Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

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

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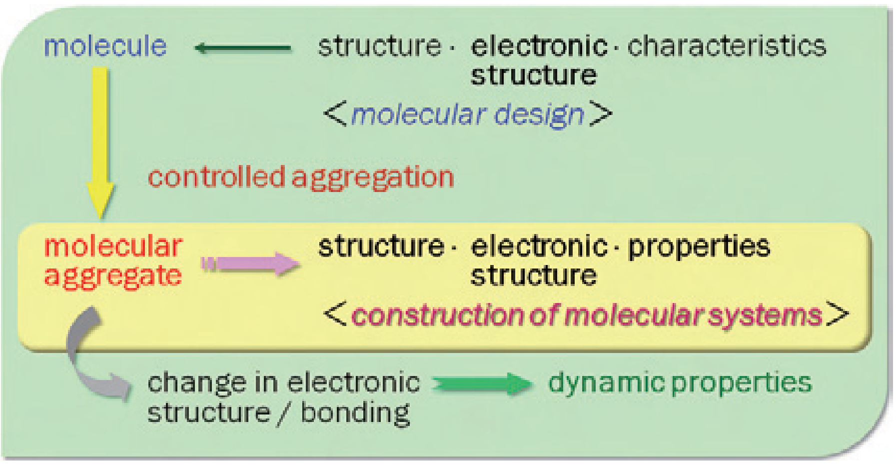
Scope of Research

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.

KEYWORDS
Dielectric Spectroscopy
Erythrocyte
Surface Potential
Thin Film
Zwitterionic Molecule



Selected Publications

Hayashi Y, Katsumoto Y, Oshige I, Omori S, Yasuda A, Asami K: Dielectric Inspection of Erythrocytes, *J. Non-Cryst. Solids*, **356,** 757-762 (2010).

Tsutsumi J, Yoshida H, Murdey R, Sato N: Spontaneous Buildup of Surface Potential with a Thin Film of a Zwitterionic Molecule Giving Non-Centrosymmetric Crystal Structure, *Appl. Phys. Lett.*, **95,** 182901 (2009).

Murdey R, Bouvet M, Sumimoto M, Sakaki S, Sato N: Direct Observation of the Energy Gap in Lutetium Bisphthalocyanine Thin Films, *Synth. Met.*, **159,** 1677-1681 (2009).

Hiramatsu T, Sasamori T, Yoshida H, Tokitoh N, Sato N: Reversible Polymorphic Crystalline Transition of a Push–Pull-Type Molecule: {4-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (BMDCM), *J. Mol. Struct.*, **922,** 30-34 (2009).

Yoshida H, Sato N: Crystallographic and Electronic Structures of Three Different Polymorphs of Pentacene, *Phys. Rev. B*, **77,** 235205 (2008).

Yoshida H, Inaba K, Sato N: X-ray Diffraction Reciprocal Space Mapping Study of the Thin Film Phase of Pentacene, *Appl. Phys. Lett.*, **90,** 181930 (2007).

Spontaneous Buildup of Surface Potential with a Thin Film of a Zwitterionic Molecule Giving Noncentrosymmetric Crystal Structure

Surface potentials were examined using the Kelvin method for thin films of zwitterionic molecules, pyridinium 1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylide (PI) or 2-*N*-pyridinium-1,3-indandione betaine (IPB) and its nitrogen substituted compounds: pyridinium 5,7-dihydro-5,7-dioxo-6*H*-cyclopenta[*b*]pyridin-6-ylide (4N-PI) and pyridinium 5,7-dihydro-5,7-dioxo-6*H*-cyclopenta[*c*]pyridin-6-ylide (5N-PI), as well as pentacene as a control material. Among the three zwitterionic compounds, we recently confirmed that only 4N-PI molecules crystallize in a noncentrosymmetric structure with a space group *Pc* where all the molecular dipole moments point in the same direction. Spontaneous buildup of the surface potential on the film 5.5 V at a film thickness of 300 nm was observed only for 4N-PI (Figure 1). The relationship between the alignment of the molecular dipole moments in the film and the measured surface potentials was investigated using grazing incidence x-ray diffraction (GIXD), pole-figure measurements, atomic force microscopy (AFM), and Kelvin probe force microscopy (KFM). These structural analyses disclosed that the 4N-PI film contains small crystallites with the noncentrosymmetric crystallographic structure which is the same as its single crystal. Further, the crystallites are oriented with the (110) axes perpendicular to the substrate surface with a broad distribution width of about 20° (Figure 2). This result indicates that polar molecules crystallizing in the noncentrosymmetric structure can also show spontaneous surface potential when a preferred film structure is realized.

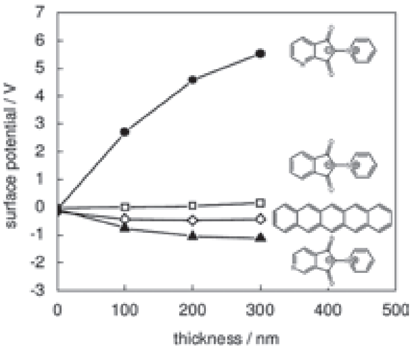


Figure 1. Surface potential measured for the films in the dark as a function of film thickness.

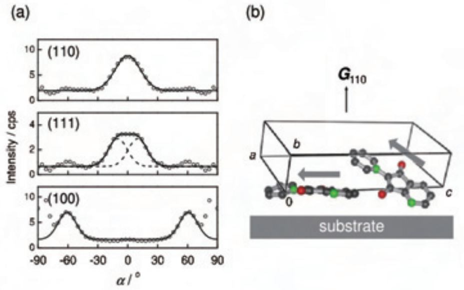


Figure 2. (a) X-ray pole figures (plotted as a function of polar angle α measured from the surface normal) of (110), (111) and (100) diffractions for the 4N-PI film. (b) Schematic of the analyzed orientation of the unit cell with 4N-PI molecules on the substrate surface.

Dielectric Spectroscopy Reveals Nanoholes of Erythrocyte Membrane Ghosts

When blood is diluted with water, erythrocytes swell and then burst to release hemoglobin molecules. The remaining membranes, called “ghosts”, are resealed under physiological conditions. About 50 years ago, Schwan and Carstensen reported that ghost suspensions showed peculiar dielectric dispersion below 10 kHz, called α-dispersion, which was not found for intact erythrocyte suspensions. The findings, however, have never been traced because of difficulty in low-frequency measurement due to electrode polarization, and therefore the origin of the α-dispersion has not been understood. This study has disclosed the α-dispersion (see Figure 3) by solving the problem in measurement using a new electrode configuration. The α-dispersion was found to be quite unstable at room temperature, being stabilized by fixation of ghosts with glutaraldehyde. The properties of the α-dispersion were exactly interpreted by the existence of a hole in each ghost membrane. The numerical simulation with a spherical cell model with a hole provided a linear relation between the characteristic frequency f_α of the α-dispersion and the hole radius R_h, and thereby the values of R_h being determined from those of f_α straightforwardly. The estimated values of R_h were close to those obtained by electron microscopy and several times larger than those from the analysis of the diffusion of probe molecules through the holes.

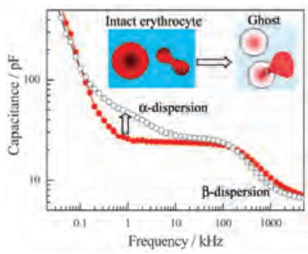


Figure 3. The capacitance of intact erythrocyte (closed circle) and ghost (open circle) suspensions plotted against the frequency of the applied ac field.