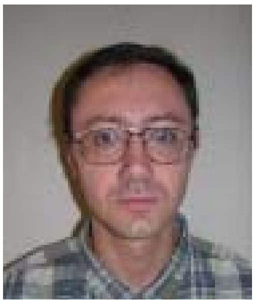
Dmitri Konarev (Division of Chemistry, Graduate School of Science)



Period

7 January, 2004 –30 November, 2004

Research

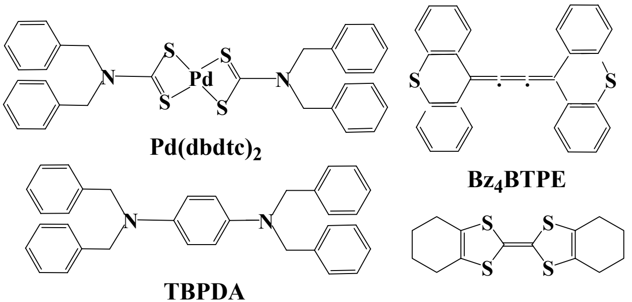


Fig. 1. Molecular structures of the

1. Sterically hindered dimerization in ionic multi-component complex: [Pd(dbdtc)$_2$]·C_{60}·$Cr(C_6H_6)_2$.

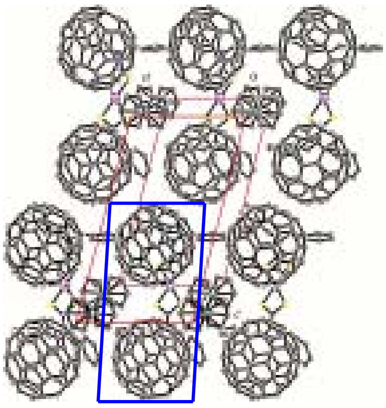


Fig. 2. Projection of the crystal structure of **1** along the *b*-axis.

New complex [Pd(dbdtc)$_2$]·($C_{60}^{\bullet-}$)·($Cr(C_6H_6)_2^{\bullet+}$) (**1**) (Pd(dbdtc)$_2$: palladium dibenzyldithiocarbamate) (Fig.1); $Cr(C_6H_6)_2$: bis(benzene)chromium) was obtained by the diffusion method. According to IR, visible-NIR and EPR spectra **1** contains neutral Pd(dbdtc)$_2$ molecules as well as $C_{60}^{\bullet-}$ and $Cr(C_6H_6)_2^{\bullet+}$ ion-radicals. Crystal structure of **1** solved at 80 K reveals a layered packing with alternation of strongly puckered $C_{60}^{\bullet-}$ layers with those composed of Pd(dbdtc)$_2$ and $Cr(C_6H_6)_2^{\bullet+}$ (Fig. 2). Within fullerene layers pairs of $C_{60}^{\bullet-}$ can be distinguishable (blue parallelogram in Fig. 2) with the shortest interfullerene C…C contact of 3.102 Å (the sum of van der Waals radii of two carbon atoms is 3.42 Å). This contact is essentially longer than the length of the intercage C-C bond in the $(C_{60}^{-})_2$ dimer (1.597 Å) indicating that $C_{60}^{\bullet-}$ are monomeric at 80 K. In contrast to X-ray diffraction data SQUID and EPR evidence the formation of the $(C_{60}^{-})_2$ dimers below 140 K. The assymetric EPR signal in this temperature range with g_1=1.9959 and g_2=1.9830 (120 K) is characteristic for isolated $Cr(C_6H_6)_2^{\bullet+}$. According to both SQUID and EPR the dimers dissociate at the heating above 140-160 K. This is accompanied by the increase of the magnetic and spin suspectibility of **1** and the change of asymmetric EPR signal from $Cr(C_6H_6)_2^{\bullet+}$ to symmetric EPR signal with g=1.9992, which can be attributed to strongly resonating signal between monomeric $C_{60}^{\bullet-}$ (g=1.9996) and $Cr(C_6H_6)_2^{\bullet+}$ (g=1.9860) due to exchange coupling. The observed dissociation temperature for the $(C_{60}^{-})_2$ dimers is the lowest among ionic complexes of C_{60} (160-250 K) showing that sterical factors hinder the formation of the

