# **Inorganic Chemistry**

# Fluorinated Biphenyldicarboxylate-Based Metal–Organic Framework Exhibiting Efficient Propyne/Propylene Separation

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Cite This: https://dx.doi.org/10.1021/acs.inorgchem.0c00003 **Read Online** ACCESS III Metrics & More Article Recommendations **SUPPORTING Information** ABSTRACT: A novel fluorinated biphenyldicarboxylate ligand of 3,3',5,5'-tetrafluorobiphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-TFBPDC) 0.8 and its terbium metal-organic framework, 0.6 ر<sup>0</sup>  $\{[Tb_2(TFBPDC)_3(H_2O)] \cdot 4.5DMF \cdot 0.5H_2O\}_n$  (denoted as JXNU-

6), were synthesized. JXNU-6 exhibits a three-dimensional (3D) framework built from one-dimensional (1D) terbium carboxylate helical chains bridged by TFBPDC<sup>2-</sup> linkers. The 3D framework of JXNU-6 features 1D fluorine-lined channels. The gas adsorption experiments show that the activated JXNU-6 (JXNU-6a) displays distinct adsorption behavior for propyne  $(C_3H_4)$  and propylene



 $(C_3H_6)$  gases. The effective removal of a trace amount of  $C_3H_4$  from  $C_3H_6$  was achieved by JXNU-6a under ambient conditions, which is demonstrated by the column-breakthrough experiments. The modeling studies show that the preferential binding sites for  $C_3H_4$  are the exposed F atoms on the pore surface in 1D channels. The strong C-H···F hydrogen bonds between  $C_3H_4$  molecules and F atoms of TFBPDC<sup>2-</sup> ligands dominate the host-guest interactions, which mainly account for the excellent C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> separation performance of **JXNU-6a**. This work provides a strategy for specific recognition toward  $C_3H_4$  over  $C_3H_6$  through the C-H…F hydrogen bond associated with the fluorinated organic ligand.

# INTRODUCTION

Metal-organic frameworks (MOFs; also denoted as porous coordination polymers) formed from metal centers and bridging organic ligands hare emerged as a unique kind of porous solid material in the past several decades.<sup>1</sup> Compared with the conventional porous solid materials of zeolites and activated carbons, MOF materials possess advantages that include well-defined structures, tailored pore sizes and shapes, and designed functional sites on pore surfaces.<sup>2</sup> Such a unique porous nature enables MOFs to exhibit promising potentials in gas storage and separation.<sup>3</sup>

Propylene  $(C_3H_6)$  with an annual output of more than 120 million tons in 2016 is one of the most productive chemicals in the world. The raw chemical of  $C_3H_6$  is primarily produced by the cracking of larger hydrocarbon molecules or petroleum distillate in the petrochemical industry, which leads to an undesirable byproduct of  $C_3H_4$  in  $C_3H_6$  gas. The separation of a C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> mixture remains a significant challenge because of the similarity of their molecular sizes  $(4.65 \times 4.16 \times$ 6.44 and 4.01  $\times$  4.16  $\times$  6.51 Å  $^3$  for C\_3H\_6 and C\_3H\_4, respectively) and kinetic diameters (C<sub>3</sub>H<sub>6</sub>, 4.68 Å; C<sub>3</sub>H<sub>4</sub>, 4.76 Å).<sup>4</sup> Current methods for the removal of a trace of  $C_3H_4$  from  $C_3H_6$  gas are cryogenic distillation or catalytic partial hydrogenation. Such methods often suffer from high cost, energy-intensive consumption, and poor efficiency.<sup>5</sup> Therefore, the development of an energy-efficient and environmentally friendly method for  $C_3H_4/C_3H_6$  separation is urgently needed. Recently, MOFs have been shown to exhibit great potential in

