

## **Supplemental Information**

# **Highly sensitive flexible metal-organic framework sets a new benchmark for separating propyne from propylene**

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**Table S1.** Crystal Structure data of TIFSIX-14-Cu-i.

Unit cell parameters	
Formula sum	C <sub>20</sub> H <sub>16</sub> Cu F <sub>6</sub> N <sub>8</sub> Ti
Formula weight	593.85 g mol <sup>-1</sup>
Crystal system	tetragonal
Space –group	I 4/m m m (139)
Cell parameters	a=13.097(3) Å; c=8.628(2) Å
Cell ratio	a/b=1.0000 b/c=1.5180 c/a=0.6588
Cell volume	1479.97(80) Å <sup>3</sup>
Z	2
Calc.density	1.33253 g cm <sup>-3</sup>

**Table S2.** Summary of the C<sub>3</sub>H<sub>4</sub> uptake, C<sub>3</sub>H<sub>6</sub> uptake and selectivity on various materials.

Adsorbents	Surface Area (m <sup>2</sup> /g)	Pore Size (Å)	C <sub>3</sub> H <sub>4</sub> uptake (mmol g <sup>-1</sup> )	C <sub>3</sub> H <sub>6</sub> uptake (mmol g <sup>-1</sup> )(1 bar)	Selectivity <sup>‡</sup>	Ref.
SIFSIX-1-Cu	1178	8.0×8.0	2.79*/8.76 <sup>†</sup>	5.94	9.17	[1a]
SIFSIX-2-Cu-i	585 <sup>#</sup>	4.4×4.4	1.94*/4.54 <sup>†</sup>	2.70	29.6	This Work
SIFSIX-3-Ni	360	3.8×3.8	2.73*/2.98 <sup>†</sup>	2.66	259	[1a]
TIFSIX-14-Cu-i	481 <sup>#</sup>	3.4×3.4 <sup>&amp;</sup>	2.18*/3.88 <sup>†</sup>	1.40	355	This Work
GeFSIX-14-Cu-i	463 <sup>#</sup>	3.4×3.4	2.12*/3.34 <sup>†</sup>	1.50	217	This Work
ELM-12	-	4.0×4.2	1.83*/ 2.74 <sup>†</sup>	1.43	84	[5]

\* the C<sub>3</sub>H<sub>4</sub> uptake at 298 K under 0.01 bar.

† the C<sub>3</sub>H<sub>4</sub> uptake at 298 K under 1 bar.

‡ the selectivity of 1/99 C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> under 298 K and 1bar.

# the surface area derived from CO<sub>2</sub> sorption data in 196 K.

& the pore size derived from the CO<sub>2</sub> sorption data in 196 K.

**Table S3.** Langmuir-Freundlich parameters fit for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> in TIFSIX-14-Cu-i at 298 K.

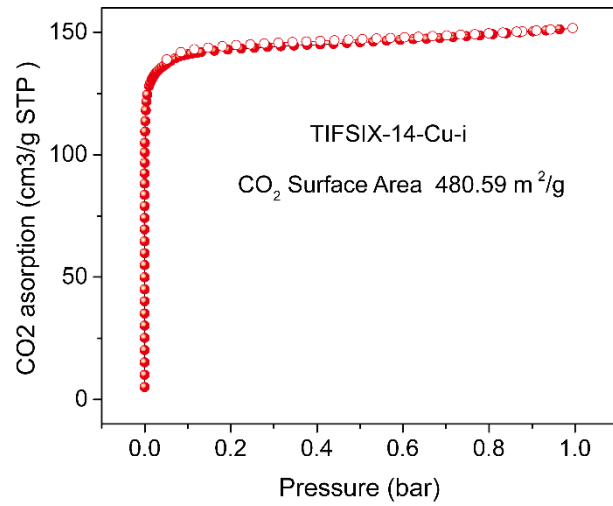
	Site A			Site B		
	q <sub>A sat</sub> (mol kg <sup>-1</sup> )	b <sub>A</sub> (KPa <sup>-1</sup> )	V <sub>A</sub>	q <sub>B sat</sub> (mol kg <sup>-1</sup> )	b <sub>B</sub> (KPa <sup>-1</sup> )	V <sub>B</sub>
C <sub>3</sub> H <sub>4</sub>	2.713	2.483	0.825	440.2	1.06E-5	0.963
C <sub>3</sub> H <sub>6</sub>	0.034	10.02	2.070	1.473	0.006	1.635

**Table S4.** Langmuir-Freundlich parameters fit for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> in GeFSIX-14-Cu-i at 298 K.

