Atsushi Seki （Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering）

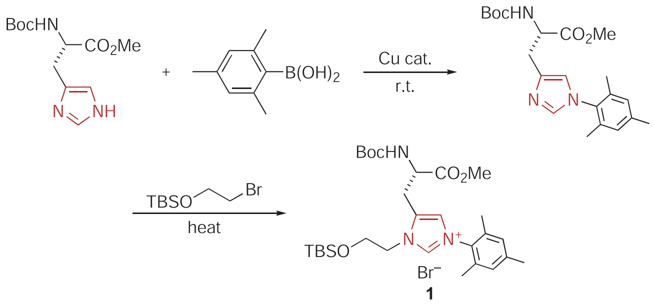
Period

May 17, 2004 – March 31, 2005

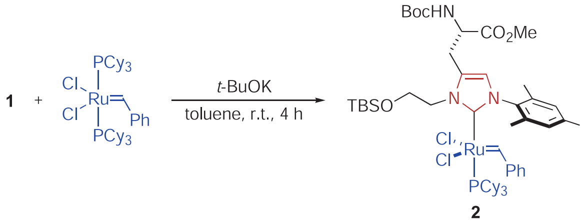
Research

The discovery of well-defined new metathesis complexes has revolutionalized organic synthesis. Ruthenium–carbene complexes by Grubbs are the most prominent of these complexes. Further advancement has been achieved by replacement of one PCy_3 group by an *N*-heterocyclic carbene (NHC). These “second-generation” catalysts show greatly improved reactivity as well as higher stability. In this study, ruthenium complexes bearing histidine-derived *N*-heterocyclic carbene were synthesized, and these catalytic activities in the olefin metathesis reaction were examined.

Mesityl group was introduced to the imidazole core of Boc-His-OMe by using copper-catalyzed arylation with arylboronic acids (eq 1). Subsequent alkylation of the resulting *N*-arylimidazole with $TBSO(CH_2)_2Br$ furnished *N*-aryl *N* '-alkyl imidazolium bromide **1**. Replacement of PCy_3 ligand of the Grubbs first-generation complex with histidine-derived *N*-heterocyclic carbene, which was generated in situ from imidazolium salt **1** and *t*-BuOK, occurred at room temperature in toluene to afford second-generation type ruthenium complex bearing histidine-derived *N*-heterocyclic carbene (eq 2).

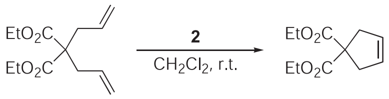


(1)



(2)

A new Grubbs type metathesis complex **2** in hand, its catalytic activity was examined. In the presence of **2**, dimethyl diallylmalonate underwent ring-closing metathesis reaction in dichloromethane at room temperature to give cyclopentane derivative (81% conv. after 45 min) (eq 3).



(3)

Encouraged by the results, we are examining incorporation of the complex **2** into peptides.

関　淳（せき　あつし）工学研究科合成・生物化学専攻有機金属化学研究室

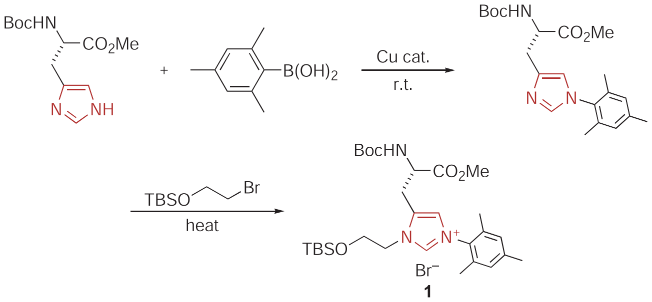
採用期間

平成 16 年 5 月 17 日～平成 17 年 3 月 31 日

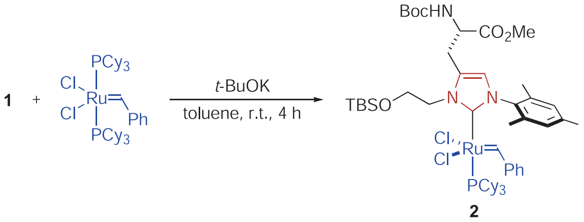
研究報告

近年、イミダゾールなどの含窒素複素環から誘導される安定カルベンを遷移金属の配位子として利用することで高い反応性や選択性を得ようとする研究が盛んである。本研究では、必須アミノ酸の一つであるヒスチジンのイミダゾール環のカルベン配位子への誘導および含ヒスチジンペプチドを配位子とする遷移金属錯体の合成を行った。さらに、これらペプチドからなる酵素様反応場における様々な遷移金属触媒反応について検討を行った。

銅触媒によるアリールボロン酸を用いるアリール化反応によってヒスチジン (Boc-His-OMe) のイミダゾール環の窒素上にメシチル基を導入し、続いて 2-シロキシブチルブロミドと反応させることで 2-シロキシエチル基を導入しイミダゾリウム塩 **1** を得た (式 1)。これの *t*-BuOK による脱 HBr によって生成した含窒素ヘテロ環カルベンを単離することなく Grubbs 錯体と反応させることでルテニウムカルベン錯体 **2** を得た (式 2)。

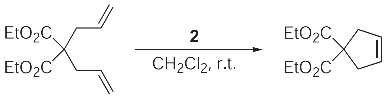


(1)



(2)

この錯体 **2** を触媒としてジアリルマロン酸ジエチルの閉環メタセシス反応を塩化メチレン中、室温で行ったところ、45 分間で 81% がシクロペンテンに転化した。



(3)

錯体 **2** のペプチド鎖への導入による酵素様反応場の構築、**1** のイミダゾール環の炭素－炭素二重結合を還元したイミダゾリン体の合成を検討している。

Teruaki Wajima （Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering）

Period

September 1 2005 – March 31 2007

Research

TRPM2 channels are activated by hydrogen peroxide, which lead to intracellular Ca^{2+} overload and cell injury. Purpose of the present study is mainly to elucidate roles of M2 on cerebral vascular and myocardial injuries in M2 knockout mice *in vivo.*

(1) Role of M2 on cerebral vascular injury: Hippocampal CA1 pyramidal neurons show vulnerability to transient cerebral ischemia and subsequently lead to delayed neuronal death. Moreover, a sustained cerebral ischemia induces cerebral infarction. Intracellular Ca^{2+} overload and reactive oxygen species are implicated in occurrence of these diseases. In the present study, effect of hydrogen peroxide on long-term potentiation (LTP) is being examined in order to elucidate roles of M2 on irreversible cerebral vascular injury. Field excitatory postsynaptic potential of wild type mice was measured using multi-channel extracellular recording system. As a result, LPT was observed (Fig. 1A). On the other hand, treatment with hydrogen peroxide completely inhibited its response (Fig. 1B). Dose finding studies of hydrogen peroxide are ongoing.

