# *Anti*-Selective Direct Asymmetric Mannich Reactions Catalyzed by Axially Chiral Amino Sulfonamide as an Organocatalyst

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Asymmetric Mannich reactions provide a powerful method for synthesizing optically active  $\alpha$ -amino carbonyl units, which are useful chiral building blocks for a number of biologically active and pharmaceutically important compounds. In particular, direct asymmetric Mannich reactions between carbonyl compounds and certain imines would be most desirable for this purpose. Among them, the proline catalyzed Mannich reaction furnished products with *syn* diastereoselectivity. Enantioselective *anti*-selective Mannich reaction are, however, considerably rarer. Therefore, we were interested in the possibility of obtaining *anti*-product, and designed a novel axially chiral amino trifluoromethanesulfonamide as a catalyst. In the presence of this catalyst, the rection between aldehydes and an  $\alpha$ -imino ester proceeded smoothly to give the functional  $\beta$ -amino aldehyde with significantly higher *anti*-diastereo and enantioselectivity than previously possible.



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# A Convenient, Enantioselective Synthesis of β-Substituted γ-Butyrolactone and Synthesis of Pregabalin

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Chiral  $\beta$ -substituted  $\gamma$ -butyrolactone is known to be an important key intermediate to many biologically active compounds such as  $\gamma$ -amino-butyric acid(GABA) derivatives and lignans. In spite of many known methods to synthesize the "lactones", many of them are laborious, in terms of efficiency, designed only for laboratory scale, or can not fulfill the desired enantiomeric purity. We have developed a general and convenient method for enantiomerically pure  $\beta$ -substituted  $\gamma$ -butyrolactone in either streochemistry. We demonstrate the usage of our method by synthesizing Pregabalin[1] ((S)-3-isobutyl- $\gamma$ -aminobutyric acid), an anticonvulsant drug that has been identified as a promising treatment for neuropathic pain.



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# Synthesis and Structure of a Bulky Silanedithiol and Its Application toward the Synthesis of Silanedithiolato Complexes

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Organosilanethiols have been extensively studied from the viewpoints of organic, organometallic, and inorganic chemistry. On the other hand, silanedithiols are very rare compounds due to their high sensitivity toward moisture in spite of the interests in not only their structures and reactivities but also their application toward the synthesis of silanedithiolato complexes, which have attracted much attention as potential precursors for the controlled synthesis of mixed-metal sulfido clusters.

Here, we report the first structural characterization of the stable examples of silanedithiol (1), hydroxysilanethiol (2), and hydroxysilaneselenol (3), bearing an effective combination of steric protection groups, Tbt and Mes, and their application toward the synthesis of silanedichalcogenolato complexes.<sup>1)</sup> Silanedichalcogenols 1, 2, and 3, which were isolated by the hydrolysis of the corresponding silanedichalcogenolato-zirconium complexes,<sup>1,2)</sup> were suggested to exist as a monomer without any intermolecular contact such as hydrogen bonds both in the solid state and in solution as judged by X-ray structural analysis and IR spectroscopy.<sup>1)</sup> Treatment of 1 with 2 molar amounts of butyllithium resulted in the quantitative formation of the corresponding dilithium silanedithiolate, Tbt(Mes)Si(SLi)<sub>2</sub> (4), the generation of which was confirmed by the trapping experiment using MeI. Furthermore, the addition of *cis*-[MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (M = Pd, Pt) or BbtEBr<sub>2</sub> (E = Sb, Bi) to a THF solution of 4 afforded the corresponding silanedithiolato complexes, [Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>M(PPh<sub>3</sub>)<sub>2</sub>] (**5a,b**) or Tbt(Mes)Si( $\mu$ -S)<sub>2</sub>EBbt (**6a,b**), respectively.



We also succeeded in the synthesis and characterization of silane(oxylato)chalcogenolato-platinum complexes [Tbt(Mes)Si( $\mu$ -O)( $\mu$ -Ch)Pt(PPh<sub>3</sub>)<sub>2</sub>] (7a,b) utilizing 2 and 3. Structures and properties of the newly isolated silanedichalcogenolato complexes will also be discussed.

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# Synthesis of Single Crystalline Tellurium Nanotubes with Triangular and Hexagonal Cross Sections

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Single crystalline tellurium (Te) nanotubes with triangular cross sections were successfully synthesized for the first time by a simple approach of vaporizing tellurium metal and condensing the vapor in an inert atmosphere onto a suitable substrate. This formation of the nanotubes was highly dependent upon the structure of the substrate surface, Ar gas flow rate, and the deposition temperature. All the observed Te nanotubes grew in a regular [0001] direction. The facile approach to nanotubes with a triangular cross section may facilitate some new applications as well as stimulate theoretical studies pertaining to the stability of this high-energy configuration.



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# Design of Multi-Functional Organic Conductors Having a Nucleobase Skeleton: Synthesis and Properties of Cytosine-Fused TTF

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Biomolecular systems have attracted much attention in the recent research for moleculebased materials, where DNA is one of the candidates of biomolecular conductors. Isocytosine- and uracil-fused TTF (tetrathiafulvalene) derivatives (1 and 2, respectively) are electron donors having nucleobase skeletons. In addition to the electron donating ability, these molecules have multiple functions, namely, amphoteric proton transfer ability and complementary hydrogen bonds that are formed in base-pairs of DNA. 1 and 2 have given neutral betainic radicals exhibiting a high conductivity of  $\sim 10^{-1}$  S cm<sup>-1</sup> as single-component organic molecules [1, 2]. In order to develop DNA-based multi-functional conducting system, we have designed and synthesized new cytosine-fused TTF derivatives **3**. In the presentation, we will report synthetic method and physical properties of *n*-butyl derivative **3b**.



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# Amphiphilic Organosilane-mediated Crystallization of Zeolites Possessing Micro-/Mesoporous Structural Hierarchy

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Zeolites are crystalline, three-dimensional framework aluminosilicates consisting of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedral primary building blocks linked each other by sharing their oxygen atoms [1]. They have been widely used as a catalyst for petroleum refinery industry and fine chemical synthesis due to a unique microporous structure with uniform diameter and shape [2]. Due to the small pore size of micropore ( $0.3 \sim 1.5$ nm), however, the catalytic application of zeolites were limited to small reactant molecules. To overcome diffusion limitation with micropore, several approaches to synthesize zeolite containing mesoporous structure have been investigated. However, there have been no successful reports on the direct synthesis of materials that possess both high crystallinity and mesoporosity within the same structure.

