

# Division of Environmental Chemistry – Chemistry for Functionalized Surfaces –

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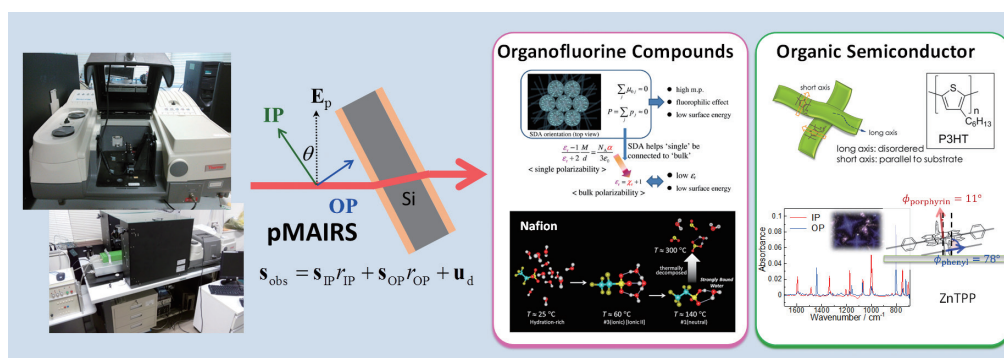
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## Scope of Research

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

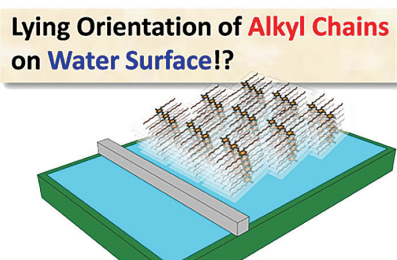


## Recent Selected Publications

Shimoaka, T.; Yamaguchi, Y.; Shioya, N.; Ajayaghosh, A.; Mori, T.; Ariga, K.; Hasegawa, T., Insights on the Molecular Orientation of Oligo(*p*-Phenylene Vinylene) Derivatives with Alkyl Chains in Langmuir Films, *J. Phys. Chem. C*, **127**, 9336-9343 (2023).  
Oka, T.; Shioya, N.; Shimoaka, T.; Hasegawa, T., Structural Rearrangement of Organic Semiconductor Molecules with an Asymmetric Shape in Thin Films, *J. Phys. Chem. C*, **127**, 7560-7564 (2023).  
Shioya, N.; Yoshida, M.; Fujii, M.; Shimoaka, T.; Miura, R.; Maruyama, S.; Hasegawa, T., Conformational Change of Alkyl Chains at Phase Transitions in Thin Films of an Asymmetric Benzothienothiophene Derivative, *J. Phys. Chem. Lett.*, **13**, 11918-11924 (2022).  
Shioya N.; Fujii M.; Shimoaka T.; Eda K.; Hasegawa T., Stereoisomer-Dependent Conversion of Dinaphthothiophene Precursor Films, *Sci. Rep.*, **12**, 4448 (2022).  
Tomita K.; Shioya N.; Shimoaka T.; Wakioka M.; Hasegawa T., Control of Supramolecular Organizations by Coordination Bonding in Tetrapyrrolylporphyrin Thin Films, *Chem. Commun.*, **58**, 2116-2119 (2022).

## Insights on the Molecular Orientation of Oligo(*p*-Phenylene Vinylene) Derivatives with Alkyl Chains in Langmuir Films

One of the oligo(*p*-Phenylene Vinylene) derivatives having alkyl chains, OPV-1, is known to form rod-shaped nanoaggregates on the water surface, and thin films with aligned nanoaggregates can be obtained by the Langmuir–Blodgett (LB) technique. Although the molecular aggregation and orientation of the “conjugated rings part” in the LB films have already been investigated, analysis of the detailed molecular structure involving the “alkyl chains” is left behind. In the present study, to reveal the role of the alkyl chains in the molecular aggregation in Langmuir films prior to the LB transfer, infrared (IR) external reflection spectroscopic measurements on the water surface are carried out. It has been revealed that not only the conjugated rings of OPV-1 but also the alkyl chains with an ordered conformation are lying on the water surface. In addition, the orientation is found to be kept on a solid substrate even after the LB transfer by IR *p*-polarized multiple-angle incidence resolution spectrometry.

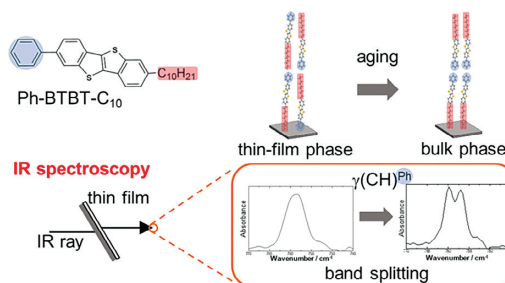


**Figure 1.** Lying orientation of oligo(*p*-phenylene vinylene) derivatives on the water surface.

## Structural Rearrangement of Organic Semiconductor Molecules with an Asymmetric Shape in Thin Films

2-Decyl-7-phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (Ph-BTBT-C10) exhibits excellent performances as an active layer in organic thin-film transistors, and its performances are greatly influenced by the molecular packing, i.e., the crystalline polymorphs. This compound has the so-called thin-film phase in a vapor-deposited film, which is different from the single-crystal structure (the bulk phase). In this work, thin films of Ph-BTBT-C10 are prepared by spin coating, and the effect of aging on the film structure is investigated by high-resolution IR spectroscopy in combination with X-ray diffraction. The results show that the as-spun film has the same thin-film phase as the vapor-deposited film and that the thin-film phase is rapidly converted to the bulk phase by aging at room temperature. This

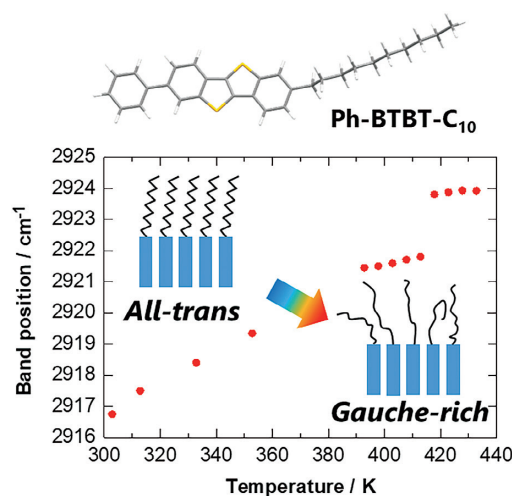
work highlights the importance of using IR spectroscopy with a high-wavenumber resolution for structural analysis of molecular thin films.



**Figure 2.** Structural rearrangement of Ph-BTBT-C10 from the thin-film phase to the bulk phase revealed by IR spectroscopy.

## Conformational Change of Alkyl Chains at Phase Transitions in Thin Films of an Asymmetric Benzothienobenzothiophene Derivative

Ph-BTBT-C10 has a highly ordered liquid crystalline state, i.e., the smectic E (SmE) phase. Although the transition from the crystalline state to the SmE phase is believed to accompany melting of the alkyl chains, no spectroscopic evidence has been found so far. In this study, the conformational change of the decyl chains in Ph-BTBT-C10 films across the phase transition is analyzed by temperature-dependent measurements in situ using IR spectroscopy. The spectral analysis reveals that the polycrystalline film has latent conformational disorder (the gauche conformer), the rate of which becomes more pronounced with the heat treatment. As expected, melting of the decyl chains is observed above the transition temperature to the SmE phase.



**Figure 3.** Conformational change of alkyl chains of Ph-BTBT-C10 with temperature.