



# A thermostable anion-pillared metal-organic framework for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separations

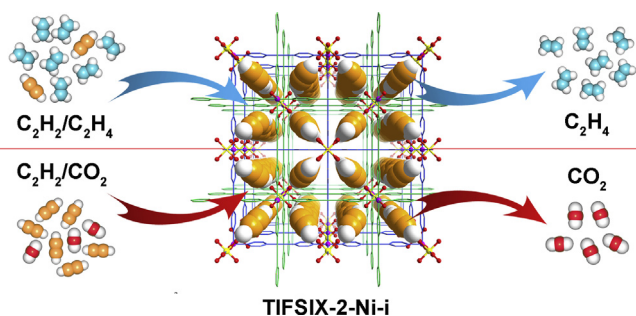
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## HIGHLIGHTS

- TIFSIX-2-Ni-i (ZU-12-Ni) has been synthesized for the first time.
- TIFSIX-2-Ni-i exhibits excellent thermal and moisture stability.
- TIFSIX-2-Ni-i displays prominent C<sub>2</sub>H<sub>2</sub> capture ability and effective separations.
- Excellent cycling stability indicates great potential in industrial separations.
- The exquisite control provides a powerful strategy to design new porous materials.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

A thermostable anion-pillared metal-organic framework TIFSIX-2-Ni-i (also referred to as ZU-12-Ni, TIFSIX = hexafluorotitanate, 2 = 4,4'-bipyridylacetylene, i = interpenetrated) has been synthesized for the first time. Structural characterizations show that TIFSIX-2-Ni-i exhibits a 2-fold interpenetrated network with narrow aperture of 5.1 Å (H-H distance) and abundant inorganic anion sites in the channel. The subtle change in metal and inorganic linkers results in the enhancement of the thermal stability of TIFSIX-2-Ni-i. Importantly, TIFSIX-2-Ni-i shows high-performing separation properties, especially for the important separations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> mixtures. Adsorption data demonstrate that TIFSIX-2-Ni-i enables effective C<sub>2</sub>H<sub>2</sub> capture (4.21 mmol/g, at 298 K and 1 bar), and achieves highly selective separation of C<sub>2</sub>H<sub>2</sub> over C<sub>2</sub>H<sub>4</sub> or CO<sub>2</sub> with the IAST selectivity of 22.7 (C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>: 1/99) and 10.0 (C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub>: 2/1) at 298 K and 1 bar. Dispersion-corrected density functional theory (DFT-D) calculations confirm the preferential adsorption of C<sub>2</sub>H<sub>2</sub> over C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>. Furthermore, the potential of industrial feasibility of TIFSIX-2-Ni-i for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation is confirmed by transient breakthrough tests (611.4 mmol/L C<sub>2</sub>H<sub>2</sub> absorbed for mixtures containing 1% C<sub>2</sub>H<sub>2</sub>). The excellent cycle performance and stable structure of TIFSIX-2-Ni-i during multiple breakthrough tests show great potential in industrial separation of light hydrocarbons.

## 1. Introduction

Separation and purification of light hydrocarbons are crucial processes to produce high-grade energy and fine chemicals [1–3]. However, the huge energy consumption during large-scale industrial

separation process account for 40–70% in a typical chemical industry, roughly equivalent to 10–15% of the world's energy consumption [1]. Conventional technologies mainly include cryogenic distillation [4] and organic solvent absorption [5]. However, both of them have some shortcomings. Cryogenic distillation is an energy-intensive process due

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to the similar physical–chemical characteristics of hydrocarbon molecules. Solvent absorption technology shows low selectivity and also suffers from the environmental pollution due to the volatile organic solvent such as N, N-dimethylformamide (DMF) or N-methylpyrrolidone (NMP).