Recently, we reported a direct synthesis route to hierarchically porous zeolites with tunable mesoporous structure using a rationally designed organic-inorganic hybrid surfactant [3]. In the present work, zeolites were synthesized using a rationally designed surfactant in conventional alkaline zeolite synthesis mixtures containing specific zeolite structure-directing species. The zeolite products were characterized by a complementary combination of X-ray diffraction (XRD), nitrogen sorption, scanning and transmission electron microscopy. The analysis result supports that the present method is suitable as a direct synthesis route to highly mesoporous MFI and LTA zeolites. In the case of the MFI zeolite, mesopore diameters were uniform and tunable, as in ordered mesoporous silica MCM-41. The mesoporous zeolite also exhibited a small-angle XRD peak corresponding to the short range correlation between neighboring mesopores.

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# 4,5-(Ethylenedithio)-2-(thiopyran-4-ylidene)-1,3-dithiole (TP-EDTT) as a Conducting Component Molecule

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The hybrid donor molecule between BEDO-TTF and BTP, TP-EDOT, has a sulfur atom with an effective atomic orbital coefficient in the HOMO at the thiopyran moiety to provide the intermolecular interaction along the molecular long axis. (TP-EDOT)<sub>2</sub>PF<sub>6</sub> is a Mott insulator, in which the head-to-head dimer along the molecular long axis accommodates one localized spin to exhibit a two-dimensional antiferromagnetic behavior [1]. The hybrid donor molecule between TTF and BTP is potentially interactive along the molecular long axis in addition to the short and stacking axes. In fact, Y. Misaki *et al.* realized the three-directional intermolecular interaction in the system referred to as a "wind mill" type [2].



Based on TP-EDOT, our molecular design to increase the intermolecular interaction along the molecular short axis requests the substitution of oxygen by sulfur to provide TP-EDTT. This molecule has been already reported by T. Otsubo *et al.*, while the complexes with inorganic anions have been almost unknown. [3] Our X-ray structural analysis revealed that the neutral TP-EDTT exhibited the shape bent at the thiopyran moiety. The optical absorption spectrum of the complex with  $PF_6^-$  low energy electronic transition at around 5000 cm<sup>-1</sup>, which should be assigned to the intermolecular charge transfer transition. The structural analysis of the complex is now underway.

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# Solid-State <sup>13</sup>C NMR Studies on Conformational Transformation of Poly(β-benzyl L-aspartate)

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We studied conformational transformation of Poly( $\beta$ -benzyl L-aspartate) (PBLA) by high resolutional solid-state <sup>13</sup>C NMR. So far, it has been shown that the  $\alpha_R$ -helical PBLA is transformed into the  $\omega_L$ -helix with a change of the helix sense by heating at about 70-140°C, and further heat treatment causes the change of conformation from the  $\omega_L$ -helix form to the  $\beta$ -sheet form[1].

Figure1 shows the C=O signal of PBLA heat-treated for various periods. The lineshape change observed for the C=O peaks indicates that the longer the heating time the more PBLA transforms into the  $\omega_L$ -helix and the  $\beta$ -sheet forms. Interestingly the  $\omega_L$ -helix didn't transform into the  $\beta$ -sheet form completely at 140°C, while at 150°C, we showed that the  $\omega_L$ -helix changed almost completely into the  $\beta$ -sheet form[2].

The relative peak intensities of these conformers are obtained by fitting the signal to a sum of Gaussian lineshapes. The reaction rate constants of the transformation from the  $\alpha_R$ -helical to the another conformers at 120, 125, 130, 135°C are obtained by analyzing the ratio of these conformers vs heat-treatment time. Using reaction rate constants at each temperatures, we obtained the transformation energy to be ca.380kJ/mol.



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## NMR study of the interaction between WRN and RPA

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Werner syndrome (WS) is an autosomal recessive disease that results in premature aging. Mutations in the WS gene (*WRN*) result in a loss of expression of the WRN protein and predispose WS patients to accelerated aging. As a helicase and a nuclease, WRN is unique among the five human RecQ helicase family members and is capable of multiple functions involved in DNA replication, repair, recombination, and telomere maintenance. The activity of Werner syndrome helicase is stimulated by human replication protein A(hRPA), a heterotrimeric single-stranded DNA binding protein. It is known that WRN has two RPA binding sites, N-terminal site and C-terminal site. We have explored the molecular basis of WRN and hRPA interaction by NMR chemical shift perturbation assay.



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# Single-molecule Study of Acetylene Adsorbed on Cu(110)

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The scanning tunneling microscopy (STM) allows us to observe individual atoms and molecules [1]. In addition, STM can be used as an energetic electron source for single-molecule vibrational excitation, which provides strategies for chemical characterization and inducing reaction of. Inelastic electron tunneling spectroscopy with STM (STM-IETS) provides vibrational information of individual acetylene molecules. Further, we show the excitation of the C-H (C-D) stretch mode of  $C_2H_2$  ( $C_2D_2$ ) at 350 meV (258 meV) induces in the hopping of the molecule along the surface. This can be attributed to energy relaxation of the C-H stretch mode to the hindered translational modes of the molecule via anharmonic coupling.



Fig. 1. (a) STM topographic image of an acetylene molecule on Cu(110) (area  $29.5 \times 29.5 \text{ Å}^2$ ,  $V_s = -107$ mV,  $I_t = 2$  nA). (b) Schematic drawing of acetylene showing side and top view of the molecular adsorption site and orientation consistent with the STM images. The dashed line represents the outline of the dumbbell shaped depression in the STM images.

Fig. 2.  $d^2I/dV^2$  difference spectra for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub> shows STM-IETS vibrational peaks at 350 and 258 mV, respectively. The tip was fixed in position vertically to give a dc tunneling current of 60 pA at 93 mV sample bias. The spectra were acquired by lock-in technique with arms modulation of 12 mV.