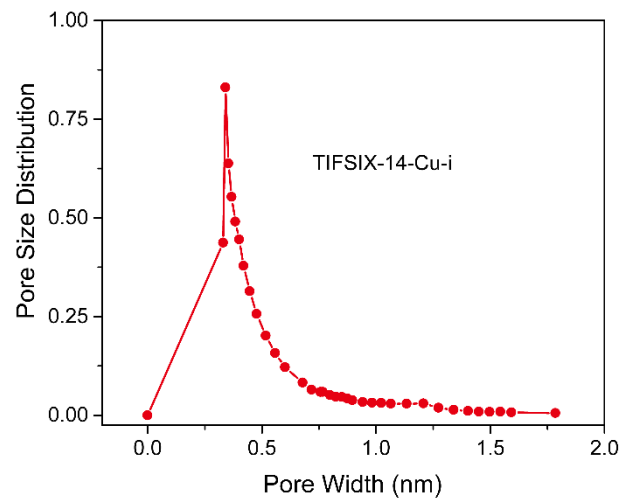
	Site A			Site B		
	q <sub>A sat</sub> (mol kg <sup>-1</sup> )	b <sub>A</sub> (KPa <sup>-1</sup> )	V <sub>A</sub>	q <sub>B sat</sub> (mol kg <sup>-1</sup> )	b <sub>B</sub> (KPa <sup>-1</sup> )	V <sub>B</sub>
C <sub>3</sub> H <sub>4</sub>	2.579	0.063	0.372	2.629	3.020	1.418
C <sub>3</sub> H <sub>6</sub>	0.911	1.72E-21	14.08	1.805	0.003	1.117

**Table S5.** Langmuir-Freundlich parameters fit for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> in SIFSIX-2-Cu-i at 298 K.

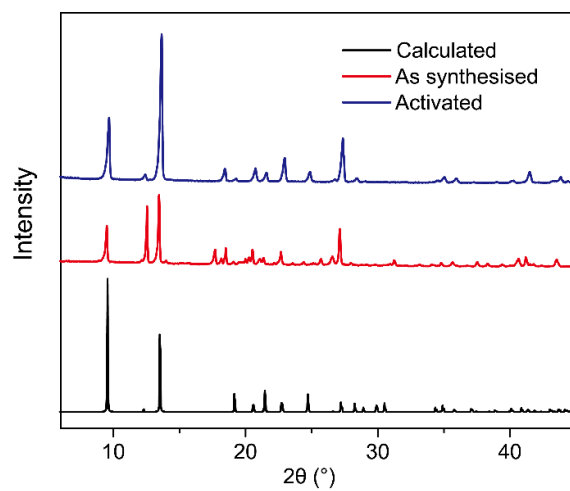
	Site A			Site B		
	q <sub>A sat</sub> (mol kg <sup>-1</sup> )	b <sub>A</sub> (KPa <sup>-1</sup> )	V <sub>A</sub>	q <sub>B sat</sub> (mol kg <sup>-1</sup> )	b <sub>B</sub> (KPa <sup>-1</sup> )	V <sub>B</sub>
C <sub>3</sub> H <sub>4</sub>	2.690	3.655	1.316	5.536	0.050	0.494
C <sub>3</sub> H <sub>6</sub>	3.224	0.062	0.951	0.257	3.61E-8	3.590



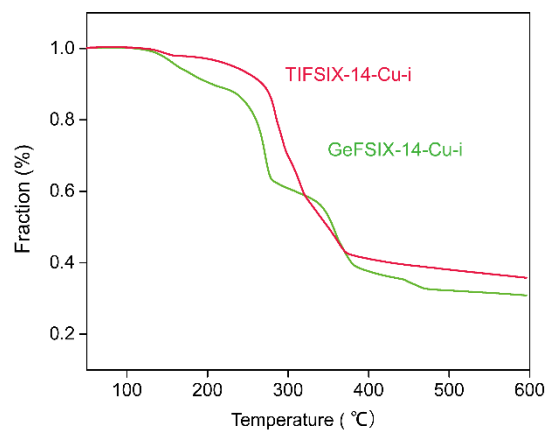
**Figure S1.** The CO<sub>2</sub> sorption data (solid symbols: adsorption; empty symbols: desorption) of TIFSIX-14-Cu-i at 196 K.



