海外における研究活動（留学支援）

学生に対する海外における研究活動の支援制度利用実績一覧および学生報告

平成 17 年 12 月～平成 18 年 11 月

7 名

氏　　　　名：川中　昇
学　　　　年：修士課程 2 回生
所　　　　属：工学研究科 分子工学専攻（指導教員：川崎 昌博 教授）
渡　航　先：ブリストル大学化学科（イギリス）
渡航先指導教員：Mike Ashfold 教授
研　究　課　題：画像分光法に関する実験
渡　航　期　間：平成 18 年 4 月 25 日～ 5 月 31 日（38 日間）

氏　　　　名：辻本　吉廣
学　　　　年：博士課程 1 回生
所　　　　属：理学研究科 化学専攻（指導教員：陰山 洋 助教授）
渡　航　先：ブリティッシュ・コロンビア大学 TRIUMF（教員帯同）
研　究　課　題：低次元正方格子磁性体の muSR 測定
渡　航　期　間：平成 18 年 6 月 21 日～ 7 月 6 日（16 日間）

氏　　　　名：永田　勇樹
学　　　　年：博士課程 3 回生
所　　　　属：理学研究科 化学専攻（指導教員：谷村 吉隆 教授）
渡　航　先：カリフォルニア大学アーバイン校（米国）
渡航先指導教員：Shaul Mukamel 教授
研　究　課　題：表面二次元分光の理論的研究
渡　航　期　間：平成 18 年 6 月 29 日～ 11 月 11 日（136 日間）

氏　　　　名：山中　崇嗣
学　　　　年：修士課程 2 回生
所　　　　属：工学研究科 分子工学専攻（指導教員：川崎 昌博 教授）
渡　航　先：フォード自動車研究所（デトロイト・米国）
渡航先指導教員：Tim Wallington 博士
研　究　課　題：大気化学研究に関する実験
渡　航　期　間：平成 18 年 7 月 31 日～ 9 月 1 日（51 日間）

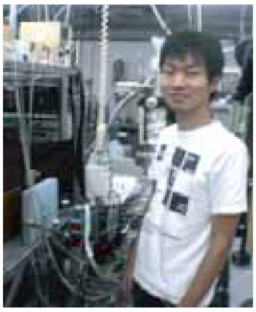
氏名：能田　洋平
学年：博士課程 3 回生
所属：理学研究科 化学専攻（指導教員：馬場 正昭 助教授）
渡航先：Akademogorodok, Novosibivsk（ロシア）
参加会議：Asia Pacific EPR/ESR Symposium 2006
発表題目：EPR Study of All-Organic Paramagnetic Liquid Crystals Showing a Smectic C or Chiral Smectic C Phase in a Surface-Stabilized Liquid Crystal Cell.
(Oral Presentation)
渡航期間：平成 18 年 8 月 22 日～ 8 月 29 日（8 日間）

氏名：藤澤　知績
学年：博士課程 2 回生
所属：理学研究科 化学専攻（指導教員：木村 佳文 助教授）
渡航先：The Politechnical University of Catalunya（バルセロナ・スペイン）
参加会議：EMLG/JMLG Annual Meeting “Liquid Systems under Extreme Conditions”
発表題目：Resonance Raman Study on the Solution of p-Nitroaniline in Supercritical Water
(Oral Presentation)
渡航期間：平成 18 年 9 月 2 日～ 9 月 9 日（8 日間）

氏名：姜　舜徹
学年：博士課程 2 回生
所属：工学研究科 分子工学専攻（指導教員：今堀 博 教授）
渡航先：ルンド大学（スウェーデン）
渡航先指導教員：Villy Sundstrom 教授
研究課題：色素増感太陽電池のフォトダイナミクスの測定
渡航期間：平成 18 年 10 月 4 日～ 12 月 9 日（67 日間）

Noboru Kawanaka

Department of Molecular Engineering,
Graduate School of Engineering, Kyoto University



