

# Joint Study Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint study 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

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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 determined the molecular structure of novel systems such as  $\text{Gd@C}_{82}$  and their spin interaction using ESR spectroscopy, and explored the functionality of the complicated molecule system. 2) We carried out an analysis of spin dynamics for functional molecular assemblies, including molecular conductors and magnetic materials. We searched for cooperative phenomena involved in intra-molecule freedom, and new functional physical-properties originating in molecular assemblies.

#### A-1 ESR Spectra of Bingel Monoadducts of $\text{Gd@C}_{82}$

Two kinds of Bingel monoadducts of  $\text{Gd@C}_{82}$  exhibited a sharp contrast in the ESR spectra. The reaction of  $\text{La@C}_{82}$  with diethyl bromomalonate in the presence of a base (the Bingel reaction) generated five mono-adducts. Akasaka and coworkers recently synthesized two monoadducts of  $\text{Gd@C}_{82}$ , mono-A and mono-E, at high purity. ESR spectra of the adducts were obtained using a high-field (W-band) ESR spectrometer at low temperature in solution, which showed remarkable contrast between mono-A and mono-E. The ESR spectrum of mono-A was unambiguously assigned to the spin state of  $S = 7/2$ , and that of mono-E to  $S = 3$ .

#### A-2 Peculiar Ground State of $\beta''$ -(BEDT-TTF)-TCNQ Revealed by ESR

One of the two segregated stack isomers of (BEDT-TTF)-TCNQ (abbreviated as ET-TCNQ),  $\beta''$ -ET-TCNQ, has been studied. Since the unit cell of  $\beta''$ -ET-TCNQ has one ET and one TCNQ molecule with a charge transfer of 0.5 electrons, a quarter-filled band with strong on-site Coulomb correlation

determines the electronic states.

It is known that (1) the  $\beta''$ -form has metallic characteristics at low temperatures with definite Fermi surfaces, (2) the charge separation within the ET layer melts away below 170 K, and (3) the 1D TCNQ stack has weak dimerization at all temperatures. However, several open questions still remain for this system, including anomalies in the electrical resistivity at 80 K and 20 K, and heat capacity anomalies at 10 K and 20 K.

Here, on the basis of ESR and  $^1\text{H}$  NMR spectra, and spin susceptibility for each of the ET and TCNQ stacks deduced from the ESR  $g$ -shift, we propose a model with partial CDW nesting in ET sheets below 80 K, spin-Peierls transition at 20 K within the TCNQ 1D stacks, and the RKKY broadening of the ESR spectra of the TCNQ soliton-like spins via conduction electrons of the ET layer with a Kondo temperature of 10 K.

#### A-3 Spin-Dynamics Investigation by Pulsed ESR for Spin-Peierls Phases in Conventional Systems and Charge-Ordered TMTTF Salts

TMTTF-based salts undergo charge-ordering (CO) transitions in the intermediate paramagnetic states between the resistivity minimum temperature and the phase-transition temperature towards the ground state. In our previous report, the charge configuration patterns of the charge-ordering phases in the intermediate paramagnetic states were determined to be  $-\text{O}-\text{o}-\text{O}-\text{o}-$  ( $4k_{\text{F}}$ ) along the stacking axes for  $(\text{TMTTF})_2\text{MF}_6$  salts ( $M = \text{P, As, Sb}$ ) by ESR linewidth anisotropy analysis. However, the charge configuration of the ground state (for example,  $(\text{TMTTF})_2\text{PF}_6$  (spin-Peierls)) has not yet been clarified. Moreover, the co-existence of the CO ( $4k_{\text{F}}$ ) and spin-Peierls ( $2k_{\text{F}}$ ) phases seems unlikely.

To determine spin dynamics in the proximity of the spin-Peierls phase, pulsed ESR investigations were carried out for one-dimensional organic conductors,  $(\text{TMTTF})_2\text{X}$ , compared to a conventional spin-Peierls system,  $\text{MEM}(\text{TCNQ})_2$ . While the ESR spin-lattice relaxation rate,  $\text{ESR}-T_1^{-1}$ , of  $\text{MEM}(\text{TCNQ})_2$  shows ordinal spin-gap behavior at around the spin-Peierls phase transition temperature,  $T_{\text{SP}}$ , the  $\text{ESR}-T_1^{-1}$  of  $(\text{TMTTF})_2\text{PF}_6$  cannot be explained within the framework of simple spin-gap formation in the proximity of  $T_{\text{SP}}$ . Possible reorientation of charge configuration is likely. We discuss the electronic properties from a microscopic point of view.

## B. Construction of the Research Methodology for Biomolecular Sensing System

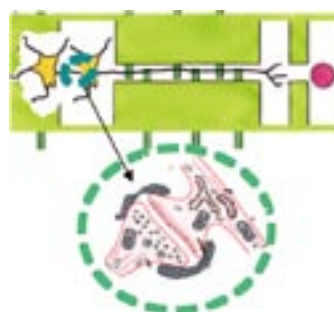
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The target of this project is the development of a kind of neural cell chips as shown in Figure 1, in which a couple of cells is combined by synapse and the detection of action potential, fluorescence or FRET signal and neurotransmitter molecules.