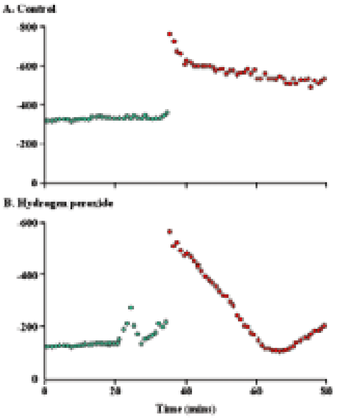


Fig. 1 Effect of hydrogen peroxide on long-term potentiation

(2) Role of M2 on myocardial injury: Intracellular Ca^{2+} overload plays an important role on cardiac ischemia/reperfusion-induced myocardial infarction. In addition, reactive oxygen species (ROS) produced by neutrophils are one of deleterious factors for development of myocardial infarction. Thus, it can be surmised that M2-deficient mice reduce the infarct size by inhibition of intracellular Ca^{2+} overload due to neutrophils-derived ROS. Establishment of mice myocardial infarction model is ongoing.

輪島　輝明（わじま　てるあき）工学研究科合成・生物化学専攻分子生物化学研究室

採用期間
平成 17 年 9 月 1 日～平成 19 年 3 月 31 日

研究報告
TRPM2 チャネル（M2）は活性酸素により活性化され、細胞内 Ca^{2+} 過負荷と細胞傷害を惹起する。本研究は、M2 のノックアウトマウスを用いて、虚血再灌流による脳血管及び心筋傷害における M2 の役割を *in vivo* において解明することを主な目的としている。

（1）脳血管傷害における M2 の役割：海馬の CA1 領域の錐体細胞は一過性の虚血においても脆弱性を示し、遅発性神経細胞死に陥る。また、脳虚血が長時間持続すれば脳梗塞を生じる。これらの疾患には、細胞内 Ca^{2+} 過負荷と活性酸素が関与している。本研究では、このような不可逆的な脳血管傷害における M2 の役割を解明するため、海馬の長期増強（LTP）に対する過酸化水素の作用に着目した。マルチチャンネル細胞外記録システムを用いて野生型マウスの細胞外興奮性シナプス後電場電位を測定した結果、LTP が認められた（図 1 A）。これに対して、過酸化水素を処置するとその反応は完全に抑制された（図 1 B）。現在、過酸化水素の条件を詳細に検討中である。

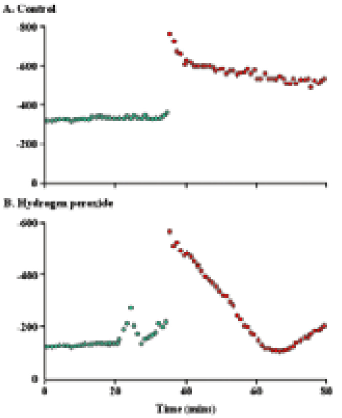


図 1　長期増強における過酸化水素の作用

（2）心筋傷害における M2 の役割：心臓の虚血再灌流による心筋梗塞には、心筋細胞への Ca^{2+} 過負荷が重要な役割を演じている。また、好中球から産生される活性酸素は心筋梗塞を進展させる要因の 1 つである。従って、M2 をノックアウトしたマウスにおいては、好中球由来の活性酸素による細胞内 Ca^{2+} 過負荷を抑制し得ることが考えられ、梗塞サイズの縮小作用が期待できる。現在、心筋梗塞モデルの条件を検討中である。

Weiping Gao （Laboratory of Chemistry of Polymer Materials, Division of Materials Chemistry, Institute for Chemical Research）

Period

1 April, 2005 –

Research

In our lab, well-defined “concentrated” polymer brushes have been prepared, for the first time, by atom transfer radical polymerization (ATRP)[1]. The surface density σ reached as large as 0.7 chains/nm^2 for common polymers like poly (methyl methacrylate) (PMMA) and polystyrene (PS). This density was more than 1 order of magnitude higher than those of typical “semi-dilute” brushes. Recent studies revealed that these concentrated brushes have structure and properties quite different and even unpredictable from those of semi-dilute brushes.

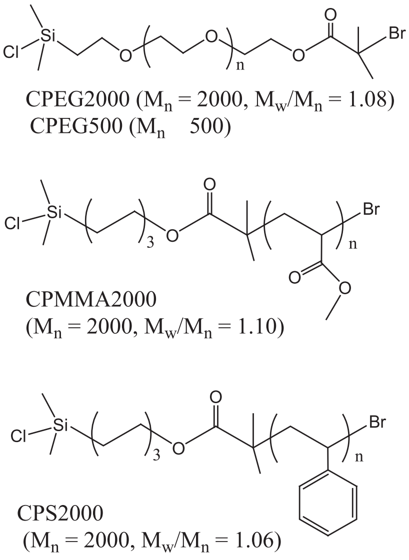


Figure 1 Surface-fixable initiators with flexible spaces

My research project is to further increase the grafting density of polymer brushes, which are expected to show more fascinating properties. In the above-mentioned successful cases, a low-mass initiator was fixed on a surface with a surface density σ_i much higher than σ. This suggests lower initiation efficiency of surface-initiated ATRP than that of the solution system, presumably because of too low mobility of the initiating moiety strictly localized on the surface. To overcome this, we planed to immobilize the initiating moiety via a flexible spacer on the surface. For this, we have newly synthesized three different types of surface-fixable initiators with flexible spacers as shown in Figure 1. These initiators were fixed on a cleaned silicon wafer and subjected to graft polymerization of MMA. Table I shows the results of σ_i and σ. They were successfully immobilized on a surface with σ_i high enough to produce a higher-density polymer brush, if the initiation efficiency is sufficiently high. After graft polymerization, the highest graft density up to now was 0.9 chains/nm^2 for the PEG initator with M$_n$ = 500. This value was improved by about 30 % as compared with the previous data. Unfortunately, the PEG initiator with M$_n$ = 2000 gave a lower σ value. This may be due to the physisorption of the spacer PEG chain on the silicon wafer, and hence will be improved by end-capping of unreacted silanol groups with an inert silane coupling agent. Further studies are going on to improve the graft density and to investigate the surface properties of such higher-density polymer brushes.

Table 1 Initiator density (σ_i), graft density (σ) and initiation efficiency

Initiators	б$_i$ chains/nm^2	б$_{PMMA}$, chains/nm^2	Initiating efficiency
CPEG2000	1.0	0.30	30%
CPEG500	2.5	0.90	36%
CPMMA2000	1.3	*	*
CPS2000	*	*	*

*to be measured

1) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, 31, 5934.

Keiichi Katoh （Kyoto Univ., Institute for Chemical Research）

Period

1 April 2005 – 31 March 2006

Research

Molecular switching materials have recently received much attention in the field of advanced materials for electrooptic devices. The spin-crossover (SC) complex shows a spin transition between the low-spin (LS) and the high-spin (HS) states as a result of external influences such as temperature and pressure changes. It has also been observed that some SC complexes can be switched between the LS and the HS states by light. This phenomenon is known as the LIESST (Light Induced Excited Spin State Trapping) effect. The transition metal complexes with organic donors such as tetrathiafulvalene (TTF) have numerous desirable or notable properties such as magnetism, electric conductivity, and optical respondence. The chemistry of TTF and its derivatives has been intensively studied since the discovery of the first metallic charge-transfer (CT) complex of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).

