 micron in diameter in the processing. The slit of 100 micron in width was obtained with it. Using this fine wire enables us to make a slit of 85 micron in the minimum width.

Table 1. Selector dimensions and technical data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of disks</td>
<td>2</td>
</tr>
<tr>
<td>Diameter of disks</td>
<td>72mm</td>
</tr>
<tr>
<td>Number of slits per disk</td>
<td>720</td>
</tr>
<tr>
<td>Length of the slits</td>
<td>2mm</td>
</tr>
<tr>
<td>Slit with</td>
<td>0.1mm</td>
</tr>
<tr>
<td>Wall width between slits</td>
<td>0.2mm</td>
</tr>
<tr>
<td>Disk thickness</td>
<td>0.1mm</td>
</tr>
<tr>
<td>Material of disks</td>
<td>stainless steel</td>
</tr>
</tbody>
</table>
Figure 1. Schematical drawing of a disk of the mechanical velocity selector.

Figure 2. Photograph of the slit.
Safety Office

IX-U  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.

IX-U-1 TTF Derivatives Containing Fused-Pyrazine Rings for Novel Donor-Acceptor Systems

Naraso1; NISHIDA, Jun-ichi1; TOMURA, Masaaki; YAMASHITA, Yoshiro2 (1Tokyo Tech; 2IMS and Tokyo Tech)


In this work, novel π-extended tetrathiafulvalen (TTF) derivatives 1-10 fused with electron-accepting pyrazine rings are described. We have succeeded in preparing two kinfs of TTF derivatives 1 and 2 containing two pyrazine rings. Furthermore, we have prepared asymmetrical TTF derivatives 3-6 containing one pyrazine ring to increase the electron-donating properties. In some cases, hydroxyl groups were introduced to intermolecular hydrogen bonds. Oxidation of hydroquinone derivatives afforded a new type of donor-acceptor compounds 7-10 with quinone units, which showed both oxidation and reduction potentials. The electrical conductivity of the donor-acceptor compound was about 10−8 S/cm as single component. We have also prepared several CT complexes based on the new TTF derivatives and investigated the structures and properties.

\[\text{Naraso1; NISHIDA, Jun-ichi1; TOMURA, Masaaki; YAMASHITA, Yoshiro2 (1Tokyo Tech; 2IMS and Tokyo Tech)}\]


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