Joint Studies Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

A. New Developments in Spin Science Using Pulsed and High-Frequency ESR

KATO, Tatsuhisa *(Josai Univ.)*
MIZOGUCHI, Kenji *(Tokyo Metropolitan Univ.)*
SAKAMOTO, Hirokazu *(Tokyo Metropolitan Univ.)*
NAKAMURA, Toshikazu *(IMS)*
FURUKAWA, Ko *(IMS)*

In order to develop advanced ESR (electron spin resonance) spectroscopy for materials science, we performed functional materials studies, both on isolated molecules and on molecular assemblies. The following two topics were investigated: 1) We investigated the electron-spin coupled states composed of Cu(II) ions in the square-planar coordination with the ligands. 2) We carried out an analysis of spin dynamics for functional molecular assemblies, including2) metal ions inserted in M-DNA and3) dye-sensitized solar cell. We searched for cooperative phenomena involved in intra-molecule freedom, and new functional physical-properties originating in molecular assemblies.

A-1 Spin Coupled State Composed of Cu(II) Ions in Square-Planar Ligand Field

The arrays of spin active metal ions are expected to lead to the coupled spin states. Herein we show two unique approaches to form copper ions' arrays, which exhibited the coupled high spin states. As the first approach, Fujita *et al*. reported a discrete homo Cu(II)–Cu(II)–Cu(II) metal array, as shown in Figure 1., through the intercalation of Cu-aza-porphines into an organic pillared coordination box, which is self assembled from two panels, three pillars and six Pd(II) hinges.1) We clarified by using an ESR spectrometer that the homo Cu–Cu–Cu array shows unique spin interaction, which is clearly reproduced by a computer simulation as a quartet spin state.2)

The other approach is owing to the efficient self-assembly properties of DNA. Shionoya *et al*. showed that upon replacement of hydrogen-bonded base pairing by metal-mediated base pairing in DNA, it is possible to align metal ions within the double helical DNA scaffold.3) They reported the alignment of up to five Cu(II) ions within the DNA scaffold by using a hydroxypyridone-metal base pair, H-MBP in Figure 2. Electron spin transient nutation (ESTN) measurement as well as cw-ESR observation exhibited that the Cu(II) centers were ferro-magnetically coupled to one another, with each Cu(II) center being in a distorted square-planar geometry.4) On the other hand Clever and Carell reported the alignment up to ten Cu(II) ions within the DNA double helix using a salicylic aldehyde metal base pair in the presence of an ethylenediamine, salen ligands metal base pair (S-MBP) in Figure 2. However, no magnetic measurements were reported for the S-MBPs.5) Recently Ono *et al*. synthesized the thymidine dimer linked DNA with N4-carboxymethylcytosine metal base pair, CA-MBP in Figure 2, having the alignment up to five Cu(II) ions. The EPR spectrum exhibited the spectra due to the coupled spin state with much smaller dipole interaction than the case of Shionoya's metal-DNA. The comparison among the cases shows that the magnetic interactions in the metal-DNA structures are strongly dependent on the conformation characteristics of the metal base pair. The formation of an extended network in the stacked array of H-MBP favors ferro-magnetic coupling, whereas the ordered pairwise-stacked arrangement of S-MBP suppresses magnetic coupling. In the case of CA-MBP, the Cu(II) array exhibits the small magnetic dipole interaction, indicating the long distance between neighboring Cu(II) ions.

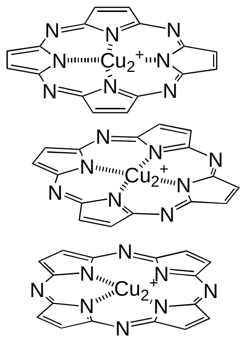

Figure 1. Stacked array of Cu-aza-porphines.

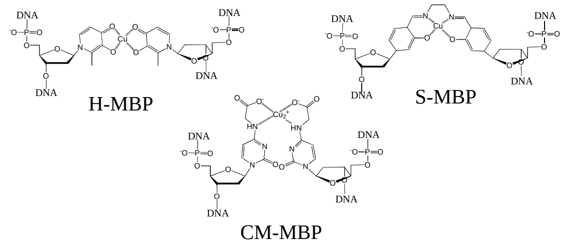

Figure 2. Three metal base pairs, hydroxypyridone MBP (H-MBP), salicylic aldehyde MBP with ethylenediamine (S-MBP), and N4-carboxymethylcytosine MBP (CA-MBP).

A-2 ESR Study of Metal Ions Inserted in M-DNA

In the view point of materials science, DNA shows several interesting properties such as self-organizing nature based on the complementarity of base pairs, arbitrariness of sequence design, and the possibility of π-electron stacking between adjacent bases. However, it has been confirmed that natural

DNA is a semiconductor with a large energy gap more than 5 eV. To introduce charge carriers into the DNA, there are several possibilities: Composite with divalent metal ions, chemical doping, and electric field induction. Here, we report an ESR study on the divalent metal ions of M-DNA.