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# **Molecular Properties of Group 1 and Group 11 Cyanides**

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Closed shell metal cyanides, Group 1 and Group 11 cyanides, were studied with abinitio calculations. For each cyanide, the most stable geometry was tracked and subjected to relativistic periodic trend. For Group 1 cyanide, triangular(T-Shaped) MNC form was obtained as the lowest energy conformer except for linear isocyanide shape of lithium cyanide. On the other hands, linear cyanide form is preferred in Group 11 cyanide. The triangular form is a very floppy structure because of one low frequency for the bending mode and strong ionic character.

Comparative relativistic calculations between nonrelativistic and relativistic levels about Group 1 and Group 11 cyanides show that relativistic effect is small for Group 1 cyanide and very large for Group 11 cyanide. These discriminated properties can be explained in terms of ionization potentials of metal atoms and molecular orbital surfaces. Especially increase of covalent character with relativistic correction is maximized for gold cyanide due to enormous relativistic effect of gold atom.[1] Generally relationship between relativistic and correlation effects is non-additive. Spin-orbit effects are not large for two kinds of cyanides. However, the most significant relativistic correction of gold molecule is consistent with the largest spinorbit correction of the same molecule.

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# Kinetics of Major Conformational Change of Photoactive Yellow Protein

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Photoactive yellow protein (PYP) is a water-soluble photo-response protein, thought to be responsible for the negative phototaxis in *Ectothiorhodospira halophila*. For sensing light, PYP has a chromophore p-hydroxycinnamyl. It is well known that PYP shows an inherent photocycle. Upon photoexcitation, the ground state species (pG) is converted into a red-shifted intermediate (pR), which decays on hundreds microseconds into blue shifted intermediate (pB'). This pB' is converted to pB on sub-millisecond time scale, and finally it returns to pG. Some previous reports suggested that the pB' and pB species correspond to a proton transferred and structural changes forms, respectively. However, there is no conclusive evidence when structural changes occur, because there has been no useful time resolved experimental technique to monitor the conformational change in time domain. Recently, a new technique that can reveal the relation between the reaction kinetics and the structural change was proposed; monitoring the time development of the diffusion coefficient (D) by using the transient grating (TG) method.<sup>[1,2,3]</sup> Here, we studied the conformational change of PYP in time domain by this method.

We have already reported that pG and pB have different D and this difference is caused by the conformational change of N-terminal domain. Therefore, if we can observe the dynamics of the D change, this dynamics should represent that of the (major) conformational change. For monitoring the D-change in a fast time scale, the TG signal should be recorded under a large q condition. Although monitoring TG signal under such condition was difficult, we successfully recorded the diffusion TG signal in a submillisecond. Our preliminary analysis of the signal based on the two state model suggests that the D of PYP starts to change in hundreds microseconds scale; i.e., N-terminal conformation may be changed by the creation of pB'. The detailed results and analysis will be presented in the conference.

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# Distinguishing Reaction Pathways: Photodissociation and Recombination Dynamics of Triiodide Ion

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Photodissociation pathway and structural dynamics of triiodide ion in methanol solution has been investigated using synchrotron based time-resolved diffraction (TRXD) technique. Although many experimental techniques have provided rich information regarding early dynamics of triiodide, the direct structural observation has been lacking. Here we show that TRXD can provide this information directly. The excitation gives diiodide ion (I<sub>2</sub>-) and iodine atom. Previous spectroscopic results reported that the three-body dissociation (I<sup>+</sup>H+I) can occur when the excitation energy is high enough. We used both 259-nm and 389-nm photons in order to investigate the excitation energy dependence of the reaction dynamics. Both 259nm and 389-nm excitation data was analyzed by the powerful global analysis which includes the all information at once.



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# Equilibrium between Monomer and Dimer Forms of Photosensor Protein Phototropin1-LOV2 Domain

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Phototropin 1 (Phot1) is a blue-light receptor in higher plants. This protein contains two photoreceptive domains, LOV1 and LOV2. Upon blue-light illumination, the LOV domains show a photocycle. By using the transient grating (TG) method, we have already reported that the LOV2 domain undergoes the association and dissociation processes between monomeric and dimeric forms.<sup>[1]</sup> We have also found that the dimer and monomer are in equilibrium and coexist in solution at the dark state. Which form is more stable? Generally, it is difficult to study such spectrally silent dimer distribution in detail. In this study, we investigated the thermodynamic characters of each form by the temperature dependence of the TG signal. This information will be useful for obtaining further insight into the photochemistry of this protein.

The temporal profiles of the TG signals at high temperatures showed that the association process (dimerization) is the main process in the photocycle. This fact indicates that the monomeric form of phot1-LOV2 is the dominant at dark state. On the other hand, interestingly, the dissociation reaction becomes dominant in the TG signal at lower temperatures. These results indicate that the dimeric form of phot1-LOV2 is energetically more stable. At the same time, we can also estimate the activation energy of the photoreaction by the temperature dependence of the rate constant. We will discuss the thermodynamics of the LOV2 domain on the basis of these results.

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# Ultrafast Exciton-Exciton Coherent Transfer in Molecular Aggregates

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We have developed the explicit non-Markovian time evolution equation which can describe the exciton-exciton coherent transfer(EECT) in strongly coupled molecular aggregates. Its solutions make it possible to derive effects caused by EECT in the nonlinear response function for four-wave-mixing experiments. We take into account two-exciton states, static disorder and a phonon heat bath coupling represented by arbitrary spectral densities. Our derivation is based on the doorway-window representation and the projection operator method which are now developed for exciton-exciton coherent states. Applications of our analytical expression to B850 monomers in the Light harvest II(LH2) antenna system shown in the figure are discussed. We have shown that EECT becomes indispensable in the ultrafast phenomena of molecular aggregates and generates the essential contribution to the nonlinear spectroscopic signals.



