

Division of Environmental Chemistry – Chemistry for Functionalized Surfaces –

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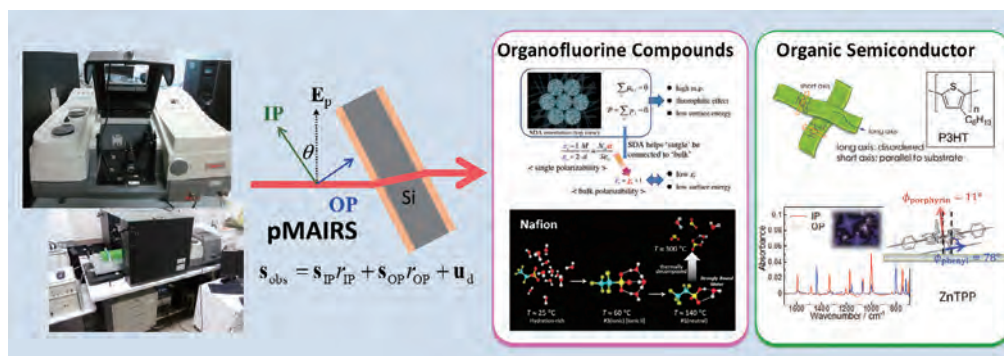
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Scope of Research

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

Tomita, K.; Shioya, N.; Shimoaka, T.; Okudaira, K. K.; Yoshida, H.; Koganezawa, T.; Hasegawa, T., Substrate-Independent Control of Polymorphs in Tetraphenylporphyrin Thin Films by Varying the Solvent Evaporation Time Using a Simple Spin-Coating Technique, *Cryst. Growth Des.*, **21**, 5116-5125 (2021).

Shioya, N.; Fujiwara, R.; Tomita, K.; Shimoaka, T.; Okudaira, K. K.; Yoshida, H.; Koganezawa, T.; Hasegawa, T., Monitoring of Crystallization Process in Solution-Processed Pentacene Thin Films by Chemical Conversion Reactions, *J. Phys. Chem. C*, **125**, 2437-2445 (2021).

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

Shimoaka, T.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Hasegawa, T., Raman Optical Activity on a Solid Sample: Identification of Atropisomers of Perfluoroalkyl Chains Having a Helical Conformation and No Chiral Center, *J. Phys. Chem. A*, **123**, 3985-3991 (2019).

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

Substrate-independent Control of Polymorphs in Tetraphenylporphyrin Thin Films by Varying the Solvent Evaporation Time Using a Simple Spin-coating Technique

Porphyrin derivatives are promising materials for various thin-film-based devices such as solar cells, field-effect transistors, and gas sensors. Since the molecular aggregation structure in a thin film significantly influences the device performance, controlling the aggregation structure is of crucial importance. In this study, we show that three different crystalline polymorphs of free-base tetraphenylporphyrin can be made to form in spin-coated thin films depending on the evaporation time of the solvent. The crystal structure in the films is identified using a combination of the two-dimensional grazing incidence X-ray diffraction (2D-GIXD) and p-polarized multiple-angle incidence resolution spectroscopy (pMAIRS) techniques. The results show that the aggregation structure in the as-spun films is controlled by the solvent evaporation time, and the initial film structure determines the polymorphs obtained after thermal annealing.

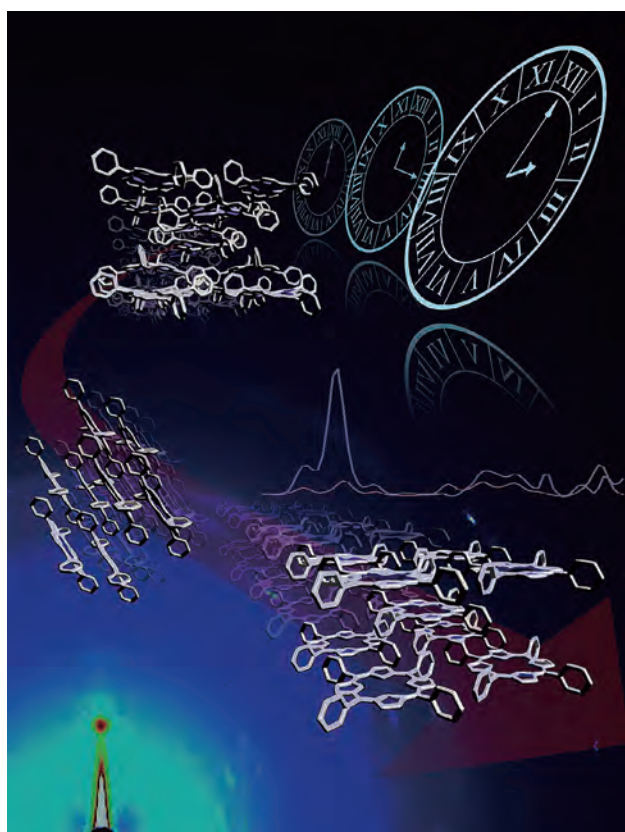


Figure 1. Three different tetraphenylporphyrin crystal structures are selectively obtained on an inert surface by varying the evaporation time of the solvent.

Monitoring of Crystallization Process in Solution-processed Pentacene Thin Films by Chemical Conversion Reactions

Solution-processable organic semiconductors having bulky substituent groups on the π -conjugated skeleton are rapidly gaining attention for their potential applications to large-area electronics. While the substituent groups contribute to the good solubility in organic solvents, they give rise to hopping sites in a thin film, affecting adversely the charge-carrier transport. As an alternative material, a solvent-soluble precursor compound with thermally cleavable functional groups is promising, which can be converted by heat treatment into a thin film to generate the desired material consisting solely of conjugated systems. This precursor approach is practically applied to various thin-film-based devices. The overall process of the thin film growth, however, remains unrevealed. In the present study, solution-processed pentacene thin films are prepared from a thermally convertible precursor, and the structural evolution during the chemical conversion reaction has been revealed by employing multiple analytical techniques of 2D-GIXD, pMAIRS, and atomic force microscopy. The highlight is that pentacene is crystallized in a stepwise manner in the thermally converted films, which is substantially different from a typical growth process. In addition, influences of the oxidation reaction of pentacene on the molecular arrangement are also discussed using the pMAIRS technique. The spectra quantitatively reveal that the presence of oxidation products disturbs molecular orientation of pentacene. This study provides a fundamental schematic of thin films grown by the precursor method.

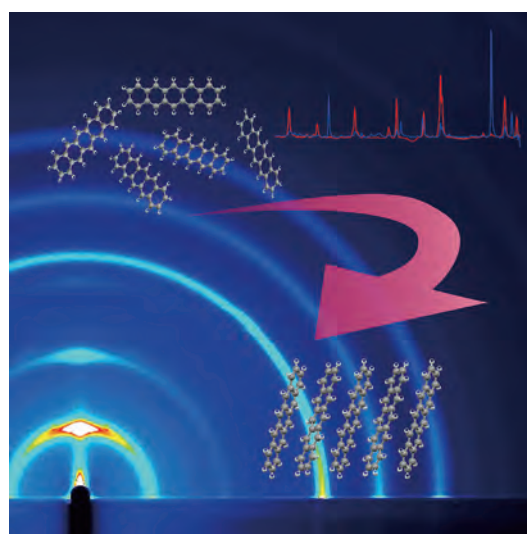


Figure 2. A combination of 2D-GIXD and pMAIRS reveal a complex growth process of solution-processed pentacene thin films, including the structural conversion reaction.