

# Division of Environmental Chemistry – Chemistry for Functionalized Surfaces –

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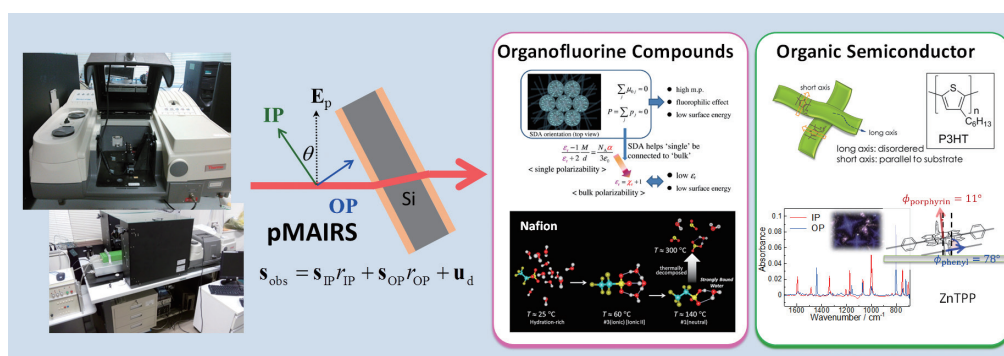
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## Scope of Research

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

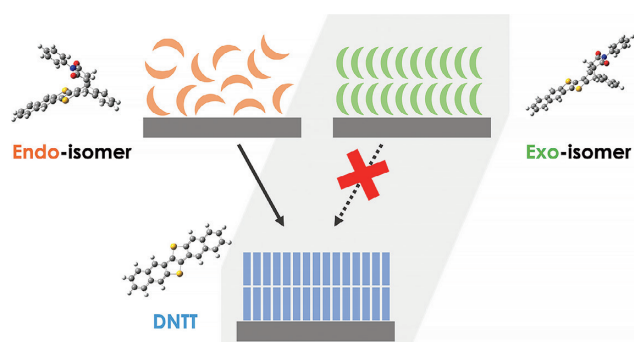


## Recent Selected Publications

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).  
Shimoaka T.; Fukumi A.; Shioya N.; Hasegawa T., Perfluoroalkanes Remain on Water Surface Even after Volatilization: Affinity Analysis of Fluorinated Solvent with Water Surface, *J. Colloid Interf. Sci.*, **611**, 390-396 (2022).

## Stereoisomer-Dependent Conversion of Dinaphthothienothiophene Precursor Films

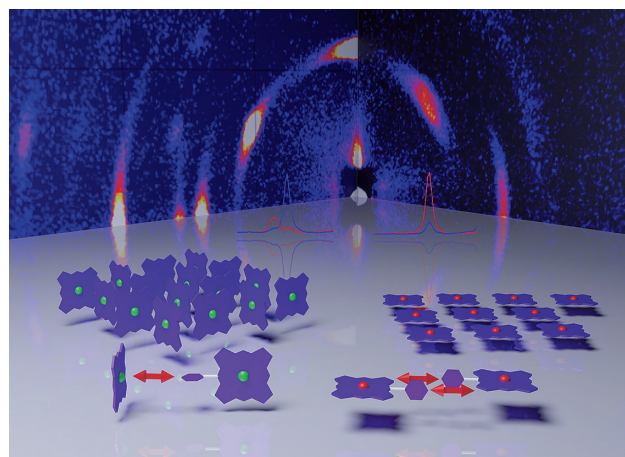
Soluble precursor materials of organic semiconductors are employed for fabricating solution-processable thin film devices. While the so-called precursor approach has already been tried for various organic electronic devices such as transistors and solar cells, understanding of the conversion process in the film lags far behind. Here, we report that molecular aggregation of the precursor compound significantly influences the thermal conversion reaction in the film. For this study, two stereoisomers of a dinaphthothienothiophene (DNTT) precursor that are the endo- and exo-DNTT-phenylmaleimide monoadducts are focused on. This study reports that the endo-isomer is readily converted to DNTT in the film by heating, whereas the exo-isomer exhibits no reaction at all (Figure 1). This finding shows a new direction of controlling the on-surface reaction.



**Figure 1.** Stereoisomer-dependent conversion reaction of dinaphthothienothiophene precursor films.

## Control of Supramolecular Organizations by Coordination Bonding in Tetrapyrrolylporphyrin Thin Films

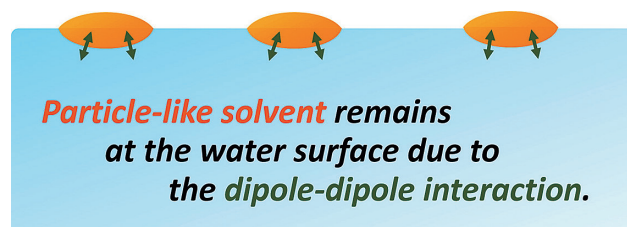
Coordination bonding has been employed to control molecular orientation in thin films and is demonstrated by using tetrapyrrolylporphyrin. Changing the central metal ion of porphyrin controls the balance of the coordination bonding and hydrogen bonding, and edge-on orientation has been realized for the first time as well as face-on orientation (Figure 2). The mechanism of the film structure formation is comprehensively explained based on the electron configuration of the central metal ion. In this manner, the present study presents a novel strategy to control 2D supramolecular structures using coordination bonding.



**Figure 2.** The edge-on and face-on orientations of tetrapyrrolylporphyrin are selectively obtained in thin films by changing the central metal ion of the porphyrin ring.

## Perfluoroalkanes Remain on Water Surface Even after Volatilization

Perfluoroalkyl ( $R_f$ ) compounds are known to have a poor solubility for most solvents except fluorinated solvents, which is known as a fluorophilic property. On the other hand, a single  $R_f$  chain with a short length such as  $C_6F_{13}$  is known to exhibit a totally different character from a condensed matter to have a strong affinity to a water molecule on the water surface via the dipole-dipole interaction, which is known as the dipole interactive (DI) property. On considering the DI property, the solvents of perfluoro- $n$ -alkanes would remain on water for a long time. In the present study, details of a liquid layer of perfluoro- $n$ -alkanes on water are investigated by using infrared external reflection spectrometry. Although the perfluoro- $n$ -alkanes are highly volatile, the relevant vibration bands did not disappear even after two hours, which means that they remain on the water surface (Figure 3).



**Figure 3.** Schematic image of fluorinated solvents remaining on the water surface.