



Enhancement of gas-framework interaction in a metal–organic framework by cavity modification

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Received: 11 May 2016/Revised: 5 June 2016/Accepted: 8 June 2016
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Abstract Originated from the pore space segmentation modification of a reported metal–organic framework (MOF) (NOTT-125), a new porous MOF ZnX was obtained and characterized by single-crystal X-ray diffraction, elemental analysis, X-ray powder diffraction and TGA. The ZnX exhibits remarkable selective CO₂ adsorption property compared with that of the NOTT-125, which should be attributed to the enhanced gas-framework interactions induced by the fragmented pore space in ZnX.

Keywords Metal–organic framework · Pore segmentation · Gas sorption · Structure modification

The use of fossil fuels promotes the development of industrial civilization. However, many environmental problems come follow it, such as the global warming which is known as the greenhouse effect. It is widely believed that the greenhouse effect is a result of the emission of carbon dioxide (CO₂) from the fossil fuel consumption [1], therefore much efforts has been devoted to the development of effective methods for CO₂ capture and sequestration (CCS) [2–7].

Electronic supplementary material The online version of this article (doi:10.1007/s11434-016-1133-8) contains supplementary material, which is available to authorized users.

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Among the various strategies developed for the CCS, physical sorption has been proved to be an effective method, and metal–organic frameworks (MOFs) has emerged as promising porous adsorbents for their readily tailorable pore characteristics, which could facilitate their performance targeted construction [8, 9]. For CO₂ adsorption in MOFs, there are three effective strategies: incorporation of unsaturated metal cation centers, metal doping and chemical functionalization [10, 11]. However, at the low pressure, the gas–framework interactions play an important role in CO₂ uptake of a framework [12, 13]. Hence a suitable pore size can maximize the gas–framework interactions to get an efficient capture of CO₂ [14]. Some tactics have been reported to realize the goal [15–17], among which the segmentation of large pore into small space by ligand insertion has been proved to be a straightforward and effective one to enhance the interaction between the gas molecule and framework [18]. It should be noted that though this method could be utilized to enhance the CO₂ separation and capture performances of MOFs, the implementation of it require MOFs with open metal sites (OMSs) decorated pore surfaces and organic ligands with matched size and configurations.

Taking the advantage of the unambiguous structures of MOFs and the diversity of organic building blocks, the structure segmentation modification of MOFs could be a useful method for the investigation of targeted materials. However, in addition to the fundamental structural requirements, the coordination behaviour of the metal centers could also be a critical factor that could determine the modification process as well as the performance of the resulted material, which has not been investigated before. Herein, we reported a porous Zn MOF (ZnX) constructed based on oxalylbis(azanediyl)diisophthalic acid (H₄L) and 4,4′-bipyridine, which was constructed aiming at the

segmentation modification and performance optimization of the reported Cu based MOF NOTT-125 (NOTT is short for Nottingham) that showing remarkable CO₂ sorption properties [19, 20]. After many attempts, it was found the targeted construction could only be achieved when the Cu²⁺ ions in the parent NOTT-125 were replaced with Zn²⁺, which emphasized the role of metal centers in the segmentation modification. Furthermore, the ZnX show remarkable selective CO₂ adsorption property as expected.

Our research originate from the segmentation modification of NOTT-125, a Cu based MOF which has been reported to show remarkable gas sorption properties. As reported, NOTT-125 possesses two different kinds of

cages. Cage A is consisted of 6 L⁴⁻ ligands and 12 Cu₂(OOCR)₄ paddlewheels units to give ellipsoidal interspace with about 1.2 nm in diameter. Cage B is constructed by 12 L⁴⁻ ligands and 6 Cu₂(OOCR)₄ paddlewheels units to show a spherical interspace with about 1.3 nm in diameter. These two types of cages were interlinked by sharing edges to result in the porous framework of NOTT-125. Structure analysis of the cage based framework show that the Cu₂(OOCR)₄ paddle-wheel units may provide OMSs for coordination of additional ligands, and the moderate distance (11.424 Å) between these sites in the Cage B (Fig. 1a) make them possible to be interconnected by 4,4'-bipyridine ligand. All these factors make NOTT-