$(C_{60}^{-})_2$ dimers in **1** probably due to incorporation of $Cr(C_6H_6)_2^{\bullet+}$ into the $C_{60}^{\bullet-}$ layers (Fig. 2). In contract to relatively stable dimers with dissociation temperature above 200 K the dimerization in **1** has large hysteresis of about 15 K (at the cooling regime from RT down to 2 K the dimerization occurs only at 145-125 K). Fast cooling from 250 down to 100 K (within 10 minutes) completely suppresses dimerization and according to EPR in this case the dimerization is observed only below 40 K. This is also the reason for the retention of monomeric phase in **1** at 80 K observed in X-ray diffraction experiment. Fast cooling of the crystal from RT down to 80 K suppresses dimerization and retains monomeric phase.

2. Antiferromagnetic interactions of spins in (OMTTF·I$_3$)·C$_{60}$.

A new ionic multi-component complex (OMTTF·I_3)·C_{60} (**2**) (OMTTF: octamethylenetetrathiafulvalene (Fig. 1)) comprising neutral C_{60} molecules and $OMTTF^{\bullet+}$ and I_3^- ions was synthesized. The complex has a layered structure with the alternation of closely packed hexagonal C_{60} layers and layers composed of $OMTTF^{\bullet+}$ and I_3^- ions arranged in chequered manner. The polycrystalline complex shows a strongly asymmetric EPR signal consisting of four components in the 4-290 K range attributable to $OMTTF^{\bullet+}$. The occurrence of magnetic susceptibility indicates an antiferromagnetic interaction of spins localized on $OMTTF^{\bullet+}$ with a antiferromagnetic hump around 4.5 K (Fig. 3). According to the one-dimensional Heisenberg antiferromagnet model the exchange interaction was estimated to be J = -3.3 K. The crystal structures of two phases of the OMTTF·I_3 salt were also studied.

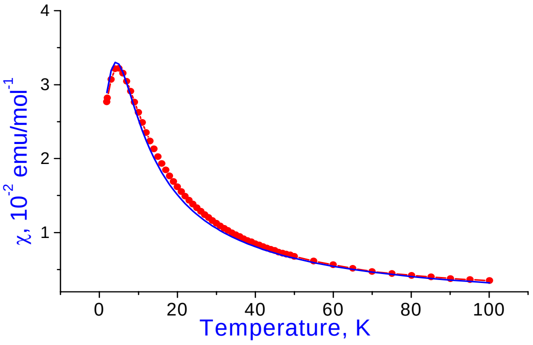


Fig. 3. Temperature dependence of magnetic susceptibility of **2** in the 1.9-100 K range in the applied field of 1 kOe. The blue line denotes theoretical fitting according to the one-dimensional Heisenberg antiferromagnet model.

3. Photocunductivity in molecular complex Bz$_4$BTPE·C$_{60}$.

A new molecular complex of C_{60} with tetrabenzo(1,2-bis[4H-thiopyran-4-ylidene]ethene) (Fig. 1), $Bz_4BTPE{\cdot}C_{60}$ (**3**) was obtained. The complex has a layered structure in which closely packed hexagonal layers of C_{60} alternate with the layers composed of Bz_4BTPE molecules. The complex has a neutral ground state according to UV-visible-NIR spectrum. It has been found that single crystals of **3** show low "dark" conductivity of $\sigma{\sim}10^{-10}$ $(\Omega{\cdot}cm)^{-1}$. A 10^2 increase in photocurrent has been observed upon illuminating the crystal with white light. Photoconductivity of **3** is sensitive to magnetic field with $B_0 < 1$ T and increases up to 5 % in magnetic field. The photoconductivity spectrum of the complex (Fig. 4) indicates that free charge carriers are generated in the UV-visible range mainly by the Bz_4BTPE excitation (the peaks at 622, 562, 472 and 348 nm) with a possible contribution of charge transfer excitations between adjacent C_{60} molecules (the peak at 472 nm).

