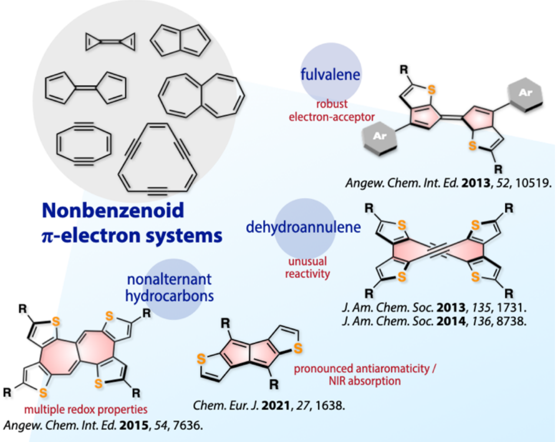
Exploring Novel Nonbenzenoid Hydrocarbons toward Unusual Yet Stable Optoelectronic Materials

([1]*WPI-iCeMS, Kyoto University*) ○Aiko Fukazawa[1]

Keywords: π-Conjugation; Nonbenzenoid hydrocarbons; Aromaticity; Antiaromaticity; Redox properties

Advancements made to date in organic optoelectronic materials are primarily attributed to aromatic hydrocarbons and their heteroaromatic analogs. These classes of compounds are highly valued for their high thermal and chemical stability as well as the desirable properties, and have stimulated the development of various synthetic methodologies, resulting in a wide variety of molecular materials. However, to achieve properties and functionalities beyond the capabilities of existing organic materials, innovative molecular designs and exploration into uncharted chemical spaces are crucial. In this context, nonbenzenoid hydrocarbons and related cross-conjugated π-electron systems are an attractive class of compounds due to their characteristic properties such as long-wavelength absorption, multistep redox properties, and distinctive behaviors in excited states, most of which are difficult to attain with benzenoid π-electron systems of comparable molecular weight. Despite their potential, nonbenzenoid π-electron systems remained unexplored as optoelectronic materials due to the difficulty in their synthesis, high reactivity, and a lack of guiding principles for molecular aimed at material applications. Our motivation is to explore the potential of nonbenzenoid π-electron systems as game-changing building blocks for next-generation functional materials, tackling the longstanding issues from three perspectives: to ensure stability without bulky substituents, to develop efficient synthetic methods, and to provide molecular design guidelines to harness their characteristic properties. This presentation will provide an overview of our strategies and some of the recent research along two major topics as follows:

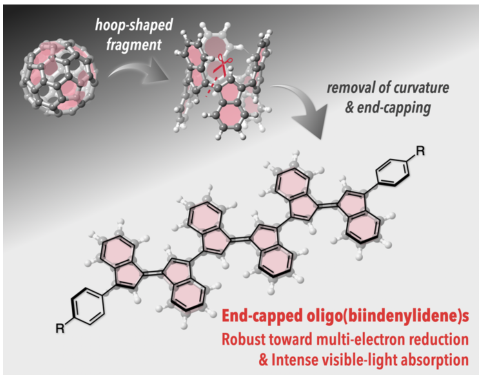
1. Strategy for the stabilization of labile nonbenzenoid π-conjugated systems without using bulky substituents. To address the first challenge in a stability issue, we have been focusing on the molecular design based on the annulation of weakly aromatic rings such as thiophene and phenanthrene on the nonbenzenoid hydrocarbons in a ring-fused manner. Based on this strategy, we have so far succeeded in synthesizing stable yet unusual π-conjugated systems including dehydroannulenes,[1] a nonaromatic[2] and antiaromatic nonalternant hydrocarbons,[3,4] and fulvalene.[5] Notably, the annulation of thiophene rings rendered these nonbenzenoid



Angew. Chem. Int. Ed. **2013**, *52*, 10519.
J. Am. Chem. Soc. **2013**, *135*, 1731.
J. Am. Chem. Soc. **2014**, *136*, 8738.
Angew. Chem. Int. Ed. **2015**, *54*, 7636.
Chem. Eur. J. **2021**, *27*, 1638.

π-electron systems high thermal stability even without bulky substituents, while maintaining the inherent characteristics of the parent π-systems. This molecular design thereby allowed us to access thermochromic behavior in near-infrared region based on exciton interactions even in solution,[3a] as well as the dense packing in the solid state.[3b] It should be also noted that most of these ring-fused nonbenzenoid π-electron systems cannot be synthesized by known methods, and we explored several new reactions and synthetic strategies for their synthesis.[1,2,4,5]

2. Novel molecular design concepts. A significant challenge lies in translating the diverse structures and properties of nonbenzenoid π-electron systems into the molecular designs for groundbreaking materials. In this context, we have recently designed and synthesized the oligo(biindenylidene)s, π-conjugated hydrocarbons that are composed of flattened one-dimensional fragments of fullerene C_{60}. Notably, the oligo(biindenylidene)s exhibit high electron affinity and the robustness against multi-electron reduction comparable to fullerenes only based on hydrocarbon scaffolds.[6] This molecular design is complementary to the conventional design of electron-accepting π-electron systems, by introducing many electron-withdrawing groups into an inherently electron-donating π-electron system. Given their potential for further structural diversification, our molecular design concepts described above would be new fundamentals in the chemistry of electron acceptors. In this presentation, I will also describe some of our recent studies based on this strategy.[7–9]



References

1) (a) A. Fukazawa, H. Oshima, S. Yamaguchi *et al. J. Am. Chem. Soc.* **2013**, *135*, 1731. (b) H. Oshima, A. Fukazawa, S. Yamaguchi *et al. J. Am. Chem. Soc.* **2014**, *136*, 8738.
2) A. Fukazawa, H. Oshima, S. Yamaguchi *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 7636.
3) (a) J. Usuba, A. Fukazawa *et al. Chem. Eur. J.* **2021**, *27*, 1638. (b) J. Usuba, A. Fukazawa, *Chem. Eur. J.* **2021**, *27*, 16127.
4) H. Oshima, A. Fukazawa, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2017**, *56*, 3270.
5) A. Fukazawa, T. Karasawa, S. Irle, S. Yamaguchi *et al. Angew. Chem. Int. Ed.* **2013**, *52*, 10519.
6) M. Hayakawa, N. Sunayama, S. I. Takagi, Y. Matsuo, S. Yamaguchi, S. Seki, A. Fukazawa *et al.*, *Nat. Commun.* **2023**, *14*, 2741.
7) S. I. Takagi, M. Hayakawa. A. Fukazawa, *Chem. Eur. J.* **2023**, *29*, e202300181.
8) K. Yasui, Y. Hartmann, A. Fukazawa, *to be submitted*.
9) (a) A. Fukazawa, M. Adachi, S. Yamaguchi *et al. Chem. Commun.* **2013**, *49*, 7117. (b) T. Mikie, M. Hayakawa, A. Fukazawa, I. Osaka, *et al. Chem. Mater*. **2021**, *33*, 8183. (c) T. Shiokawa, A. Fukazawa, *to be submitted*.