Synthesis of Trihetero[7]Helicenes and Their Photophysical and Mechanical Properties

([1]*Graduate School of Engineering, Kyoto University*) ○JiaJian Gu,[1] Takashi Hirose[1]
Keywords: Helicene; Heteroatoms; Emissive properties; Mechanical properties

Helicenes are polycyclic aromatic hydrocarbons (PAHs) characterized by a non-planar, helical backbone formed through the *ortho*-fusion of benzene or other aromatic rings. An effective strategy to modulate their electronic and optical properties involves directly incorporating non-carbon main-group elements—such as N, O, S, Se, or SO_2—into the π-conjugated framework. This substitution significantly influences the electronic structure, resulting in optical, electrical, and mechanical properties distinct from those of carbohelicenes. Despite these advantages, the precise effects of heteroatom doping on the specific properties remain unclear, with only a limited number of examples reported.[1] To uncover general trends, an effective synthetic strategy for introducing various heteroatoms at the same position is required.

In this work, we demonstrate that fluorine-heteroatom annulative reactions[2] provide an effective approach for incorporating heteroatoms into the helicene framework. Using this approach, we synthesized triple-heteroatom-doped [7]helicenes containing nitrogen, oxygen, sulfur, selenium, and sulfone in a single step from *ortho*-substituted difluorobenzene oligomers. The emission maxima in THF were found to shift significantly, from 384 nm for oxa derivative **O7H** to 462 nm for sulfone derivative **$SO_2$7H** (Figure 1). In this presentation, we also discuss the mechanical properties of trihetero[7]helienes depending on the type of heteroatoms, using quantum chemical calculations.

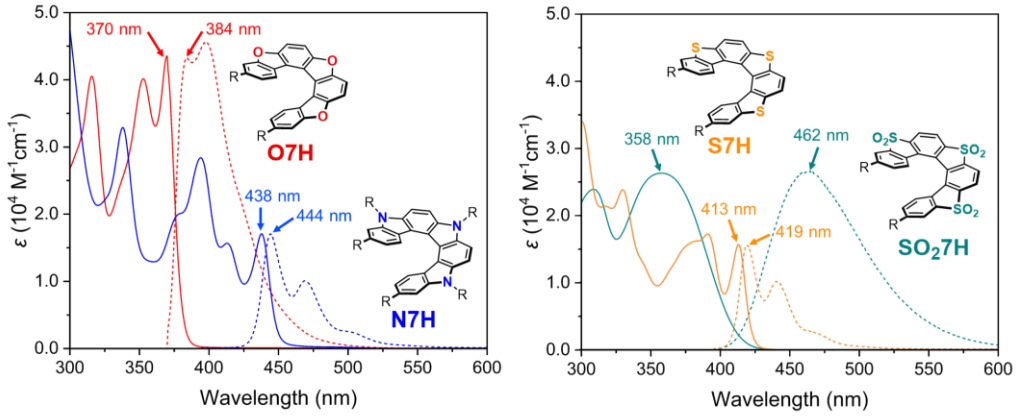

Figure 1. UV-vis absorption (solid line) and emission (dashed line) spectra of hetero[7]helicenes in THF.

1) a) T. Yanagi, T. Tanaka, H. Yorimitsu, *Chem. Sci.* **2021**, *12*, 2784–2793. b) L. Zhou, H. Liu, J. Tan, C. Liu, X.-Y. Cao, A. Narita, Y. Hu, *Chem. Asian J.* **2022**, *17*, e202200336. 2) Y. Zhu, C. Lin, C. Zhao, Y. Ou, Z. Li, K. Zhu, J. Wang, *Angew. Chem. Int. Ed.* **2024**, e202420073.