

# Division of Synthetic Chemistry – Organoelement Chemistry –

<https://www.scl.kyoto-u.ac.jp/~oec/en/index.html>



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## Scope of Research

$\pi$ -Extended aromatic compounds such as higher acenes and porphyrins are attractive as organic functional materials. In particular, we focus on the control of thin-film structure by self-assembly of the materials to investigate the correlation between packing structure and charge carrier mobility. We are also interested in the compounds including heavy main group elements to elucidate the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners.

### KEYWORDS

Organic Semiconductor

Self-Assembly

Reactive Intermediate

Aromatic Compound

Main Group Element



## Recent Selected Publications

Miyazaki, K.; Matsuo, K.; Hayashi, H.; Yamauchi, M.; Aratani, N.; Yamada, H., An Unsymmetrical 5,15-Disubstituted Tetrabenzoporphyrin: Effect of Molecular Symmetry on the Packing Structure and Charge Transporting Property, *Org. Lett.*, **25**, 7354-7358 (2023).

Nishino, R.; Tokitoh, N.; Sasayama, R.; Waterman, R.; Mizuhata, Y., Unusual Nuclear Exchange within a Germanium-Containing Aromatic Ring That Results in Germanium Atom Transfer, *Nature Commun.*, **14**, 4519 (2023).

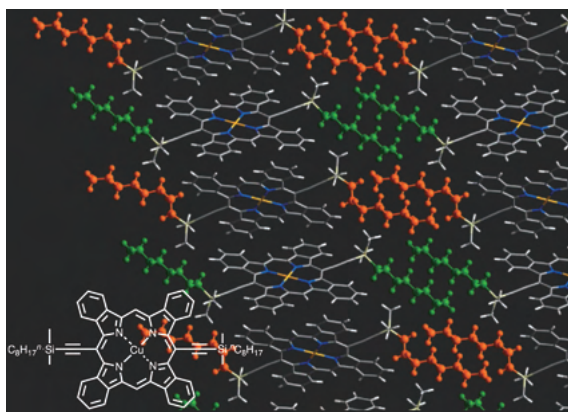
Iwai, K.; Mizuhata, Y.; Nakamura, T.; Goto, M.; Wakamiya, A.; Shimakawa, Y.; Tokitoh, N., Solid-State Chromism of Zwitterionic Triarylmethylium Salts, *Eur. J. Inorg. Chem.*, **26**, e202300337 (2023).

Jeong, E.; Ito, T.; Takahashi, K.; Koganezawa, T.; Hayashi, H.; Aratani, N.; Suzuki, M.; Yamada, H., Exploration of Alkyl-Group Effects on the Molecular Packing of 5,15-Disubstituted Tetrabenzoporphyrins toward Efficient Charge-Carrier Transport, *ACS Appl. Mater. Interfaces*, **14**, 32319-32329 (2022).

Eimre, K.; Urgel, J. I.; Hayashi, H.; Giovannantonio, M. D.; Ruffieux, P.; Sato, S.; Otomo, S.; Chan, Y. S.; Aratani, N.; Passerone, D.; Gröning, O.; Yamada, H.; Fasel, R.; Pignedoli, C. A., On-Surface Synthesis and Characterization of Nitrogen-Substituted Undecacenes, *Nat. Commun.*, **13**, 511 (2022).

## Exploration of Alkyl Group Effects on the Molecular Packing of 5,15- Disubstituted Tetrabenzoporphyrins toward Efficient Charge-Carrier Transport

The high design flexibility of organic semiconductors should lead to diverse and complex electronic functions. However, currently available high-performance organic semiconductors are limited in variety; most of p-type materials are based on thienoacenes or related one-dimensionally (1D) extended  $\pi$ -conjugated systems. In an effort to expand the diversity of organic semiconductors, we are working on the development of tetrabenzoporphyrin (BP) derivatives as active-layer components of organic electronic devices. BP derivatives can afford field-effect hole mobilities of  $>4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the resulting thin films show high thermal stability wherein the field-effect hole mobility stays above  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  even after heating at  $160 \text{ }^\circ\text{C}$  in air, reflecting the tight packing of large BP units. These findings will serve as a good basis for extracting the full potential of 2D extended  $\pi$ -frameworks and thus for increasing the structural or functional diversities of high-performance organic semiconductors.

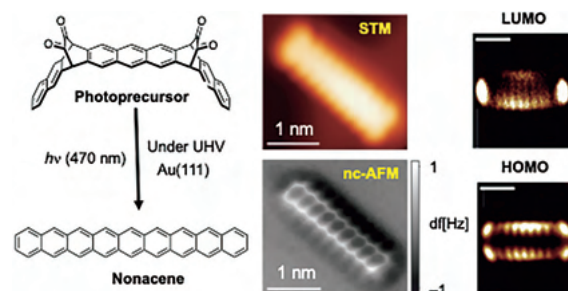


**Figure 1.** Packing structure of 5,15-bis(*n*-octyldimethylsilyl)ethynyl tetrabenzoporphyrin in the solution processed thin film.

## On-Surface Light-Induced Generation of Higher Acenes and Elucidation of Their Open-Shell Character

Acenes are an important class of polycyclic aromatic hydrocarbons which have recently gained exceptional attention due to their potential as functional organic semiconductors. Fundamentally, they are important systems to study the convergence of physico-chemical properties of all-carbon  $\text{sp}^2$ -frameworks in the one-dimensional limit; and by virtue of having a zigzag edge topology they also provide a fertile playground to explore magnetism in graphenic nanostructures. We have demonstrated the on-

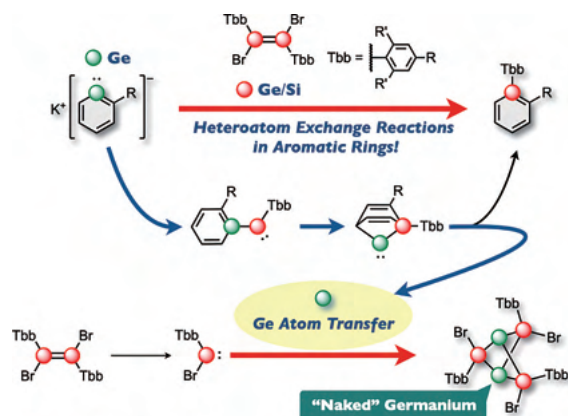
surface formation of heptacene and nonacene via visible-light-induced photo-dissociation of  $\alpha$ -bisdiketone precursors on an Au(111) substrate under ultra-high vacuum conditions. Through combined scanning tunneling microscopy/spectroscopy and non-contact atomic force microscopy investigations, we provide insight into the chemical and electronic structure of these elusive compounds.



**Figure 2.** On-surface synthesis of nonacene from photoprecursor and its STM, AFM, and STS images.

## Development of Germanium Atom Transfer Reaction

In organic synthesis, the synthetic strategy relies on the division of the target molecule into simpler substructures, the feasibility of which depends on the availability of the necessary building blocks. A single atom is the simplest and most ideal building block for all molecules, but for most elements, obtaining individual atoms for synthesis is impractical. We have demonstrated that single atomic germanium can be introduced into various molecules by taking advantage of the reactivity of the germabenzenyl anion, in which the anionic carbon of the phenyl anion is replaced by germanium. The method discovered in this research enables the controlled synthesis of molecules with “naked” germanium and is expected to lead to the development of various functional materials involving germanium.



**Figure 3.** Germanium atom transfer reaction utilizing a germabenzenyl anion.