



Adsorptive separation of xenon/krypton mixtures using ligand controls in a zirconium-based metal-organic framework



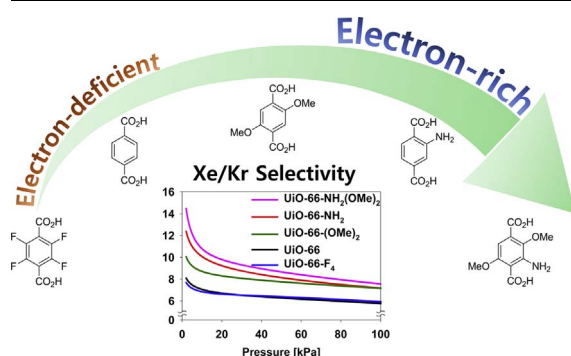
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GRAPHICAL ABSTRACT



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ABSTRACT

A Zr-based metal-organic framework (MOF), UiO-66, is considered to be one of the most stable MOFs and has recently been shown to be a good candidate for adsorptive separation of Xe/Kr mixtures. Since the ability to impart chemical functionalities is an attractive characteristic of MOFs, herein, we prepared a series of functionalized UiO-66 materials (UiO-66-NH₂, UiO-66-(OMe)₂, UiO-66-NH₂(OMe)₂, and UiO-66-F₄) by incorporating several polar functionalities into UiO-66. We found that series of electron-rich and electron-deficient UiO-66 materials have stronger interactions with Xe and Kr atoms than pristine UiO-66. We also found that Xe/Kr selectivity increases with the electron density of the ligand. Although there was a reduction in surface area, UiO-66-NH₂(OMe)₂ exhibited the highest Xe/Kr Henry's constant ratio (14.4), possibly due to having the highest electron density as well as an unsymmetrical arrangement of functional groups of the ligands. Furthermore, the breakthrough experiments show that UiO-66-NH₂(OMe)₂ can effectively separate Xe from Kr under dynamic mixture conditions and can be easily regenerated under a mild regeneration condition.

1. Introduction

Radioisotopes of Xe (¹²⁷Xe, ¹³³Xe, and ¹³⁵Xe) and Kr (⁸⁵Kr), which are strong beta or gamma emitters, are generated during the

reprocessing of used nuclear fuels [1]. Release of these gases into the atmosphere or sea results in the contamination of food chains, and inhalation can cause fatal health problems, such as cancer [2]. Because the half-life of ⁸⁵Kr (10.7 y) is much longer than that of Xe (¹²⁷Xe:

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36.3d; ^{133}Xe : 5.2 d; ^{135}Xe : 9.1 h), capturing and separating radioactive ^{85}Kr is an important issue [3]. Since reliance on nuclear energy has gradually increased over the past few decades [4], the amount of ^{85}Kr produced is continuously increasing [5].

To remove radioactive noble gases from off-gas streams, energy-intensive cryogenic distillations are currently used. Hence, adsorption has been considered to be a cost- and energy-effective alternative [6–9]. However, to develop an efficient adsorption process, an adsorbent with high selectivity as well as a large adsorption capacity is required. Due to their attractive properties, such as permanent porosity and tunable functionality, metal-organic frameworks (MOFs) have attracted great interest as potential adsorbents for gas separations [10–14].

Until now, several experimental and computational studies have been reported for Xe/Kr separation using MOFs. The initial studies focused on the evaluation of the potentials of existing MOFs for Xe/Kr separation. In a dynamic breakthrough experiment, Muller et al. showed that a prototype MOF, HKUST-1, could separate Xe/Kr mixtures [15]. Greathouse et al. computationally showed that IRMOF-1 could selectively adsorb Xe over Kr (selectivity: 2.5–3.0) due to the difference in van der Waals interactions [16]. From a computational screen of eight MOFs, Ryan et al. identified MOF-505 as a promising adsorbent for Xe/Kr separation (selectivity: ~ 11.2) [17]. As a follow-up study which combines experiments and simulations, Bae et al. confirmed that MOF-505 could effectively separate Xe/Kr mixtures (selectivity: 9–10) due to small pores with unsaturated Cu^{2+} sites [18]. Thallapally et al. experimentally showed that Ni-MOF-74 has a higher Xe/Kr selectivity (~ 4.0) than IRMOF-1, HKUST-1 and activated carbon due to the high density of its open metal sites [1,19]. In a combined experimental and computational study, Li et al. showed that $\text{Co}_3(\text{HCOO})_6$ has high Xe/Kr selectivity (~ 12) due to the size and shape of its pores [20].

There have been very few reports suggesting new MOFs or new functionalization strategies of MOFs for Xe/Kr separations. Liu et al. experimentally determined that loading silver nanoparticles into Ni-MOF-74 could enhance Xe/Kr selectivity (6.8) [21]. Chen et al. recently reported that a new MOF, SBMOF-2, exhibited high Xe/Kr selectivity (~ 10) due to the pores containing phenyl rings and $-\text{OH}$ groups, both of which work as strong adsorption sites for polarizable Xe gas [22]. More recently, Mohamed et al. introduced a new ultra-microporous MOF, CROFOUR-2-Ni, which exhibited very high Xe/Kr selectivities (22) [23].

