Design of a highly-stable cobalt (II) porous framework based on aromatic stacking strategy for efficient SF$_6$ capture and SF$_6$/N$_2$ mixture separation

Yong-Peng Li$^a$,*, Xiao-Jie Zhang$^a$, Jing-Jing Ni$^a$, Wen-Juan Ji$^b$, Shuo-Li$^a$, Yu-Lin Li$^a$, Wen Wen$^a$, Jian Wang$^a$, Zhu-Yin Sui$^a$,*, Xiu-Feng Xu$^a$,*

$^a$School of Chemistry and Chemical Engineering, Yantai University, Yantai, 264005, China

$^b$School of Chemistry & Materials Science, Shanxi Normal University, Taiyuan, Shanxi, 041004, China

*Corresponding authors

liyongpeng@ytu.edu.cn (Y.-P, Li),

suizy@ytu.edu.cn (Z.-Y, Sui),

xxf@ytu.edu.cn (X.-F, Xu)
ABSTRACT: Effective capture and separation of the greenhouse gas SF₆ from N₂ is extremely important to attenuate the greenhouse effect and bring economic benefits to the semiconductor industry. Herein, a highly stable “pillar-layer” MOF (YTU-30) with multiple \( \lambda - \lambda \) stacking aromatic rings as pillar in the pores was prepared by mixed ligand strategy. Static equilibrium isothermal adsorption results display that YTU-30 possesses a high SF₆ uptake capacity (68.6 cm\(^3\) cm\(^{-3}\)), while nearly negligible N₂ adsorption (3.3 cm\(^3\) cm\(^{-3}\)) at 298 K and 1 bar. The substance ratio of SF₆-to-N₂ uptake reached 20.8. Dynamic breakthrough experiments also demonstrate that YTU-30 can achieve the effective separation of SF₆/N₂ (10/90) mixture. The breakthrough interval between SF₆ and N₂ can be up to 233.0 min/g. The calculated SF₆ adsorption amounts in the breakthrough experiments were 1.6 mmol g\(^{-1}\) for YTU-30. Cycling experiments of static and dynamic were unchanged with a very simple process, which further confirmed the feasibility and directly capture SF₆ and separate the SF₆/N₂ mixture for YTU-30. The dense aryl rings with \( \lambda - \lambda \) stacking in the pores not only increases the stability of MOF, but also contributes to its high SF₆ adsorption. These results provide a new strategy to achieve the construction of a stable MOF for the separation SF₆/N₂ gas mixture.

Keywords: metal-organic frameworks, mixed ligand strategy, structural stability, SF₆ purification
1. Introduction

Sulfur hexafluoride (SF₆) be widely used as the insulating gas, plasma etching contrast agent, thermoacoustic insulator and so on because of its good chemical stability, non-toxic, non-flammable and good arc extinguishing.[1-3] However, SF₆ emissions into the atmosphere can cause serious greenhouse effect with an estimated to be 800 to 3000 years lifetime in the atmosphere. The Intergovernmental Panel on Climate Change found that the greenhouse potential of SF₆ is 23900 times than the emission of the same volume of CO₂.[4-7] At present, SF₆/N₂ gas mixture is widely used in industry to replace pure SF₆ gas, which can maintain sufficient dielectric strength while achieving the expected environmental and economic benefits.[8, 9] Undoubtedly, recovery and further recycling of SF₆ from SF₆/N₂ mixture is an essential process to prevent its release into the atmosphere. Therefore, it is an urgent need to find an effective method to achieve efficient SF₆ adsorption and SF₆/N₂ separation to reduce its long-term adverse environmental impact.

Compared to the widely used cryogenic distillation and liquefaction, adsorptive separation is considered an energy-saving strategy for gas separation, and the key is to discover efficient absorbents.[10-13] The majority of traditional porous materials, such as conventional zeolites, and carbon-based adsorbents have been developed for SF₆/N₂ separation.[14-16] However, conventional porous adsorbents cannot fulfill SF₆/N₂ separation due to low SF₆ capacity or poor SF₆/N₂ selectivity. Thus, it is still necessary new adsorbents with high adsorption, separation and stability.

