

Division of Multidisciplinary Chemistry – Molecular Aggregation Analysis –

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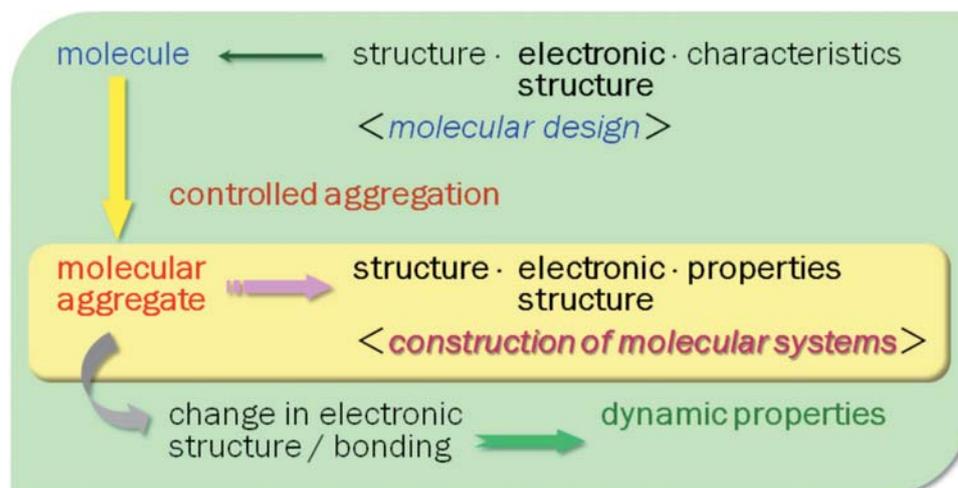
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Scope of Research

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 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.

KEYWORDS

Activation Energy
Bilayer Lipid Membrane
Dielectric Spectroscopy
Organic Semiconductor
Trap State



Selected Publications

Murdey, R.; Sato, N., Interpretation of the Thermal Activation Energy of Conduction for Molecular Semiconductor Thin Films with Blocking Contacts, *Jpn. J. Appl. Phys.*, **53**, 05FY04 (2014).

Yoshida, H., Low-energy Inverse Photoemission Study on the Electron Affinities of Fullerene Derivatives for Organic Photovoltaic Cells, *J. Phys. Chem. C*, **118**, 24377-24382 (2014).

Hidaka, Y.; Asami, K., Measurement of Dipole Potential in Bilayer Lipid Membranes by Dielectric Spectroscopy, *J. Membrane Biol.*, **247**, 721-727 (2014).

Asami, K., Low-Frequency Dielectric Dispersion of Bacterial Cell Suspensions, *Colloids Surf. B*, **119**, 1-5 (2014).

Interpretation of the Thermal Activation Energy of Conduction for Organic Semiconductor Thin Films with Blocking Contacts

A two-terminal lead phthalocyanine (PbPc) thin film device exhibited reversible rectification *in situ* when a high bias stress potential was applied to the electrodes, as shown in Figure 1. The current rectification was associated with a shift of the thermal activation energy of conductance by about -0.1 eV (forward bias) and $+0.1$ eV (reverse bias) from the pre-bias value of 0.67 eV as the equilibrium one. The rectification ratio of the conductance was changed less than that predicted from the observed change in activation energy, indicating that the system obeyed the Meyer–Neldel rule normally associated with charge carriers in thermal equilibrium with a logarithmic tail of trap states. Annealing the sample at 175 °C removed the rectification behavior, providing further indication that trap states play a significant role in the transport mechanism. Rectification implies blocking electrodes and injection limited current at both electrodes, under which conditions the activation energy is expected to correlate with the energy barrier for charge injection—the energy separation between the Fermi level of the electrode and the mobility edge of the organic semiconductor (see Figure 2). Neither of these energy levels, however, depends explicitly on an excess of trapped charge in the logarithmic density of tail states induced by the bias stress. A change in the trap filling level induced by the space charge injection during the bias stress should not, therefore, influence either state in a way that satisfactorily explains the observed rectification. The most likely interpretation that explains our results is that the metal Fermi level is pinned to the trap filling level in the organic thin film.