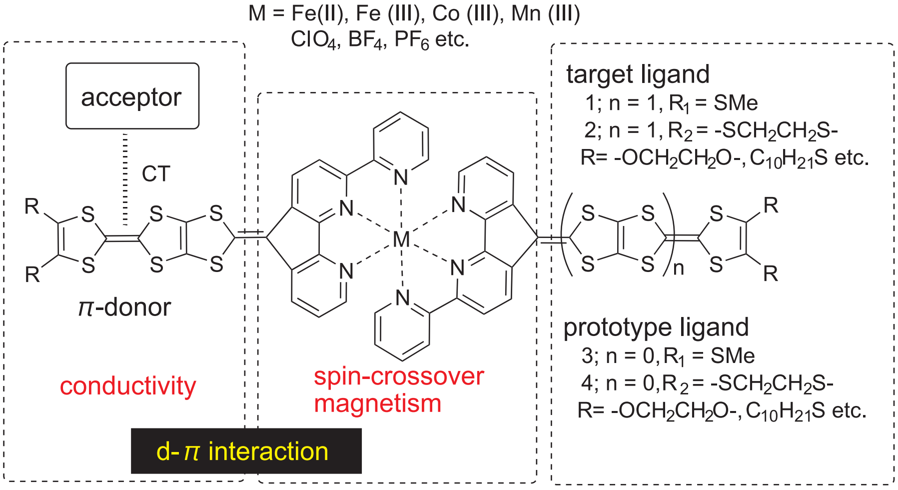


Figure 1 optically switchable magnetic-conductive conjugated molecular system

In order to combine photomagnetic properties and electric conductivity, the author designed an optically switchable magnetic-conductive conjugated molecular system (**Figure 1**). First, however, the author synthesized a prototype ligand to search the coordination function which is constructed by *N,N,N*-tridentate ligand and 1,3-dithiole ring (**3** and **4**), and the analysis of its chemical properties is now in progress. It could be possible that a π-donor combined with coordination functionality can be used as a ligand for transition metals. The synthesis of such a hybrid ligand is an important challenge for the development of an optically switchable magnetic-conductive conjugated molecular system.

Qing Luo （Laboratory of Molecular Materials Chemistry, Division of Environmental Chemistry, Institute for Chemical Research）

Period

1 May, 2004 – 31 March, 2006

Research

(1) New solid-state NMR pulse methods. For solid organic and polymeric materials, homonuclear correlations, e.g. ^{13}C-^{13}C interaction, contain important structural information. Normally, such homonuclear interaction can only be studied by two-dimensional NMR methods, e.g. two-dimensional double-quantum NMR (2D DOQSY) and spin diffusion spectroscopy. However, 2D NMR experiments are usually time-consuming and almost impossible for natural abundant samples. We have developed a new 1D experiment, namely homonuclear cross polarization, which is based on the selective soft pulses and Hartmann-Hahn magnetization transfer, to explore the homonuclear correlations. This method has been verified in a ^{13}C enriched β-alanine sample. The methyl carbon was selectively excited and then the magnetization was transferred to carbonyl carbon through a spin locking RF. The intensity of the carbonyl carbon as a function of the contact time presents a typical CP dynamic curve. Furthermore, a modified selective excitation pulse method to completely suppress artifacts, which are serious problems in studying natural abundant samples, was also designed as shown in Figure 1. As a result, the artifacts in the homonuclear cross polarization experiment for the natural abundant adamantane solids can be suppressed to a negligible level. Signal from the ^{13}C-^{13}C pairs isolated from others, which presents a J-coupled splitting, can be selectively observed. More effective methods for other organic materials are being developed by employing different selective excitation pulse sequences.

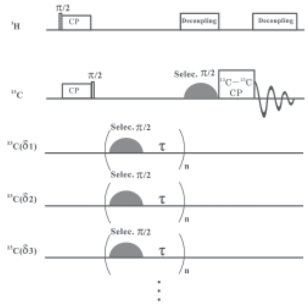


Figure 1

(2) Solid-state ^{13}C/^{1}H NMR experiments under ultrahigh magnetic field (930 MHz). To obtain higher resolution and higher signal noise ratio (S/N) in solid-state NMR spectroscopy, the static magnetic field is kept increasing. The world highest 930 MHz solid-state NMR spectrometer (ECA930) has been equipped in National Institute of Material Science (NIMS). We have joined to the cooperative project to establish the new system, including modifications and developments of probes, power amplifiers, and RF controls for precise pulse technologies and higher sensitivities. Different organic materials including polymer and cellulose samples have been measured by using 1D and 2D NMR methods on the ECA930.

(3) Characterization of polymer thin films by 2D solid-state NMR. Some 2D solid-state NMR methods, for example DOQSY and CSA spin exchange, can be used to quantitatively characterize the local structure, i.e. torsion angle and internuclear distance, of organic materials. Now, we are trying to prepare ^{13}C enriched thin films divided from the substrate with proper thickness to study the relationship between the orientation, conformation and the thickness of the films.

Publications

- **Qing Luo**, Hironori Kaji, and Fumitaka Horii, One-dimensional solid-state NMR methods using selective soft pulses to detect the through-space ^{13}C-^{13}C correlation: Homonuclear cross polarization, *The 1st Asia-Pacific NMR Symposium*, **2005**, p. 195.
- **Qing Luo**, Fumitaka Horii, Solid-State NMR, *Kobunshi (High polymers)*, in press

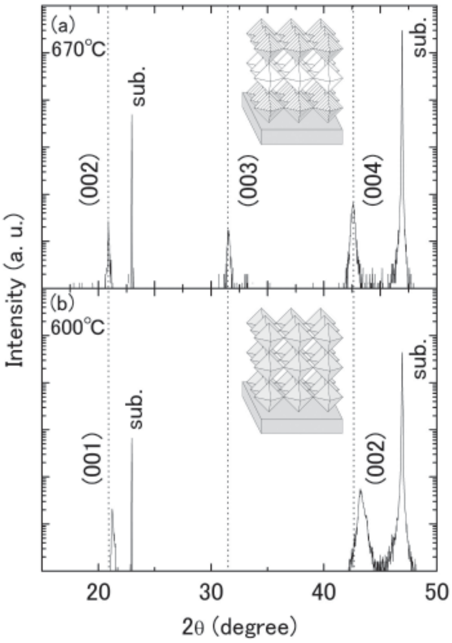
Atsunobu Masuno （Advanced Inorganic Synthesis, Division of Synthetic Chemistry, Institute for Chemical Research）

Period

1 April, 2005 – 31 March, 2006

Research

(1) Layered double perovskite thin films



Among many double perovskites with the formula $A_2BB'O_6$, La_2CuSnO_6 (LCSO) is the only double perovskite with a layered configuration of B-cations that can be prepared at ambient pressure. The layered LCSO with a two-dimensional structure is expected to exhibit extraordinary anisotropic physical properties. In this work, epitaxial LCSO films were successfully synthesized by a pulsed laser deposition (PLD) method. In figure, we show θ-2θ X-ray Diffraction patterns for typical LCSO films deposited on LSAT (001) substrates at substrate temperature = (a) 670 ℃ and (b) 600 ℃ . In figure (a), a superlattice peak corresponding to the (003) reflection of layered double perovskite unit cell is found at around $2\theta \approx 32^\circ$, which assures the successful alternation of Cu^{2+} and Sn^{4+} ions perpendicular to the film plane, as illustrated in the inset. In contrast, no superlattice peak is observed as shown in figure (b), indicating the film has simple perovskite structure with random arrangement of Cu^{2+} and Sn^{4+} ions. Thus, we can control the degree of B-cations arrangement by changing substrate temperature during deposition.

