Construction of a honeycomb two-dimensional metal-organic framework composed of C_1-symmetric macrocyclic ligands and interlayer molecular arrangement

(^{1}*Graduate School of Science, The University of Tokyo*) ○Keiichi Nakagawa,[1] Shohei Tashiro,[1] Mitsuhiko Shionoya[1]
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Metal-organic frameworks (MOFs) are porous materials that exhibit high designability based on the design of ligands and metal nodes, and various functions have been developed by precisely ordering guest molecules in their confined space. In particular, the space created in the layered structure allows for molecular recognition and arrangement of guest molecules, which can be applied to template synthesis. Therefore, the use of macrocyclic building blocks should be an effective approach to construct layered MOF structures with unique molecular arrangement capabilities.

In this study, a new 2D MOF, metal-benzimidazole[3]arene framework-3 (MBAF-3, $[Ag_{1.17}\mathbf{L}](OTs)_{1.17}\cdot(solv)_x$), simply by mixing a C_1-symmetric macrocyclic ligand ((P/M)-benzimidazole[3]arene, $\mathbf{L}$) and AgOTs in the solvent ($CHCl_3$/MeCN = 2 : 1), has been synthesized together with a reported 3D MOF (MBAF-1). Single-crystal X-ray diffraction analysis revealed that, the asymmetrically arranged coordination sites of the chiral macrocyclic ligand results in the formation of two homochiral (P)- and (M)-honeycomb layers in the MBAF-3 structure, which are stacking alternately. Various molecular recognition sites, such as hydrogen bonding sites and pocket sites, were located between the layers. In these recognition sites, interlayer molecular arrangements were achieved, such as hydrogen bonding sites recognizing chloroform molecules and pocket sites recognizing cyclohexane molecules. In this presentation, we will also report on the recognition and arrangement of other guest molecules.