Metal-organic frameworks (MOFs) are excellent candidates for high-performance gas storage and separation applications owing to their tunable pore size and modifiable pore environment.[17-22] Despite the potentially vast benefits of MOFs, their application in industry is significantly hindered by their inherent instability in aqueous solutions.[23-27]
Considering that most of the separation processes are carried out in the humid, somewhat acidic and alkaline corrosive environments, relatively poorly stabilized MOF materials are suboptimal for adsorption and separation applications. This drawback necessitates the development of alternative methods to improve their resilience and enhance their potential for industrial use.

In light of the above challenges, herein, we synthesized a stable “pillar-layer” MOF (YTU-30, YTU=Yantai University), \([\text{Co}_2(\text{ABTC})(\text{TPP})_2]_n\) by a mixed ligand strategy using 3,3′,5,5′-azobenzene tetracarboxylic acid (H₄ABTC) and 2,4,6-tris(4-pyridyl)pyridine (TPP). Multipyridyl ligands have been triumphantly introduced in the synthesis of porous MOFs in combination with polycarboxylic ligands. In previous work, we have shown the systematic research of mixed ligand MOFs by modifying connection modes and size-matching multipyridyl ligands, which not only strengthen the robustness of MOFs, but also introduce Lewis basic sites. Tetracarboxylate linkers have a multiple coordination modes through complete or partial deprotonation of the -COOH groups, thus allowing for the construction of a rich variety of MOFs. Hence, H₄ABTC was chosen for the construction of two-dimensional layer through the ability of multiple coordination of the -COO group with the Co(II) center. Whereas, the TPP contain 4-pyridyl building elements, which are usually used as pillars for framework extension with good stability. And the presence of off-domain \(\pi-\pi\) interactions in the aryl ring can increase the stability of the MOF.
2. Experimental

2.1. Materials and general methods

All solvents and starting materials used for synthesis were commercially supplied. Infrared spectra were obtained in KBr slices on a Bruker INVENIO FTIR spectrometer in the 400-4000 cm⁻¹ range. Thermogravimetric Analyses (TGA) were performed in a nitrogen stream using a Netzsch TG209F3 instrument at a heating rate of 10 °C min⁻¹. Powder X-ray diffraction (PXRD) data were obtained on a MSXD-3 X-ray powder diffractometer. Single crystal diffraction data were acquired on a Bruker SMART APEX II CCD single crystal diffractometer. Sorption measurements were performed by Micrometrics 3Flex. Breakthrough experiments were performed on a self-built instrument.

Additional detailed experimental steps and methods are provided in the supporting information.

2.2. Synthesis of YTU-30 single crystals

A mixture of CoCl₂·6H₂O (35.0 mg, 0.15 mmol), H₄ABTC (35.8 mg, 0.10 mmol), TPP (62.0 mg, 0.20 mmol), DMF (3 mL), EtOH (2 mL), H₂O (1 mL) and HBF₄ (100 μL) was sonicated continuously at room temperature for 10 min until it became a uniform purple solution and sealed in a 20 mL reaction bottle. The reaction mixture was heated to 140 °C and kept for 72 hours. Subsequently, the reactor was naturally cooled down to room temperature, resulting in the formation of purple crystals of YTU-30 with a yield of 52%. The crystal structure was determined using single crystal X-ray diffraction, while the powder sample was analysed through powder X-ray diffraction (PXRD). The thermal stability was evaluated using thermogravimetric (TG) analysis.

3. Results and discussion
3.1. Crystal Structures of YTU-30

YTU-30 crystallizes in triclinic $P\bar{1}$ space group and the asymmetric unit contains two Co (II), one ABTC$^{4-}$, and two TPP (Table S1 and Fig. S1). Each Co (II) adopts distorted octahedrally coordinated, having CoO$_4$N$_2$ coordination where four oxygen atoms from three carboxylate groups of ABTC$^{4-}$ and two nitrogen atoms from two TPP. Both nitrogen atoms are situated at axial positions. The binuclear [Co$_2$(COO)$_3$N$_2$] can be generated by two independent Co1 and Co2 (Fig. 1a). Four carboxylate groups of ABTC$^{4-}$ have two different binding fashions, in which two -COOH groups on the diagonal have the same models of holds two metal centers or holds only one metal center, respectively. The [Co$_2$(COO)$_3$N$_2$] clusters are cross-linked by ABTC$^{4-}$ to form the 2D layer stretching along the crystallographical $a$-$c$ plane (Fig. 1c). Then, the 2D layers are pillared by terminal N-atoms from the triangular TPP ligand generating a 3D framework (Fig. 1d). Two [Co$_2$(COO)$_3$N$_2$] clusters connected by two meta-carboxylate groups from one ABTC$^{4-}$ and four TPP ligands as pillars paralleling to each other. Interestingly, strong $\pi$–$\pi$ stacking interactions around the range of 3.3-4.0 Å are observed between aromatic rings of these four parallel TPP pillars (Fig. 1e). This $\pi$–$\pi$ stacking interactions also act the vital factor for the stability of the YTU-30 framework. There exists a narrow channel of $9.7 \times 6.9$ Å$^2$ (measured by the distance between atoms) along $a$ direction with the solvent accessible void up to 30.6% calculated using a probe of 1.8 Å (N$_2$ kinetic radius) by PLATON (Fig. 1d).