Period

25 April 2006 - 31 May 2006

Place

University of Bristol, Bristol, England, UK

Research

The threshold for photoabsorption spectra of water ice bulk appears around 165 nm. However Dressler and Schnepp reported a region of weak and continuous absorption extending from 180 to 210 nm with a shallow maximum near 195 nm.[1] An *ab initio* theoretical calculations of the electronic excitation energy of water dimer structure on a model ice surface predicted that the photoabsorption of this surface species appears at around 200 nm. In the present experiment, we have investigated the UV photodissociation dynamics of water ice at 157 and 193 nm, observing the formation of hydrogen atoms from the *bulk* ice and the *surface* species.

The photodissociation of polycrystalline and amorphous ice films at 157 and 193 nm has been investigated by measuring the time-of-flight (TOF) spectra of photofragment hydrogen atoms with resonance enhanced multiphoton ionization.[2]

The TOF spectrum for the polycrystalline ice film at 157 nm consists of a combination of three different Maxwell- Boltzmann energy distributions, *T* = 5000, 600, and 110 K, while those at 193 nm represented simply by *T* = 3000 K.

The spectra from the amorphous ice film at 157 and 193 nm consist mainly of one distribution represented by T = 110 K.

The slow components come from the photodissociation of the ice *bulk* while the fast ones from the *surface* species.[3]

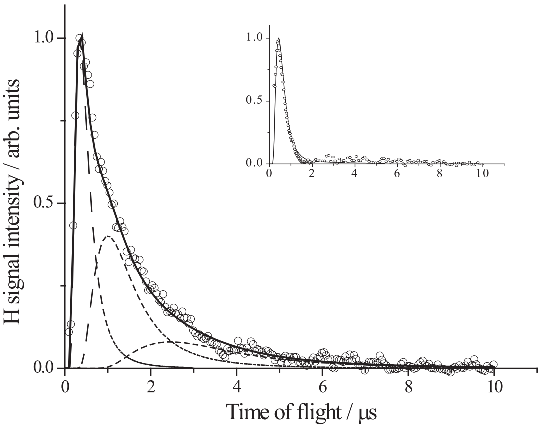


Figure 1 Time-of-flight spectra of H atoms from the crystalline ice film at 157 nm. Inset: at 193 nm.

References

[1] Dressler and Schnepp., *J. Chem. Phys*. **1960**, 33, 270.
[2] Yabushita andd Kawasaki . et al., *J. Chem. Phys*. **2004**, 120, 5463
[3] Kawanaka, Yabushita , Kawasaki and Ashfold. *J. Chem. Phys*., in press

Yoshihiro Tsujimoto

Department of Chemistry,
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Period

21 June 2006 - 6 July 2006

Place

TRIUMF, University of British Columbia, Canada

Research

(1) Unusual ground states in double-layered perovskites (CuX)LaNb$_2$O$_7$ (X=Cl, Br): We are interested in the physical properties of square-lattice antiferromagnets designed by ion-exchange reactons. Recently we have prepared spin 1/2 frustrated antiferromagnets (CuX)LaNb$_2$O$_7$ (X =Cl, Br) that exhibit unusual ground states: spin liquid state with a finite spin gap and collinear order at 32K, respectively[1,2]. To obtain further insight to understanding the magnetic properties, I had an opportunity to visit TRIUMF in UBC for the μSR measurements on (CuX)LaNb$_2$O$_7$. μSR stands for Muon Spin Relaxation, Rotation and Resonance. μSR measurements can detect dynamical spin fluctuations as well as static magnetic order, even in systems with very small ordered moment and/or random spin configurations. Zero-field μSR spectra for (CuCl) LaNb$_2$O$_7$ show Gaussian-like decay even at 20mK, which indicates the absence of long-range order, while that for (CuBr) LaNb$_2$O$_7$ show a clear precession below 32K due to a static internal magnetic field from the ordered magnetic moments surrounding the muon site. These experimental results provide firm evidence of the aforementioned ground states.