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# Asymmetric Electrophile-promoted Cyclizations

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Asymmetric functionalization of olefinic double bonds is considered as the prime challenging subject in modern synthetic organic chemistry. The most reverend achievements in this area have been procured by asymmetric epoxidation, dihydroxylation, aminohydroxylation, hydrogenation and hydroboration. Another efficient installation of versatile functional groups at olefinic double bonds has been consummated by intra- and intermolecular electrophile-promoted addition reactions. Most of the stereoselective addition reactions have been effected through substrate-controlled diastereoselectivity. Since reagent-controlled asymmetric addition reactions can be more efficacious and complementary, development of the corresponding version is of great value and has been arduously pursued. The reagent-controlled reactions have been mostly executed by organoselenvlation using chiral selenium reagents prepared from binaphthalene, o-substituted benzene, ferrrocene and camphor derivatives. Other rarely explored asymmetric addition reactions comprise iodolactonization with iodonium ion-dihydroquinine complexes, oxymercuration with chiral Hg(II) carboxylates, chlorohydroxylation with Pd(II)-BINAP complexes and iodocyclization with iodine in the presence of chiral Ti(IV) alkoxides. Among them, the last may belong to substrate-controlled version due to the probable formation of substrate-chiral Ti(IV) alkoxide complexes. Herein, we describe unprecedented asymmetric mercuriocyclization<sup>1,2,5</sup> using chiral bisoxazolines as ligands, and catalytic enantioselective intramolecular iodoetherification<sup>35</sup> to form 2-substituted tetrahydrofurans with high enantioselectivity, and its synthetic application to pyrrolidine alkaloids.



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## **Practical Asymmetric Synthesis with Designer Chiral Organocatalysts**

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Asymmetric synthesis by chiral phase transfer catalysis has provided an attractive method of preparing a variety of useful optically active compounds. Accordingly, sructurally rigid, chiral spiro-type ammonium salts (*R*,*R*)-1 or (*S*,*S*)-1 derived from commercially available (*R*)or (*S*)-binaphthol have been already prepared and successfully applied to the highly efficient, catalytic enantioselective alkylation of *tert*-butyl glycinate-benzophenone Schiff base under mild phase transfer conditions.<sup>14</sup> Recently, we successfully designed simplified, chiral quaternary ammonium salts (*S*)-2 with *C*<sub>2</sub>-symmetry as a new, yet very active chiral phase transfer catalyst for practical asymmetric synthesis of  $\alpha$ -alkyl- and  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids.<sup>5</sup> Various alkyl halides were employable where enantioselectivities generally exceeded 97% ee. We also developed a new, asymmetric Strecker reaction by designing a new type of chiral, helical phase transfer catalyst (*S*)-3 for the efficient asymmetric synthesis of sterically hindered  $\alpha$ -alkyl- $\alpha$ -amino acids.<sup>6</sup>



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# The Total Synthesis of (±)-ceratopicanol

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In 1988, Hansen and Abraham<sup>1</sup> reported the isolation from the fungus *Ceratocystis Piceae* Ha 4/82 of (+)-ceratopicanol (1), a novel triquinane sesquiterpene. They also elucidated its chemical structure. The uncommon presence of two vicinal bridgehead quaternary carbons among the five contiguous chiral centers, on a *cis,anti,cis* triquinane framework makes 1 an attractive synthetic challenge. Its structure represents evidence for the biosynthetic generation of hirsutene and related natural products associated with the humulene cascade.<sup>2</sup>



Recently, we designed and developed a new efficient way to generate TMM divis from allenes and N-aziridinylimines and successfully utilized in [2+3] cycloaddition reaction with olefins. The novel one pot sequential transformation of thermally labile pyrazoles obtained through [2+3] cycloaddition reaction of diazoalkanes with allenes produced TMM divis and the generated divis were trapped by olefin to form polyquinanes. With this novel synthetic methodology, we tried to total synthesis of (±)-Ceratopicanol.



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# Palladium-Catalyzed Asymmetric [3 + 3] Cycloaddition of Trimethylenemethanes with Nitrones

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Intermolecular cycloaddition reactions are powerful methods for the convergent construction of cyclic materials from relatively simple organic fragments, and achieving such transformations by the use of transition-metal catalysts is highly desirable in view of efficiency of the process and mildness of the reaction conditions. We recently reported the development of a palladium-catalyzed [3 + 3] cycloaddition of trimethylenemethane (TMM) with azomethine imines to produce highly functionalized hexahydropyridazine derivatives under simple and mild conditions.<sup>1</sup> We also found that these [3 + 3] cycloaddition reactions are applicable to the couplings with nitrones.

This presentation describes a novel synthetic method for optically active functionalized 1,2oxazines via palladium-catalyzed asymmetric [3 + 3] cycloaddition of trimethylenemethanes (TMMs) with nitrones. Synthesis of bulky phosphoramidite ligand L and its application to the palladium-catalyzed asymmetric [3 + 3] cycloaddition gave the desired products in excellent yield with high diastereo- and enatioselectivity.



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# Synthetic Studies on Dysiherbaine

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Dysiherbaine (1) is a neuroexcitotoxic amino acid isolated from the Micronesian marine sponge, *Dysidea herbacea*. Since the isolation and structure determination of this compound in 1997, it has received much attention from medicinal and synthetic chemists as well. This interest arises from its potent biological activity, hence, prospective pharmacological utility and its structural novelty posing a significant synthetic challenge.

Dysiherbaine contains six chiral centers on a novel bicyclic skeleton making it a quite challenging target. Its unique structural feature prompted many research groups, including ours, to be engaged in its synthesis.



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# Electrochemical Properties of Kinetically Stabilized Silaaromatic Compounds

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Aromatic compounds containing a silicon atom have attracted considerable interest from the viewpoint of fundamental and material chemistry. However, it has been known to be difficult to synthesize and isolate silaaromatics due to their extremely high reactivity toward self-

oligomerization. We have succeeded in the synthesis of several kinds of stable silaaromatic compounds, i.e., silabenzene 1, 1- and 2silanaphthalenes 2 and 3, 9-silaanthracene 4, and 9silaphenanthrene 5 by taking advantage of an efficient steric protection group, Tbt (2,4,6-tris[bis--(trimethlsilyl)methyl]phenyl), and revealed their aromatic character [1].

On the other hand, one-electron reduction is known to be one of the characteristic reactivities of aromatic hydrocarbons. Systematic elucidation of the electrochemical properties of silaaromatic compounds should be of great interest. Particularly, we report here the Redox behavior of silabenzene 1.

