

# 学位論文の要約

題目 Study on the Regulation of Gas Selectivity and Ionic Conductivity by Chemical Modifications of Isorecticular Zn-based Metal-organic Frameworks

(亜鉛系等網目状金属-有機構造体の化学修飾によるガス選択性ならびにイオン伝導性制御に関する研究)

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## 序論

Metal-organic frameworks (MOFs), consisting of metal ions (clusters) and organic ligands, are a family of materials with ultrahigh porosity. One of the most attractive advantages of MOFs is their abundant internal free volume (up to 90%), which is capable of the incorporation and adsorption of diverse guest molecules. In addition, during structural design and synthesis, the arrangement and coordination of various components bring infinite possibilities for tailoring properties and applications. All these benefits have endowed MOFs with excellent potential in domains, such as gas adsorption and separation, catalysis, energy storage, and so on. Under specific circumstances, chemical modification of MOFs is necessary for customized properties. Fluorine, with the highest electronegativity and small atom radius, has attracted much interest in MOF modification. However, it should be mentioned that the fluorination of ligands greatly affects the framework structure in many cases, which will hamper our research to examine the fluorination effect in isorecticular MOFs. Besides, appropriate pore size is also a decisive factor affecting the results. If the pores are too large, the inner wall of pores cannot effectively influence the introduced guest molecules; if the pores are too small, they cannot effectively incorporate guest molecules. Therefore, in order to investigate the effects of fluorination on guest molecules in isorecticular MOFs, it is crucial to judiciously select a series of MOFs with chemical stability during fluorination and appropriate pore size.

To this end, in this thesis, a series of Zn-based microporous MOFs,  $\text{Zn}_2(\text{xFBDC})(\text{tmBDC})(\text{DABCO})$  (hereafter **DMOF-xFs**), where  $x$  denotes the number of fluorine on the terephthalate ligands ( $\text{xFBDC}^{2-}$ ;  $x = 0, 1, \text{ and } 2$ ), was chosen as the MOF

materials (tmBDC<sup>2-</sup>: tetramethylterephthalate, DABCO: 1,4-diazabicyclo[2.2.2]octane). Single-crystal X-ray diffraction measurements (SCXRD) have shown that all the **DMOF-*x*F**s exhibit nearly the same crystal structure, with the fluorine atoms slightly protruding into the channels. To recap briefly, the three **DMOF-*x*F**s are isomorphous in the tetragonal system, with terephthalate-based linkers (*x*FBDC<sup>2-</sup> or tmBDC<sup>2-</sup>) bridging the Zn dimers in the *ab* plane and DABCO units pillaring the dimers along the *c* axis. Besides, all the **DMOF-*x*F**s possess micropores, which is optimal for us to investigate the effect of fluorine on the wall.

## 1 . Increased CO<sub>2</sub>/N<sub>2</sub> Selectivity by Stepwise Fluorination in Isorecticular Ultramicroporous Metal-organic Frameworks

In this section, we selected the ultramicroporous **DMOF-0F** as a parent MOF because of its high stability against water vapour. The substitution of BDC<sup>2-</sup> with 1FBDC<sup>2-</sup> or 2FBDC<sup>2-</sup> ligands leads to the successful synthesis of **DMOF-1F** or **DMOF-2F**, respectively, while maintaining the framework structure, which is verified by crystallographic, optical, and sorption studies. Sorption measurements show that **DMOF-2F** exhibited the highest CO<sub>2</sub>/N<sub>2</sub> selectivity among three MOFs, followed by **DMOF-1F** and then **DMOF-0F**. Theoretical calculations based on sorption isotherms also demonstrated that increasing the fluorine content leads to a pronounced increase in CO<sub>2</sub>/N<sub>2</sub> selectivity under low CO<sub>2</sub> concentration conditions, primarily driven by intermolecular interaction between the fluorine atoms and adsorbed CO<sub>2</sub> molecules. The present work would provide deeper insights into the rational design of ultramicroporous MOFs for controlling CO<sub>2</sub>/N<sub>2</sub> selectivity.

## 2 . Rational Control of Ionic Conduction of Encapsulated Ionic Liquid by Fluorination of Isorecticular Metal-organic Frameworks

In this section, we focused on the control of ionic conductivity in ionic liquid-encapsulated MOFs (IL@MOFs) through the chemical modification of ligands. The difference in binding energy between C–H···F and C–F···F interactions, primarily arising from the low polarizability of fluorine, was utilized to realize the control of ionic conductivity. To this end, a series of Zn-based microporous MOFs, **DMOF-*x*F**s; *x* = 0, 1, and 2, was chosen as the host materials. Then, we introduced a certain amount of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ((EMI)(TFSA)), which is one

of the most widely used fluorinated ILs in electrochemical applications, as the guest materials largely because of its excellent electrochemical and thermal stability. Electrochemical impedance measurements revealed that (EMI)(TFSA)-encapsulated **DMOF-2F** (hereafter **IL@DMOF-2F**) exhibits the highest ionic conductivity, which is one order of magnitude higher than the other two hybrid materials. Vibrational measurements and computational simulations indicate that the mobility of (EMI)(TFSA) in non-fluorous framework is significantly restricted due to abundant C–H···F interactions, whereas the introduction of fluorine atoms on the ligands suppresses the C–H···F interactions, thereby showing the highest ionic conductivity. The present work would provide a new strategy for developing and understanding the ionic conducting hybrid materials.