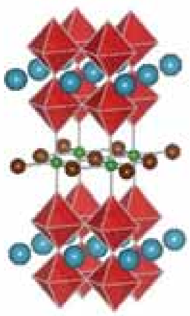


Figure 1 Crystal Structure of (CuX)LaNb$_2$O$_7$ (X=Cl, Br)

(2) Successive phase transitions in a triple-layered perovskite (CuBr)Sr$_2$Nb$_3$O$_{10}$:(CuBr) Sr$_2$Nb$_3$O$_{10}$ exhibits successive phase transitions at 7.3K and 9.1K as probed by specific heat experiments. To investigate the origin of the phase transitions, we performed μSR measurements for the copper bromide. The spectra showed that exponential decay appeared at temperatures below 7.3K, which indicates the static long-range magnetic order sets in at the lower critical temperature. Investigations on the intermediate phase for 7.3-9.1K are in progress.

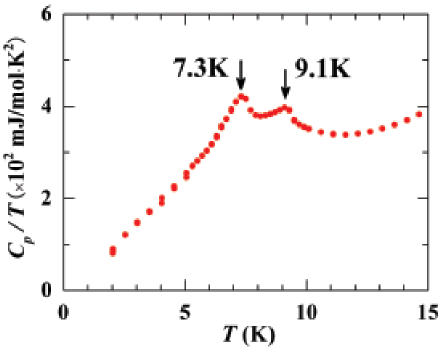


Figure 2 Heat capacity of (CuBr)Sr$_2$Nb$_3$O$_{10}$ in zero magnetic field.

References

1. Spin-Singlet Ground State in Two-Dimensional S = 1/2 Frustrated Square Lattice (CuCl)LaNb$_2$O$_7$, H. Kageyama, T. Kitano, N. Oba, M. Nishi, S. Nagai, K. Hirota, L. Viciu, J. B. Wiley, J. Yasuda, Y. Baba, Y. Ajiro, and K. Yoshimura, Journal of the Physical Society of Japan., **74** (2005) 1702-1705
2. Collinear Order in Frustrated Quantum Antiferromagnet on Square Lattice (CuBr)LaNb$_2$O$_7$, N. Oba, H. Kageyama, T. Kitano, J. Yasuda, Y. Baba, K. Hirota, Y. Narumi, M. Hagiwara, K. Kindo, T. Saito, Y. Ajiro, and K. Yoshimura, Journal of the Physical Society of Japan., **75** (2006) 113601

Yuki Nagata

Division of Chemistry,
Graduate School of Science, Kyoto University

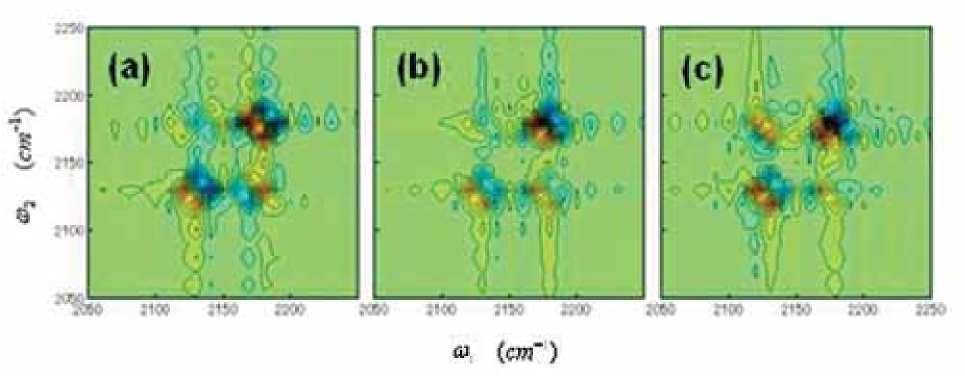
Period
31 June 2006 - 11 November 2006

Place
University of California, Irvine, USA

Research

I have conducted theoretical research on a two-dimensional (2D) surface infrared (IR) spectroscopy at Shaul Mukamel Group in the University of California, Irvine.