The redox behavior of silabenzene **1** was revealed by cyclic voltammetry (Figure 1). The voltammogram of **1** showed a quasi-reversible redox couple at  $E_{1/2} = -2.96$  V (vs. Fc/Fc<sup>+</sup>), which lies between those of naphthaene ( $E_{1/2} = -3.37$  V) and anthracene ( $E_{1/2} = -2.74$  V) under the same conditions.

Treatment of silabenzene 1 with lithium naphthalenide (1.0 eq) in 1,2dimethoxyethane at room temperature afforded a dark-red solution. The ESR spectrum of the resulting solution showed characteristic signals as shown in Figure 2, indicating the generation of the corresponding anion radical species of 1.

The trapping reactions of the anion radical species will also be described.

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Figure 2. ESR spectrum of the reaction mixture of 1 with lithium naphthalenide in THF at r.t.



# Synthesis and Properties of Metal and Metal Silicide Nanowires

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Synthesis of metal nanowires (NWs) are difficult, because catalysts are not available. We were able to synthesize metal NWs such as Te, Cd, and Bi by using gas phase method. Also metal silicides show interesting physical properties. Whereas MnSi shows low temperature helimagnetic order, FeSi is a small gap semiconductor with anomalous temperature dependant magnetic moment and CoSi is a diamagnetic semimetal. The recent discovery of unusual positive magnetoresistance and large anomalous Hall Effect in Fe<sub>1-x</sub>Co<sub>x</sub>Si alloys shows the possibility of using these materials in the future Si-based spintronics technology. Synthesis of single crystal high quality NWs, realization of the desired physical properties, and assembly and integration into the device architecture are among the major challenges in the field of nanotechnology.

Cobalt silicide is a promising material for advanced thermoelectric applications with large thermoelectric power (80  $\mu$ V/K) comparable to that of bismuth (50 to 100  $\mu$ V/K). While there has been progress in utilizing Bi NWs in thermoelectric devices, CoSi NWs could be another prospective candidate for effective thermoelectric materials. We demonstrate the successful synthesis of freestanding high density CoSi and FeSi NWs with ordered crystal structure and unusual ferromagnetic properties.



Fig. 4-probe measurements of the resistance of FeSi NW.

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# Phase Diagram and In-plane Spin Fluctuation in Novel Superconducting System, Na<sub>x</sub>Co<sub>2</sub>·yH<sub>2</sub>O

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Recent studies on the physical and chemical properties of the bilayer hydrated (BLH) triangular lattice superconductor  $Na_x CoO_2 \cdot yH_2O$  have revealed the fact that the superconductivity would occur near the ferromagnetic electron correlations. We newly synthesized the non-superconducting and superconducting BLH Na<sub>x</sub>CoO<sub>2</sub>·yH<sub>2</sub>O compounds by the systematic sample preparation with time-controlling duration effect in high humidity atmosphere [1]. A non-superconducting BLH phase compound shows the magnetic transition around 4.2 K with broadening of the <sup>59</sup>Co nuclear quadrupole resonance (NQR) spectrum as well as the anomaly in temperature dependence of the <sup>59</sup>Co-NQR spin-lattice relaxation rate,  $1/T_1$ . Furthermore, we succeeded in constructing the electronic phase diagram as a function of the NQR frequency, and found that superconducting phase exists very close to the nonsuperconducting magnetic BLH phase in the vicinity of quantum critical point of magnetic correlations [2]. These results strongly suggests that the superconductivity in BLH Na<sub>x</sub>CoO<sub>2</sub>. yH<sub>2</sub>O originates from the ferromagnetic fluctuation within the CoO<sub>2</sub> layer. This result is also supported by the results of  $1/T_1$  of <sup>23</sup>Na NMR which can be explained by a part of the A-type spin fluctuations observed in the mother compound Na<sub>x</sub>CoO<sub>2</sub> by the neutron scattering experiment [3].

We will give a review of the physical and chemical properties of the superconducting BLH compound,  $Na_xCoO_2 \cdot yH_2O$ , and discuss the occurrence mechanism of the exotic superconductivity having the possibly anomalous spin-triplet electron pairings with the *p* or *f* -wave symmetry [4]. This work was done as collaborations with Hiroto Ohta, Chishiro Michioka, Yutaka Itoh from my group in Kyoto University.

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# Density Functional Study of Carbon Cluster C<sub>20</sub>

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Density functional calculations have performed for many isomers of neutral carbon cluster  $C_{20}$  using both local density approximation and gradient-corrected approximations to the exchange-correlation energy. The stable isomers include ring, cage, double ring and graphitic structure. The local density approximation yields the cage to be the most stable isomer with the bowl and ring forms being significantly higher in energy. However, the inclusion of gradient corrections completely reverses the energy ordering of the isomers. The gradient correction alters the relative energy between the cage and ring isomers by more than 6 eV and yields the ring as the most stable form.



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# Geometry, Bonding Nature, and Stability of $\eta^3$ -Silaallyl and $\eta^3$ -Silapropargyl/Silylalkynyl Tungsten Complexes: Theoretical Study

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Multiple bond including Si element is very interesting in comparison to its carbon analogue, because it is very different from the C analogue. Synthesis and isolation of such chemical species are interesting and challenging in recent chemistry. For instance, the synthesis of Si analogue of acetylene has not been succeeded until 2004.<sup>1</sup> Silaallyl is also interesting species because it is the simplest of all conjugated systems including Si. Though silaallyl would not be stable, the interaction with transition metal complex is expected to stabilize the silaallyl species. Recently, a  $\eta^3$ -silaallyl tungsten complex, Cp\*(CO)<sub>2</sub>W( $\eta^3$ -Si(Me)<sub>2</sub>CH=CMe<sub>2</sub>) **A** was isolated experimentally for the first time,<sup>2</sup> but similar  $\eta^3$ silapropargyl tungsten complex, Cp\*(CO)<sub>2</sub>W( $\eta^3$ -Si(Ph)<sub>2</sub>C=C<sup>t</sup>Bu) **B**, was not, while **B** proposed as intermediate in formation of Cp\*(CO)<sub>2</sub>W(C=C<sup>t</sup>Bu)(SiPh<sub>2</sub>) **C**. We theoretically investigated Cp(CO)<sub>2</sub>W(Si(H)<sub>2</sub>C=CH) **3** and Cp(CO)<sub>2</sub>W(C=CH)(SiH<sub>2</sub>) **4** with DFT, MP2 to MP4(SDTQ), and CCSD(T) methods.