It has been confirmed that several alkaline earth and transition metal ions, such as Mg, Ca, Mn, Fe, Co, Ni, and Zn, could form composites with DNA, locating in between the bases of a base pair. The magnetic transition metal ions are useful as a probe to investigate the electronic states of metal ions in the M-DNAs. Especially, Mn^{2+} ions are the ideal magnetic probe with S = 5/2 which gives ESR signal around the free electron g-value, g ~ 2. Analysis of ESR spectra in M^{2+}-DNA has led us to the conclusion that the charge transfer from the metal ions to the DNA base pairs did not occur, keeping DNA semiconducting after M^{2+} introduction. Only the exception has been found in Fe-DNA, where Fe^{2+} ion introduced into DNA base pairs changed to Fe^{3+}, as confirmed by its color and ESR g-value just near g ~ 2, corresponding to S = 5/2 expected for a high-spin state of Fe^{3+}, as demonstrated in Figure 3. Thus, one could conclude that one electron should transfer to DNA in Fe-DNA. Fe-DNA also shows another curious behaviors in magnetization and ESR spectra, which suggest a mixture of high-spin state, S = 5/2 and low-spin state, S = 1/2 of Fe^{3+}, especially as a function of Fe concentration.

On the location of metal ions are suggested to be in between the bases of a base pair from several experimental facts. However, the bonding state of the metal ion is still open question. We have succeeded to study the bonding state of Mn in Mn-DNA from the analysis of six hyperfine split spectra of $Mn_{0.01}Ca_{0.99}$-DNA taken at Q-band in Figure 2. It is known that the separation of the central two spectra represents the bonding nature of metal ion. Isolated Mn^{2+} ion in the ionic crystal CaF_2 shows the separation of more than 100 G, but in the crystal, ZnS made of mainly covalent bond indicates the separation of around 70 G. From the separation of 96 G in $Mn_{0.01}Ca_{0.99}$-DNA in Figure 4, we can clearly conclude that the bonding of Mn ion with surrounding bases in Mn-DNA is ionic in character. The present observation of the bonding nature of metal ions in M-DNA strongly supports further investigation and understanding of M-DNA, experimentally and theoretically.

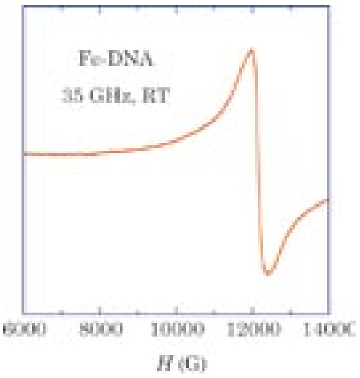

Figure 3. (left) ESR spectrum of Fe-DNA located at about g = 2, suggesting that S = 5/2 for Fe^{3+}.

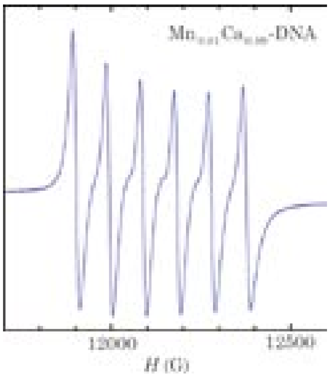

Figure 4. (right) ESR spectra of Mn ion in $Mn_{0.01}Ca_{0.99}$-DNA show the six hyperfine peaks. The separation of the center two spectra could be a measure of bonding nature, ionic or covalent.

A-3 ESR Study of Spin Dynamics for Dye-Sensitized Solar Cell

In dye-sensitized solar cells (DSSC), dye molecules are excited from the ground state S to the excited state S* by photo energy. The electron transfer from the excited dye molecules to the electrode plays an important role of the photoelectric transfer characteristic in DSSC. A various type of dye molecules were investigated. Time-resolved ESR measurements give us to detailed information of the photoelectric transfer characteristic. The aim of the present study is to reveal the relationship between the photoelectric transfer characteristic and the spin dynamics of electron in DSSC. The spin dynamics of the various organic dye molecules such as the eosin-Y was investigated by time-resolved ESR spectroscopy with laser photolysis (Nd:YAG 2nd harmonics, 532 nm). We discuss the spin dynamics of the various organic dye molecules with TiO_2.

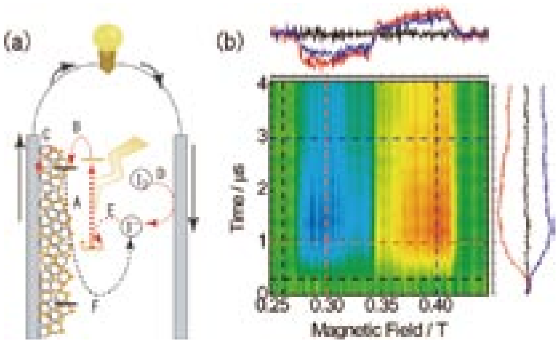

Figure 5. (a)Schematic image of the DSSC and (b)TR-ESR spectra for eosin-Y.