separation performances for ethane/ethylene,<sup>6</sup> carbon dioxide/ acetylene,<sup>7</sup> and acetylene/ethylene mixtures.<sup>8</sup> However, in view of their similar kinetic diameters and molecular sizes,  $C_3H_4/C_3H_6$  separation is difficult and is rarely explored for MOFs.<sup>9</sup> In this contribution, we present a novel fluorinated biphenyldicarboxylate ligand for the construction of a lanthanide MOF, { $[Tb_2(TFBPDC)_3(H_2O)] \cdot 4.5DMF \cdot$  $(0.5H_2O)_n$  (JXNU-6; DMF = N,N-dimethylformamide). The design of 3,3',5,5'-tetrafluorobiphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-TFBPDC) is aimed at providing the binding sites (the exposed F atoms) for the recognition of specific molecules. The present three-dimensional (3D) structure of JXNU-6 constructed from the terbium carboxyalte chains and a TFBPDC<sup>2-</sup> ligand exhibits one-dimensional (1D) fluorinelined channels. The efficient removal of a trace amount of  $C_3H_4$  from  $C_3H_6$  gas is realized by JXNU-6a (activated as JXNU-6). The exposed electronegative F atoms on the pore surface of JXNU-6a are found to be favorable sites for the weakly acidic alkynyl H and methyl H atoms of the C3H4 molecule. Thus, we present a new approach for the specific

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recognition of  $C_3H_4$  over  $C_3H_6$  via the C-H…F hydrogen bond based on the fluorous organic ligand.

#### EXPERIMENTAL SECTION

**Chemicals.** All chemicals were obtained commercially, except for  $H_2$ -TFBPDC, which was prepared as given in Scheme S1.

**Gas Sorption Studies.** The gas sorption experiments were performed on a Micromeritics ASAP2020 HD88 surface area analyzer.  $N_2$  (99.999%),  $C_3H_4$  (99.95%), and  $C_3H_6$  (99.999%) were used. The as-prepared **JXNU-6** samples were washed with DMF five times and then soaked with dichloromethane for 8 days. The dichloromethane-exchanged **JXNU-6** was first vacuumed for 3 h at 30 °C and then immediately vacuumed for 27 h at 98 °C to yield the activated sample of **JXNU-6a**.

Adsorption Selectivity and Isosteric Heat of Adsorption Calculations. The adsorption selectivity was calculated with the ideal adsorbed solution theory (IAST). The experimental pure-component gas adsorption isotherms at 273 and 298 K were fitted by a single-site Langmuir–Freundlich model.<sup>10</sup> The isosteric heat of adsorption was calculated from the fitting parameters of the adsorption isotherms using the virial method.<sup>11</sup>

**Column-Breakthrough-Separation Experiments.** Gas separation experiments were performed on our previously reported apparatus for gas mixtures.<sup>12</sup> A gas chromatograph with a thermal conductivity detector was used for monitoring the effluent gas from the adsorption column. The separation experiments were carried out at 298 K and 1 atm. The adsorption column has a length of 100 mm and an inner diameter of 4 mm and was loaded with 0.347 g of sample. The mixed gas with a total flow rate of 2 mL min<sup>-1</sup> was continuously fed into the adsorption column.

**Synthesis of {**[**Tb**<sub>2</sub>(**TFBPDC**)**,(H**<sub>2</sub>**O**)]**,4.5DMF,0.5H**<sub>2</sub>**O**}*,***n** (**JXNU-6**). A mixture of TbCl<sub>3</sub>·6H<sub>2</sub>O (7.46 mg, 0.02 mmol), H<sub>2</sub>-TFBPDC (3.12 mg, 0.01 mmol), and 2-fluorobenzoic acid (7 mg, 0.05 mmol) in 2 mL of DMF was screw-capped in a 10 mL vial and heated at 100 °C for 24 h. After cooling to room temperature, colorless crystals were obtained. Yield: 48% based on H<sub>2</sub>-TFBPDC. Elem anal. Calcd/found for **JXNU-6** (1610.31): C, 41.39/41.13; H, 2.91/2.78; N, 3.91/3.81. IR spectrum (cm<sup>-1</sup>): 3415 (w), 1633 (s), 1589 (s), 1398 (s), 1280 (w), 1251 (w), 1147 (w), 1111 (w), 1035 (s), 858 (s), 845 (s), 804 (w), 723 (m), 681 (m), 585 (s), 522 (w), 422 (m).