From the geometry and frontier orbitals, **1** can be understood as tungsten  $\eta^3$ -alkenylsilyl complex rather than tungsten  $\eta^3$ -silaallyl complex. Also, **3** can be understood to be 50% of tungsten  $\eta^3$ -silapropargyl and 50% of tungsten  $\eta^3$ -alkynylsilyl complex.<sup>3</sup> Complex **1** is much more stable than **2** by 21 kcal/mol, while **3** 



is less stable than **4** by 4.9 kcal/mol. These differences can be interpreted, as follows: The interaction of  $Cp(CO)_2W$  with  $H_2SiCHCH_2$  moiety in **1** is stronger than that with  $H_2SiCCH$  moiety in **3**. The W-vinyl bond is considerably weaker than the W-acetylide bond. Formation of silacyclopropene from silylene and acetylene is much more exothermic than that of silacyclopropane from silylene and ethylene, indicating weaker interaction of silylene with vinyl than that with acetylide.

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# **Probing Solution-phase Reaction Pathways** with 100-ps Time-resolved X-ray Diffraction

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Here we report direct structural observation of the long-sought bridged radical in solution using synchrotron-based time-resolved liquid-phase x-ray diffraction. The structural dynamics spanning picosecond to microsecond time scale has been experimentally determined in unprecedented structural details (1-3). In addition, we further extended this technique to study protein structural dynamics in solution. We obtained time-resolved MAXS (medium angle x-ray diffraction) data from heme proteins such as myoglobin and hemoglobin and preliminary analysis showed that the 3D structural changes of proteins can be monitored by time-resolved x-ray diffraction even in solution.



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# Molecular Mechanism of the Primary Photochemical Reactions in Rhodopsin Photoreceptor Proteins

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Rhodopsin proteins function as photo-receptors in vision and bio-energetic processes. For example, visual receptor rhodopsin (Rh) resides in the retina of the eye, and is responsible for vision. The rhodopsin proteins possess inside the proteins a common chromophore molecule, the retinal protonated Schiff base. The activation of rhodopsin proteins starts with an extremely fast (50-500 fs) photo-induced isomerization of the chromophore around a double bond of its polyene chain, which is one of the fastest reactions in nature. In addition to the fast rate, the photoisomerization reaction is highly selective; e.g., the photoisomerization in Rh takes place exclusively around the  $C_{11}=C_{12}$  bond, whereas the polyene chain includes several double bonds that are capable of undergoing isomerization. Such ultrafast rate and high chemical selectively furnish the rhodopsin proteins with high sensitivity to incoming light.

Unveiling the molecular dynamics in electronic and atomic details is requisite for understanding of the reaction mechanism. For the purpose, we have developed an ab initio quantum mechanical/molecular mechanical molecular dynamics (QM/MM-MD) method, and applied it for molecular simulations of the retinal photoisomerization in the rhodopsin proteins. The method combines ab initio multi-electronic state molecular dynamics of retinal chromophore models with molecular mechanics of the protein motion, allowing us to simulate the reaction dynamics in the proteins without imposing empirical assumptions for multidimensional forces of retinal in the electronically excited and ground states.

The QM/MM-MD simulations were carried out for the photoisomerization in Rh. Similar to another rhodopsin protein, bacteriorhodopsin (bR), which was examined in a previous study [1], the simulated photoisomerization in Rh is highly bond-selective; only the  $C_{11}=C_{12}$  bond undergoes the isomerization. In contrast to bR, the reaction kinetics of Rh was found to be coherent. All decays of electronically excited states associated with the photoisomerizations complete within 100 fs without losing the coherence. The simulations have elucidated that the photoisomerization around  $C_{11}=C_{12}$  is accelerated by co-rotation around the  $C_6-C_7$  bond in an extended Hula-Twist fashion, which contributes to the fast photoisomerization.

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# Photodissociation Dynamics of Sulfur Containing Heteroaromatic Compounds

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Specific heteroaromatics such as DNA and RNA bases have been widely investigated under the curiosity of their stability against solar UV. Especially, a photodissociation of the phenol (C<sub>6</sub>H<sub>5</sub>OH) and indole (C<sub>8</sub>H<sub>7</sub>N), which are two of most simple heteroaromatics, are intensively studied by both experimental and theoretical approach. The character of the photochemistry of heteroaromatics is determined by the relative location of  $\pi\pi^*(n\pi^*)$  and  $\pi\sigma^*$ states. This reveals that different character of the electronic transition comes from different degree of  $\pi$  conjugation between carbon and hetero atoms (oxygen and nitrogen).<sup>1,2</sup> In contrast, the sulfur constituent has highly nonbonding character as compared with the oxygen and nitrogen. This may show unique properties when sulfur takes part in the photochemical dynamics. Nevertheless, studies about the photochemistry of sulfur containing heteroaromatics are unfortunately rare.

Based on this motivation we have been carried out the study of the photodissociation dynamics of thiophenol and its several derivatives by using the conventional velocity map ion imaging coupled with Doppler reduced deuterium detection. We could figure out large nonbonding character in the thiophenol-d<sub>1</sub> (C<sub>6</sub>H<sub>5</sub>SD). This was reported as the intramolecular orbital alignment of nascent phenylthiyl radical (C<sub>6</sub>H<sub>5</sub>S·) after the photodissociation at 243.1 nm.<sup>3</sup> Here, the D atom abstraction channel through  $n\pi^*$  and  $n\sigma^*$  states, which is strongly correlated S-D dissociation coordinate, may be competed at the early stage of dissociation pathway. Firstly wavepacket may be prepared on both the  $n\pi^*$  and  $n\sigma^*$  states, then propagated on the repulsive potential energy surface. Together, photodissociation dynamics at several wavelength such as 224, 266 nm and vibrational adiabaticity will be discussed.