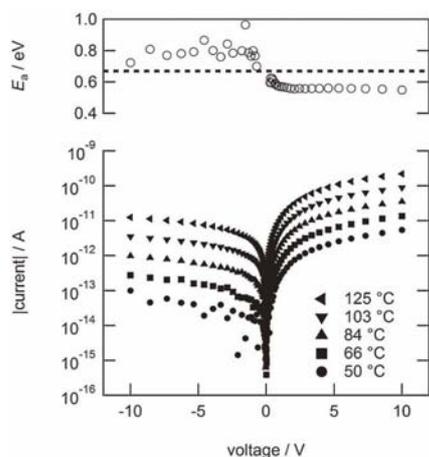


Figure 1. *In situ* I - V curves and activation energies obtained for an 8 nm-thick PbPc film deposited at 50 °C and annealed at 125 °C for 48 h. The forward rectification was observed when a $+500$ V bias applied for 2–3 h at 125 °C. The dotted line indicates the pre-stress activation energy of 0.67 eV.

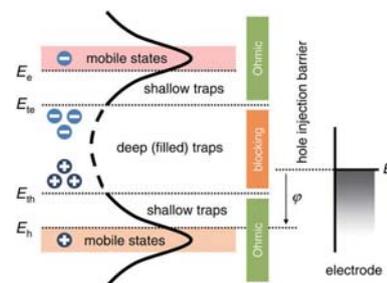


Figure 2. A schematic energy diagram for the interface between an organic semiconductor and a metal electrode. The organic semiconductor has trap states distributed throughout the transport energy gap, $E_c - E_v$. An electrode Fermi level within the trap filling states is expected to result in blocking contacts, whereas Fermi levels falling closer to either mobility edge are likely to form an Ohmic contact for either holes or electrons.

Measurement of Dipole Potential in Bilayer Lipid Membranes by Dielectric Spectroscopy

It is known that there is a positive electrostatic potential within a bilayer lipid membrane (BLM) originating from alignment of dipolar residues of lipids and water molecules. The potential is termed the dipole potential (DP) and is thought to be important in regulating the functions of membrane proteins and the interactions of various bioactive compounds with the membranes. To understand the DP, we studied dielectric properties of planar BLMs using dipicrylamine (DPA) (hydrophobic anion) as a probe for the DP. The BLMs doped with DPA showed dielectric relaxation due to the translocation of DPA between the membrane interfaces (Figure 3). Incorporating either cholesterol (CL) or 6-ketocholestanol (KC) into the membranes increased the characteristic frequency of the dielectric relaxation, which is proportional to the translocation rate constant of DPA. The results suggested that the sterol dipoles induced positive potential changes within the membrane interior. The changes of the DP were 70 mV for CL and 150 mV for KC when the sterol mole fraction was 0.67 . The opposite effect was caused by phloretin added to the aqueous media, and the maximum DP change was -90 mV at 100 μ M.

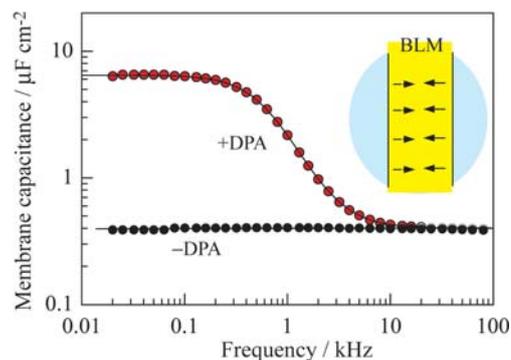


Figure 3. Dielectric relaxation of bilayer lipid membranes in the absence and presence of DPA. Inset: sterol dipoles in the membrane are illustrated.