Due to the improvement of computing power, several high-throughput screening studies have recently been reported. Sikora et al. computationally screened 137,000 hypothetical MOFs and suggested that structures with cylindrical pores with 4–8 Å diameters would be ideal for Xe/Kr separation [24]. Van Heest et al. computationally screened over 3400 MOFs and identified 70 candidates for seven different noble gas separations [25]. More recently, Banerjee et al. also carried out molecular simulations to screen over 125,000 MOF structures and identified SBMOF-1 as an outstanding material for Xe/Kr separation (selectivity: 16) [26].

Most research including high-throughput screening studies has focused on the geometrical properties of MOFs, such as the surface area, pore size, and pore morphology. Few studies have studied polar adsorption sites, such as polar functional groups and open metal sites. In a combined experimental and computational study, Meek et al. systematically investigated the effect of monohalogenated ligands on noble gas adsorption and showed that the polarizability of a ligand correlates well

with Xe/Kr selectivity [27]. By using ten MOFs with open metal sites, Perry IV et al. systematically explored the effect of the metal identity and pore size and suggested that a series of MOF-74 materials is the preferred choice for the further development of improved noble gas sorbents because of their high densities of open metal sites as well as proper pore sizes [28]. This conclusion was further supported by our follow-up study combining first principles calculations and breakthrough experiments [29].

In our recent study, we revealed that zirconium-based UiO-66 is one of the best candidate MOFs for Xe/Kr separation because of its good hydrothermal and radioactive stabilities as well as high Xe/Kr selectivity (~ 8) [30]. We reasoned that the Xe/Kr selectivity of UiO-66 could be enhanced by introducing additional functionalities into MOFs on organic linker molecules. A variety of polar functional groups (e.g., alkoxy, amine, and halogen) have been successfully incorporated into UiO-66 frameworks, and chemical tags can be used to change the binding affinity of the framework to the guest molecules and pore environments [31]. In this study, we strategically synthesized and introduced polar organic functionalities into the UiO-66 framework to improve the Xe/Kr selectivity and see the effect of electron-donating and electron-withdrawing groups in the ligands on the Xe/Kr selectivity. Methoxy, amino-, fluoro- groups and combinations thereof were incorporated into a benzene-1,4-dicarboxylic acid (BDC) moiety in a controlled manner. Although several functionalized UiO-66 materials have already been reported, tri-functionalized UiO-66- $\text{NH}_2(\text{OMe})_2$ has not been reported to date. From this study, we found that this new MOF, UiO-66- $\text{NH}_2(\text{OMe})_2$, exhibits the highest Xe/Kr selectivity among the entire series MOFs investigated.

2. Experiments

2.1. Preparations and syntheses

We prepared four different functionalized BDC ligands (BDC- NH_2 , BDC- F_4 , BDC-2,5-(OMe) $_2$, and BDC-3- NH_2 -2,5-(OMe) $_2$) as well as the pristine BDC ligand (Fig. 1). BDC (1), BDC- NH_2 (2), and BDC- F_4 (5) were purchased from chemical companies (Sigma-Aldrich or Alfa Aesar) and used without further purification. BDC-2,5-(OMe) $_2$ (3) was synthesized from BDC-2,5-(OH) $_2$ through methylation of the ester form, and BDC-3- NH_2 -2,5-(OMe) $_2$ (4) was prepared by nitration of BDC-2,5-(OMe) $_2$ followed by reductions. The detailed procedures for the preparation, synthesis and characterizations of the ligands can be found in the Supporting Information. By using these ligands, a series of UiO-66 materials was prepared and activated using modified methods based on previously reported methods (see the Supporting Information for details) [32].

2.2. Characterizations

Powder X-ray diffraction (PXRD) patterns were obtained at ambient temperature on a Bruker D8 Discover at 40 kV, 40 mA for CuK α ($\lambda = 1.5406 \text{ \AA}$). The thermal stabilities of the series of UiO-66 materials were measured by a thermogravimetric analyzer model 8000 (Perkin Elmer Inc., Waltham, MA) over the temperature range of 25–700 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

To obtain the BET surface areas and pore size distributions, N_2 adsorption and desorption isotherms at 77 K were measured up to 1 bar by

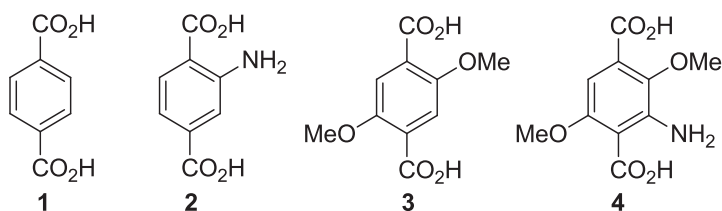


Fig. 1. Pristine benzene-1,4-dicarboxylic acid ligand (BDC, 1) and a series of functionalized ligands: 2-amino benzene-1,4-dicarboxylic acid (BDC- NH_2 , 2); 2,5-dimethoxyterephthalic acid (BDC-2,5-(OMe) $_2$, 3); 3-amino-2,5-dimethoxyterephthalic acid (BDC-3- NH_2 -2,5-(OMe) $_2$, 4); 2,3,5,6-tetrafluoro benzene-1,4-dicarboxylic acid (BDC- F_4 , 5).

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