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# **Theoretical Study of Human Telomeric G-quadruplex Structure**

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The human telomeric sequence d[AGGG(TTAGGG)<sub>3</sub>] forms the G-quadruplex structure. The formation and stabilization of DNA G-quadruplexes in human telomeric sequence have been shown to inhibit the activity of telomerase, that is activated in 80-90% in cancer cells. Thus G-quadruplex DNA have become an attractive target for the development of anticancer drugs. The various conformations of G-quadruplex have been proposed. The 22 nt sequences d[AGGG(TTAGGG)<sub>3</sub>] forms an antiparallel structure in Na<sup>+</sup> solution, with one diagonal and two lateral loops (a).<sup>1</sup> The same 22 nt sequence forms a parallel structure, with double-chain - reversal loops in a  $K^+$  containing crystal (b).<sup>2</sup> The G-quadruplex structure in  $K^+$  solution is considered to be biologically more relevant than  $Na^+$  because  $K^+$  predominant in cells. Recently, three groups, including our group, proposed mixed-chair G-quadruplex structure in  $K^+$  solution(c, d).<sup>4-6</sup> The structure are termed intramolecular human telomeric (3+1) Gquadruplexes, in which three G-tracts are oriented in one direction with syn, syn, anti guanines and the fourth in the opposite direction with anti, syn, syn.<sup>5</sup> More recently, Patel *et al.* proposed four possible intramolecular human telomeric (3+1) G-quadruplexes, in which 5' end starts from different corners of the same G-tetrad core.<sup>6</sup> The two major (3+1) Gquadruplex structures have one double-chain-reverasal and two lateral loops. In other arrangements of (3+1) G-quadruplex, the G-quadruplex structures have two double-chainreversal loops and one lateral loop.

The purpose of this study is to find the folding pathways of Gquadruplex and the (3+1) G-quadruplex structure in K<sup>+</sup> solution. In this



study, the stabilization energies of G-quadruplex were examined using MO calculation and molecular modeling. Examining for the folding pattern, the stabilization energy of GG base pair and cation interaction were calculated by *ab initio* calculation. The GG base pair and G-tetrad plane were stabilized by a network of Hoogsteen base pair. The Na<sup>+</sup> ion prefers to be located in the central cavity of the G-quartet. On the other hand, the K<sup>+</sup> ion prefers to sit outside the plane of the G-quartet. Then the four (3+1) structure were calculated by Minimization and Molecular Dynamics simulation.

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# Analyzing Solution-phase Time-resolved X-ray Diffraction Data by Isolated-solute Models

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Extracting transient structural information of a solute from time-resolved x-ray diffraction (TRXD) data is not trivial because the signal from a solution contains not only the solute-only term as in the gas phase, but also solvent-related terms. To obtain structural insights, the diffraction signal in q space is often Fourier sine transformed (FT) into r space, and molecular dynamics (MD) simulation-aided signal decomposition into the solute, cage, and solvent terms has so far been indispensable for a clear-cut assignment of structural features. Here we present a convenient method of comparative structural analysis without involving MD simulations by incorporating only isolated-species models for the solute. FT is applied to both the experimental data and candidate isolated-solute models, and comparison of the correlation factors between the experimental FT and the model FTs can distinguish the best candidate among isolated-solute models for the reaction intermediates. The low q region whose influence by solvent-related terms is relatively high can be further excluded, and this mode of truncated Fourier transform (TFT) improves the correlation factors and facilitates the comparison. TFT analysis has been applied to TRXD data on the photodissociation of C<sub>2</sub>H<sub>4</sub>I<sub>2</sub> in two different solvents (methanol and cyclohexane),  $HgI_2$  in methanol, and  $I_3^-$  in methanol excited at 267 nm. The results are consistent with previous conclusions for C<sub>2</sub>H<sub>4</sub>I<sub>2</sub> in methanol and HgI<sub>2</sub> in methanol, and the new TRXD data reveal that the C<sub>2</sub>H<sub>4</sub>I transient radical has a bridged structure in cyclohexane and  $I_3^-$  in methanol decomposes into  $I+I_2^-$  upon irradiation at 267 nm. This TFT method should greatly simplify the analysis because it bypasses MD simulations.

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# Resonance Raman Study on the Solvation of p-Nitroaniline in Supercritical Water

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Although solvation in supercritical water (SCW) is an important subject in understanding unique chemical processes which occur in SCW, spectroscopic approaches to this problem are still limited due to the experimental difficulties. Most studies until now are those on solvatochromic shift or the fluorescence stokes shift, and the local density enhancement near the critical point has been discussed based on the density dependence of the peak shift. We worked on the vibrational spectroscopic study of the solvation in SCW. We applied the resonance Raman spectroscopy to the solution in SCW for the first time. As a target probe molecule, we chose p-nitroaniline (PNA).

Figure 1 shows the results of the Raman spectra in SCW at 668K. The band which assigned to the NO<sub>2</sub> stretching mode shows a strong density dependence and other bands shown here do not show the density dependence. The band shift of the NO<sub>2</sub> stretching mode is about 10 cm<sup>-1</sup> from the highest density to the lowest density in the measurement, although the bandwidth of this mode is not so significant.

Figure 2 shows that a correlation exists between the peak frequency of the UV absorption of pNA and the frequency of the dominant (high-frequency) component of the NO<sub>2</sub> mode. In conventional solvents the NO<sub>2</sub> vibrational frequency shows a V-shaped dependence on the absorption frequency, and the results in SCW span the region from tetrahydrofuran to cyclohexane. Solvation of pNA in SCW is thus apparently similar to that found in nonpolar solvents when assessed either by the absorption peak (relative stabilization of the excited state) or by the NO<sub>2</sub> frequency (relative contribution of charge separated character in the ground state).



