Room-temperature Conversion of CO_2 into Metal-Organic Frameworks

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Facile conversion of CO_2 into valuable chemicals and materials is a significant challenge to a carbon-neutral society. CO_2 is an attractive renewable carbon resource with the high natural abundance.[1] Due to the inherent inertness of CO_2, conversion of CO_2 into functional materials at ambient conditions is a significant challenge regardless of the materials.

Metal−organic frameworks (MOFs) are porous materials that consist of metal ions and bridging linkers. CO_2 storage/separation and catalysts using MOFs have been extensively studied last few decades. On the other hand, MOF synthesis from CO_2 remains unexplored. Carboxylates are a representative MOF linker, e.g. benzene-1,4-dicarboxylate. Meanwhile, the di- or tri-carboxylates, which are suitable as MOF linkers, present difficulties in the synthesis from CO_2 because the high-energy reaction conditions and multistep reactions are required.

We focused on carbamate as a CO_2-derived MOF linker instead of conventional carboxylates. Amines (*R*-NH_2) readily react with CO_2 to produce carbamates (*R*-$NCOO^-$). In this work, piperazine (H_2PZ) was employed as a source of CO_2-derived carbamate linker, piperazine 1,4-dicarbamate ($[PZ(CO_2)_2]^{2-}$: PDC). We demonstrated one-pot, room-temperature synthesis of MOFs, $[Zn_4O(PDC)_3]$ (**1**), from CO_2 (**Figure 1**). We comprehensively studied the crystal structure of **1** by synchrotron X-ray analysis and the stabilization of PDC in the MOF lattice by temperature-programmed desorption and DFT calculations.[2]

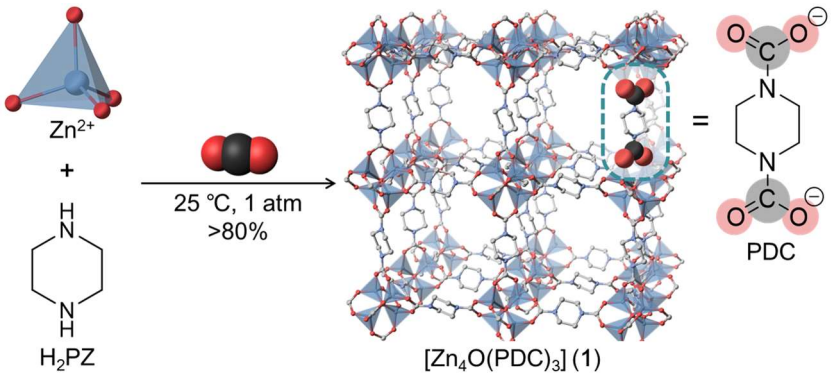

Figure 1. Schematic illustration of formation of **1** via *in situ* conversion of CO_2 into PDC.

1) Q. Liu *et al*., *Nat. Commun.*, 2015, **6**, 5933. 2) K. Kadota *et al*., *J. Am. Chem. Soc.*, 2021, **143**, 16750.