(2) Multiferroic double perovskite thin films

Double perovskite Bi_2NiMnO_6 (BNMO) thin films were prepared by a PLD method. BNMO is a new multiferroic (ferromagnetic and ferroelectric) compound with Ni^{2+} and Mn^{4+} ions ordered in a rock-salt configuration. Magnetic measurements revealed that the obtained films were ferromagnets. Measurements of ferroelectric properties are now in progress.

Publications

- “Control of physical properties of micro-fabricated perovskite-type manganese oxide thin films by spin-polarized current” **A. Masuno**, T. Terashima, Y. Shimakawa, M. Takano, *J. Jpn. Soc. Powder Powder Metal.*, 52(2005)
- “New ferromagnetic ferroelectric Bi_2NiMnO_6 compound with double-perovskite structure” Y. Shimakawa, M. Azuma, K. Takata, M. Hashisaka, D. Kan, **A. Masuno**, M. Sakai, T. Terashima, K. Mibu, and M. Takano, *Proc. in 12th US-Japan Seminar on Dielectric & Piezoelectric Ceramics* (2005) 203-206
- “Blue-Light Emission at Room Temperature from Ar+-Irradiated $SrTiO_3$” D. Kan, T. Terashima, R. Kanda, **A. Masuno**, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, and M. Takano, *Nature Materials*, 4 (2005) 816-819

  1 article in preparation (Appl. Phys. Lett.)

Noriyoshi Nagahora （Division of Synthetic Chemistry, Institute for Chemical Research）

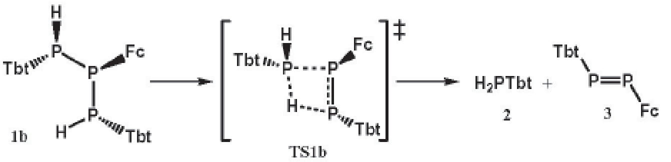
Period

1st April, 2005–31st March, 2006

Research

Remarkable progress has been made in the chemistry of open-chain phosphorus compounds because of their unique structures and properties. In most cases, open-chain phosphorus hydrides are thermally unstable and difficult to be treated under ambient temperature due to the weak phosphorus–hydrogen bonds. On the other hand, in the course of our studies on kinetically stabilized doubly bonded systems between heavier Group 15 elements using original steric protection groups, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups, we found that the Tbt group is applicable to the kinetic stabilization of $(TbtHP)_2PFc$ (**1**). We report here the synthesis and structure of kinetically stabilized 1,3-dihydrotriphosphane **1**, which can be isolated at room temperature, together with its unique thermal disproportionation reaction leading to the formation of H_2PTbt (**2**) and (*E*)-TbtP=PFc (**3**).

Addition of LiP(H)Tbt to THF solution of dichloroferrocenylphosphine at –78 °C gave a diastereomer mixture of **1** as orange crystals in 73% isolated yield. The molecular structure of **1** was determined by X-ray crystallographic analysis (Figure 1). We carried out the thermolysis of **1** in toluene-d_8 to investigate the thermal stability of **1**. Heating of toluene solution of **1** in a sealed tube at 130 ℃ afforded both **2** and **3** in the ratio of 1:1. Plots of a logarithm of the concentration of **1** against time show the linear decay of **1** through >90% consumption in toluene-d_8 solution at 130 ℃, indicating that the thermolysis is the first-order reaction depending on the concentration of the substrate with the rate constant $k = (6.39 \pm 0.22) \times 10^{-5}$ s^{-1}. The activation parameters were estimated by the Eyring plot as $\Delta H^{\ddagger} = 28.8 \pm 0.86$ kcal/mol, $\Delta S^{\ddagger} = -6.8 \pm 1.8$ cal/mol • K, and $\Delta G^{\ddagger}$ (298 K) = 30.8 ± 0.86 kcal/mol, respectively. We have performed theoretical calculations on the reaction mechanism for the disproportionation reaction of the parent P_3H_5 giving PH_3 and (*E*)-HP=PH as a model system. Consequently, the reaction mechanism of the thermal disproportionation reaction of **1** is most likely interpreted in terms of the pathway from **1b** leading to the formation of **2** and **3** via **TS1b** with a four-membered ring geometry.



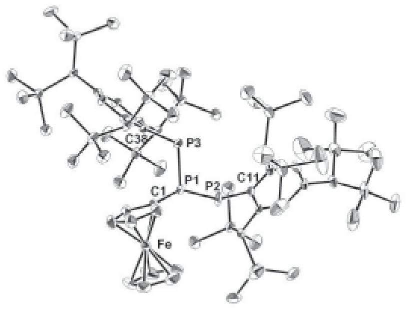


Fig. 1 ORTEP drawing of **1** with thermal ellipsoid plots (50% probability). Hydrogen atoms are omitted for clarity.

Publications

1. "Synthesis and Structure of a Stable 1,3-Dihydrotriphosphane and Its Thermal Decomposition Leading to the Formation of the Corresponding Phosphine and Diphosphene" **Nagahora, N.**; Sasamori, T.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 3074–3080.
2. "Systematic Studies on Redox Behavior of Homonuclear Double-bond Compounds of Heavier Group 15 Elements" Sasamori, T.; Mieda, E.; **Nagahora, N.**; Takeda, N.; Takagi, N.; Nagase, S.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 166–167.

長洞　記嘉（ながほら　のりよし）化学研究所有機元素化学研究領域

採用期間

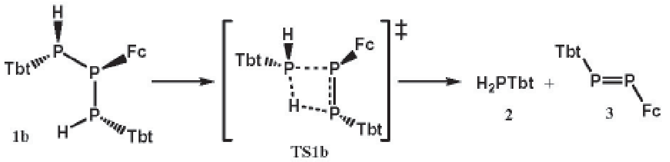
平成 17 年 4 月 1 日～平成 18 年 3 月 31 日

研究報告

これまでにジホスファンやトリホスファン等の直鎖状リン化合物に関する多くの報告があり、その特異な構造や物性に注目が集まっている。その中でもホスフィン上に水素原子を有する phosphorus hydride 類は、室温溶液中で容易に分解することが報告されている。一方、既に我々は非常に有効な立体保護基である 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) および 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) 基を用い、種々の高周期 15 族元素間二重結合化合物を安定な化合物として合成・単離することに成功し、系統的な研究を行ってきた。その研究の途上において、1,3-ジヒドロ-2-フェロセニルトリホスファン **1** の安定化に Tbt 基が有用であるとこを見出した。さらに、1,3-ジヒドロトリホスファン **1** の熱分解反応において対応するホスフィン **2** とジホスフェン **3** が生成することを明らかにし、速度論および理論計算を用い反応機構について考察した。

