

## Planar Chirality of Pillar[5]arene Controlled by Dynamic Covalent Bond

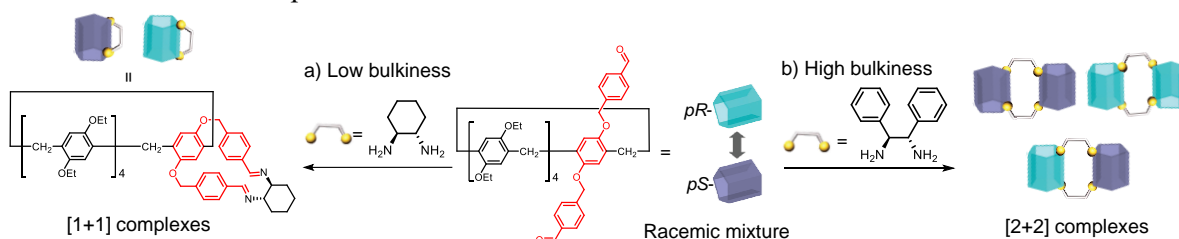
(<sup>1</sup>Graduate School of Engineering, Kyoto University, <sup>2</sup>Nano Life Science Institute, Kanazawa University) ○Cheng Peng, <sup>1</sup>Kenichi Kato, <sup>1</sup>Shunsuke Ohtani, <sup>1</sup>Tomoki Ogoshi<sup>1,2</sup>

**Keywords:** Covalent Dynamic Bond; Pillararene; Diastereomeric Selectivity; Planar Chirality

Pillar[5]arene exhibits planar chirality due to its two stable enantiomeric conformations. However, the free rotation of benzene units makes it challenging to stabilize its chirality, as racemization can occur easily.<sup>1</sup> In this work, we proposed a new way to generate diastereomers selectively and stabilize the conformation through reversible imine formation with a chiral diamine linker.

A pillar[5]arene-based dialdehyde was synthesized and used as the reactant. By mixing the dialdehyde and a chiral diamine with low bulkiness in a stoichiometric ratio with a catalytic amount of trifluoroacetic acid and heating the mixture at 323K in the presence of molecular sieves, a pair of [1+1] diastereomers were formed exclusively (**Figure 1a**), proving the high selectivity of the dynamic covalent method.<sup>2</sup> No other byproducts were observed in the system because the [1+1] diastereomers are the most thermodynamically stable products. In comparison, when no acid was added to the system, the final products would be a mixture of kinetic products, consisting of [1+1], [1+2], [2+1] complexes and other oligomers since the imine formation was not reversible in the absence of acid. Once the [1+1] products were formed, the rotation of benzene units would be inhibited by the bulky imine unit. No racemization occurred at room temperature even after a week, demonstrating the effective chirality fixation by dynamic covalent method.

When we used a diamine with high bulkiness, [2+2] diastereomers were obtained exclusively (**Figure 1b**). Thus, this strategy allowed us to easily obtain various pillar[5]arene-based chiral porous materials with different stoichiometry by changing the bulkiness of the diamine.<sup>3</sup> The diastereoselectivity can also be improved as the number of building blocks increases in the complex.



**Figure 1.** Planar chiral control of pillar[5]arene by reversible imine formation.

1) a) T. Ogoshi et al, *J. Org. Chem.* **2010**, 75, 3268. b) N. L. Strutt et al, *J. Am. Chem. Soc.* **2012**, 134, 17436. 2) H. Qu et al, *Chem. Sci.* **2018**, 9, 8814. 3) M-H. Li et al, *Chem. Commun.* **2021**, 57, 13429.