Division of Environmental Chemistry
– Solution and Interface Chemistry –

http://www.scl.kyoto-u.ac.jp/~yoeki/

Prof
HASEGAWA, Takeshi
(Ph D)

Assist Prof
WAKAI, Chihiro
(D Sc)

Assist Prof
SHIMOAKA, Takafumi
(D Sc)

Students

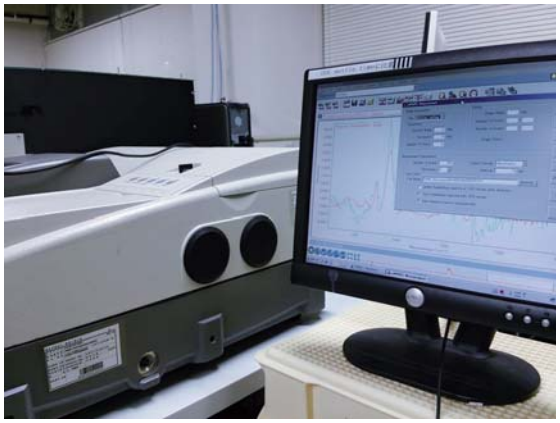
TU, Kai-min (D3)
SHIOYA, Nobutaka (M2)
TANAKA, Yuki (M2)

Scope of Research

To understand the chemical structure, property and reactions in a two-dimensional molecular aggregate, the keywords of molecular interactions and orientation are focused on, and the fluctuated molecular aggregates are investigated by using originally developed spectroscopic and theoretical techniques. The current major topics are: (1) a new chemical model accounting for bulk properties specific to perfluoroalkyl compounds; (2) analysis of molecular orientation and conformation in a thin film of organic semiconductor polymer; (3) study on a novel surface selection rule for discussing the molecular orientation in a thin film adsorbed on a rough surface.

KEYWORDS

Infrared and Raman Spectroscopy
Surface and Interface Chemistry
Perfluoroalkyl Compounds
Organic Semiconductor
Polymer Electrolyte Membrane
Nano Particle and Fibril Analysis



Selected Publications

Hasegawa, T.; Shimoaka, T.; Shioya, N.; Morita, K.; Sonoyama, M.; Takagi, T.; Kanamori, T., Stratified Dipole-Arrays Model Accounting for Bulk Properties Specific to Perfluoroalkyl Compounds, *ChemPlusChem*, **79,** 1421-1425 (2014).

Nakata, S.; Ueda, T.; Miyaji, T.; Matsuda, Y.; Katsumoto, Y.; Kitahata, H.; Shimoaka, T.; Hasegawa, T., Transient Reciprocating Motion of a Self-Propelled Object Controlled by a Molecular Layer of a *N*-Stearoyl-*p*-nitroaniline: Dependence on the Temperature of an Aqueous Phase, *J. Phys. Chem. C*, **118(27),** 14888-14893 (2014).

Shioya, N.; Shimoaka, T.; Hasegawa, T., Analysis of Molecular Orientation and Conformation of Poly(3-hexylthiophene) Thin Films on Silicon by Infrared p-Polarized Multiple-Angle Incidence Resolution Spectrometry, *Chem. Lett.*, **43(8),** 1198-1200 (2014).

Morimine, S.; Norimoto, S.; Shimoaka, T.; Hasegawa, T., Surface Selection Rule of Infrared Diffuse Reflection Spectrometry for Analysis of Molecular Adsorbates on a Rough Surface of a NonAbsorbing Medium, *Anal. Chem.*, **86,** 4202-4208 (2014).

Tu, K.-M.; Ishizuka, R.; Matubayasi, N., Spatial-decomposition Analysis of Electrical Conductivity in Concentrated Electrolyte Solution, *J. Chem. Phys.*, **141,** [044126-1]- [044126-9] (2014).

Stratified Dipole-Arrays Model Accounting for Bulk Properties Specific to Perfluoroalkyl Compounds

Perfluoroalkyl compounds are known to exhibit a hydrophobic character on the surface of the material, although the C-F bond has a large dipole, which should make the molecular surface polar and hydrophilic. This inconsistency has long been a chemical matter to be solved. Herein, a stratified dipole-arrays model is proposed: the molecular polar surface can be fully hidden by forming a two-dimensional aggregate of perfluoroalkyl (Rf) groups; this aggregate is spontaneously induced by dipole–dipole interaction arrays owing to the helical structure of the Rf group. In this model, a 'short' Rf group should play the role of a single Rf group with a hydrophilic character, whereas a 'long' Rf group should spontaneously form a hexagonal aggregate. To examine this model, Rf-containing myristic acids with various Rf lengths have been synthesized and their aggregation properties are analyzed by using the Langmuir monolayer technique aided by precise IR spectroscopic analysis.