**Crystallographic Study.** Single-crystal X-ray diffraction experiments were carried out with a Rigaku Oxford SuperNova diffractometer equipped with an EOS detector (Mo K $\alpha$  radiation;  $\lambda = 0.71073$  Å). Absorption correction and data reduction were handled with a *CrysAlisPro* package.<sup>13</sup> *SHELXT*<sup>14</sup> and *SHELXTL*<sup>15</sup> were applied to structure solution and refinement. All H atoms were modeled geometrically and refined with a riding model. Non-H atoms were refined anisotropically. The guest H<sub>2</sub>O and DMF molecules (3549 Å and 741 e<sup>-</sup> per unit cell) are highly disordered and treated by *SQUEEZE* of *PLATON*.<sup>16</sup> The crystallographic data are provided in Table 1, and the important bonds are presented in Table S1.

# RESULTS AND DISCUSSION

**Structural Description.** JXNU-6 exhibits a 3D framework featuring the 1D terbium carboxylate helical chains and 1D fluorine-lined channels. One and a half TFBPDC<sup>2–</sup> ligands, half a coordinated H<sub>2</sub>O molecule, and two Tb<sup>III</sup> ions with half-occupation compose the asymmetric unit of JXNU-6. Both Tb1 and Tb2 atoms are located at 2-fold axes but display different coordination geometries. The Tb1 atom is nine-coordinated by eight O atoms from six carboxylate groups of six TFBPDC<sup>2–</sup> ligands and one O atom of an aqua ligand (Figure 1a), while Tb2 is bound to eight carboxylate O atoms from six TFBPDC<sup>2–</sup> ligands. The Tb–O bond distances fall into the typical range varying from 2.336(5) to 2.623(5) Å. The two crystallographically unique TFBPDC<sup>2–</sup> ligands exhibit two coordination modes binding four metal ions with two  $\mu_2$ -

#### Table 1. Crystallographic Data for JXNU-6<sup>a</sup>

	formula	$C_{42}H_{14}F_{12}O_{13}Tb_2$
	fw	1272.37
	temp (K)	293(2)
	cryst syst	tetragonal
	space group	P4 <sub>1</sub> 22
	Ζ	4
	a (Å)	15.8993(2)
	b (Å)	15.8993(2)
	c (Å)	27.5708(7)
	$\alpha$ (deg)	90
	$\beta$ (deg)	90
	γ (deg)	90
	V (Å <sup>3</sup> )	6969.6(2)
	$D_{\rm calcd} \ ({\rm g \ cm^{-3}})$	1.213
	$\mu \ (\mathrm{mm}^{-1})$	2.085
	no. of reflns collected	38062
	no. of indep reflns	7126
	no. of obsd reflns $[I > 2\sigma(I)]$	6660
	F(000)	2432
	R <sub>int</sub>	0.0382
	$R_1 \left[ I > 2\sigma(I) \right]$	0.0332
	wR <sub>2</sub> (all data)	0.0886
	CCDC number	1975059
${}^{a}R_{1} = \sum   F_{o}  -  F_{c}   / \sum  F_{o} $ and $wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum [w(F_{o}^{2})^{2}]\}^{1/2}$ .		