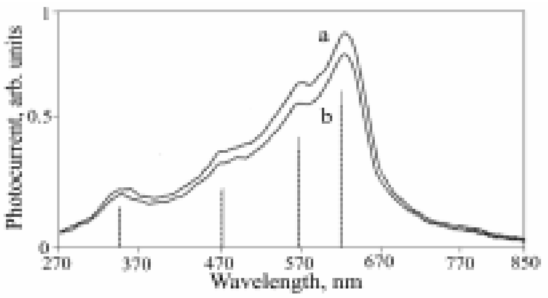


Fig. 4. Photoconductivity spectra of **3** in the absence (b) and in the presence (a) of the magnetic field with B_0 = 0.5 T. Continuous and dotted vertical lines show position of optical transitions in the magnetic field and its absence, respectively.

4. Antiferromagnetic interaction of spins in isostructural complexes $(TBPDA)_2 \cdot C_{60} \cdot D$.

Series of ionic multi-component complexes of general formula $(TBPDA)_2 \cdot (C_{60}^{\bullet-}) \cdot (D^+)$ (**4-6**) (TBPDA: tetrabenzyl-*p*-phenylenediamine (Fig. 1); D are tetrakis (dimethylamino) ethylene (TDAE, **4**), decamethylchromocene (Cp^*_2Cr, **5**) and decamethylcobaltocene (Cp^*_2Co, **6**)) were obtained as single crystals. The presence of D^+, $C_{60}^{\bullet-}$ and neutral TBPDA in **4-6** was proved by optical absorption spectra in the IR and UV-vis-NIR ranges. The crystal structures of **4** and **5** studied by single crystal X-ray diffraction are isostructural. D^+ and $C_{60}^{\bullet-}$ are spatially separated by bulky TBPDA molecules as shown in Fig. 5. Complexes has EPR signals with g = 2.0009 and the line halfwidth (ΔH) of 29.3 G (**4**), g = 2.2526 and ΔH = 2150 G (**5**) and g = 1.9999 and 67 G (**6**) at RT. EPR signal in **6** was attributed to $C_{60}^{\bullet-}$ (g = 1.9996), whereas those in **4** and **5** can be attributed to strongly resonating signals between $C_{60}^{\bullet-}$ (g = 1.9996) and D^+ ($TDAE^{\bullet+}$ has EPR signal with g = 2.0035 and $Cp^*_2Cr^+$ has asymmetric EPR signal with $g_{\perp}$ = 4.02(1) and g_{II} = 2.001(1)) due to exchange coupling. The EPR signals from **4** and **6** are split into two components below 60 and 40 K, respectively, which shift in the opposite directions to lower and higher fields with the temperature decrease. This is accompanied by the decrease of the magnetic moment of the complex. This phenomenon is explained by the formation of field-induced short-range antiferromagnetically ordered clusters.

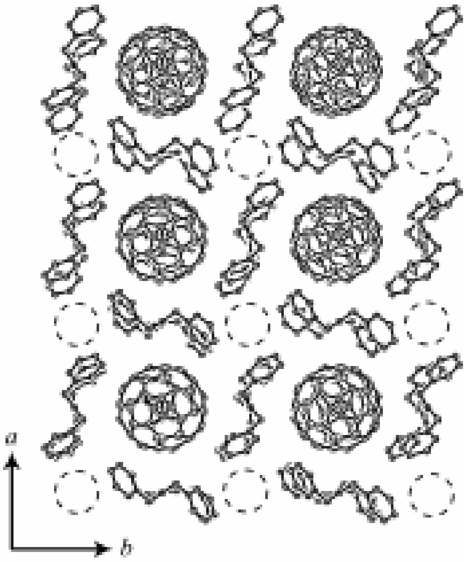


Fig. 5. View of the layers composed of D^+, $C_{60}^{\bullet-}$ and TBPDA in the *ab*-plane. The positions of disordered D^+ are shown by dashed circles (TDAE (**4**) and Cp^*_2Cr (**5**)).

Publications.

