Theoretical study on stereo recognition of thiaheterohelicene on Ag(111)

C. Ye[1], T. Hattori[1], Y. Hamamoto[1], P. Krukowski[2], A. Saito[1], H. Osuga[3], Y. Morikawa[1], Y. Kuwahara[1]

[1] *Department of Precision Engineering, Graduate School of Engineering, Osaka Univ.*
[2] *Department of Solid State Physics, Faculty of Physics and Applied Informatics, Univ. of Lodz*
[3] *Department of Materials Science and Chemistry, Faculty of Systems Engineering, Wakayama Univ.*

yechangqing@ss.prec.eng.osaka-u.ac.jp

Chiral molecular recognition plays a critical role in many chemical and biochemical processes. Introducing chirality onto surface enables the development of two-dimensional chiral systems, providing a unique platform to investigate the chiral recognition mechanism among molecular systems at the nanoscale. This opens up new opportunities to design novel chiral materials and devices with tailored properties for potential applications such as enantioselective heterogeneous synthesis and asymmetric catalysis [1].

The adsorption and self-assembled structure of helicene on surface have become one of the model systems for studying the basic principles of chiral recognition due to its simple helical structure [2]. To obtain a better understanding of the dynamic process of molecular recognition among these helical molecules, molecular dynamics simulation was used to investigate the initial stage of the ordered structures formed by racemate [7]thiaheterohelicene ([7]TH) on the Ag(111) surface.

First, the arrangement of two molecules demonstrated that two different [7]TH enantiomers formed heterochiral dimers, which was more stable than homochiral ones in energy, revealing the preference in heterochiral interaction. As the number of molecules was gradually increased, a zigzag-chain structure similar to the STM observations appeared, in which different enantiomers arrange alternatingly (Fig. 1). It was considered that the heterochiral dimer formed as a building block and the π-π interaction between partially overlapped skeletons contributed to the stable growth of the chain structures. This structural expansion suggested the hierarchical progress of chiral recognition within two-dimensional chiral systems.

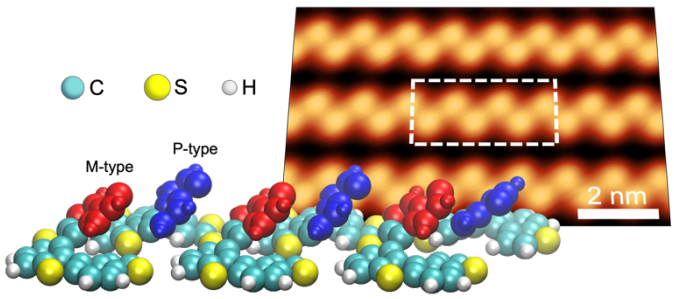

Fig. 1. The STM image (9 nm x 6 nm, V_s = 2.0 V, I_t = 50 pA) and the possible molecular model of zigzag chain structure formed by [7]TH on Ag(111).

[1] T. Mallat. *et al*. *Chem. Rev*., **107**, 4863−4890 (2007).

[2] P. Krukowski. *et al. Appl. Surf. Sci*., **589**, 152860. (2022).