 $\eta^2:\eta^1$  carboxylate groups or with one  $\mu_2-\eta^2:\eta^1$  and one  $\mu_2-\eta^1:\eta^1$ carboxylate groups (Figure S1). The dihedral angles between the benzene planes and their attached carboxylate moieties are 44.3 and 88.7°. In contrast to its analogue, the benzene rings with their attached carboxylate groups in the biphenyl-4,4'dicarboxylate ligand are nearly coplanar. Such large torsion angles in the TFBPDC<sup>2-</sup> ligand result from the large size of the F atoms and the electrostatic repulsion between carboxylate O atoms and F atoms with negative charge. As displayed in Figure 1b, Tb<sup>III</sup> ions are bridged by the carboxylate groups to generate a 1D right-handed helical chain propagating along the *c* axis. Within the helix, the Tb1 and Tb2 atoms are alternately arranged and the separation between the neighboring  $\mathrm{Tb}^{\mathrm{III}}$ atoms is 4.07 Å. The pitch length of 27.2 Å for the helix is identical with the c-axis length. Such a helical chain is generated around the crystallographic 41 screw axis (Figure S2), which is consistent with a  $P4_122$  space group for JXNU-6. Each helix is connected to four adjacent helixes with the same handedness through tetrafluorobiphenyl moieties to generate a 3D structure (Figure 1c). The 3D framework has 1D square channels extending to the c axis, with the inner wall full of F atoms, which generates the fluorine-lined channels. The 1D channels are occupied by the disordered DMF and H<sub>2</sub>O molecules, which are accounted for 50.5% of the unit cell volume.<sup>16</sup> The PXRD pattern of the bulk materials was close to the simulated one generated from single-crystal X-ray diffraction data (Figure S3). The thermogravimetric analysis (TGA) curve showed that the loss of DMF and  $H_2O$ molecules occurred between 30 and 185 °C (weight loss: measured 22.2%, theoretical 22.1%; Figure S4). The TGA curve of the dichloromethane-exchanged sample showed that the DMF and H<sub>2</sub>O molecules in the channels can be successfully exchanged by dichloromethane (Figure S4). Thus, the dichloromethane-exchanged sample was degassed



Figure 1. (a) Coordination environments for Tb<sup>III</sup>, (b) a 1D right-handed helical chain, and (c) the 3D framework of JNXU-6.

at 98 °C under high vacuum to yield the guest-free phase of **JXNU-6a**.

**N<sub>2</sub> Adsorption.** Examination of the structure of **JXNU-6** shows that it has 1D pore channels. Thus, the porous nature of **JXNU-6** was demonstrated by a N<sub>2</sub> adsorption isotherm at 77 K for the guest-free phase of **JXNU-6a**. When  $P/P^{\circ} < 0.01$ , **JXNU-6a** adsorbs N<sub>2</sub> sharply, and then the N<sub>2</sub> uptake increases slowly with increasing gas pressure (Figure 2). The largest uptake of 249.8 cm<sup>3</sup> (STP) g<sup>-1</sup> for N<sub>2</sub> was obtained. Such a N<sub>2</sub>



Figure 2.  $N_2$  adsorption (closed circle)/desorption (open circle) curves for JXNU-6a at 77 K (inset: pore-size distribution).

isotherm confirms the microporous character of **JXNU-6a**. From the N<sub>2</sub> adsorption data, the Brunauer–Emmett–Teller and Langmuir surface areas were calculated to be 865.3 and 1029.1 m<sup>2</sup> g<sup>-1</sup>, respectively (Figure S5). The experimental total pore volume of 0.38 cm<sup>3</sup> g<sup>-1</sup> derived from the N<sub>2</sub> adsorption data is very close to the calculated one (0.39 cm<sup>3</sup> g<sup>-1</sup>). The narrow distribution of the micropore at 9.2 Å was obtained by the nonlocal density functional theory model (Figure 2, inset) based on the N<sub>2</sub> adsorption data. The pore size is comparable to the pore aperture of 10.4 Å derived from the crystal structure. After adsorption, the **JXNU-6a** bulk material was checked by powder X-ray diffraction (PXRD), which shows that the PXRD pattern of **JXNU-6a** after adsorption is close to the synthesized one (Figure S3), suggesting that the crystalline framework remains intact during the adsorption process.