References

1) K. Ono, M. Yoshizawa, T. Kato and M. Fujita, *Angew. Chem., Int. Ed.* **46**, 1803–1806 (2007).

2) K. Ono, M. Yoshizawa, T. Kato and M. Fujita, *Chem. Commun.* 2328–2330 *(*2008).

3) K. Tanaka, Y. Yamada and M. Shionoya, *J. Am. Chem. Soc.* **124**, 8802–8803 (2002).

4) K. Tanaka, A. Tengeiji, T. Kato and M. Shionoya, *Science* **299**, 1212–1213 (2003).

5) G. H. Clever and T. Carell, *Angew. Chem., Int. Ed.* **46**, 250–253 (2007).

B. Construction of the Research Methodology for Biomolecular Sensing System

URISU, Tsuneo *(IMS)*
TERO, Ryugo *(IMS)*
ASANO, Toshifumi *(IMS)*
UNO, Hidetaka *(SOKENDAI)*
SHIBASAKI, Koji *(OIIB)*
TOMINAGA, Makoto *(OIIB)*
SHIGEMOTO, Ryuichi *(NIPS)*
FUKAZAWA, Yugo *(NIPS)*
YAWO, Hiromu *(Tohoku Univ.)*
ISHIZUKA, Toru *(Tohoku Univ.)*

The neurodegenerative diseases are intractable diseases for which neither of the cause and the treatment method is clarified. Statistically, 20% of more than 85 years old persons get dementia. Thus developments of treatment method and clarification of the cause are the urgent problem of human beings. Concerning this point, it is one of the problems to be solved that there is no suitable screening device of neural systems. In this program, we have started the research to develop a screening device which have the function of in vitro neural network analysis.

B-1 Development of Cell Culture Type Planar Ion Channel Biosensor for Nerve Cell Signaling Analysis

Cells growing on SOI substrates with and without the FN coating are compared. The FN coating clearly promoted cell growth. Although we did not control the cell positions, a cell was often positioned on the micropore.

The sequence of steps in the incubation mode recording is as follows. The culture mediums in the upper and lower chambers were exchanged to the extracellular and intracellular solutions, respectively, for the ion channel current measurements. Perforated patch mode recordings were formed by nystatin (100–200 µg/ml). The increase of capacitance (5–10 pF) of the cell membrane was observed 5–10 min after addition of the nystatin solution.

The whole-cell current of the TRPV1 activated by capsaicin stimulation was recorded. The first capsaicin application induced a large current increase, and the current increase induced by the second application was weaker than the first one. The decrease in the sensitivity unique to the capsaicin stimulation of TRPV1 with a Ca^{2+}-containing solution was observed.

B-2 Fabrication of Light Gated Ion Channel Biosensor

In the investigation of the electrically excitable cells, photo-stimulation provides a versatile alternative to electrode stimulation. Channel of the excitable cell by the photo-stimulation is especially useful in constructing the neural network analysis device. In the present work, we have expressed Chlamydomonas reinhardii channelrhodopsin 2 (ChR2) on the cell membrane of a kind of excitable cell C2C12, and measured the basic characteristics of the photo-response. ChR2 has a light absorbance peak at 460 nm and forms a non-selective cation channel, the gating of which is triggered by the photo-isomerization of the all-trans retinal to 13-cis configuration. To investigate the photo-response characteristics of ChR2-expressed C2C12 cell, we have constructed the planer-type ion channel biosensor by putting a single C2C12 cell on the micropore of the Si substrate and successfully observed the light-gated whole cell channel current. We are now measuring the basic characteristics of this system such as, effects of cell-cell interaction and coupling of the cell's own characteristics and the chamber's electric characteristics on the time dependence of the whole cell current.

(2) Research Symposia

(From Oct. 2008 to Sep. 2009)

Dates	Theme	Chair
Jan. 22–23, 2009	Plasmonic Materials for Molecular Science	**UENO, Kosei** **IMURA, Kohei**
Mar. 5– 6, 2009	Workshop on Biradical Chemistry and Its Future Perspect	**ABE, Manabu** **SAKURAI, Hidehiro**
Jul. 23, 2009	Preparatory Meeting for Molecular Science Summer School	**TANAKA, Midori** **HISHIKAWA, Akiyoshi**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2008–Mar. 2009	Apr. 2009–Sep. 2009	Total
Special Projects		0	1	1
Research Symposia		2	0	2
Research Symposia for Young Researchers		0	1	1
Cooperative Research		44	60	104
Use of Facility	Instrument Center	36	18	54
	Equipment Development Center	4	9	13
Use of UVSOR Facility		85	70	155
Use of Facility Program of the Computer Center				147*

* from April 2008 to March 2009