Topologically, the ABTC$^{4-}$ can be viewed as 4-coordinated, the SBU of [Co$_2$(COO)$_3$N$_2$] can be simplified to the 6-connected node, and the TPP ligand can be considered as a linker. Thus, the YTU-30 can be simplified as a (4,6)-connected fsc topology network (Fig. S2).
Fig. 1 (a) Inorganic \([\text{Co}_2(\text{COO})_2\text{N}_2]\) cluster; (b) ABTC\(^4\)- linker; (c) View of the 2D layer constructed from ABTC\(^4\) and Co (II) centers; (d) 3D pillar-layer framework of YTU-30 with narrow channels.

3.2. The Stability of YTU-30

The stability of YTU-30 was tested before gas adsorption experiments, being of great importance for the application of porous MOFs. The thermal stability was examined by thermogravimetric analysis. As shown in Figure S4, the thermal stability of YTU-30 can be achieved at 386 °C. The PXRD patterns of the synthesized samples were in good agreement with the simulation results, indicating the successful synthesis of high purity YTU-30 (Fig. 2a). More importantly, there are not significant changes in the PXRD patterns after soak the
samples in water and different pH solutions, confirmed that YTU-30 has remarkable chemical stability. PXRD indicates the structural stability of YTU-30, contrasting with the framework distortion or flexibility typically seen in layer-pillared MOFs constructed from dicarboxylates and diamines. The robustness of the framework in YTU-30 is attributed to the strong π–π stacking interactions between TPP pillars, which inhibit interlayer slippage.

3.3. Static Gas Uptake Performance

The pore characteristics of YTU-30 were assessed by N\textsubscript{2} ad-desorption experiments at 77 K. Its isotherm exhibited reversible type I adsorption behavior (Fig. 2b), which is consistent with the microporous nature. Based on the N\textsubscript{2} adsorption, the BET (Brunauer-Emmett-Teller) surface area and pore size distributions were estimated to be 714.0 m\textsuperscript{2} g\textsuperscript{-1}, and 7.7 Å, respectively. The pore size distribution was analyzed using the Horvath-Kawazoe cylindrical model, and the result was similar to the crystal structure prediction. It's worth noting that the kinetic diameter of SF\textsubscript{6} is 0.52 nm, implying that YTU-30 may be suitable for capturing SF\textsubscript{6}.

![Fig. 2 (a) PXRD patterns of YTU-30 after treatment under different treatments; (b) N\textsubscript{2} adsorption isotherms at 77 K (solid symbols: adsorption, open symbols: Desorption) and pore size distribution (inset).](image)

