

## Helical Inversion Dynamics in a Metal–Peptide Framework

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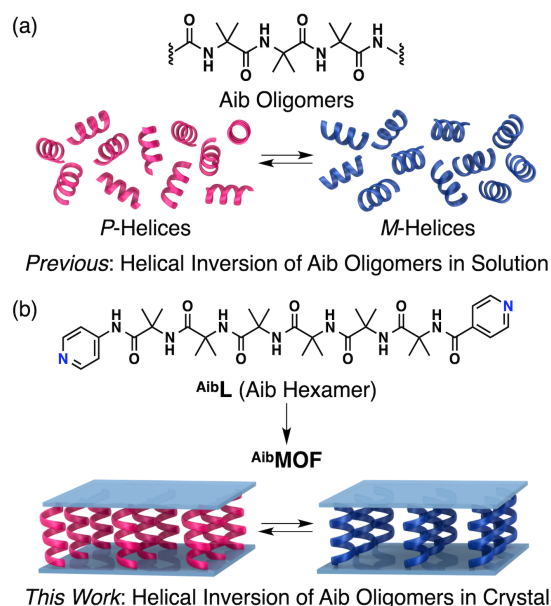
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Helix is a unique structural motif in nature and its structurally dynamic behavior plays a crucial role in various events such as chiral sensing. Inspired by the helical structures in nature, a great interest has been paid to the design of artificial systems with helical motifs that exhibit dynamic behaviors.<sup>1</sup> Peptides containing achiral amino acids such as 2-aminoisobutyric acid (Aib) that adopt stable hydrogen-bonded helical conformations can undergo helix inversion between right-handed (*P*) and left-handed (*M*) helices by external stimuli.<sup>2</sup> However, helix inversion processes have been exclusively investigated in solution (Fig. 1a), while there are only few studies in solid, especially in the crystalline state where molecular motions are greatly restricted (Fig. 1b).

We designed <sup>Aib</sup>L composed of an Aib hexamer with terminally appended pyridyl groups (Fig. 1b). <sup>Aib</sup>MOF, [Zn<sub>2</sub>(<sup>Zn</sup>Por)(<sup>Aib</sup>L)], was synthesized by the reaction of <sup>Aib</sup>L, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and tetrakis(4-carboxyphenyl)porphyrin (<sup>2H</sup>PorH<sub>4</sub>) in a mixture of DMF/EtOH. Single-crystal X-ray analysis revealed that <sup>Aib</sup>MOF consists of stacked 2D double layers. Each double layer contains two porphyrin sheets pillared by 3<sub>10</sub>-helical <sup>Aib</sup>L. A racemic mixture of *P* and *M* helices are present in the crystal due to a 2-fold disorder.

<sup>13</sup>C-labeled <sup>Aib</sup>L was synthesized as an NMR helicity detector, and <sup>Aib</sup>MOF prepared from the <sup>13</sup>C-labeled ligand was subjected to variable temperature solid state <sup>13</sup>C NMR spectroscopy. The spectra showed that the signals assigned to *P* and *M* helical structures reversibly coalesce and split with a coalescence temperature (*T*<sub>c</sub>) of 333 K, indicating that the helices are dynamically inverting even in the crystalline state as a function of temperature. It is noteworthy that such dynamic motion of <sup>Aib</sup>L in <sup>Aib</sup>MOF do not deteriorate the crystalline framework of <sup>Aib</sup>MOF. This is accomplished by the intrinsic porosity of <sup>Aib</sup>MOF, allowing the space required for the inversion motion.

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**Figure 1** (a) Helix inversion of Aib oligomers in solution. (b) Molecular structure of <sup>Aib</sup>L composed of an Aib hexamer modified with terminal pyridyl groups and schematic representation of <sup>Aib</sup>MOF to realize helical inversion even in the crystalline state.