ジヒドロホスフィン **2** とブチルリチウムから調製したリチウムホスフィドをジクロロフェロセニルホスフィンに作用させることで化合物 **1** を 73% の単離収率で得た。化合物 **1** の ^{31}P NMR を測定したところ、一つの ABX および二つの ABC パターンが観測された。これらは 3 種の異性体に由来するシグナルであり、前者は (1*R**,3*R**) 体、後者は (1*S**,3*R**) および (1*R**,3*S**) 体として帰属可能であった。最終的な構造決定は単結晶Ｘ線構造解析にて行い、構造パラメーターを得ることに成功した (図１)。次に、**1** の重トルエン溶液を脱気封管し加熱したところ、対応するホスフィン **2** とジホスフェン **3** が定量的に 1：1 の比で生成することを見出した。観測された不均化反応の反応速度は基質濃度に対し 1 次であり、活性化エンタルピーおよびエントロピーはそれぞれ約 +29 kcal/mol, –6.8 cal/mol･K と見積もられた。

さらに、P_3H_5 モデル分子の不均化によるホスフィン (H_3P) および (*E*)-ジホスフェン (HP=PH) 生成過程に関して理論計算を用い考察を行った。P_3H_5 分子の不均化過程において見積もられた$\Delta S^{\ddagger}$は –2.3 cal/mol･K であり、1,3-ジヒドロトリホスファン **1** の熱分解において実験的に観測された$\Delta S^{\ddagger}$と類似している。つまり、**1** の熱分解反応においても分子内水素移動により四員環遷移状態を経由し、不均化反応が進行しているものと考えられる。



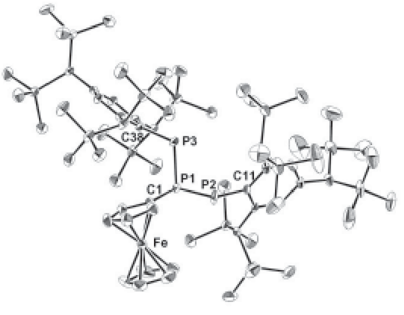


図 1 化合物 **1** の ORTEP 図

論文発表

1. “Synthesis and Structure of a Stable 1,3-Dihydrotriphosphane and Its Thermal Decomposition Leading to the Formation of the Corresponding Phosphine and Diphosphene” **Nagahora, N.**; Sasamori, T.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 3074–3080.
2. “Systematic Studies on Redox Behavior of Homonuclear Double-bond Compounds of Heavier Group 15 Elements” Sasamori, T.; Mieda, E.; **Nagahora, N.**; Takeda, N.; Takagi, N.; Nagase, S.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 166–167.

Toyonari Yaji （Advanced Research Center for Beam Science, Institute for Chemical Research）

Period

1 April, 2005 – 31 March, 2006

Research

(1) Scanning tunneling spectroscopy of Pt-1D-chainBQD

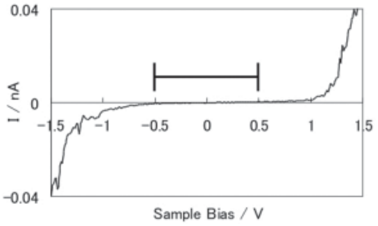


Figure 1 An STS of PTBQD thin film of 10 nm thickness on HOPG.

we measured current-voltage (I-V) curves of Pt-1D-chain in bis(1, 2-benzoquinonedioximato)platinum (II) (PTBQD) thin films on highly ordered pyrolytic graphite (HOPG) and molybdenum disulfide (MoS_2) by scanning tunneling spectroscopy (STS) to investigate the molecular scale electronic property of the thin films in application to a molecular wire for molecular electronics.

An I-V curve has two important features (figure 1). The first is an almost flat region over ca. 1 eV from -0.5 V to +0.5 V. This value of 1 eV corresponds roughly to the optical band gap of d-p transition. The second feature is that the resistivity in a region out of the energy gap is of the order of 10^2 Ω・cm. The value is comparable to that of PTBQD α-form single crystal. At molecular scale, the good electrical properties are kept up. In case of MoS_2 substrate, we obtained the same results.

(2) Nano-structure fabrication of a diacetylene

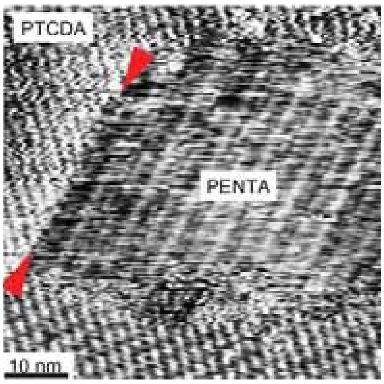


Figure 2 An STM image of PENTA domain embedded into PTCDA layer on HOPG (60nm x 60nm).

We investigated controlling of nano-structure of 10, 12-pentacosadiynoic acid diacetylene (PENTA) embedded in a perylene-3, 4, 9, 10-tetracarboxylic-dianhydride (PTCDA) mono-molecular layer at solid-liquid interface on HOPG for the purpose of fabrication of highly ordered one-dimentional nano-wire.

Figure 2 shows a scanning tunneling microscopic (STM) image of PENTA molecules adsorbed into the hole area of the PTCDA layer scratched by an STM tip. The nano-domain composed of PENTA molecules is formed and PENTA columns are highly ordered on HOPG although the scratched area has usually an irregular shape. This is concluded to be due to re-adsorption of PTCDA. We will fabricate the one-dimentional nano-wire by photo-polymerization in the future.

Publications

1. “STM and STS Studies on Platinum Chains in Bis (1,2-benzoquinonedioximato) platinum” **T. Yaji**, K. Yoshida, M. Tsujimoto, T. Nemoto, H. Kurata and S. Isoda, *Mol. Cryst. Liq. Cryst.*, submitted.
2. “Regularly-shaped diacetylene nano-structures on surfaces” O. Franco, T. Nemoto, **T. Yaji** and S. Isoda, *Mol. Cryst. Liq. Cryst.*, submitted.
3. “Structural Analysis of Bis (1, 2-benzoquinonedioximato) platinum (II) Polymorphs Formed Epitaxially on Alkali Halides” K. Yoshida, **T. Yaji**, M. Koshino and S. Isoda, *Jpn. J. Appl. Phys.*, 2005, **44**, 491-494.