Ethylene ( $C_2H_4$ ) and acetylene ( $C_2H_2$ ) are the core petrochemical products and have been widely utilized as basic raw materials in various industries. Currently,  $C_2H_4$  is typically produced during steam cracking which is unavoidable to contain some impurities such as acetylene [6]. In addition, carbon dioxide ( $CO_2$ ) is produced together during the production of acetylene by thermal cracking process [7]. Existence of  $C_2H_2$  will deactivate the catalysts during ethylene polymerization [8]. Therefore, the removal of small amount of  $C_2H_2$  from  $C_2H_4$ -rich mixture and the separation of  $CO_2$  from  $C_2H_2$  is the key to the preparation of polymer-grade ethylene and high-quality acetylene, respectively. However, the similar size and physical properties of ethylene, acetylene, and carbon dioxide make it very challenging to find alternative technologies to energy-intensive distillation process.

Considering of energy conservation and environmental protection, a method based on selective adsorption which works at ambient temperature and pressure become an attractive solution for gas separation. Up to now, multifarious porous materials such as porous polymers [9,10], zeolites [11–13], carbon materials [14,15], metal-organic frameworks (MOFs) and/or porous coordination polymers (PCPs) [16–35], and hydrogen-bonded organic frameworks [36–38] have been studied for  $C_2H_4/C_2H_2$  and  $C_2H_2/CO_2$  separations and purifications. Among numerous adsorbents, metal-organic frameworks (MOFs) are splendid due to their properties of abundant types, highly permanent porosity, tailorable pore size and pore surface functions [39–48]. In the past decades, more and more researches have been focused on the  $C_2H_2/C_2H_4$  [16–24] and  $C_2H_2/CO_2$  separations [25–30] with MOFs. For instance, the mixed MOFs (M'MOFs) family exhibit very high selectivity for  $C_2H_2/C_2H_4$  separation (up to 24.0 for M'MOF-3a), but relatively low  $C_2H_2$  capacity (1.9 mmol/g) at room temperature which attribute to the narrow micropore windows [49,50]. On the contrary, the famous MOF-74 series possess extremely high  $C_2H_2$  uptake (e.g. 8.37 mmol/g for Mg-MOF-74) due to the high densities of open metal sites, while the pores are too large to achieve size-sieving effect and have strong interaction with both  $C_2H_2$  and  $C_2H_4$  which lead to a bit low selectivity (2.18, at 1 bar) [51,52]. Therefore, optimal MOF materials for the challenge separations of  $C_2H_2/C_2H_4$  and  $C_2H_2/CO_2$  should integrate high selectivity and capacity. Recently, our lab has found that SIFSIX-2-Cu-i is a benchmark material which achieves a trade-off between high selectivity and capacity [16]. This stimulates us to explore more new MOFs which can recognize the subtle difference between similar molecules, achieving efficient separations for  $C_2H_2/C_2H_4$  and  $C_2H_2/CO_2$  mixtures.

Herein, we report an anion-pillared metal-organic framework TIFSIX-2-Ni-i (ZU-12-Ni, TIFSIX = hexafluorotitanate, 2 = 4,4'-bipyridylacetylene, i = interpenetrated) which is the first example to introduce Ni node into interpenetrated hexafluoroanion-pillared ultramicroporous materials. As expected, TIFSIX-2-Ni-i exhibits enhanced thermal stability and  $C_2H_2$  capacity (4.21 mmol/g at 298 K, 1 bar) than the previous benchmark SIFSIX-2-Cu-i, and achieves highly efficient separations of  $C_2H_2/C_2H_4$  and  $C_2H_2/CO_2$ . The small uniform pore aperture of 5.1 Å (H-H distance) and high concentration of electro-negative F groups in the pore increase the affinity to  $C_2H_2$  [5,16,53], resulting exceptional acetylene capacity. These advantages were demonstrated by gas sorption isotherms and breakthrough tests. Overall, TIFSIX-2-Ni-i is among the best materials that can separate trace  $C_2H_2$  from  $C_2H_2/C_2H_4$  mixtures efficiently and achieve good separation of  $C_2H_2$  and  $CO_2$ .