The vibrational energy dissipation and intermolecular coupling of CO on various surfaces have attracted much attention as the CO-CO interaction is crucial to resolve the underlying mechanism of surface dynamics. During my visit, we have proposed the 2D IR surface spectroscopy and applied to the mixture of CO and isotopic CO on Cu(100). Since the fifth-order Raman response function has the same form as the response function of surface 2D spectroscopy, similar techniques and discussions developed in 2D Raman spectroscopy are expected to be useful in 2D surface IR spectroscopy. We have calculated the temperature dependence of the 2D signals, where the cross peaks representing the coupling between CO and isotoped CO stretching modes. The results have showed the frustrated rotational modes activated by increasing temperature cause the change of the cross peaks.



Publications

[1] “Two-dimensional Raman spectroscopy of atomic liquids and solids”, Yuki Nagata and Yoshitaka Tanimura, J. Chem. Phys. **124**, 024508 (2006).
[2] “Analyzing atomic liquids and solids by means of two-dimensional Raman spectra in frequency domain”, Y. Nagata, T. Hasegawa, and Y. Tanimura, J. Chem. Phys. **124**, 194504 (2006).
[3] “Two-dimensional surface infrared spectroscopy: classical simulation of CO on Cu(100).”, Y. Nagata, Y. Tanimura, and S. Mukamel, in preparation.

Takashi Yamanaka

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Period

13 July 2006 - 31 August 2006

Place

Ford Motor Company, Dearborn, USA

Research

FTIR smog chamber techniques have been used to investigate the kinetics and mechanism of the reaction of Cl atoms with *i*-propanol in 700 Torr of N_2 at 296 K.

Cl atoms were generated from the photolysis of molecular chlorine by the UV irradiation of $CH_3CH(OH)CH_3/Cl_2/N_2$ mixtures. Chloropropanols are formed as the result of photochemical chain chlorination reactions.

$Cl + CH_3CH(OH)CH_3 \rightarrow CH_3C(OH)CH_3 + HCl$ (1a)
$Cl + CH_3CH(OH)CH_3 \rightarrow CH_3CH(OH)CH_2 + HCl$ (1b)
$CH_3C(OH)CH_3 + Cl_2 \rightarrow CH_3CCl(OH)CH_3 + Cl$ (2)
$CH_3CCl(OH)CH_3 \rightarrow CH_3\ C(O)CH_3 + HCl$ (3)
$CH_3CH(OH)CH_2 + Cl_2 \rightarrow CH_3CH(OH)CH_2Cl + Cl$ (4)

The kinetics of reaction (1) was studied using relative rate techniques. The observed loss of $CH_3CH(OH)CH_3$ versus those of the reference compounds (C_2H_4 and C_2H_2) is shown in Figure 1. It gives rate constant $k_1 = (8.28 \pm 0.97) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The branching ratio was determined by measuring the Products. Figure 2 shows the observed formation of $CH_3CH(OH)CH_2Cl$ and the sum of $CH_3CCl(OH)CH_3$ and $CH_3C(O)CH_3$ versus loss of CH3CH(OH)CH3. It gives $k_{1a}/(k_{1a} + k_{1b}) = 0.85 \pm 0.07$ and $k_{1b}/(k_{1a} + k_{1b}) = 0.15 \pm 0.07$.

Using the data presented in the present work we can calculate site specific rate constants of $k_{1a} = (7.04 \pm 1.01) \times 10^{-11}$ and $k_{1b} = (1.24 \pm 0.60) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.Comparing this with the reactivity of Cl atoms towards $–CH_3$ groups in C_2H_6, 2.95×10^{-11}, the reactivity of a $–CH_3$ group in i-propanol, $(6.20 \pm 3.05) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, is substantially (approximately a factor of 5) less because of the presence of the –OH functional group.

