

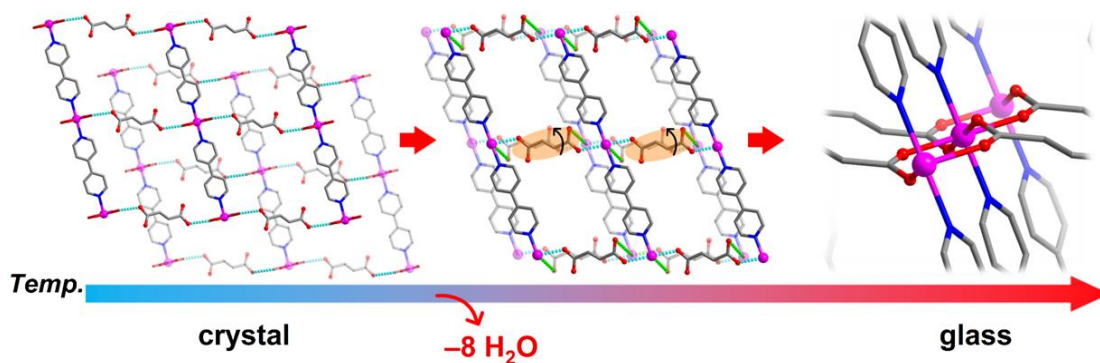
Glass formation of coordination polymers driven by dehydration treatment

(¹Graduate School of Engineering, Kyoto University, ²Institute for Advanced Study, Kyoto University) ○Zeyu Fan,¹ Yong-Sheng Wei,² Satoshi Horike^{1,2}

Keywords: coordination polymers, metal-organic frameworks, glass, phase transition

Coordination polymer (CP) and metal-organic framework (MOF) glasses have been emerged as new class of glass materials. Their structures and functionalities can be adjusted by changing the inorganic and organic building blocks. The high processability, structural dynamics and grain boundary free character enable them to form monoliths and membranes for ion conductivity, gas separation and optical applications.¹ Similar with conventional inorganic glasses, CP/MOF glasses are usually obtained by melt-quenching process. However, most CP/MOFs did not melt and directly decompose irreversibly upon heating.² It is essential to develop new method to fabricate CP/MOF glasses.

One of the most used ligands for constructing CP/MOFs are carboxylate ligands. Nevertheless, there is no carboxylate-based CP/MOF glasses until now, which is due to the alternative coordination environment and strong coordination bond between metal and carboxylates. Here we develop the direct glass-formation process through thermal dehydration of a series of carboxylate (fumarate, fum and terephthalate, bdc) and pyridine (4,4'-bipyridine, bpy and 1,2-di(pyridin-4-yl)ethene, bpee) based Co^{2+} one-dimensional (1D) CPs which contain water molecules as ligands. Loss of coordination water through heat treatment causes local structural rearrangement of the 1D coordination networks, which is monitored by *in-situ* variable-temperature (VT) PXRD, FT-IR and synchrotron X-ray. Glass transition is confirmed by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). These glasses form bulk monoliths through hot-press technique and their grain-boundary free character is examined by cross-section SEM.



1) S. Horike et al., *Chem. Rev.* **2022**, *122*, 4163. 2) J. A. Mason et al., *J. Am. Chem. Soc.* **2021**, *143*, 2801.