## 2. Experimental

### 2.1. Synthesis of TIFSIX-2-Ni-i

A methanol solution (4.0 mL) of 4,4'-dipyridylacetylene (0.286 mmol) and a methanol solution (4.0 mL) of  $Ni(BF_4)_2 \cdot xH_2O$  (0.26 mmol) and  $(NH_4)_2TiF_6$  (0.26 mmol) were mixed at room temperature, then the mixtures were settled for 4 h. The obtained sample in 67.8% yield (according to dissolved  $(NH_4)_2TiF_6$ ) was exchanged with methanol for 1 day.

An alternative method of room temperature diffusion was used to produce single crystals of TIFSIX-2-Ni-i. A methanol solution (2 mL) of  $Ni(BF_4)_2 \cdot xH_2O$  (0.149 mmol) and  $(NH_4)_2TiF_6$  (0.149 mmol) were carefully layered onto a DMSO solution (2 mL) of 4,4'-dipyridylacetylene (0.115 mmol). Glaucon crystals were obtained after two weeks.

### 2.2. Characterization of TIFSIX-2-Ni-i

To illuminate the structure of TIFSIX-2-Ni-i, Powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction data were collected on a SHIMADZU XRD-6000 diffractometer and Bruker APEX-II CCD diffractometer, respectively. The morphology of TIFSIX-2-Ni-i was observed on a SU8000 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) indicated the thermal stability was conducted on an instrument of TGA Q500. Surface area was based on the nitrogen adsorption and desorption isotherms at 77 K using micromeritics ASAP 2020 adsorption apparatus. More details could be seen in [Supplementary information](#).

### 2.3. Gas adsorption and separation measurements

The single-component adsorption isotherms of  $C_2H_2$ ,  $C_2H_4$  and  $CO_2$  at different temperatures were performed on micromeritics ASAP 2020 instruments. The fixed bed breakthrough experiments and multicycle tests were carried out on dynamic gas breakthrough equipment. The details of methods and conditions in each experiment were described in [Supplementary information](#).

### 2.4. Dispersion-corrected density-functional theory (DFT-D) calculations

To further understand the interaction between guests and TIFSIX-2-Ni-i framework, DFT-D method was utilized to calculate the optimized adsorption binding sites of  $C_2H_2$  and  $C_2H_4$  in TIFSIX-2-Ni-i. Detailed methods and conditions were described in [Supplementary information](#).

## 3. Results and discussion

### 3.1. Structure descriptions

TIFSIX-2-Ni-i was readily synthesized by self-assembly of 4,4'-dipyridylacetylene (dpa),  $(NH_4)_2TiF_6$  and  $Ni(BF_4)_2$  in methanol. Structure of TIFSIX-2-Ni-i had been confirmed by single-crystal X-ray diffraction, and the purity of bulk material was identified by powder X-ray diffraction (PXRD). The result of single-crystal X-ray diffraction indicated that TIFSIX-2-Ni-i was a doubly interpenetrated **pcu**-type framework. The crystallographic details of TIFSIX-2-Ni-i were summarized in [Table S1](#). As showed in [Fig. 1](#), the metal nodes of Ni and organic linkers of dpa constitute two-dimensional networks which were then pillared by  $TiF_6^{2-}$  to form a three-dimensional framework. These independent nets were staggered with each other to form two-fold interpenetrated structures in which the node of the second net was just located in the cavity center of the first net ([Fig. 1c](#)). The interpenetrated geometry of TIFSIX-2-Ni-i contributes to the highly uniform micropore. The quasi-maximal diameter in the unit cell of TIFSIX-2-Ni-i was 4.57 Å (F-F distance) while the maximal aperture size was 5.1 Å (H-H distance). The Ni-dpa-Ni distance of TIFSIX-2-Ni-i was 13.897 Å ( $a = b$ ), which

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