

# Division of Environmental Chemistry

## – Chemistry for Functionalized Surfaces –

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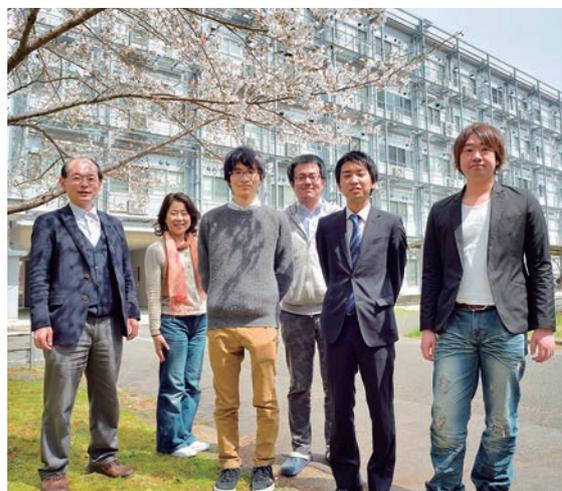
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### Scope of Research

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) Vibrational spectroscopy on fluorine chemistry; (2) controlling factors of a molecular packing and orientation in a thin film of an organic semiconductor compound; (3) the optimal experimental condition and the correlation factor of pMAIRS based on electrostatics for estimating an accurate quantitative molecular orientation in a thin film.

#### KEYWORDS

Infrared and Raman Spectroscopy    Surface and Interface Chemistry  
Perfluoroalkyl Compounds            Organic Semiconductor  
pMAIRS



### Selected Publications

Shioya, N.; Shimoaka, T.; Eda, K.; Hasegawa, T., Controlling Mechanism of Molecular Orientation of Poly(3-alkylthiophene) in a Thin Film Revealed by Using pMAIRS, *Macromol.*, **50**(13), 5090-5097 (2017).

Hasegawa, T., Physicochemical Nature of Perfluoroalkyl Compounds Induced by Fluorine, *Chem. Rec.*, **17**, 903-917 (2017).

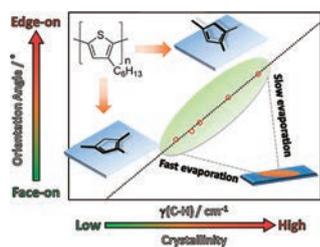
Shimoaka, T.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Hasegawa, T., Study of Perfluoroalkyl Chain-Specific Band Shift in Infrared Spectra on the Chain Length, *J. Phys. Chem. A*, **121**, 8425-8431 (2017).

Shioya, N.; Norimoto, S.; Izumi, N.; Hada, M.; Shimoaka, T.; Hasegawa, T., Optimal Experimental Condition of IR pMAIRS Calibrated by Using an Optically Isotropic Thin Film Exhibiting the Berreman Effect, *Appl. Spectrosc.*, **71**(5), 901-910 (2017).

Shioya, N.; Shimoaka, T.; Murdey, R.; Hasegawa, T., Accurate Molecular Orientation Analysis Using Infrared pMAIRS Considering the Refractive Index of the Thin Film Sample, *Appl. Spectrosc.*, **71**(6), 1242-1248 (2017).

## Controlling Mechanism of Molecular Orientation of Poly(3-alkylthiophene) in a Thin Film Revealed by Using pMAIRS

A face-on oriented thin film of poly(3-hexylthiophene) (P3HT) is suitable for an organic semiconductor layer in a photovoltaic device, and thus analysis of the film structure in terms of molecular orientation is crucial. Although the face-on film often has a poor crystallinity, diffraction techniques have long been employed for the structural analysis, and only very minor crystal parts have been discussed. In our previous study, P3HT was revealed to have a uniquely oriented structure even in an amorphous film by using p-polarized multiple-angle incidence resolution spectrometry (pMAIRS), which is powerful to analyze the molecular orientation, crystallinity, and the conjugation length of P3HT. With the best use of the potential of pMAIRS, in the present study, the controlling mechanism of the molecular orientation of P3HT correlated with the crystallinity in a spin-coated thin film is revealed. As a result, by employing a high-spin speed at 8,000 rpm, a highly face-on oriented thin film having a very low crystallinity is obtained, which readily reveals that the face-on component has a strong correlation with the amorphous aggregates.