1. Ionic multi-component complexes containing $TDAE^{\bullet+}$ and $C_{60}^{\bullet-}$ radical ions and neutral D_1 molecules: $D_1 \cdot TDAE \cdot C_{60}$. **D. V. Konarev**, I.S. Neretin, G. Saito, Yu.L. Slovokhotov, A. Otsuka, and R.N. Lyubovskaya, *Dalton Trans.,* 2003, 3886-3891.

2. Fullerene complexes with cobalt (II) tetraphenylporphyrin: from molecular to ionic crystals. **D.V. Konarev**, S.S. Khasanov, G.Saito, R.N. Lyubovskaya. *J. Porph. Phth.*, 2003, **7**, 801-806.

3. Synthesis, crystal structure and photoconductivity of new molecular complex of C_{60} with tetrabenzo(1,2-bis[4H-thiopyran-4-ylidene]ethene): $Bz_4BTPE \cdot C_{60}$. **D.V. Konarev**, S.S. Khasanov, G. Saito, D.V. Lopatin, V.V. Rodaev, A.V. Umrikhin, A.L. Litvinov, R.N. Lyubovskaya, *J. Phys. Chem. Solids*, in press.

4. The synthesis, crystal structure and optical properties of an ionic multi-component C_{60} complex $(OMTTF \cdot I_3)C_{60}$ and simple $OMTTF \cdot I_3$ salts. **D.V. Konarev**, S.S. Khasanov, R.N. Lyubovskaya, A. Otsuka, G. Saito, *J. Mat. Chem*, submitted

5. Review: The formation of σ-bonded $(fullerene^-)_2$ dimers and $(Co^{II}TPP \cdot fullerene^-)$ anions in ionic complexes of C_{60}, C_{70}, and $C_{60}(CN)_2$. **D.V. Konarev**, S.S. Khasanov, G. Saito, R.N. Lyubovskaya, *Recent Res. Devel. in Chem.*, 2004, 2, 105-140

(Dr.) T. J. Wallington

Senior Research Fellow
Scientific Research Laboratory,
Ford Motor Company, Dearborn, MI, USA

Staying Period: January 10, 2004 - January 14, 2004
Host: Masahiro Kawasaki (Dept. Mol. Eng., Grad. Sch. Eng.)

Stratospheric ozone depletion is an example of a global scale problem. Stratospheric ozone loss is caused by the release of chlorofluorocarbons (e.g., CF_2Cl_2) and Halons (e.g., CF_3Br and CF_2ClBr). CFCs and Halons have no significant loss mechanisms in the lower atmosphere and within several years of their release they become uniformly distributed in the lower atmosphere on a global scale. CFCs and Halons are transported into the stratosphere as part of the natural air circulation. In the stratosphere the CFCs encounter harsh solar UV irradiation ($\lambda < 250$ nm) which is blocked from the lower atmosphere by absorption by the ozone layer. UV irradiation of CFCs and Halons releases Cl and Br atoms which then participate in ozone destruction reactions.

The recent search for environmentally acceptable CFC replacements provides a good example of how detailed studies of the atmospheric degradation mechanism of a class of chemical compounds lead to an understanding of their environmental impact. Hydrofluorocarbons (e.g., CF_3CFH_2, also known as HFC-134a) and hydrochlorofluorocarbons (e.g., CF_3CCl_2H, also known as HCFC-123) are important classes of chemical compounds which are used as replacements for CFCs in a variety of applications.

Collaboration paper:
Atmospheric Chemistry of CH_3CHF_2 (R-152a): Mechanism of the $CH_3CF_2O_2$+HO_2 Reaction
Y. Hashikawa, M. Kawasaki, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, *Chem. Phys. Letters,* 391(1-3), 165-169 (2004)