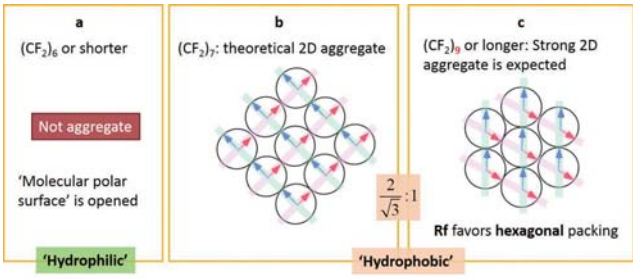


Figure 1. Top views of the 2D molecular aggregates as a function of the Rf length.

Analysis of Molecular Orientation and Conformation of Poly(3-hexylthiophene) Thin Films on Silicon by Infrared p-Polarized Multiple-angle Incidence Resolution Spectrometry

Infrared (IR) p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) has been employed for the first time to reveal the molecular orientation in two different poly(3-hexylthiophene) (P3HT) thin films having face-on and edge-on orientations. The CH out-of-plane deformation vibration mode (ca. 820 cm^{-1}) of the thiophene ring is found to be highly localized on the ring, which is quite useful for molecular orientation analysis coupled with IR p-MAIRS. On the other hand, the CH stretching vibration region is useful for determining the molecular order, conformation, and folding of the hexyl chain via MAIRS dichroism.

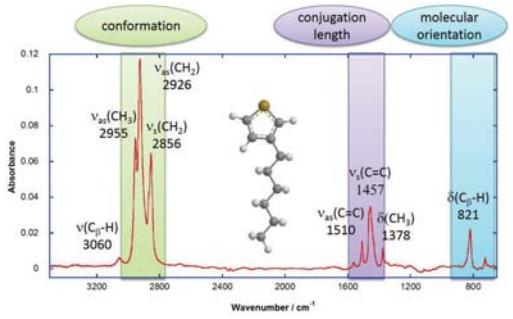


Figure 2. IR p-MAIRS spectra of a P3HT thin film deposited on a Si substrate prepared by using a chloroform.

Surface Selection Rule of Infrared Diffuse Reflection Spectrometry for Analysis of Molecular Adsorbates on a Rough Surface of a Nonabsorbing Medium

The surface selection rule (SSR) for discussing the molecular orientation in a thin film adsorbed on a rough surface is determined by analyzing a surface monolayer by defining the angle of incidence and polarizations. As the standard sample, a highly organized self-assembled monolayer (SAM) on a rough alumina surface is employed. By introducing crossed-Nicol polarizers in the incident and detection paths, the specular reflection and diffuse reflection components are readily separated. To fully understand the spectra of the SAM, a new idea is proposed that the incidental light can be excluded from the discussion when the angle of incidence is small, which is named the pseudotransmission (pd-Tr) model. Another important idea is that a part of a spectrum is degraded in the signal-to-noise ratio by the suppression of incidental light on the rough surface via a deconstructive interference, which can experimentally be revealed by the crossed-Nicol measurements of single-beam spectra depending on the angle of incidence. Through the experiments of all the combinations of polarizations and angles of incidence, the pd-Tr model and the light suppression are found to be an important base to fully understand the SSR of molecular adsorbates on a rough surface of a nonabsorbing medium.

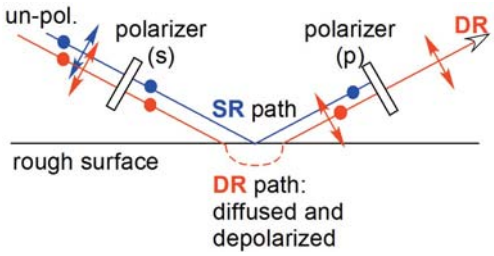


Figure 3. A schematic of the DR filter consisted of two mutually orthogonal (crossed-Nicol) polarizers. The incidental and detection angles are set to be equal to each other. The solid circle (●) and the two-direction arrow (↔) indicate the s- and p-polarizations, respectively. Only the DR component passes through the second polarizer.