

## Interface Science - Molecular Aggregates -



Prof  
SATO, Naoki  
(D Sc)



Assoc Prof  
ASAMI, Koji  
(D Sc)



Instr  
KITA, Yasuo  
(D Sc)



Instr  
YOSHIDA, Hiroyuki  
(D Sc)

### Students

TSUTSUMI, Kiyohiko (D3)    KITA, Hiroki (M2)    SAKOU, Machiko (M2)    YAMAMOTO, Daisuke (M2)  
HIRAMATSU, Takaaki (M1)    TSUTSUMI, Jun'ya (M1)    YOSHIDA, Tadashi (M1)

### Visitor

Prof ZHAO, Kongshuang    South China Normal University, China, 26 December 2000-25 March 2001.

## Scope of Research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectroscopies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

## Research Activities (Year 2001)

### Presentations

Characterization of biological cells by dielectric spectroscopy, Asami K, 1st International Conference on Dielectric spectroscopy in Physical, Chemical and Biological Applications (Jerusalem, Israel), 13-15 March.

Unoccupied states of organic semiconductor thin films examined by inverse photoemission spectroscopy, Sato N, Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications (Glumslöv, Sweden), 4-7 June.

Dielectric monitoring of cell growth in culture using an inductive probe, Asami K, Zhao KS, XI International Conference on Electrical Bio-Impedance (Oslo, Norway), 17-21 June.

Electronic structures of unoccupied states in metallo-phthalocyanine thin films studied by inverse photoemission spectroscopy, Sato N, Yoshida H, Tsutsumi K, The 7th China-Japan Joint Symposium on Conduction and

Photoconduction in Organic Solids and Related Phenomena (Guangzhou, China), 18-22 November.

Thin film growth of bis(1,2-dimethylglyoximate)-platinum(II) on pseudo-Ag(111) studied by X-ray photoemission spectroscopy, Yoshida H, Takahashi R, Kita H, Sato N, The 7th China-Japan Joint Symposium on Conduction and Photoconduction in Organic Solids and Related Phenomena (Guangzhou, China), 18-22 November.

### Grants

Sato N, Precise analyses of extended electronic structures in organic thin films by means of in situ normal and inverse photoemission spectroscopies, Grant-in-Aid for Scientific Research (A) (2), 1 April 1999 - 31 March 2002.

Asami K, Bio-impedance imaging by scanning dielectric microscopy, Grant-in-Aid for Scientific Research (C)(2), 1 April 2000-31 March 2002.

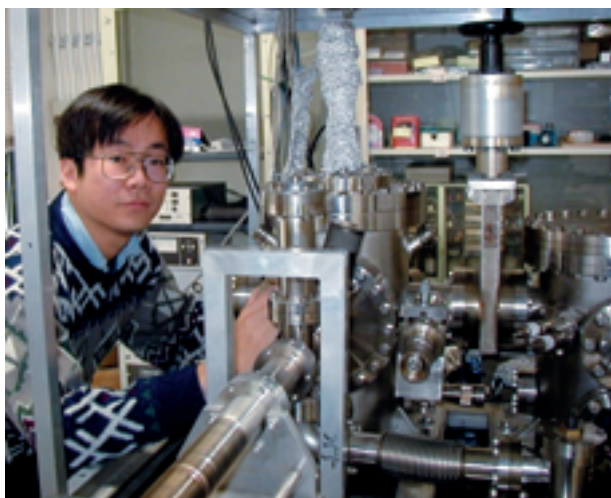
## Topics

### Unoccupied electronic states of 3d-transition metal phthalocyanines (MPc: M = Mn, Fe, Co, Ni, Cu and Zn) studied by inverse photoemission spectroscopy

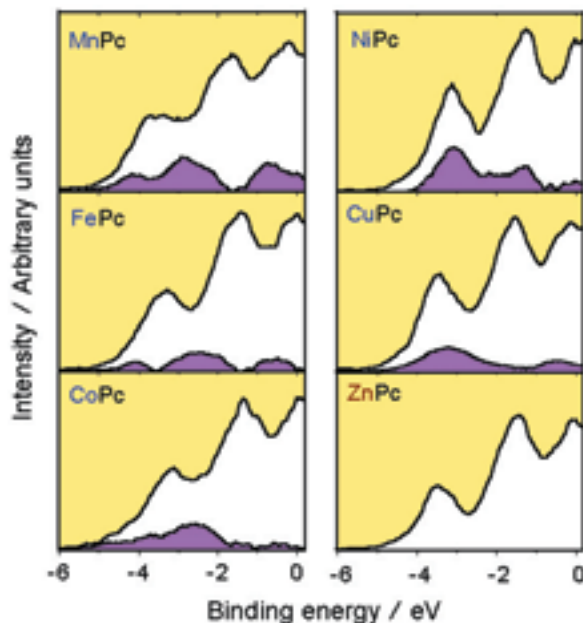
Unoccupied electronic states of thin films of 3d-metal phthalocyanines (MPc: M = Mn, Fe, Co, Ni, Cu and Zn) were systematically investigated in the energy range from the Fermi level to the vacuum levels using inverse photoemission spectroscopy: obtained spectra are shown in Fig. 1. The spectra obtained for NiPc and CuPc were in good agreement with spectra previously reported. Overall the features of the observed spectra were similar to each other, regardless of the substitution of the central metals. This is explained by the dominant contribution to the spectra from the macrocyclic  $\pi$  orbitals of the Pc framework.

Changes in the contribution of the central metal, however, cause small variations in the spectra. In our analysis of the metal contribution, we examined the difference spectra obtained by subtracting a ZnPc reference spectrum (as shown as purple-colored areas in Fig. 1). The choice of ZnPc as a reference was made because the d orbitals of the zinc ion in ZnPc are fully occupied.

The difference spectra of MnPc, FePc, NiPc and CuPc were found to agree well with the reported X-ray absorption spectra. It is thus concluded that the difference spectra reflect the density of unoccupied states derived from the central metals. The difference spectra of MnPc, FePc, CoPc, NiPc and CuPc were further tentatively assigned with the help of reported results from extended Hückel and density functional calculations.



K. Tsutsumi working on our home-built inverse photoemission apparatus; the bellows coupling seen in the front of the apparatus accommodates a low-energy electron source.



**Fig. 1.** Inverse photoemission spectra observed for evaporated thin films of MPc (M = Mn, Fe, Co, Ni, Cu and Zn). Purple-colored areas show difference spectra obtained by subtracting the ZnPc spectrum from the MPc spectra.

### Ion channels of alamethicin dimers N-terminally linked by disulfide bond

Because of structural resemblance, the helix-bundle type channels formed by alamethicin, 20-residue antibiotic peptide, in lipid bilayers are available as a model of biological channels. The channels, however, have drawbacks in single channel analysis: the multi-conductance behavior that are due to transient changes in molecularity of peptides in a helix bundle, and the voltage-gated channel formation preventing characterization of the current-voltage relation.

To overcome the drawbacks we adopted covalent alamethicin dimers, that restrict the peptide molecularity and form long lasting channels that allow us to measure the current-voltage relations by applying a fast voltage ramp during channel opening. The dimers, N-terminally linked by a disulfide bond, revealed the relationship between the channel conductance and the peptide molecularity, and demonstrated that negative fixed charges at the narrowest part of the pore much more enhanced cation-selectivity in ion permeation than those at the pore mouth.