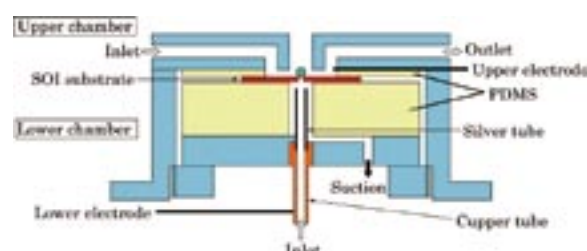
Figure 2 is shown the first device which we have developed last year.<sup>1)</sup> Transient receptor potential V1 (TRPV1) transfected HEK293 cell is positioned on the micropore of the Si chip. The chip is integrated into the microfluidic circuit. Channel current triggered by capsaicin was successfully observed. The desensitization unique to the TRPV1 channel was observed.

### Reference

1) Z. L. Zhang *et al.*, *Thin Solid Film* (2007) in press.



**Figure 1.** Schematic image of the target neural cell chip in this project.



**Figure 2.** Planer patch clamp device fabricated in this project using Si-SOI substrate.

## (2) Research Symposia

(From 2006 Oct. to 2007 Sep.)

Dates	Theme	Chair
Nov. 7– 8, 2006	Approach from Interstellar and Molecular Sciences to the Origin of Homochirality	<b>KAWAGUCHI, Kentaro</b> <b>OHSHIMA, Yasuhiro</b>
Nov. 17–18, 2006	Workshop on Research for VUV Luminescence	<b>ITOH, Minoru</b> <b>SHIGEMASA, Eiji</b>
Nov. 29–30, 2006	Large-Amplitude Vibration by High-Resolution Molecular Spectroscopy	<b>BABA, Masaaki</b> <b>OHSHIMA, Yasuhiro</b>
Dec. 5– 6, 2006	Recent Advances in Molecular Science via Sum Frequency Generation Spectroscopy	<b>OUCHI, Yukio</b> <b>MORITA, Akihiro</b>
Dec. 21–22, 2006	Hierarchy of Molecular Interactions in Complicated Systems: A Basis for Understanding of Biological Functions	<b>TAHARA, Tahei</b> <b>NISHI, Nobuyuki</b>
Mar. 11–12, 2007	New Development of Materials Molecular Science	<b>KATO, Reizo</b> <b>YAKUSHI, Kyuya</b>
Mar. 14–15, 2007	Functions and Properties of Nano-Structure Controlled Hybrid Inorganic-Organic Composites	<b>OHBA, Masaaki</b> <b>TANAKA, Koji</b>
Mar. 19–20, 2007	Progress in Science of Nanoclusters and Nanoparticles —Reactivity, Structure, and Dynamics	<b>MAFUNE, Fumitaka</b> <b>TSUKUDA, Tatsuya</b>
Mar. 19–20, 2007	Molecular Science of Enzymes Relating to Heme Degradation	<b>FUJII, Hiroshi</b>

May 22–23, 2007	Molecular Science for Living Cells	<b>OHTA, Nobuhiro</b> <b>OZAWA, Takeaki</b>
Jun. 1– 3, 2007	Metals and Molecular Assemblies —The Way to Frontier of Supramolecular Science—	<b>UENO, Takashi</b> <b>KAWAGUCHI, Hiroyuki</b>
Jun. 23, 2007	Physical Chemistry Symposium for Young Scientists in Molecular Science	<b>HAMAGUCHI, Hiroo</b> <b>HISHIKAWA, Akiyoshi</b>
Aug. 29–31, 2007	Coupled Simulation in Molecular Science: Theories and Applications	<b>AOYAGI, Mutsumi</b> <b>SAITO, Shinji</b>
Sep. 10–11, 2007	Synchrotron Radiation and Surface Electron Emission Microscopy: Recent Progress in Microscopic Techniques for Nanomaterials Science	<b>ASAKURA, Kiyotaka</b> <b>YOKOYAMA, Toshihiko</b>
Sep. 28–29, 2007	Scientific Basis of New Field “Molecular Communication”	<b>URISU, Tsuneo</b>

### (3) Numbers of Joint Study Programs

Categories		2006 Oct.–2007 Mar.	2007 Apr.–2007 Sep.	Total
Special Projects		0	2	2
Research Symposia		9	6	15
Cooperative Research		39	44	83
Use of Facility	Laser Research Center for Molecular Science	1	–	1
	Research Center for Molecular Scale Nanoscience	21	–	21
	Instrument Center	–	23	23
	Equipment Development Center	5	2	7
Use of UVSOR Facility		62	70	132
Use of Facility Program of the Computer Center				141