(Dr.) David Beratan

Professor, Department of Chemistry, Duke University, USA
Staying Period: June 19, 2004-June 20, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to our laboratory to give a lecture for graduate students and faculties in Katsura campus. The title of his talk was “Dynamic docking and inter-protein electron transfer” and the outline was as follows. Horse myoglobin (Mb) provides a convenient workbench for probing the effects of electrostatics on binding and reactivity in the dynamic [Mb, cytochrome b5] electron-transfer (ET) complex. We have combined mutagenesis and heme neutralization to prepare a suite of six Mb surface-charge variants: the Mb(S92D) and Mb(V67R) mutants introduce additional charges on the front face; and incorporation of the heme di-ester into each of these neutralizes the charge on the heme propionates which further increases the positive charge on the front face. For this set of mutants, the nominal charge of Mb changes by -1 to +3 units relative to native Mb. For each member of this set, we have measured the bimolecular quenching rate constant (k_2) for the photoinitiated ET reaction as a function of ionic strength. We find: i) a dramatic decoupling of binding and reactivity, in which the bimolecular rate varies 1,000-fold within the suite of Mbs without a significant change in binding affinity; ii) the ET reaction occurs within the thermodynamic or rapid exchange limit of the dynamic-docking model, as shown by the fact that the zero-ionic-strength bimolecular rate constant varies exponentially with the net charge on Mb; iii) Brownian Dynamics docking profiles allow us to visualize the microscopic basis of dynamic docking; iv) a new theoretical approach which mathematically couples docking with reactivity (Functional Docking) successfully describes changes of bimolecular ET rates upon protein modification and the ionic strength variations. He had opportunity to talk with many graduate students and faculties who are involved in ET chemistry. We think that he inspired many graduate students and young scientists in Kyoto University.

(Dr.) Micheal J. Therien

Professor, The Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA
Staying Period: June 18, 2004-June 23, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to our laboratory to give a lecture for graduate students and faculties in Katsura campus. In his talk, he demonstrated that in aqueous solution, hydrophobic conjugated-multi(porphyrin)-based near-infrared fluorophores (NIRFs) cooperatively self assemble with amphiphilic diblock copolymers to form polymersomes (100 nm - 20 mm diameter polymer vesicles). The thick membranes of these synthetic vesicles uniquely segregate and uniformly disperse large numbers of high emission dipole strength NIRFs. Long-wavelength optical excitation of such assemblies generates intense, highly localized emissive signals capable of penetrating through the dense tumor tissue of a live animal. Robust, NIR-emissive polymersomes thus define a soft matter platform with exceptional potential to facilitate deep-tissue fluorescence-based imaging for in vivo diagnostic and drug-delivery applications.

The second task of Prof. Therien was to give an invited lecture in CREST International Symposium on Radical Ion Reactivity (ISRIR 2004), which was supported by our COE program. The title of his talk was “Photoinduced Electron Transfer in Unusual Donor-Spacer-Acceptor Structural Motifs Interrogated by Visible Pump/IR Probe Spectroscopy”. He focused on the current research in his laboratory including synthesis and photophysical properties of porphyrin-acceptor dyads. In particular, he emphasized that visible pump/IR probe spectroscopy is powerful technique for monitoring transient species. During his stay he had chance to discuss with many graduate students who are involved in synthesis of porphyrins and related compounds. We believe that he encouraged many graduate students and young scientists during his visit in Kyoto University.

(Dr.) Nazario Martín

Professor, Universidad Complutense de Madrid, Spain
Staying Period: June 20, 2004-June 28, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to our laboratory to give a lecture for graduate students and faculties in Katsura campus. He talked about synthesis and physical properties of tetrathiafulvalene (TTF) and its derivatives, which have been used as the most important electron donor component in the formation of electrically conducting materials. These molecules have been also used as electroactive units in the construction of molecules exhibiting a wide variety of different properties. In his presentation the synthesis of novel highly conjugated TTF (exTTF) derivatives and other exTTF/fullerene derivatives as well as their application in fields such as photoinduced electron transfer (PET), supramolecular chemistry, molecular wires, and non-linear optics, was discussed.

The second task of Prof. Martín was to give an invited lecture in CREST International Symposium on Radical Ion Reactivity (ISRIR 2004), which was supported by our COE program. The title of his talk was “Mimicking Photosynthesis: The Quest for Highly Stabilized Radical-Ion Pairs in Functionalized Fullerenes”. He focused on the current research in his laboratory including synthesis and photophysical properties of donor-linked fullerene dyads and triads. In particular, he emphasized that π-conjugated oligomers are potential building blocks for the creation of molecular wires. During his stay he had chance to contact with many graduate students who are involved in synthesis of fullerene derivatives and related compounds. We believe that he inspired many graduate students and young scientists during his visit in Kyoto University.