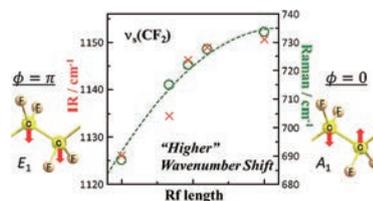


**Figure 1.** Beautiful correlation between the orientation angle of the thiophene ring and the crystallinity of P3HT thin films.

## Study of Perfluoroalkyl Chain-Specific Band Shift in Infrared Spectra on the Chain Length

The  $\text{CF}_2$  symmetric stretching vibration ( $\nu_s(\text{CF}_2)$ ) band of a perfluoroalkyl (Rf) group in an infrared (IR) spectrum exhibits a unique character, that is, an apparent high wavenumber shift with increasing the chain length, which is an opposite character to that of the CH stretching vibration band of a normal alkyl chain. To reveal the mechanism of the unusual IR band shift, two vibrational characters of an Rf chain are focused: (1) a helical conformation of an Rf chain, (2) the carbon (C) atoms having a smaller mass than the fluorine (F) atom dominantly vibrate as a coupled oscillator leaving F atoms stay relatively unmoved. These indicate that a “coupled oscillation of the skeletal C atoms” of an Rf chain should be investigated considering the helical structure. In the present study, therefore, the coupled oscillation of the Rf chain dependent on the chain length is investigated by Raman spectroscopy, which is suitable for

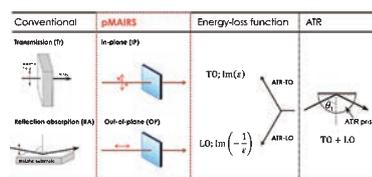
investigating a skeletal vibration. The Raman-active  $\nu_s(\text{CF}_2)$  band is found to be split into two bands, the splitting is readily explained by considering the helical structure and length with respect to group theory, and the unusual peak shift is concluded to be explained by the helical length.



**Figure 2.** Higher wavenumber shift of the  $\nu_s(\text{CF}_2)$  band with increasing the chain length is induced by the conformational change of the Rf skeleton.

## Optimal Experimental Condition of IR pMAIRS Calibrated by Using an Optically Isotropic Thin Film Exhibiting the Berreman Effect

Infrared (IR) p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) is a useful spectroscopic tool for revealing the molecular anisotropic structure in a thin film, which is used for the molecular orientation analysis of many functionalized organic thin films. Infrared pMAIRS provides both in-plane (IP) and out-of-plane (OP) vibrational mode spectra, which are influenced by the choice of the angles of incidence, i.e., angle set. To obtain quantitatively reliable pMAIRS spectra, therefore, the optimal angle set must be revealed. In a former study, an optimization study was carried out on a silicon substrate by using the band intensity ratio of the IP and OP spectra of highly oriented molecules in a thin film, which has a problem that the optimized results cannot be used for another substrate. In the present study, a totally new idea using an optically isotropic thin film as a standard sample is proposed to comprehensively explore the optimal angle set on various substrates: the band shift due to the Berreman effect of a strongly absorbing compound is used, instead of the band intensity. This new approach makes the pMAIRS calibration for various substrates a much easier task. With the optimal angle set, the molecular orientation angle in the film calculated by the pMAIRS spectra is also found to be reliable quantitatively. This technique opens a user-friendly way to a reliable molecular orientation analysis in an ultrathin film using IR pMAIRS.



**Figure 3.** Interrelationship between pMAIRS and the representative infrared spectroscopic techniques via energy-loss functions.