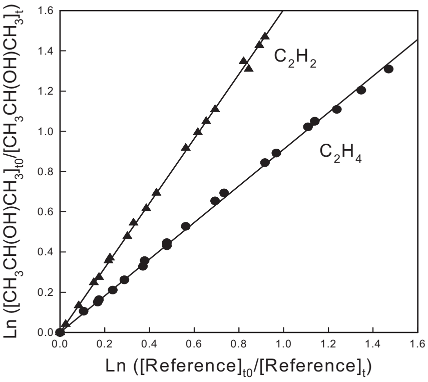

Figure 1: Loss of $CH_3CH(OH)CH_3$ versus C_2H_2 and C_2H_4

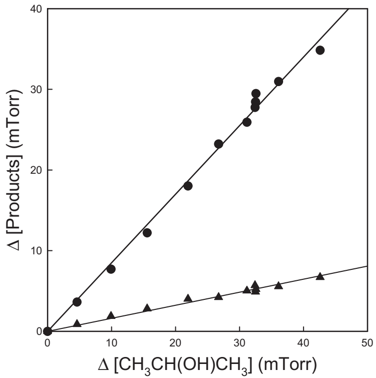

Figure 2: Formation of $CH_3CCl(OH)CH_2Cl$ (triangles) and $CH_3C(O)CH_3 + CH_3CCl(OH)CH_3$ (circles) versus $CH_3CH(OH)CH_3$ loss

Yohei Noda

Division of Chemistry,
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Period

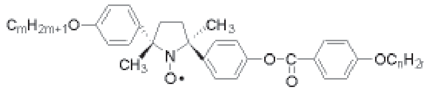
24 August 2006 - 27 August 2006

Conference

Asia Pacific EPR/ESR Symposium (APES2006), Novosibirsk, Russia

Presentations

(1) EPR Study of All-Organic Paramagnetic Liquid Crystals Showing a Smectic C or Chiral Smectic C Phase in a Surface Stabilized Liquid Crystal Cell (Oral Presentation): We have studied the molecular orientation of chiral paramagnetic liquid crystals (LCs) **1** and **2** in a surface-stabilized LC cell (4 μm thickness, antiparallel configuration) by EPR. We have already determined the molecular orientation in an LC cell at the nematic (N) and chiral nematic (N*) phases of (±)- and (*S,S*)-**1**, respectively. The angular dependence of the *g*-value clearly showed the uniform alignment in the N phase and the existence of helical superstructure in the N* phase. In this presentation, we reported the molecular orientation of the smectic C (SmC) and chiral smectic C (SmC*) phases of (±)- and (*S,S*)-**2**, respectively. For the SmC phase, the angles, θ and ϕ were determined as $24 \pm 2°$ and $\pm 40 \pm 1°$, respectively (Figure 1). For the SmC* phase, the disappearance of a helical structure due to the surface stabilization effect on the LC cell surface was observed.



(*S, S*) - **1** (m=7,n=8)
(*S, S*) - **2** (m=n=13)

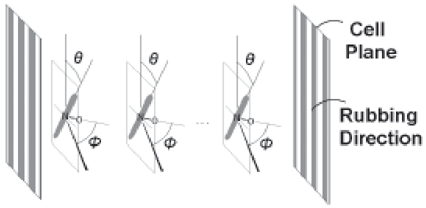
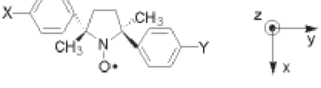


Figure 1 Schematic view of the tilting of an SmC phase. The definition of the angles, θ and ϕ is shown.

(2) EPR Study of the Single Crystal of PROXYLs (Poster Presentation): We also reported the results of the anisotropic EPR study of single crystals of PROXYLs. The principal g-values were determined. Comparing with the simulation by Anderson-Weiss theory with the crystallographic data, we found out the anomalous behaviour of the linewidth at the direction of the axis of the one-dimensionality of the antiferromagnetism of **1**.