**C**<sub>3</sub>**H**<sub>4</sub> and **C**<sub>3</sub>**H**<sub>6</sub> Adsorption. JXNU-6a shows a porous structure; therefore, the gas adsorption potential of JXNU-6a was investigated. As depicted in Figure 3, JXNU-6a exhibits different C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> adsorption behavior, indicating potential applications in gas separation. The largest C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> uptakes for JXNU-6a at 273 K are 128.8 and 93.2 cm<sup>3</sup> g<sup>-1</sup>, respectively. At 298 K, the adsorption amounts for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> are 113.6 and 79.9 cm<sup>3</sup> g<sup>-1</sup> (Figure 3b). The C<sub>3</sub>H<sub>4</sub> adsorption amount for JXNU-6a (5.07 mmol g<sup>-1</sup>) at 298 K is much higher than those of ELM-12 (2.77 mmol g<sup>-1</sup>), <sup>9b</sup> UTSA-200 (3.58 mmol g<sup>-1</sup>), <sup>9c</sup> ZU-62 (3.64 mmol g<sup>-1</sup>), <sup>17</sup> SIFSIX-3-Ni (2.85 mmol g<sup>-1</sup>), <sup>9a</sup> and NKMOF-1-Ni (3.5 mmol g<sup>-1</sup>), <sup>18</sup> suggesting that JXNU-6a is a good candidate for the sorption



Figure 3.  $C_3H_4$  and  $C_3H_6$  adsorption isotherms of JXNU-6a.



Figure 4. Experimental column breakthrough curves for 1/99 (a) and 0.1/99.9 (b) C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> mixtures for JXNU-6a at 298 K and 1 atm.

of C<sub>3</sub>H<sub>4</sub>. As depicted in Figure 3, the C<sub>3</sub>H<sub>4</sub> adsorption isotherm exhibits a sharper increase than that of C3H6 at a pressure lower than 10 kPa (Figure 3). The C<sub>3</sub>H<sub>4</sub> uptakes for **JXNU-6a** are 90.7 cm<sup>3</sup> g<sup>-1</sup> (273 K) and 57.4 cm<sup>3</sup> g<sup>-1</sup> (298 K) at 10 kPa. Such different adsorption behaviors of C3H4 and C<sub>3</sub>H<sub>6</sub> for JXNU-6a indicates that JXNU-6a has the potential for  $C_3H_4$  and  $C_3H_6$  separation. As depicted in Figure 3, the  $C_3H_6$  adsorption isotherms are fully reversible at 273 and 298 K, while hysteretic desorption behavior is observed in the C<sub>3</sub>H<sub>4</sub> isotherms at both temperatures. Such a phenomenon suggests that C<sub>3</sub>H<sub>4</sub> molecules have strong interactions with the host framework, which is confirmed by the large isosteric heat of adsorption Q<sub>st</sub> for C<sub>3</sub>H<sub>4</sub> (C<sub>3</sub>H<sub>4</sub>, 39.9 kJ mol<sup>-1</sup>, and C<sub>3</sub>H<sub>6</sub>, 27.1 kJ mol<sup>-1</sup>, near zero loading) fitted by the corresponding adsorption isotherms at 273 and 298 K using the viral method (Figures S6 and S7). The  $C_3H_4/C_3H_6$  uptake ratios for JXNU-6a are 1.79 (at 1 kPa) and 1.42 (100 kPa) at 298 K, respectively. The  $C_3H_4/C_3H_6$  uptake ratio for JXNU-6a is comparable with those of SIFSIX-2-Cu-i (1.43), SIFSIX-1-Cu (1.46), and Mg-MOF-74 (1.44) at 298 K and 100 kPa<sup>9c</sup> but larger than those of SIFSIX-3-Ni (1.04), ZU-62 (1.35), Ni-MOF-74 (1.15), Cu-BTC (1.25), and Cr-BTT (1.24).9c Although the  $C_3H_4/C_3H_6$  uptake ratios for ZJUT-1,<sup>9c</sup> UTSA-200,9c ELM-12,9b and NKMOF-1-Ni<sup>18</sup> are larger than that of JXNU-6a (Figure S8), their  $C_3H_4/C_3H_6$  separation performance is hampered severely by their much lower total adsorption capacities. The MOF-74 series<sup>9c</sup> and Cu-BTC<sup>9c</sup> have larger adsorption capacities but exhibit small  $C_3H_4/C_3H_6$ uptake ratios (Figure S8). Therefore, JXNU-6a with a large uptake and a suitable  $C_3H_4/C_3H_6$  uptake ratio is considered to be a promising material for  $C_3H_4/C_3H_6$  separation.