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採用期間

平成 17 年 4 月 1 日 – 平成 18 年 3 月 31 日

研究報告

(1) 1 次元白金鎖の STS による電気的特性の研究

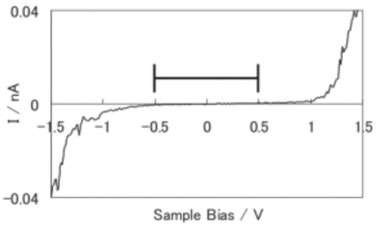


図 1　HOPG 基板上 PTBQD 薄膜（膜厚 10nm）の STS。

分子エレクトロニクスへの応用を目的として、高配向焼結グラファイト（HOPG）や二硫化モリブデン（MoS$_2$）基板上の Bis (1, 2-benzoquinonedioximato) platinum (II)（PTBQD）薄膜中の 1 次元白金鎖の分子レベルでの電気的な特性を調べるために、その電流 - 電圧 (I-V) 特性を走査トンネル分光法 (STS) によって測定した。

結果、その I-V 曲線には 2 つの特徴が認められた（図 1）。1 つは、-0.5V から +0.5V にかけて約 1eV の範囲で電流変化がほぼ一定であった。この約 1eV という値はバンドギャップ（d-p 遷移）にほぼ対応している。2 つ目の特徴は、この I-V 曲線から求められた抵抗率である。特に、バンドギャップの領域より大きな電圧印加領域では、$10^{2}\ \Omega\cdot\mathrm{cm}$ のオーダーにまでなり、この抵抗率値は PTBQD の α 形バルク単結晶の値に相当する。以上のように分子レベルにおいても良好な電気的特性を示すことを明らかにした。これらの特徴は、MoS$_2$ 基板についても同様に得られた。

(2) ジアセチレンのナノ構造構築

高配向の 1 次元ナノワイヤー作製のために、HOPG 基板上の perylene-3, 4, 9, 10-tetracarboxylic-dianhydride（PTCDA）単分子膜中に埋め込まれた 10,12-pentacosadiynoic acid（PENTA）ジアセチレンの固液界面におけるナノスケールでの構造化過程を研究した。

図 2 は走査トンネル顕微鏡（STM）の探針によって剥離された PTCDA 層部分に吸着された PENTA 分子の STM 像である。PENTA 分子のナノスケールのドメインが形成され、また剥離された領域は不規則であるが、PENTA 分子のカラムと PTCDA の境界は再吸着機構により急峻なものとなることを見出した。我々は、この状態の PENTA 分子を光重合して 1 次元ナノワイヤーの作製を行う予定である。

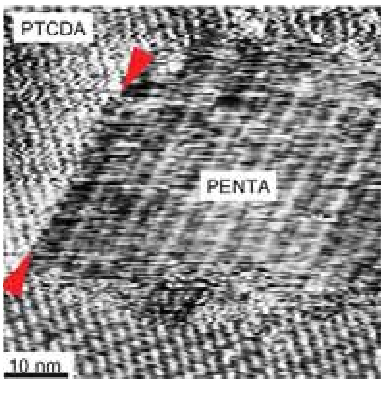


図 2　HOPG 上の PTCDA 層に埋め込まれた PENTA 分子の STM 像（60nm x 60nm）。

論文発表

1. “STM and STS Studies on Platinum Chains in Bis (1,2-benzoquinonedioximato) platinum” **T. Yaji**, K. Yoshida, M. Tsujimoto, T. Nemoto, H. Kurata and S. Isoda, *Mol. Cryst. Liq. Cryst.*, submitted.
2. “Regularly-shaped diacetylene nano-structures on surfaces” O. Franco, T. Nemoto, **T. Yaji** and S. Isoda, *Mol. Cryst. Liq. Cryst.*, submitted.
3. “Structural Analysis of Bis (1, 2-benzoquinonedioximato) platinum (II) Polymorphs Formed Epitaxially on Alkali Halides” K. Yoshida, **T. Yaji**, M. Koshino and S. Isoda, *Jpn. J. Appl. Phys.*, 2005, **44**, 491-494.

Taiyo Yoshioka （Division of Materials Chemistry, Institute for Chemical Research）

Period

1 April, 2005 – 31 March, 2006

Research

Uniaxially oriented thin films of poly(butylene terephthalate) (PBT) were studied by transmission electron microscopy (TEM). The specimen films were prepared by applying share to the melt: share rate was about $4 \times 10^6 s^{-1}$.

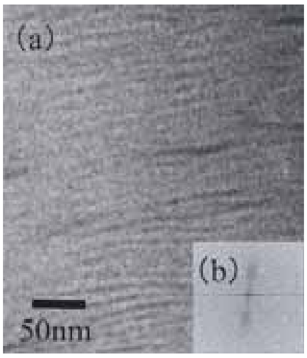


Figure 1
(a) Bright-field image of the uniaxially oriented thin film. (b) Fast Fourier transformation (FFT) pattern computed from a small area cut out from the image (a). The shearing direction is vertical.

In a conventional bright-field image of the uniaxially oriented thin film of PBT (see Figure 1(a)), the stacked-lamellar structures are recognized over a whole image. Two-dimensional fast Fourier transformation (FFT) was applied to a small area which was cut out from the image (a). The resulting FFT pattern is shown in Figure 1(b). The long period of the stacked-lamellar structures in image (a) is estimated from this pattern to be about 18nm.

A set of dark-field (DF) images, in which one is taken from the un-tilted film and the other is from the film tilted by 15 ° around the shearing direction, was obtained from the identical specimen region and compared with each other. Both of the DF images were taken by using a 100_α equatorial reflection. It was confirmed that appearance or disappearance of the stacked- lamellar structures as shown in Figure 2 occurred by tilting the specimen film. Figure 2 shows a DF image taken from the tilted film. In this image a well-defined stacked-lamellar structure can be clearly recognized, although any remarkable morphology was not found at the same region in the DF image taken from the un-tilted film. That is to say, it was demonstrated that all of the lamellae in one observed group as a stacked-lamellar structure have a same crystallographic orientation against the direction of incident electron beam. This result strongly indicates that the lamellae grow epitaxially from the backbone entity with a same crystallographic orientation between the backbone entity and the lamellae, since it was confirmed by selected-area electron diffraction study that this specimen film does not have any preferential orientation of a specific lattice plane at least in the tilting range from 0° to 40°. On the basis of these comparisons, it was concluded that shish-kebab structures are formed in the film and that each shish-kebab structure is composed of the lamellae which have a same crystallographic orientation.

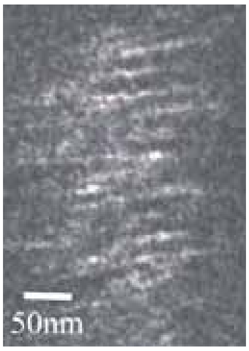


Figure 2
Dark-field TEM image of the uniaxially oriented thin film tilted by 15° around the shearing direction. The shearing direction is vertical.