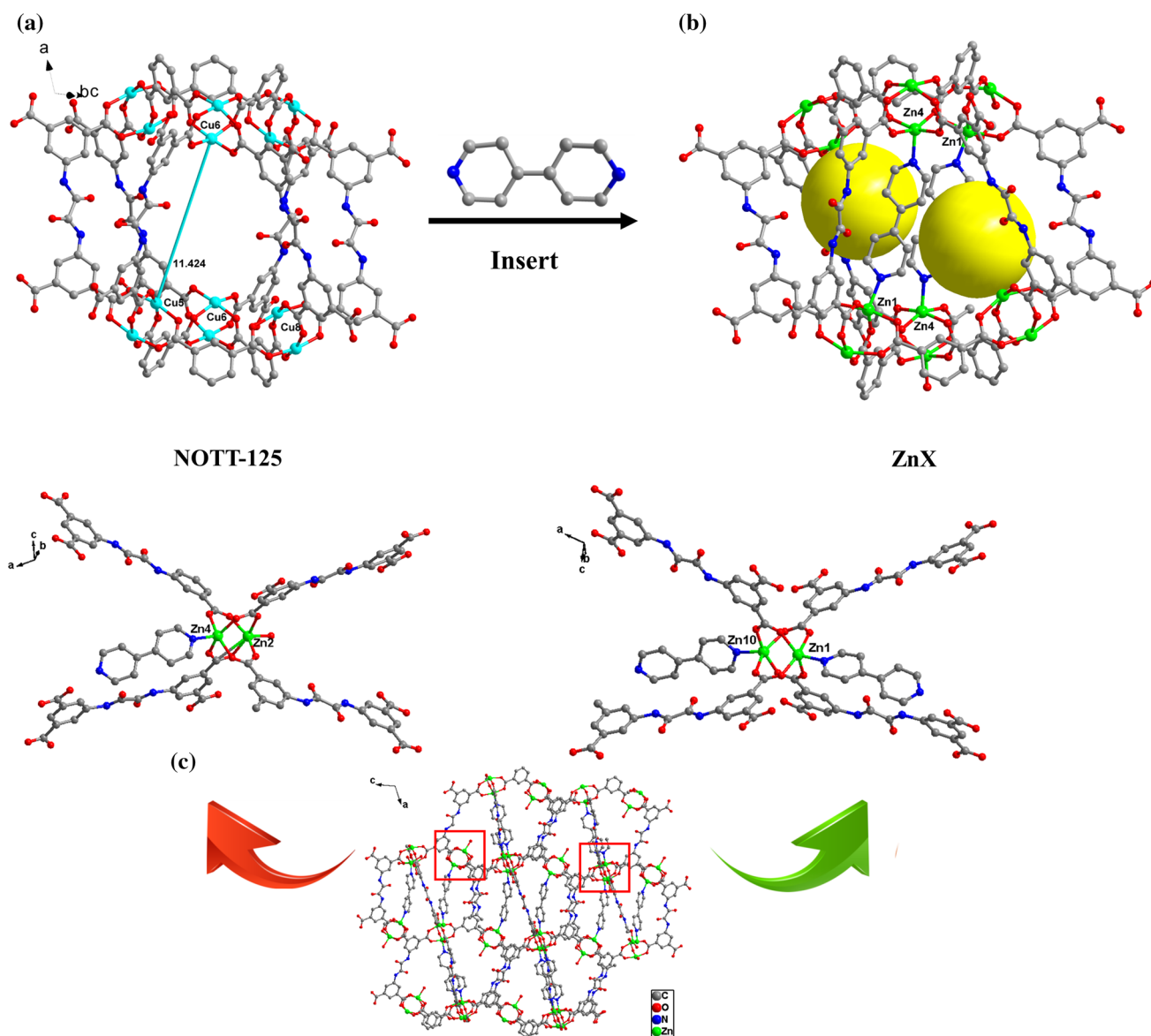


Fig. 1 a The distance between the neighboring OMSs in NOTT-125. b The fragmented cage in ZnX. c The coordination environments of two kinds of Zn₂(OOCR)₄ paddle-wheel units in ZnX

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