 $C_3H_4/C_3H_6$  Separation. To predict the feasibility of the separation performance for  $C_3H_4/C_3H_6$  mixed gases, IAST calculation<sup>10</sup> was conducted on a  $C_3H_4/C_3H_6$  mixture for JXNU-6a (Figure S9). The adsorption selectivities  $(S_{ads})$  at low pressure are 3.1 and 3.1 for 1/99 and  $0.1/99.9 C_3H_4/C_3H_6$ mixtures at 298 K (Figure S10). The  $S_{ads}$  value with the 1/99 ratio is larger than those of Cu-BTC  $(1.1)^{9c}$  and ZIF-8  $(1.3)^{9c}$ Experimental column-breakthrough studies based on the  $C_3H_4/C_3H_6$  mixtures were conducted with a total gas flow of 2 mL min<sup>-1</sup> under 298 K and 1 atm. The experimental breakthrough curves for C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> with 1/99 and 0.1/99.9 (v/v) are shown in Figure 4.  $C_3H_6$  was detected first at the outlet effluent from the packed column, while C3H4 gas was kept in the adsorption bed. Thus, highly pure  $C_3H_6$  with a C<sub>3</sub>H<sub>4</sub> concentration below 10 ppm monitored at the outlet effluent can be obtained. For a 1/99  $C_3H_4/C_3H_6$  mixture, the  $C_3H_6$  productivity for JXNU-6a is 8.84 mol L<sup>-1</sup> calculated from the breakthrough curves (Figure 4a). Such a result means that  $C_3H_6$  with a purity of 99.999% is realized by the JXNU-6a material. The  $C_3H_4$  breakthrough started at 124 min g<sup>-1</sup> for a  $1/99 \text{ C}_3\text{H}_4/\text{C}_3\text{H}_6$  mixture. The breakthrough time for JXNU-**6a** is comparable to those of SIFSIX-1-Cu (125 min  $g^{-1}$ ) and ZJUT-1  $(125 \text{ min g}^{-1})^{9c}$  but is much larger than those of MIL-100(Cr) (70 min g<sup>-1</sup>), UiO-66 (40 min g<sup>-1</sup>), and ZIF-8 (35 min  $g^{-1}$ ).<sup>9</sup> However, because of its large  $S_{ads}$  value for the  $C_{3}H_{4}/C_{3}H_{6}$  mixture, ELM-12 (210 min g<sup>-1</sup>)<sup>9b</sup> shows a breakthrough time longer than that of JXNU-6a. For the

0.1/0.99  $C_3H_4/C_3H_6$  mixture, the  $C_3H_4$  breakthrough occurred 248 min g<sup>-1</sup>, which is close to that of SIFSIX-2-Cu-i (240 min g<sup>-1</sup>)<sup>9c</sup> but is larger than that of ELM-12 (120 min g<sup>-1</sup>).<sup>9b</sup> From the breakthrough curves of Figure 4a, the amount of  $C_3H_4$  captured by the **JXNU-6a** material is 111.2 mmol L<sup>-1</sup>. Clearly, a trace of  $C_3H_4$  can be efficiently removed from the  $C_3H_4/C_3H_6$  mixtures by the **JXNU-6a** material. Thus, **JXNU-6a** demonstrates a highly efficient separation performance toward the  $C_3H_4/C_3H_6$  mixture.