Publications

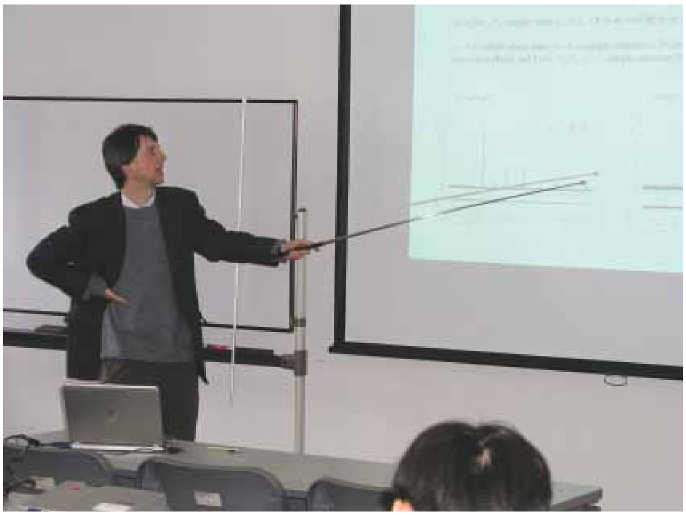
- “Morphological study by TEM on uniaxially oriented thin films of PBT” , T. Yoshioka, M. Tsuji, Y. Kawahara, S. Kohjiya, N. Manabe, Y. Yokota, *Polymer*, 2005, **46**, 4987-4990.

(Dr.) John Paul Attfield

Professor, Center for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK.
Staying Period: January 1, 2005 - March 31, 2005

Host: M. Takano (Int. Res. Cent. Elements Sci., Inst. Chem. Res.)

Professor J. P. Attfield came to my laboratory to discuss about the solid state chemistry of transition metal oxides. He gave us two lectures at Uji campus. The first one was focused on the chemical control of electronic oxides. He talked about the cation size effect of some perovskite-related manganese oxides, and charge ordering in manganese and iron oxides. He showed that the variations in property of $Ln_{1-x}M_x\text{MnO}_3$ perovskites, which show colossal magnetoresistances at the metal-insulator transition, and superconducting $Ln_{2-x}M_x\text{CuO}_4$ oxides, can be described using three parameters. These are the hole doping level x, the average radius of the trivalent Ln and divalent M (= Ca, Sr, Ba) cations at the A sites, $<r_A>$, and a new parameter - the variance in the A cation radius distribution, σ^2. Metal-insulator transition in $Ln_{1-x}M_x\text{MnO}_3$ perovskites and superconducting properties of $Ln_{2-x}M_x\text{CuO}_4$ materials are both sensitive to changes in these quantities. The second lecture was about some of his recent works on cobalt double perovskites $(\text{La}, M)_2\text{Co}M'\text{O}_6$ (M = Ca, Sr, Ba and M'= Ru, Nb). These compounds were shown to have geometrical spin frustration, due to the rock salt-type configuration of Co and Ru/Nb, which explains their magnetic behavior. He also talked about his recent works on perovskite-related chromium (IV) oxides synthesized using high pressure technique. These compounds are metastable at ambient pressure, and require high pressure during their syntheses. We had a collaboration on the synthesis of the series $\text{Sr}_{n+1}\text{Cr}_n\text{O}_{3n+1}$ during his stay, using the high pressure apparatus at our laboratory. We also started a collaboration on the study of a novel layered cobalt oxide $\text{SrCo}_6\text{O}_{11}$, which was recently found in my laboratory using high pressure technique and shows very uniue magneto-transport property. Prof. Attfield specializes in crystal structure study of oxides, and we are collaborating on the neutron powder difraction study of above compound.



Pei Tang, Ph.D.

Associate Professor of Anesthesiology and Pharmacology
University of Pittsburgh School of Medicine, Pittsburgh, PA 15261, USA
Staying Period: February 28, 2005

Host: M. Nakahara (Inst. Chem. Res.)

One of the greatest challenges to the scientific community in the past 150 years is to understand the action of a class of seemingly nonspecific drugs on the central nervous system to produce the physiological state of mind referred to as “general anesthesia” . How volatile anesthetics exert their action in the central nervous system to produce general anesthesia is not fully understood. Professor Tang gave us a lecture in Uji campus entitled “Protein dynamics and molecular mechanisms of general anesthesia” and suggested that the anesthetic effects on protein dynamics on the timescale corresponding to the characteristic time of protein function might underlie a unitary molecular mechanism of general anesthesia. The lecture covered the most recent structure and dynamics studies in her laboratories on neuronal nicotinic acetylcholine receptors and glycine receptors using nuclear magnetic resonance (NMR) spectroscopy and large-scale computer simulations. These studies, combined with the detailed analyses of anesthetic modulation of several soluble protein models, including firefly luciferase, calmodulin, and ketosteroid isomerase, pointed to a universal link between changes in protein global dynamics and the action of general anesthetics.

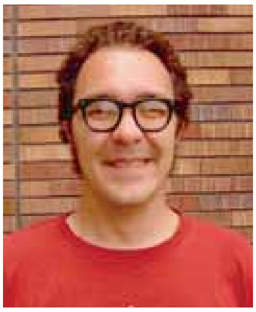
Michael L. Klein, Ph.D.

Director of The Laboratory for Research on the Structure of Matter
University of Pennsylvania, Philadelphia, PA 19104-6202, USA
Staying Period: April 14, 2005

Host: M. Nakahara (Inst. Chem. Res.)

Professor Klein's research is focused on quantum and classical computer simulation of condensed matter and biophysical systems at the atomic level with emphasis on the relationship between intra- and inter-molecular interactions and physical properties. The focus is on applications to realistic systems as well as developing new simulation methodologies. Areas of interest in the field of quantum simulations include the behavior of electrons in disordered materials using *ab initio quantum* simulation techniques with specific application to the metal-insulator transition and the use of path integral Monte Carlo calculations to probe quantum phenomena in solids, fluids and clusters. He gave a lecture in Uji campus entitled "Computer simulation of self-assembling amphiphilic systems: From natural to synthetic membranes". His lecture covered the approach to develop coarse grain models for synthetic and natural molecules that assemble into membranes and other morphologies. An overview was presented of recent applications of the methodology in probing the interaction of pore forming molecules with natural and synthetic membranes. Applications of the approach to cylinder forming molecules were also presented.

(Dr.) Simone Aloisio



Assistant Professor, California State University,
Staying Period : July 7 - August 13

Host: Masahiro Kawasaki (Dept. Mol. Eng., Grad. Sch. Eng.)

During my visit to the Kawasaki Lab at Kyoto University, I have worked closely with Mr. Enami, Mr. Hoshino, Mr. Yamanaka, and Mr. Imahama, in addition to Prof. Kawasaki and Dr. Hashimoto. We have worked on two projects. Both use the time resolved cavity ringdown spectroscopy (CRD) method to measure the kinetics of gas phase species. In the CRD method, the output of a pulsed laser enters a cavity formed by two highly reflective mirrors, creating a long effective path. A small amount of light leaks out of one end of the cavity, with its intensity falling off exponentially with each pass. In the presence of an absorbing species, the time it take for the intensity of light to decrease becomes shorter. This allows for extremely low limits of detection. Furthermore, when coupled with a photolysis laser shot, the kinetics of radical species can be observed. The Kawasaki lab has successfully measured the kinetics of many important reactions in this way.

One of the projects involved the study of the equilibrium constant for the formation of N_2O_4 from NO_2. While this process is well known to occur, there have been relatively few studies of this benchmark reaction. Furthermore, there are no published studies of this reaction using CRD. This reaction is important in the atmosphere, and the results of this study will have significant impact. Promising results have been obtained in this study, in that NO_2 was detected with the CRD instrument at low concentrations. The loss of NO_2 signal at lower temperatures, which is to be expected per the equilibrium reaction, was observed and quantified. Studies of this reaction continue.