古賀 忠典（こが ただのり）　理学研究科化学専攻物理化学研究室

採用期間

平成１６年７月２２日～平成１６年８月２５日

研究報告

中性子反射率法を用いた「その場」観察により、溶媒（二酸化炭素、CO_2）の臨界点近傍での高分子超薄膜の急激な膨潤率増加が明らかにされている(図１)。この異常な膨潤率の増加は、ポリマーと溶媒の相互作用用パラメーターに依存せず、超臨界流体を特徴づける「密度揺らぎ」（クラスター構造）と強い相関を持ち、溶媒の密度揺らぎが極大になる熱力学的状態(「尾根」)で最も顕著に現れる事が分かっている。本研究では、高分子/超臨界二酸化炭素溶液中における溶媒和構造をラマン分光法を用いて解析し、超臨界流体中のの溶媒和構造と異常な膨潤度との対応関係の有無を明らかにすることを研究目的とした。

ラマンスペクトル測定は、日本分光製レーザーラマン分光光度計を用い、励起光源として、Ar レーザー（励起波長 488nm、出力 300mW）を用いた。また、高圧ラマン測定用にサファイア窓及びステンレス本体から構成される圧力セルを作製した。本研究に用いた高分子は、poly(propylene oxide) (PPO, M_w=400g/mol)で、この高分子の室温付近での CO_2 に対する相溶性は、他の高分子に比較して格段に良いことが分かっている。ラマン測定用の試料としては、あらかじめトルエン溶液に溶かしてフィルター処理を行い、高分子試料中の不純物を除去したものを使用した。図２に、バルク PPO のラマンスペクトルを示す。図から分かるように、$1456cm^{-1}$ に PPO の CH_2 scissor に対応する強いピークが観測された。次に、高圧セル中に PPO（重量分率 10%）を詰め、CO_2 溶媒中でのラマンスペクトルを測定した。測定は、等温（36 度）条件下で行った。図２に P=8.2MPa（36 度での「尾根」に対応する）の結果を示している。このように、バルク PPO で観測された $1456cm^{-1}$ のピークは消滅し、代わりに $1400cm^{-1}$ 付近に数本の鋭いピークが観測された。しかし、これらのピークは溶媒（CO_2）のみのラマンスペクトルでも観測されており、PPO 固有のバンドではない可能性が大きい。CO_2 の圧力を変えたラマン測定でも同様の結果が得られた。

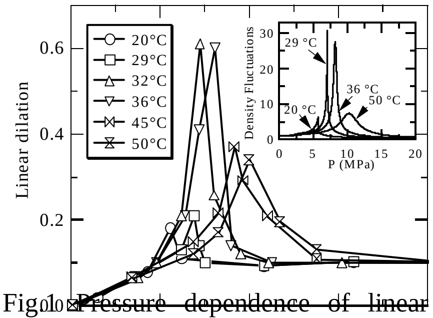


Fig.1 Pressure dependence of linear dilation for deuterated deuterated styrene-butadiene random copolymer thin film in CO_2. In the inset, calculated density fluctuations of CO_2 are shown

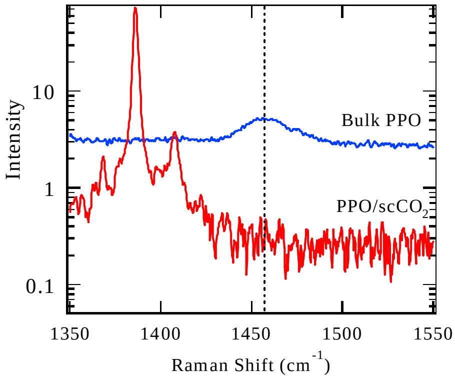
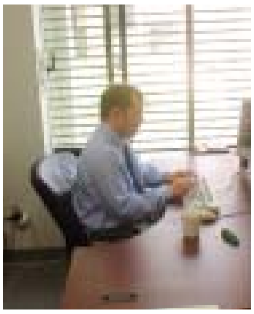