The single-component adsorption isotherms for SF\textsubscript{6} and N\textsubscript{2} were determined for YTU-30 at 273 K, 283 K and 298 K and 1 bar. Since industrial applications focus more on the volume of
the adsorbent than on its weight, the volume uptake capacity is usually a suitable criterion for evaluating gas adsorption capacity. YTU-30 adsorbs a large amount of SF$_6$ at low pressures, in contrast, the adsorption of N$_2$ shows a linear relationship for N$_2$ adsorption under the whole test pressures, indicating the preferential affinity for SF$_6$ molecules. As shown in Figure 3a, the SF$_6$ and N$_2$ uptake amounts are 50.0 and 1.3 cm$^3$ cm$^{-3}$, respectively, for YTU-30 at 298 K and 0.40 bar (304 mmHg). When the pressure up to 1 bar, the YTU-30 can uptake 68.6 and 3.3 cm$^3$ cm$^{-3}$ of SF$_6$ and N$_2$, respectively, at 298 K. Based on the volumetric absorption of SF$_6$, the safe storage density of YTU-30 at 298 K and 1 atm is 1.55 kg/L, which is higher than the safe storage density of SF$_6$ at 8 MPa at room temperature (< 1.17 kg/L). At 1.0 bar, the SF$_6$ uptakes on YTU-30 were 80.8 cm$^3$ cm$^{-3}$ at 273 K. The adsorption performance of YTU-30 increased with the temperature reduce, which also indicates that it is physisorption. More surprisingly, the total SF$_6$ uptake decreases to 77.7 cm$^3$ cm$^{-3}$ with a small loss of 3.1 cm$^3$ cm$^{-3}$ as the temperature increases from 273 to 283 K. The above result indicates relatively strong interactions between SF$_6$ molecules and the pore space in YTU-30. The corresponding total N$_2$ adsorption (5.6, and 4.7 cm$^3$ cm$^{-3}$) was negligible in comparison. The significant difference in adsorption of SF$_6$ and N$_2$ suggests that YTU-30 can be an excellent separating material for SF$_6$/N$_2$ mixture. The SF$_6$ uptake amount at 298 K and 1.0 bar for YTU-30 surpassed those of many other MOFs, including UiO-66-Br$_2$ (45.8 cm$^3$ cm$^{-3}$)[12], UiO-66 (44.0 cm$^3$ cm$^{-3}$)[12], MIL-100(Fe) (38.9 cm$^3$ cm$^{-3}$)[28], and SBMOF-1 (36.6 cm$^3$ cm$^{-3}$)[29]. To evaluate the regeneration abilities of YTU-30 for SF$_6$ adsorption, five consecutive SF$_6$ adsorption-desorption cycles were conducted and without any activation process at each interval. The adsorption amount of SF$_6$ was almost the same in five consecutive cycles (Fig. 3c). Undoubtedly, the regeneration conditions in this work can save more energy compared with other materials that require reactivation.
Fig. 3 SF$_6$ (a) and N$_2$ (b) adsorption isotherms for YTU-30 at 273 K, 283 K and 298 K; Cyclic regeneration tests toward SF$_6$; $-\Omega_{st}$ of SF$_6$ and N$_2$ adsorption as a function of the surface coverage.

To further evaluate the adsorption affinity between SF$_6$/N$_2$ and YTU-30, the isosteric heat of adsorption ($-\Omega_{st}$) were calculated by virial fits of their experimental single-component gas sorption isotherms (273, 283, and 298 K). As show in Fig. 3d, the SF$_6$ isosteric heat is 22.8 kJ mol$^{-1}$ is higher than the N$_2$ (14.0 kJ mol$^{-1}$) at zero coverage, indicating the higher affinity toward SF$_6$ than N$_2$. The high affinity of YTU-30 for SF$_6$ can be attributed to the unique porous surfaces decorated with the dense aryl rings of organic ligands and the accessible high H sites from TPP and ABTC$^4$-, which provide strong attractions for SF$_6$ molecules.

The difference in the adsorption capacities and affinity of YTU-30 for SF$_6$ and N$_2$ inspired
us to further explore the separation performance for SF₆/N₂ mixtures through ideal adsorbed solution theory (IAST) selectivities, which were calculated upon fitting the single-component isotherms by the single-site Langmuir-Freundlich equation. The volume concentrations of SF₆/N₂ (10/90) mixtures was studied in consideration of the usual industrial requirement. The predicted selectivity of SF₆/N₂ for YTU-30 were calculated to be 68.0 at 298 K and 1 bar. It is worth noting that the SF₆/N₂ selectivity of YTU-30 under ambient conditions is also higher than the other MOFs, such as MOF-74(Zn) (46.0)⁴⁰, MOF-74(Co) (40)⁴⁰, CAU-17 (31.0)⁵¹, and MIL-100(Fe) (24.4)²⁸, and UiO-67(21.6)⁹.

In addition to the uptake capacity and selectivity, the separation potential, which incorporates both of these factors, is used as a metric to evaluate the performance of separation. It indicates the highest amount of pure N₂ (6.8 mmol g⁻¹) can be recovered from the mixture in a fixed bed absorber at 298 K and 100 kPa. Separation potentials can be calculated using Equation S5 in the supporting information for the IAST method.