It was significant for us to give a presentation in Russia, which is a leading country of EPR researches. I experienced many international contacts. I am deeply grateful for the trip assistance by 21st Century COE Program (Kyoto University Alliance for Chemistry).



1: X=Y=CH_3
2: X=CH_3, Y=H

Publications

1. EPR Studies on Molecular Orientation in a Surface-Stabilized Paramagnetic Liquid Crystal Cell, Y. Noda, S. Shimono, M. Baba, J. Yamauchi, N. Ikuma, and R. Tamura. *J. Phys. Chem. B*, **110**, 23683-23687 (2006)
2. Molecular Orientation of All-Organic Paramagnetic Liquid Crystals Showing a Smectic C or Chiral Smectic C Phase in a Surface-Stabilized Liquid Crystal Cell, Y. Noda, S. Shimono, J. Yamauchi, N. Ikuma, Y. Uchida and R. Tamura. *Appl. Magn. Reson.*, (Submitted)
3. EPR Study of the Single Crystal of PROXYLs, Y. Noda, S. Shimono, M. Baba, J. Yamauchi, Y. Uchida, N. Ikuma, and R. Tamura. *Appl. Magn. Reson.*, (Submitted)

Tomotsumi Fujisawa

Division of Chemistry,
Graduate School of Science, Kyoto University

Period
3 - 7 September 2006

Conference
EMLG/JMLG Annual Meeting
"Liquid Systems under Extreme Conditions", Barcelona, Spain

Presentation

Resonance Raman Study on the Solvation of p-Nitroaniline in Supercritical Water: 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_2 stretching mode shows a strong density dependence and other bands shown here do not show the density dependence. The band shift of the NO_2 stretching mode is about 10 cm^{-1} 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_2 mode. In conventional solvents the NO_2 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_2 frequency (relative contribution of charge separated character in the ground state).

I was very glad to have a chance to attend the meeting.

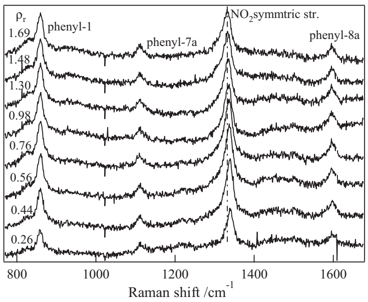


Figure 1

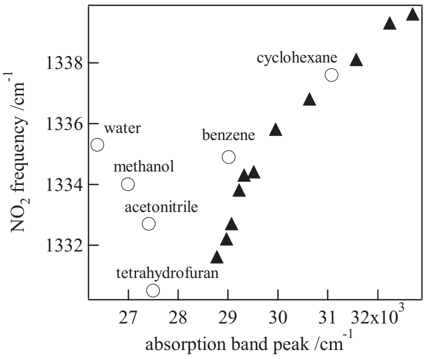


Figure 2

Publications

1. Fujisawa, T., Maru, E., Amita, F., Harada, M., Uruga, T., and Kimura, Y., "Development and application of the multipurpose optical flow cell under supercritical condition of water" , in *proceedings of the 14th International Conference on the Properties of Water and Steam, 2004, 445.*
2. Kimura, Y., Amita, F., and Fujisawa, T., "Non-linear Laser Spectroscopy in Supercritical Fluids" , in *Review of High Pressure Science and Technology*, 16, 87 (2006)
3. Fujisawa, T., Terazima, M., and Kimura, Y., "Excitation Wavelength Dependence of the Raman Stokes Shift of N,N-dimethyl-p-nitroaniline" , *Journal of Chemical Physics*, 124, 184503 (2006)
4. Fujisawa, T., Terazima, M., and Kimura, Y., "Resonance Raman Study of the Solvation of p-Nitroaniline in Supercritical Water" , *Chemical Physics Letters*, 430, 303 (2006)

Soonchul Kang

Department of Molecular Engineering,
Graduate School of Engineering, Kyoto University