To understand the separation performance toward the  $C_3H_4/C_3H_6$  mixture, modeling studies using first-principles dispersion-corrected density functional theory (DFT-D) were conducted on **JXNU-6a**. The modeling results evidence that the  $C_3H_4$  molecules locate in the 1D channels and the preferential adsorption sites for the  $C_3H_4$  molecule are the F atoms of the organic ligands. The  $C_3H_4$  molecule interacts with the host framework through strong C–H…F hydrogen bonds (Figure 5). The distance between the alkynyl H atom of the



Figure 5. C<sub>3</sub>H<sub>4</sub> favorable adsorption binding sites in JXNU-6a.

 $C_3H_4$  molecule and the F atom of the TFBPDC<sup>2-</sup> ligand is 2.50 Å. In addition, the methyl H atom of the  $C_3H_4$  molecule is synergistically bound with the F atoms of the ligands through C-H…F hydrogen bonds with the H…F distances of 2.53, 2.75, and 2.82 Å (Figure 5). The electropositive nature of the alkynyl H atom of the C3H4 molecule enables a strong binding interaction with the electronegative F atom of the organic ligand of the host framework. Such strong hydrogen bonds enable a high adsorption energy of 63.2 kJ mol<sup>-1</sup> for  $C_3H_4$ . The high adsorption energy is accounted for the high  $C_3H_4$ capacity at low pressure for JXNU-6a. In the reported MOFs for  $C_3H_4/C_3H_6$  separation, the sulfonate O atoms and the F atoms of the inorganic anions of  $SiF_6^{2-}$  and  $NbOF_5^{2-}$  of the host MOF frameworks were found to be favorable sites for the  $C_3H_4$  molecule,<sup>9</sup> while in the present case, the F atoms are derived from the fluorinated organic ligand. Therefore, we provide the first example of a MOF for the separation of a  $C_3H_4/C_3H_6$  mixture through the C-H...F hydrogen-bond strategy with the fluoro organic ligand. In contrast to the  $C_3H_4$ molecule, the C<sub>3</sub>H<sub>6</sub> molecule interacts with the host framework through weak interactions such as  $\pi \cdots \pi$  stacking between the alkenyl and the benzene rings of the organic ligands with centroid-to-centroid distances of 3.79 and 4.01 Å and the weak C-H…F hydrogen bond (H…F = 2.96 Å) between the methyl H atom of the  $C_3H_6$  molecule and the F

atom of the TFBPDC<sup>2-</sup> ligand (Figure S11). The weak interactions between the  $C_3H_6$  molecule and host framework result in a low adsorption energy of S1.7 kJ mol<sup>-1</sup> for the  $C_3H_6$  molecule. Therefore, quite different interactions between gas molecules and the framework of **JXNU-6a** lead to an excellent separation performance toward the  $C_3H_4/C_3H_6$  mixture for **JXNU-6a**.

#### CONCLUSIONS

In summary, a novel fluorinated biphenyldicarboxylate ligand and its terbium metal-organic framework of JXNU-6 have been synthesized. JXNU-6 with 1D channels is constructed from helical terbium carboxylate chains. The F atoms attached to the benzene rings point to the inner wall of the 1D channels, thus giving highly fluorophilic 1D channels. JXNU-6a exhibits an excellent gas separation performance toward the C3H4/ C<sub>3</sub>H<sub>6</sub> mixture, as established by gas adsorption and separation experiments. Strong C-H--F hydrogen bonds between the weakly acidic alkynyl H atom of C3H4 molecules and the weakly basic F atoms of fluorinated biphenyldicarboxylate ligands are mainly responsible for the efficient gas separation performance. This work demonstrates an elegant example of MOF materials showing efficient separation toward  $C_{3}H_{4}/$  $C_{3}H_{6}$  through the C-H...F hydrogen-bond strategy associated with the organic fluoro ligand.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00003.

Synthesis information for the ligand, PXRD patterns, TGA curves,  $Q_{st}$  of  $C_3H_4$  and  $C_3H_6$  adsorption, and modeling studies (PDF)

#### Accession Codes

CCDC 1975059 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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