

Division of Environmental Chemistry – Chemistry for Functionalized Surfaces –

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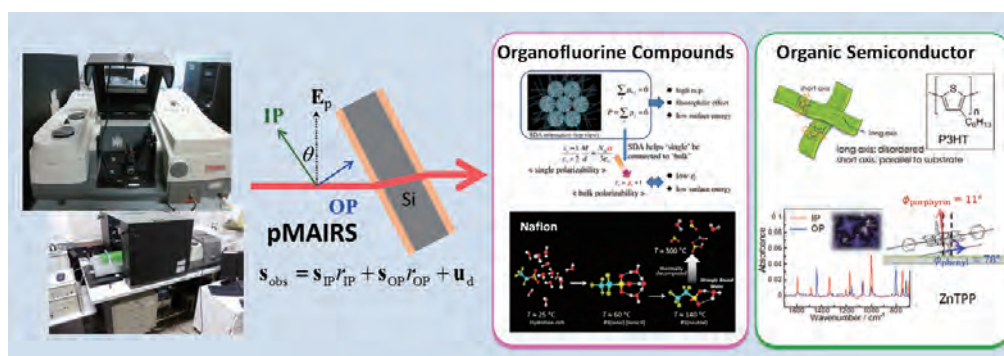
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Scope of Research

To understand the chemical structure and properties of a molecular aggregated system, the keywords of molecular interactions and orientation are focused on, and the molecular aggregates are investigated by using originally developed spectroscopic techniques. The current major topics are: (1) perfluoroalkyl-specific properties in a condensed system; (2) controlling factors of molecular packing and orientation in a thin film of an organic semiconductor compound; (3) development of new molecular orientation analytical technique “MAIRS2.”

KEYWORDS

Infrared and Raman Spectroscopy
Surface and Interface Chemistry
Perfluoroalkyl Compounds
Organic Semiconductors
pMAIRS and MAIRS2



Selected Publications

Shioya, N.; Eda, K.; Shimoaka, T.; Hasegawa, T., Hidden Thin-Film Phase of Dinaphthothienothiophene Revealed by High-Resolution X-Ray Diffraction, *Appl. Phys. Express*, **13**, 095505 (2020).

Fukumi, A.; Shimoaka, T.; Shioya, N.; Nagai, N.; Hasegawa, T., Infrared Active Surface Modes Found in Thin Films of Perfluoroalkanes Reveal the Dipole–Dipole Interaction and Surface Morphology, *J. Chem. Phys.*, **153**, 044703 (2020).

Hasegawa, T.; Shioya, N., MAIRS: Innovation of Molecular Orientation Analysis in a Thin Film, *Bull. Chem. Soc. Jpn.*, **93**, 1127-1138 (2020).

Shioya, N.; Fujiwara, R.; Tomita, K.; Shimoaka, T.; Hasegawa, T., Simultaneous Analysis of Molecular Orientation and Quantity Change of Constituents in a Thin Film Using pMAIRS, *J. Phys. Chem. A*, **124**, 2714-2720 (2020).

MAIRS: Innovation of Molecular Orientation Analysis in a Thin Film

Multiple-angle incidence resolution spectrometry (MAIRS), originally developed in our group, is a unique spectroscopic technique for analyzing the structure of molecular aggregates in a thin film, which requires only the refractive index of the film for attaining an analytical accuracy of three significant digits (Figure 1). Since MAIRS is robust to the surface roughness of the film, rough films prepared by using the spin-coating, bar-coating, or drop-casting techniques can be analyzed with a good reproducibility. MAIRS makes the best use of a Fourier transform infrared (FT-IR) spectrometry, which enables us to discuss molecular conformation, packing, polymorphs etc. as well as the molecular orientation. At the moment, MAIRS has two options, pMAIRS and MAIRS2. pMAIRS has already been established and the application is spreading. MAIRS2 is the newest technology, which frees us from FT-IR specific problems, that is to say, interference of water-vapor peaks and of optical fringes.

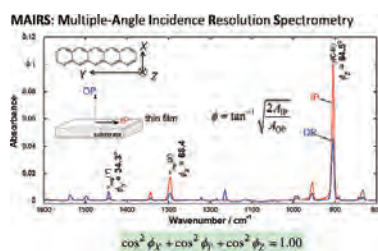


Figure 1. A pMAIRS spectrum of a pentacene film deposited on a Si substrate.

Infrared Active Surface Modes Found in Thin Films of Perfluoroalkanes Reveal the Dipole–Dipole Interaction and Surface Morphology

Infrared (IR) spectra of an organic thin film are mostly understood by considering the normal modes of a single molecule, if the dipole–dipole (D–D) interaction is ignorable in the film. When the molecules have a chemical group having a large permanent dipole moment such as the C=O and C–F groups, the D–D interaction induces vibrational couplings across the molecules, which produces an extra band as a surface phonon or polariton band because of the small thickness. Since the dipole moment of an organic compound is much less than that of an inorganic ionic crystal, we have a problem that the extra band looks like a normal-mode band, which are difficult to be discriminated from each other. In fact, this visual similarity sometimes leads us to a wrong direction in chemical discussion because the direction of the transition moment of the extra band is

totally different from those of the normal modes. We reveal useful selection rules for discussing IR spectra of a thin film without performing the permittivity analysis. The apparent change in the spectral shape on decrease in the thickness of the sample (Figure 2) can be correlated with the morphological change in the film surface. This analytical technique has effectively been applied for studying the chemical properties of perfluoroalkanes as a chemical demonstration, which readily supports the stratified dipole-array theory for perfluoroalkyl compounds.

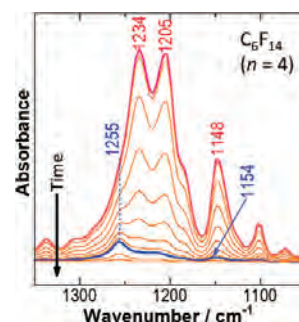


Figure 2. Time-dependent IR ATR spectra of C₆F₁₄ deposited on Ge during the evaporation process at ambient temperature.

Hidden Thin-Film Phase of Dinaphthothienothiophene Revealed by High-Resolution X-Ray Diffraction

Dinaphthothienothiophene (DNNT) has attracted considerable attention as a next-generation material for organic thin-film transistors, replacing the conventional basic material of pentacene. Although the performance of DNNT devices is higher than that of pentacene, and has been reported numerously, a comprehensive understanding of thin-film growth is lacking. In fact, thin-film structures have long been believed to be identical to single-crystal structures. In the present study, the thickness-dependent structural evolution is revealed by means of high-resolution X-ray diffraction. This technique apparently discriminates the thin-film structure from the conventionally known bulk structure (Figure 3). Thus, we have revealed the thin-film phase of DNNT for the first time.

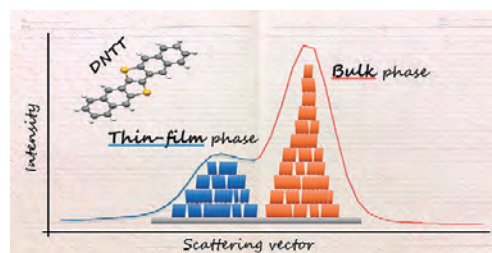


Figure 3. High-resolution X-ray diffraction measurements show two distinct peaks, which are newly assigned due to the thin-film and bulk phases.