The other project involved the study of the elusive Cl_3 radical. The Cl_3 radical is a so-called tri-halogen formed from the reaction of chlorine atom (Cl) and chlorine gas (Cl_2). Previously, a few laboratories had reported the detection of this species. Recently, however, some theoretical calculations have been published that dispute these observations as being attributed to Cl_3. There had been no direct absorption measurements of the Cl_3 radical. Prior to my arrival, the Kawasaki lab had been able to make the first direct absorption measurement of the Cl_3 radical. The rise and decay profiles of the formation and reaction of this species has also been observed, allowing for kinetic interpretation of the data. Work also continues on this project.

Thank you for supporting this visit. I feel that it was mutually beneficial to all parties involved.

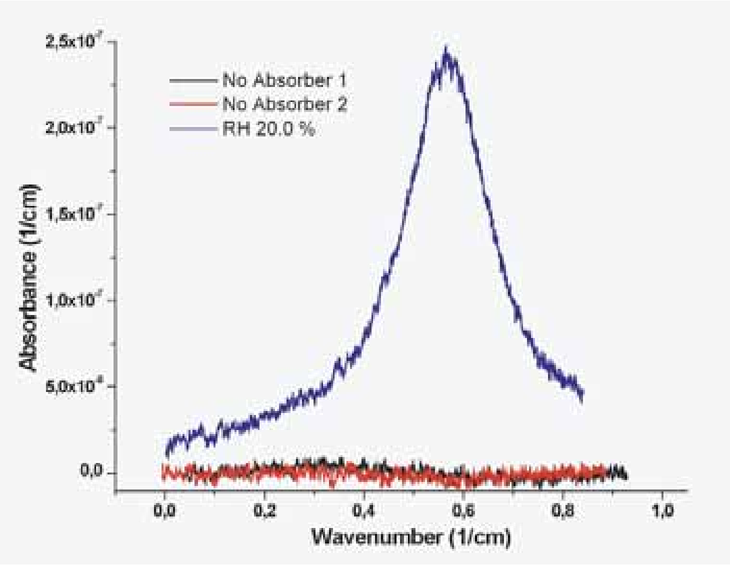
(Dr.) Mario Bitter

Post-Doctorial Research Associate
University of Cambridge, UK
Staying Period: July11 - August.2, 2005

Host: Masahiro Kawasaki (Dept. Mol. Eng., Grad. Sch. Eng.)

The application of cavity ringdown spectroscopy (CRDS) to atmospherically important species was studied employing two separate CRDS techniques. Cavity Enhanced Absorption (CEA) spectroscopy was employed in a laboratory study of rotationally resolved water vapour absorption lines around 652 nm. One isolated water line centred at 15337.8729 cm^{-1} was recorded at different water vapour concentrations in a nitrogen bath gas and fitted with a Voigt line profile. Together with ancillary measurements the line strength could be calculated (5.86×10^{-25}cm) and compared to data in three line parameter sets HITRAN, ESA and BR. (See the foot note for these abbreviates) An underlying continuum absorption was found whose absorbance increased linearly with water vapour. Its average cross section was $1.00 \times 10^{-25} cm^2$. Only $0.34 \times 10^{-25} cm^2$ of this continuum cross section could be accounted for by far line wing contributions. The measurements were affected by the employed diode laser's multimode operation. Numerical model simulation provided further evidence for this.

It was shown that from the three H_2O line parameter sets HITRAN, ESA and BR, the BR data base provided the best parameterisation in the probed spectral region.



HITRAN: HIgh-resolution TRANsmission molecular data base.
ESA: European Space Agency water vapour line parameter data set.
BR: Collaboration of Universities of Brusells and Reims data set.

(Dr.) Jean-Paul le Crane

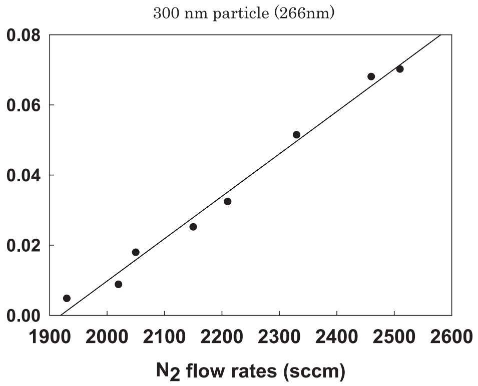
PhD student University of Bordeaux I
Staying Period: July27 - August.27

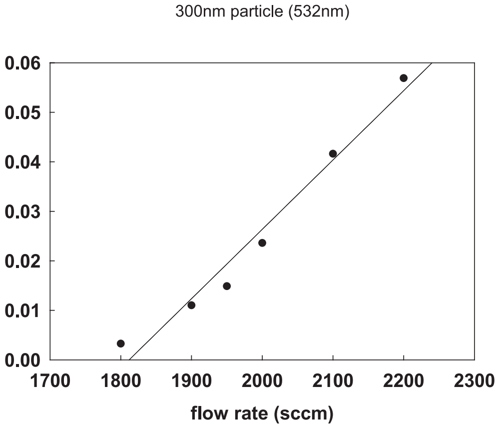
Host: Masahiro Kawasaki (Dept. Mol. Eng., Grad. Sch. Eng.)

Human activities result in the emission of a large quantity of compounds and species. Among these emissions, particulate matter is of particular interest in order to understand theirs impacts in the atmosphere. A large quantity of studies have been made on the atmospheric measurement of PM2.5 and PM10 particle size nevertheless smaller the particle is, deeper it is able to enter into the lung and more effective could be its activity in the human being. This is the reason why it is important to develop an experimental setup capable of measuring 100 nm particle size.

The experimental setup consists in a cavity ring down where styrene particles (500 nm or 300 nm or 100 nm size) are introduced owing to a nebulizer in which a flow of nitrogen circulate. A part of the light, coming from a YAG laser, which the wavelength could be adjusted at 266, 532 and 1064 nm, is scattered by particle and the remaining light is detected by a photomultiplier tube and then the signal is digitalized by an oscilloscope. The scattered light, due to particles, increase the cavity ring down decay rate (β) allowing us to detect particles in measuring the $\Delta\beta$ value (corresponding to the difference between the β values obtain with and without particles).

Figures 1 and 2 are examples of $\Delta\beta$ values obtained as a function of the flow of nitrogen in the nebulizer using 300 nm particle size and 266 nm and 532 nm wavelength light. In the case of styrene particles, the $\Delta\beta$ value is only due to scattered light, for 532 nm wavelength light, whereas, for 266 nm wavelength light, the $\Delta\beta$ value is due to both scattered light and absorption of styrene particles at this wavelength.





The next step of this study will be to link the $\Delta\beta$ value to the concentration of particles inside the cavity ring down (instead of the flow rate of nitrogen) by measuring the absorption coefficient of styrene particles at 266 nm and comparing both $\Delta\beta$ values obtain at 266 nm and 532 nm, for the same conditions (concentrations and particles size).