Fig.2 Raman spectra at T=36°C

論文発表:なし

(Dr.) O. J. Nielsen



Professor, Atmospheric Chemistry Division
Plant Biology and Biogeochemistry Department
Risø National Laboratory
DK-4000 Roskilde, Denmark
Staying period: July 1, 2004

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

Human activities result in the release of a large quantity and variety of chemical compounds into the atmosphere. These compounds are degraded in a complex series of reactions. The atmosphere is a highly oxidizing environment and degradation proceeds via a sequence of reactions in which the pollutants are oxidized in successive steps resulting in increasingly polar and less volatile products. Eventually the pollutant is either completely oxidized, or it is converted into partially oxidized species which are removed via wet and/or dry deposition to the earth's surface. While the degradation reactions are beneficial because they remove pollutants from the air, they can have unwanted side effects. The degradation products and intermediates can lead directly, or indirectly, to environmental impacts on local, regional, or global scales. Stratospheric ozone depletion is an example of a global scale problem. Stratospheric ozone loss is caused by the release of chlorofluorocarbons (e.g., CF_2Cl_2) and Halons (e.g., CF_3Br and CF_2ClBr). CFCs and Halons have no significant loss mechanisms in the lower atmosphere and within several years of their release they become uniformly distributed in the lower atmosphere on a global scale. CFCs and Halons are transported into the stratosphere as part of the natural air circulation. In the stratosphere the CFCs encounter harsh solar UV irradiation ($\lambda < 250$ nm) which is blocked from the lower atmosphere by absorption by the ozone layer. UV irradiation of CFCs and Halons releases Cl and Br atoms which then participate in ozone destruction reactions.

Collaboration Paper:

Gas Phase UV and IR Absorption Spectra of $C_xF_{2x+1}CHO$ (x = 1--4)
Y. Hashikawa, M. Kawasaki, R. L. Waterland, M. P. S. Andersen, O. J. Nielsen, M.D. Hurley, J. C. Ball, T.J. Wallington, *J. Fluorine Chem.* 125 (12), 1925-1932 (2004)

(Dr.) Young Kuk

Professor, School of Physics, Seoul National University, Seoul, Korea
Staying Period: August 3, 2004-August 4, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to my laboratory to discuss about porphyrin chemistry. In Katsura campus, he talked with ours about the joint project relating the development of molecular electronics based on porphyrins. We had a positive agreement to start the collaborative work including the exchange of graduate students between the two universities.

The second task of Prof. Kuk was to give a lecture for graduate students in Katsura campus of Kyoto University. The title of his talk was “One-dimensional wires and their interconnections”. The contents of the lecture were as follows. As electronic devices shrink down to nanometer scale, we face not only processing problems but also conceptual limits in the integration process. Accurate alignment of nano-devices, routing of the interconnecting wires and increasing access time to each transistor are three most frequently asked problems. With these conceptual barriers ahead, it is time to think about alternate devices and their integration schemes. Scientists found interesting transport properties in 1-D systems as early as in 1974. Organic, metal, semiconductor and biological wires have shown metallic or semiconducting properties. These observations have opened ways to make 1-D active devices and functional 1-D systems by interconnecting semiconducting wires with gate oxides and metals to metallic interconnection wires. So far, many different configurations have been proposed to produce switching devices. But all these devices still suffer from poor signal to noise ratio and undesirable characteristic curves because of defects in the 1-D wires. The integration of 1-D active devices is even more difficult than the construction of the devices themselves. The devices are too small to make wire-bondings to their electrodes and the spaces between neighboring devices are too small to route the interconnecting wires around the devices. Among many functional 1-D systems, we chose to study carbon nanotube as a test 1-D system for its well-known geometrical structure, symmetric property, electrical properties and synthesis technology. Recently, it has been shown experimentally that fullerenes, metals or insulators can be inserted into single wall nanotubes, forming a chemically modified carbon nanotubes1. These newly developed materials can be used as parts of active electronic devices. We can produce junctions between metal and semi-conductor or semiconductor and semiconductor. In this presentation, geometric, electronic and transport properties of several 1-D wires will be given. Lastly, we show our new network logic that integrates these 1-D wires.

