

Crystal structure of triptycene-based metal-organic frameworks and their properties

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Metal-organic frameworks (MOFs) are porous coordination materials that are composed of organic ligands and metal ions. Their structures can be controlled via the choice of the organic ligands, metal ions, and reaction conditions, and therefore, numerous studies on MOFs have been conducted in recent years. Triptycene, the smallest member of the ipitycene family, is an example of such a rigid molecular unit with a unique paddle-wheel like arrangement of three phenyl rings fused via a bicyclo[2.2.2]octane unit. Triptycene and its derivatives, which exhibit a three-dimensionally rigid framework, have been widely used as building blocks for the creation of advanced supramolecular systems. As a result triptycene-based polymers have “internal molecular free volume” and these porous three-dimensional polymeric materials have large surface area and thermal stability. For example, in 2019, the synthesis and adsorption properties of a series of MOFs based on trivalent metals (Al^{3+} , Fe^{3+} , Cr^{3+} , and Sc^{3+}) and peripherally expanded triptycene ligands (PET) has been reported by Farha and co-workers [1]. These MOFs exhibit hydrolytic stability due to the high rigidity of the triptycene ligands. The high porosity and surface area of the MOFs using PET ligands yielded impressive storage performances for H_2 and CH_4 . Moreover, porous materials that capitalize on the hydrogen bonds on the same PET ligands have attracted particular attention due to their large guest-accessible volume (~80%) [2]. In our group, various organic molecules have been synthesized by utilizing the rigidity and three-dimensional bulkiness of triptycene. Therefore, we have been attracted to the potential gas-storage properties of MOFs that contain triptycene-based ligands, given their extended three-dimensional rigidity. A major advantage of MOFs in comparison to other porous materials is the relative ease of functionalization, where organic moieties can generally be installed on the linker molecules as substituents. Particularly, functionalization of MOFs with the functional group (CH_3 , NH_2 , NO_2 , Cl , Br , CO_2H , OCH_3 , or SO_3H) enhances their adsorption performances for various gases (mainly H_2 , CO_2 , and CH_4) [3]. In this study, we report the synthesis of the novel Zinc-based metal-organic frameworks ($\text{Zn-X}_2\text{Trp}$, $\text{X} = \text{H}$, alkyl, halogen), which were obtained from the solvothermal reaction of bi-functionalized triptycene hexacarboxylates, $\text{H}_6\text{X}_2\text{Trp}$, with Zinc nitrate (Fig. 1). Single crystal X-ray structural analysis of $\text{Zn-X}_2\text{Trp}$ revealed that they have an isomorphic three-dimensional network structure with *nia* topological structure (Fig. 2). The N_2 , H_2 , and CO_2 gas-adsorption properties of $\text{Zn-X}_2\text{Trp}$ will also be discussed.

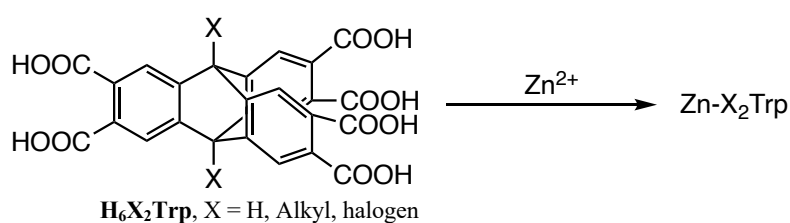


Figure 1. Synthesis of $\text{Zn-X}_2\text{Trp}$ using $\text{H}_6\text{X}_2\text{Trp}$.

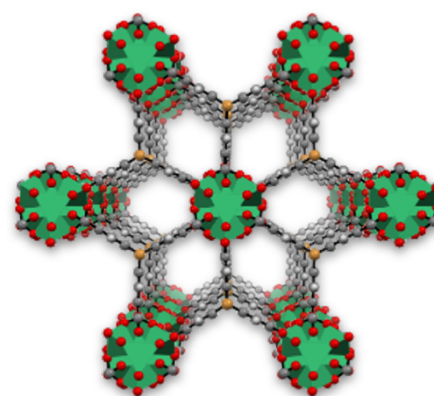


Figure 2. Network structure of $\text{Zn-X}_2\text{MOF}$

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