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# Photoionization Spectroscopy of the Metal-benzene Sandwich Complex and Its Ar and Benzene Clusters /Photodissociation Dynamics of Thiophenol

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Pulsed-field ionization spectroscopy of a metal-benzene sandwich complex, bis(n6benzene)chromium has been carried out to give the accurate ionization potential (IP) of  $5.4665 \pm 0.0003$  eV and cationic vibrational frequencies [1,2]. The low-n Rydberg states of n<100 are found to be also optically excited and those are ascribed to the *nf*-Rydberg series. Ionization behavior strongly depends on the electric field conditions. Many inter- and intramoiety vibrational modes are identified in the ionization spectrum. Ab initio results are compared with the experiment. Additionally, the Cr(Bz)<sub>2</sub>-Ar<sub>n</sub> clusters are found in the supersonic jet. The magic number of 6 is experimentally found. The shift of the ionization potential as a function of the cluster size indicates that the clustering site is equivalent until n = 6. For the larger clusters, the IP shift shows the different behavior, indicating that the clustering site becomes diverse. The finding of the magic number in the van der Waals cluster is quite rare, and theoretical calculations are carried out for the explanation of the experiment. The other type of the cluster,  $Cr(Bz)_2$ -Bz<sub>n</sub>, is also formed in the beam and its IP dependence on the cluster size is investigated. Contrary to the case of the Cr(Bz)<sub>2</sub>-Ar<sub>n</sub> cluster, the Cr(Bz)<sub>2</sub>- $Bz_n$  cluster shows the exponential decrease of the  $\Delta IP$  as the number of benzene solvent increases. The plausible structures of the clusters will be discussed.

In the second part of the talk, photodissociation dynamics of thiophenol will be discussed. The S-H bond dissociation dynamics has been investigated using the velocity-map ion imaging method [3,4]. The detachment of H from the thiophenol gives rise to the radical with the orbital which is either parallel with or perpendicular to the molecular plane. The Dopplerfree detection of H atom is also demonstrated. The intramolecular orbital alignment will be explored in other thiophenol with different chemical substitutions.

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# Nanoscale Chemistry: From Single Molecule to Self-assembled Structures

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Scanning tunneling microscopy (STM) has been used not only to image but also to manipulate and characterize individual molecules on metallic surfaces. The capability of studying a single molecule provides nanoscale information such as environmental effect that cannot be obtained from macroscopic measurements. In this talk, I introduce recent advances in nanoscale chemistry using STM. My first talk is on the wetting behavior of water on Cu(110) surface<sup>1)</sup>. At 5 K, water migrates very slowly on the surface and predominantly appears as a monomer. The molecules diffuse on the surface at elevating temperature, and aggregate into dimer, trimer and larger clusters. When adsorbed at 78 K, water molecules can migrate fast enough to make hydrogen bonds with each other and form ice-like structure. Reflecting the structural anisotropy of Cu(110), water molecules aggregate into self-assembled one-dimensional (1D) ice along the specific direction of the surface (Fig.1). The origin of this unique 1D growth will be discussed in terms of stress relaxation.

The second talk is a single-molecule study of acetylene on Cu(110). An acetylene molecule appears as a dumbbell shape (Fig.2). Single-molecule vibrational spectroscopy was conducted and  $\sim sp^3$  rehybridization was found. Hopping motion of an acetylene molecule can be induced by injecting energetic tunneling electron. The motion was found to be mainly initiated by vibrational excitation of C-H stretch.



Fig. 1 Water chain on Cu(110), 90x90A<sup>2</sup>



Fig.2 Acetylene molecules on Cu(110), 48x38 A<sup>2</sup>

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# **Reaction of Amino Acids on the Ge(100) Surface**

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The adsorption of amino acids on the Ge(100) surface was investigated with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, scanning tunneling microscopy (STM) and density functional theory. All amino acids consist of a carboxylic acid (-COOH) and an amino (-NH<sub>2</sub>) functional group attached to the same tetrahedral  $\alpha$ -carbon atom. Amino acids are distinguished by the different R-groups attached to the  $\alpha$ -carbon. The simplest amino acid is glycine, with an H as the R-group. Our MIR-FTIR results indicate that for glycine, the principal surface product is formed by OH dissociation of the carboxylic acid group. This result is consistent with calculations, which indicate that the OH dissociation product is the most thermodynamically stable. More than one surface product is evident in the spectra, however, with the results suggesting products containing nitrogen dative bonds. Based on the understanding of glycine, the effect of the side chain can be probed in more complex amino acids. Histidine ( $C_6H_9N_3O_2$ ), a basic amino acid, has an imidazole group as the R-group. STM results reveal the ordering of histidine molecules on the Ge(100) surface. At saturation coverage, the STM images show globally ordered arrays consisting of dumbbell shape features that are independent of the direction of the underlying dimer rows of the Ge (100) surface. We will present the adsorption structures and discuss the role of adsorbateadsorbate intermolecular interactions based on the experimental results and ab initio calculations of glycine. The studies of glycine and histidine allow us to understand the competitive tendencies of the amine and carboxylic acid functional groups in amino acids and also identify the reactivity of the moieties present in the side chain. These results provide a basis for future studies of amino acid polymers, i.e. proteins, which can be used in biocompatible materials of the future.



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# **Condensed Phase Chemical Dynamics Detected by Multidimensional Spectroscopy**

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Ultrafast nonlinear spectroscopy plays a pivotal role in investigating inter- and intramolecular motions in complex molecular systems. Over the last decade, extensive theoretical, computational, and experimental efforts have been made for multidimensional vibrational spectroscopy [1] to have a variety of information for molecular motion and interactions. Consequently, multidimensional spectroscopy has been proven to be a valuable and versatile tool for diverse topics in condensed phases as the anharmonicity of potentials, vibrational mode coupling, vibrational dephasing mechanisms, and structural changes of large molecules. The distinctive advantage of the multidimensional vibrational spectroscopy is due to the multiple pumping and probing processes, which can be described by the multipoint correlation functions of the porlarizability and the dipole moments of relevant vibrational coordinates.

In this poster, we show two-dimensional infrared (2D-IR) spectra, which are defined by the four-point correlation function of dipole moments, for such various chemical systems

as reactive systems, anharmonic mode coupling systems, and so on. We then demonstrate the possibility to scrutinize certain aspects of condensed phase chemical dynamics by means of multidimensional spectroscopy. [2,3]

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Fig1. 2D-IR spectrum from a tunneling reaction system. [2]

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