Supramolecular Assemblies and Systems Based on Pillar-Shaped Macrocyclic Compounds "Pillar[*n*]arenes"

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Pillar[*n*]arenes have become one of the important key players in supramolecular chemistry. In this study, organic reactions based on molecular recognition in crystalline pillar[*n*]arenes are introduced. First, complexation of linear polymer chains using crystalline state pillar[*n*]arenes is discussed. Using the complexation in crystalline state, ring-opening polymerization of cyclic monomers is also discussed. Second, formation of planar-chiral inter-locked molecules resulting from supramolecular structures in solid state is discussed.

Complexation of linear polymers using crystalline pillar[5]arenes: Pillar[5]arenes have a π-electron-rich space enclosed by π-planes. Consequently, multiple C–H/π interactions work with guest molecules with C–H groups. Almost all organic compounds and polymers contain C–H groups, thus pillar[5]arenes can encapsulate nearly all organic compounds and polymers with suitable size for their cavity. However, C–H/π interactions are inherently weak in normal solvent system. For instance, polyethylene oxide (PEO) has a thickness of approximately 3.7 Å, which fits within the pore size of pillar[5]arene (approximately 4.7 Å). However, pillar[5]arene **1** cannot form complex with PEO in solvent system. In the solvent system, solvation inhibited the complexation due to the weak nature of C–H/π interactions. On the other hand, when polyethylene oxide (PEO) was melted and directly immersed in crystalline pillar[5]arene **1**, crystalline pillar[5]arene **1** took up PEO. In this system, weak multiple C–H/π interactions work for the complexation due to no solvation. Interestingly,

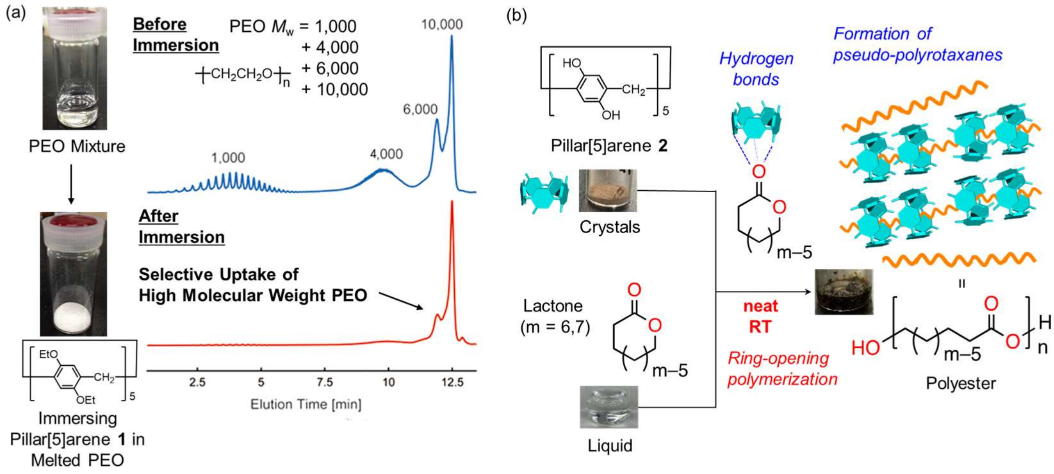

Figure 1 (a) High mass fractionation by crystalline pillar[5]arene **1**. Liquid chromatography traces of an equal-weight mixture of PEOs (upper) and host–guest complex crystals after the immersion in the mixture (lower). (b) Ring-opening polymerization of lactones with crystalline pillar[5]arene **2** and formation of pseudo-polyrotaxanes.

when PEO containing various molecular weights was immersed, crystalline pillar[5]arene **1** selectively took up high-molecular-weight PEO.1) The complexation with linear polymer can be used for initiation of polymerization. When lactone monomers were directly immersed in crystalline pillar[5]arene with phenolic groups **2**, ring-opening polymerization occurred (Figure 1b), while the polymerization did not occur with solvent. The results were obtained because the phenolic hydroxy groups have catalytic activity via hydrogen bonds and the pillar[5]arene cavities prefer linear guests. After the reaction, pillar[5]arenes **2** and polyesters formed pseudo-polyrotaxanes.2)

Planar-chiral inter-locked molecules from supramolecular structures in solid states: Pillar[*n*]arenes exhibit planar chirality i.e., *pS* and *pR* forms, due to the position of the alkoxy groups. Pillar[5]arene with (*S*)-2-methylbutoxy groups in the side chains **3** (Figure 2) exhibits diastereomeric relationships referred to as (*S*, *pR*)-**3** and (*S*, *pS*)-**3**, and two diastereomers can interconvert in solution via the rotation of benzene units (stereodynamic). As a result, an energy difference is generated between *pR* and *pS* forms and the *pR*/*pS* ratio can be changed by inversion between the (*S*, *pR*) and (*S*, *pS*) forms. However, in our previous work, pillar[5]arene **3** with high *pR*/*pS* ratios could not be generated even in various solvents. This is because the energy difference between (*S*, *pR*)-**3** and (*S*, *pS*)-**3** is too small in solution to show diastereoselectivity. However, when crystallization of **3** was conducted in the presence of long axis C16 with amino groups at both ends, a [3]pseudorotaxane was obtained, where two (*S*, *pS*)-**3** rings penetrated one axle. [3]Pseudorotaxanes consisting of either two (*S*, *pS*)-**3**, two (*S*, *pR*)-**3**, or (*S*, *pS*)-**3** and (*S*, *pR*)-**3** wheels are the three possible supramolecular diastereomers. By the co-crystallization, the [3]pseudorotaxane consisting of two (*S*, *pS*)-**3** wheels diastereoselectively formed in the solid state because higher effective molarity worked in the solid state with aid by packing effects to form the [3]pseudorotaxane, and the [3]pseudorotaxane consisting of two (*S*, *pS*)-**3** wheels was most stable among the three [3]pseudorotaxane diastereomers. Subsequent end-capping reactions of the polycrystalline [3]pseudorotaxane with high de in solvent-free conditions successfully yielded rotaxanes while maintaining the high de generated by the co-crystallization.3)

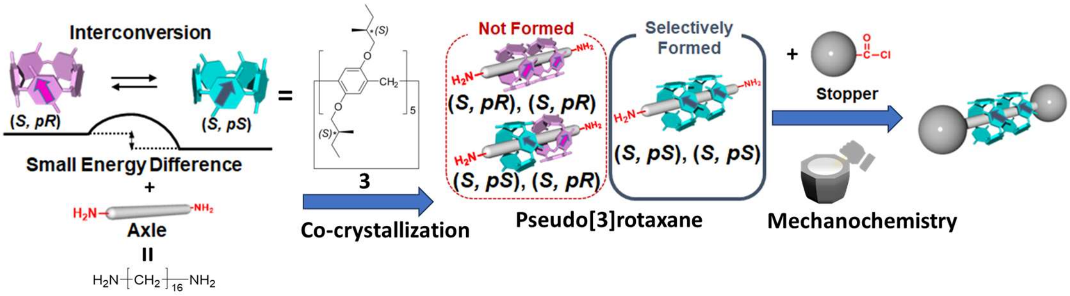

Figure 2 Selective formation of the [3]pseudorotaxane with two (*S*, *pS*)-**3** wheels by the co-crystallization and chiral [3]rotaxane formation by the mechanochemical reaction in the solid state.

1) *Nature Commun.* **2019**, *10*, 479. 2) *Angew Chem. Int. Ed.* **2022**, *61*, e202212874. 3) *J. Am. Chem. Soc.* **2023**, *145*, 15324.