(Dr.) James M. Mayer

Professor, The Department of Chemistry, University of Washington,
Seattle, WA 98195-1700, USA
Staying Period: October 20, 2004-October 30, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to our laboratory to give three lectures for graduate students and faculties in Katsura campus. The title of his first talk is "Oxidations of C–H and O–H bonds by metal complexes: from hydrogen atom transfer to Marcus theory", in which he demonstrated that some oxidation reactions including the C–H or O–H bond cleavage by transition metal complexes proceed through the hydrogen atom transfer mechanism. The reaction rates are closely related to both the ability of accepting an electron (the redox potential) and the ability of accepting a proton (pKa values) of the respective components. He rationalized the mechanism of these fundamentally important reactions based on the Marcus theory. The title of the second talk is "Hydrogen atom transfer, proton-coupled electron transfer, and related reactions: the importance of intrinsic barriers". He showed the relationship between two conceivable mechanisms, hydrogen atom transfer and proton-coupled electron transfer (PCET) and pointed out the importance of the intrinsic barriers for determining the above mechanisms. The title of the last talk is "Electrophilic ligands: two-electron oxidations by osmium complexes". In this lecture, he demonstrated that the nitrogen atom of the high-valent osmium complexes bearing a Tp ligand possesses the electrophilic character to react with some nucleophiles. He also showed us his recent results on the C–H bond activation chemistry of the osmium complexes. The most important finding is that the C–H bond is activated catalytically by using a co-oxidant.

During his stay he had chance to discuss with many faculties and graduate students who are involved in the chemistry of transition metal complexes and electron transfer reactions. We believe that he encouraged many graduate students and young scientists during his visit in Kyoto University.

(Dr.) Itamar Willner

Professor, Institute of Chemistry, The Hebrew University of Jerusalem, Israel
Staying Period: November 13, 2004-November 16, 2004

Host: H. Imahori (Dept. Mol. Eng., Grad. Sch. Eng.)

The invited researcher came to our laboratory to give a lecture for graduate students in Katsura campus. The outline of his talk was as follows. Integrated biomolecule/metal or semiconductor nanoparticles (NPs) hybrid systems act as active units for biosensing, nano-circuitry and nano-motors. Electronic or photonic biosensors based on biomolecule-NPs hybrid systems were developed. The elctrical contacting of redox-enzymes, e.g. glucose oxidase, was accomplished by the reconstitution of the apo-enzyme on a flavin adenine dinucleotide (FAD)-functionalized Au-NP (1.2 nm). The enzyme reconstituted with the Au-NP was assembled on an Au-electrode, and the system revealed unprecedented electron transfer efficiency (turnover rate 4500 s^{-1}), and effected the bioelectrocatalyzed oxidation of glucose. Metal nanoparticles may be used as effective labels to follow biocatalytic processes and to quantitatively analyze the enzyme substrate. For example, the catalytic enlargement of Au-NP by NADH or H_2O_2 was employed to develop biosensing paths involving NAD^+-dependent enzymes and flavin-based oxidases, respectively. This concept will be addressed by presenting systems to follow inhibitors of acetylcholine esterase by the catalytic growth of Au- or Ag-NPs. An interesting example will involve the identification of NAD^+-dependent biocatalyzed transformations by following the shape of NPs. The biocatalytic transformations generate tripode and tetrapode Au-NP. The formation of the NPs is imaged by HRTEM or absorption spectroscopy (λ=670 nm). Biomolecule/semiconductor NP hybrid systems are employed for optical biosensing of DNA and of telomerase activity present in cancer cells. The replication of hybridized DNA on CdSe/ZnS NPs or the telomerization of a telomerase primer linked to the semiconductor NPs in the presence of the dye (Texas-Red)-labeled dNTP results in the dye labeled replica or telomers. Fluorescence resonance energy transfer (FRET) provides, then, the imaging signal for the sensing process. Biomolecules provide organized templates for the assembly of metal or semiconductor nanocircuitry. We believe that many students and scientists in Kyoto University were inspired by his impressive lecture.