Period

4 October 2006 - 7 December 2006

Place

Department of Chemical Physics, Lund University, Sweden

Research

(1) Electron Injection and Recombination in Porphyrin Sensitized Titanium Dioxide: Extensive studies have been carried out in the 1990s with the intension to understand the processes within the dye-sensitized nanocrystalline semiconductor photoelectrochemical solar cell (DSSC), and by this to improve its performance. In spite of these efforts no breakthrough was achieved, and nanocrystalline TiO_2 films sensitized with Ru(II) complexes remain to be the most successful light-to-electricity converts employed in DSSCs. These solar cells are clearly not ideal, as the absorption spectra of these Ru-complexes incompletely match the spectrum of the solar emission. An overall conversion efficiency of ~10 % from sunlight to electricity has been accomplished with a DSSC based on RuN3 adsorbed to nanocrystalline TiO_2, compared to theoretical conversion limit of ~27 % for such devices. The limitations of DSSC performance as well as new approaches to more efficient light-to-electricity conversion remain to be found.

The operation of DSSCs is directly related to the photoinduced primary processes of electron transfer at the dye-semiconductor interface. Perhaps the most essential process, the one that leads to the charge separated state, is electron injection. Even through RuN3-sensitized TiO_2 films are extensivery studied and it is known that electron injection in these samples occurs on the femto- and picosecond time scales with a quantum efficiency of close to 100 %, the exact mechanism and rate are still unclear. This is motivating detailed studies of electron injection, and the parameters controlling it. Understanding the influence of these parameters will facilitate the design of the DSSC, other molecular-based photovoltaic devices, and artificial photosynthetic assemblies.

The aim of this work is to study the electron injection dynamics between dyes and nanocrystalline TiO_2 films, with special interest paid to porphyrins-sensitized TiO_2 films, and understand which parameters influence and control this reaction. Especially, relationship between the molecular structure, the photodynamics, and the photovoltaic properties has been examined.

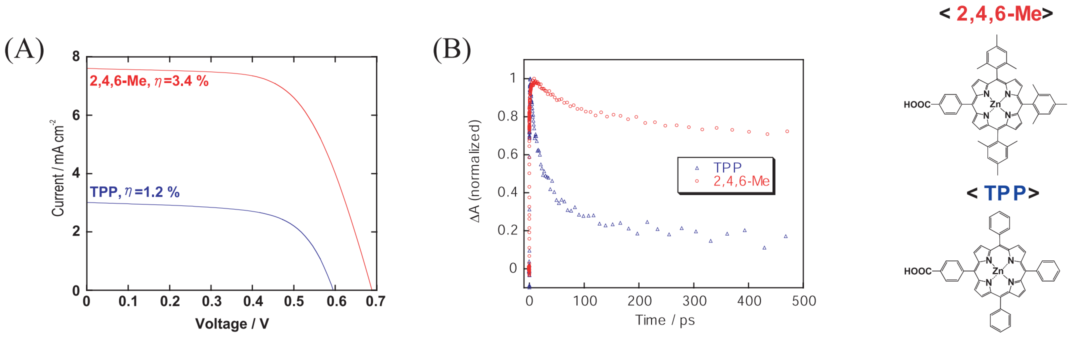


Figure 1 (A) Current-voltage characteristics of porphyrin-sensitized TiO_2 cells under AM 1.5 conditions. (a) 2,4,6-Me, *t*-BuOH/CH_3CN, 1 h, and (b) TPP, *t*-BuOH/CH_3CN, 1 h. Conditions: electrolyte 0.1 M LiI and 0.05 M I_2, 0.6 M 2,3-dimethyl-1-propyl imidazolium iodide, and 0.5 M 4-*t*-butylpyridine in CH_3CN; input power: AM 1.5 under simulated solar light. (B) Comparison of transient absorption kinetics for TiO_2 films sensitized by TPP and 2,4,6-Me at probe wavelength of 660 nm.