Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

http://www.kuicr.kyoto-u.ac.jp/labos/is2/scope.html

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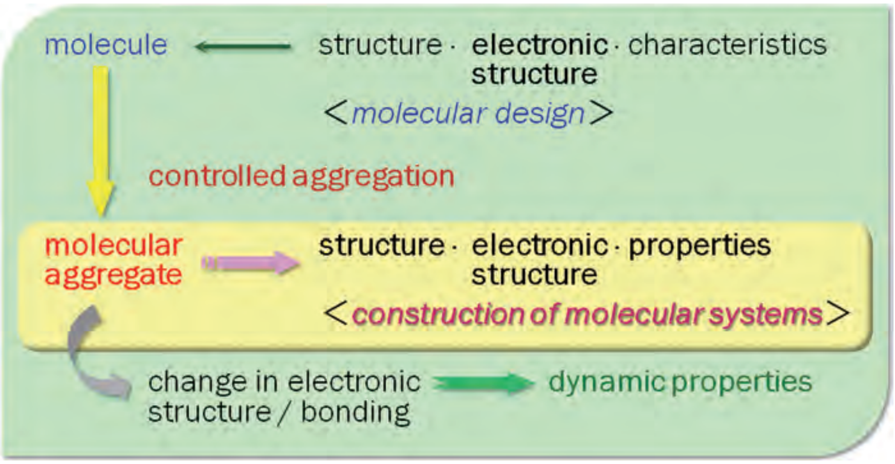
Scope of Research

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 spectrosocpies 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 sturcutres in mocrocapsules, boipolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

KEYWORDS

α-Dispersion
Cell Suspension
Diode Behavior
Pentacene Thin Film
Voltage Stress



Selected Publications

Tsuzuki, S.; Sato, N., Origin of Attraction in Chalgogen-Nitrogen Interaction of 1,2,5-Chalcogenadiazole Dimers, *J. Phys. Chem. B*, **117,** 6849–6855 (2013).

Fabiano, S.; Yoshida, H.; Chen, Z.-H.; Facchetti, A.; Loi, M. A., Orientation-Dependent Electronic Structures and Charge Transport Mechanisms in Ultrathin Polymeric n-Channel Field-Effect Transistors, *ACS Appl. Mater. Interfaces*, **5,** 4417-4422 (2013).

Han, W.-N.; Yoshida, H.; Ueno, N.; Kera, S., Electron Affinity of Pentacene Thin Film Studied by Radiation-Damage Free Inverse Photoemission Spectroscopy, *Appl. Phys. Lett.*, **103,** [123303-1]-[123303-5] (2013).

Noshiro, D.; Sonomura, K.; Yu, H.-H.; Imanishi, M.; Asami, K.; Futaki, S., Construction of a Ca^{2+}-Gated Artificial Channel by Fusing Alamethicin with Calmodulin-Derived Extramembrane Segment, *Bioconjugate Chem.*, **24,** 188-195 (2013).

Asami, K., Dielectric Properties of Dipicrylamine-Doped Erythrocytes, Cultured Cells and Lipid Vesicles, *Bioelectrochemistry*, **92,** 14-21 (2013).

Voltage Stress Induced Reversible Diode Behavior in Pentacene Thin Films

Recently, there has been renewed interest in the current–voltage (*I–V*) behavior of organic materials under low electric potentials applied, where many conditions used to derive the space charge limited current model will cease to apply. Current flow is regulated there by charge injection at one or both electrodes and, as a result, interfacial effects become the dominant factor behind the measured *I–V* relationships. Changing the barrier energy for charge carrier injection at one or both electrodes will result in diode or diode-like behavior. This is normally achieved by using electrodes with different work functions.

In the course of *in situ* measurement of the dark conductance of pentacene films deposited under ultrahigh vacuum between two nominally identical titanium electrodes in bottom contact geometry, we consistently observed a small difference between the measured conductance for positive and negative applied voltages. A vacuum-deposited 100 nm thick pentacene film provided us with the asymmetric *I–V* curves and the direction and degree of the diode-like behavior vary with sample and measurement history. On further investigation it was discovered that "stressing" the sample at high voltage could reliably cause the sample to exhibit rectification in one direction or the other, depending on the polarity of the applied voltage stress. The rectification behavior, once set, was essentially permanent until reversed by a subsequent voltage stress in the opposite direction.

Analysis of the voltage and temperature dependence suggests that the current is injection limited under both forward and reverse bias. The bias stress acts to raise or lower the energy barrier for charge carrier injection, most likely through the injection of space charge into the bulk film.

Modification of the electrical properties of organic devices from sustained applied voltage bias is well known though the mechanisms are not always well understood. To our knowledge, however, bias stress induced, reversible rectification has not been reported previously for organic films.

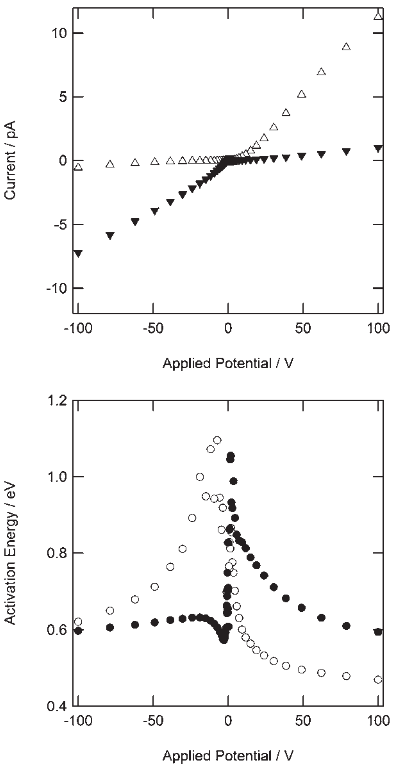


Figure 1. Variation in device current (upper) and the activation energy of electrical conductance (lower) as a function of applied potential, for the system after positive bias stress (△,○) and after negative bias (▼,●).

Electrical Properties of *E. coli* Cells Revealed by Dielectric Spectroscopy

To understand the electrical properties of the plasma membrane and the cell wall of *E. coli* cells, dielectric spectra of the cell suspensions were measured over a frequency range from 10 Hz to 10 MHz. Low-frequency dielectric dispersion, so-called the α-dispersion, was found below 10 kHz in addition to the β-dispersion, due to interfacial polarization, appeared above 100 kHz. When the cells were killed by heating at 60 ºC for 30 min, the β-dispersion disappeared completely, whereas the α-dispersion was little influenced. The disappearance of the β-dispersion suggests that the plasma (or inner) membranes in the dead cells are no longer the permeability barrier to small ions, and that the α-dispersion is not related to the membrane potential produced by diffusion of specific ions along their gradients across the plasma membrane. The intensity of the α-dispersion depended on both of the pH and ionic strength of the external medium, supporting the model that the α-dispersion results from the deformation of the ion clouds formed outside and inside the cell wall containing charged residues.

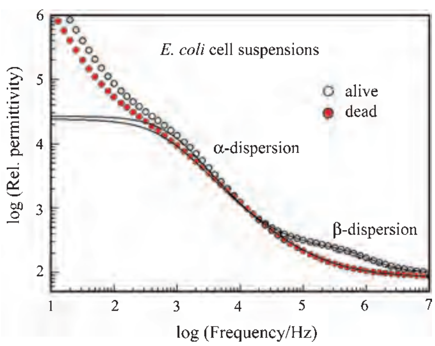


Figure 2. Dielectric spectra of *E. coli* cell suspensions.