Fig. 4 (a) Comparison of experimental isotherms and simulated isotherms (Left Y axis), and adsorption selectivity predicted by IAST (Right Y axis) of YTU-30 for SF₆/N₂ (10/90) mixture at 298 K; (b) Separation potential for SF₆/N₂ (10/90) mixture.

3.4. Dynamic Breakthrough experiments

Laboratory-scale breakthrough experiments were conducted following these promising
results. A binary gas mixture of SF$_6$/N$_2$ (10/90) was introduced into the system with a flow rate of 2 mL min$^{-1}$ at 298 K and 1.0 bar. As shown in Fig. 5a, nitrogen flows rapidly out of the breakthrough column and can be detected at 12.0 min/g. In contrast, the SF$_6$ breakthrough time was significantly longer, which is not detected until 245.0 min/g, and reaches adsorption saturation at 400.0 min/g. The breakthrough interval between SF$_6$ and N$_2$ can be up to 233.0 min/g, which are higher than the most of reported MOF materials. The significantly long interval time implied the preferential adsorption of SF$_6$ over N$_2$ in YTU-30, consistent with the high -$Q_{st}$ and adsorption amount of SF$_6$. During the breakthrough interval, the outlet N$_2$ concentration exceeds 99.9% can be up to 7.2 mmol g$^{-1}$, which close to the theoretical value. The production of polymer-grade N$_2$ from actual industrial SF$_6$/N$_2$ (10/90) mixtures strongly indicates that SF$_6$/N$_2$ can be completely separated and further enables SF$_6$ reused using dynamic flow conditions. The calculated SF$_6$ adsorption amounts in the breakthrough experiments were 39.0 cm$^3$/cm$^3$ for YTU-30. Recoverability and reusability of adsorbents are imperative for actual industrial applications. YTU-30 can be regenerated at room temperature with He (20 mL min$^{-1}$) purging for 2 h. The cycling breakthrough experiment of SF$_6$/N$_2$ (10/90) mixture exhibits no significant loss at least three times under the same conditions (Fig. 5b). Given its less energy demand for desorption (low -$Q_{st}$) and water stability, it is potential competent for achieve SF$_6$/N$_2$ separation at normal temperature and pressure conditions. The PXRD patterns after cycling experiments are in good agreement with the simulated patterns, it also confirms the structural stability of YTU-30.
3.5. GCMC Simulations

To further understand the interactions between gas molecules and YTU-30, Grand Canonical Monte Carlo (GCMC) simulations were used to calculate the adsorption density distributions, and adsorption binding sites. As shown in Fig. 6, both SF$_6$ and N$_2$ are preferentially located around the channel consisting of multiple pyridine rings. The SF$_6$ molecule can interact with the pyridine ring through S-F-π and C-H···F interactions with the distances of 3.77 and 2.71 ~ 3.95 Å, respectively. The adsorption sites for N$_2$ are also calculated for comparison. N$_2$ interacts with one pyridine ring with the distances of 4.81 Å and three C-H···N with the distances of 4.11-4.98 Å. The above results indicated the formation of stronger interactions between SF$_6$ molecules and the YTU-30.
4. Conclusions

In summary, by the mixed ligand strategy, a novelty “pillar-layer” microporous cobalt-based MOF (YTU-30) together with multiple π–π stacking interactions between dense aryl rings was synthesized toward the SF$_6$/N$_2$ separation. The MOF displays high chemical stability (pH 3~11, and water) as well as effective capture of SF$_6$ from binary SF$_6$/N$_2$ mixtures, as confirmed by IAST selectivity, separation potential, and dynamic breakthrough curves. GCMC simulations revealed that this particular separation ability for SF$_6$ can be mainly attributed to the dense aryl rings on the pore inner wall, which can favorable preferential adsorb SF$_6$ molecules through S-F-π and C-H···F interactions. This contribution not only reports a new stable MOF that can efficiently separate SF$_6$ from SF$_6$/N$_2$ mixture, but also provides an alternative effective strategy for the assembly of MOFs applied in gas separation, that is, introducing dense aryl rings as bridging ligands by mixed ligand strategy.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (22101244), and
the Natural Science Foundation of Shandong Province (ZR2021QB044).

**Conflict of interest**

The authors declare that they have no conflict of interest.

**Supplementary Data**

Detailed experimental steps and methods, tables of crystal data, PXRD, TGA data. The Supplementary Data is available free.

**References**


This preprint research paper has not been peer reviewed. Electronic copy available at: https://ssrn.com/abstract=4696626