**Figure S2.** The pore size distribution of TIFSIX-14-Cu-i derived from the CO<sub>2</sub> BEsorption data in 196 K.



**Figure S3.** The XRD patterns of the synthesised and activated TIFSIX-14-Cu-i.



**Figure S4.** The TGA curve of TIFSIX-14-Cu-i and GeFSIX-14-Cu-i.

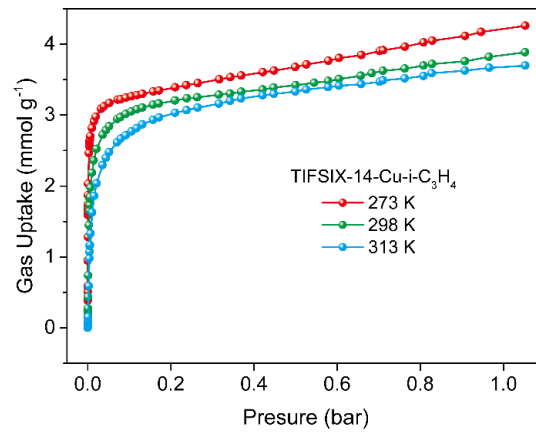


Figure S5. The adsorption isotherms of  $C_3H_4$  on TIFSIX-14-Cu-i at temperature from 273 to 313 K.

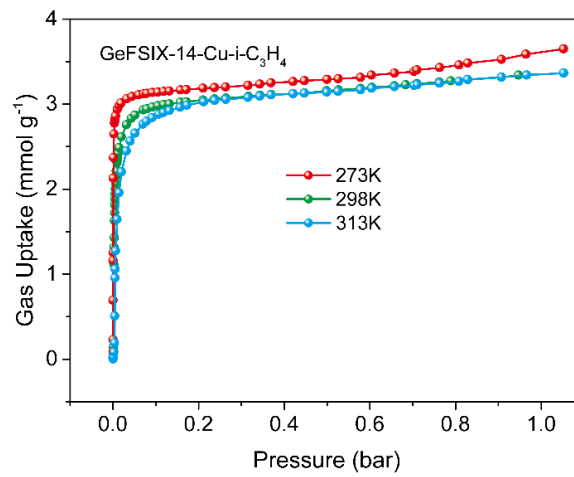


Figure S6. The adsorption isotherms of  $C_3H_4$  on GeFSIX-14-Cu-i at temperature from 273 to 313 K.

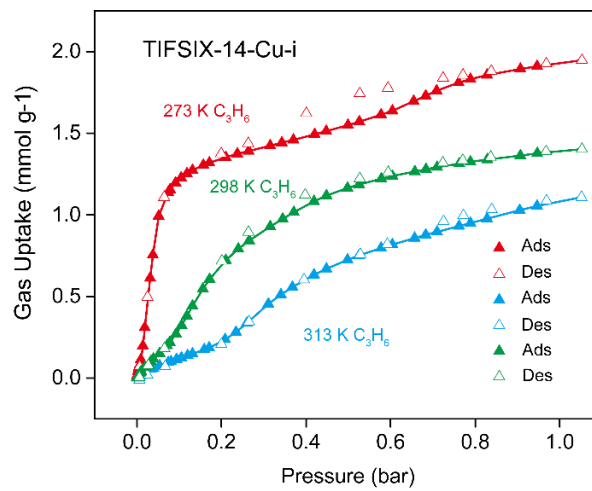
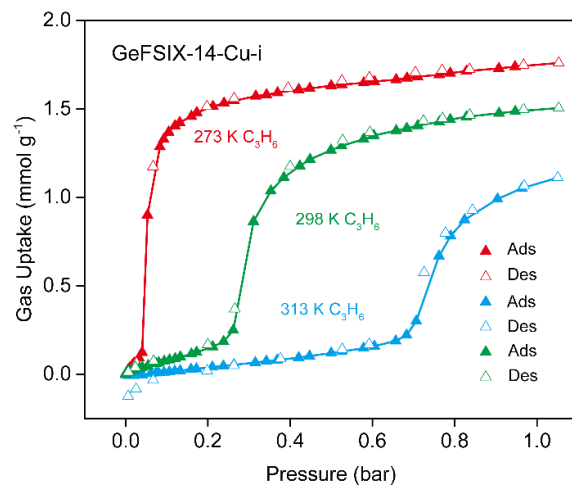
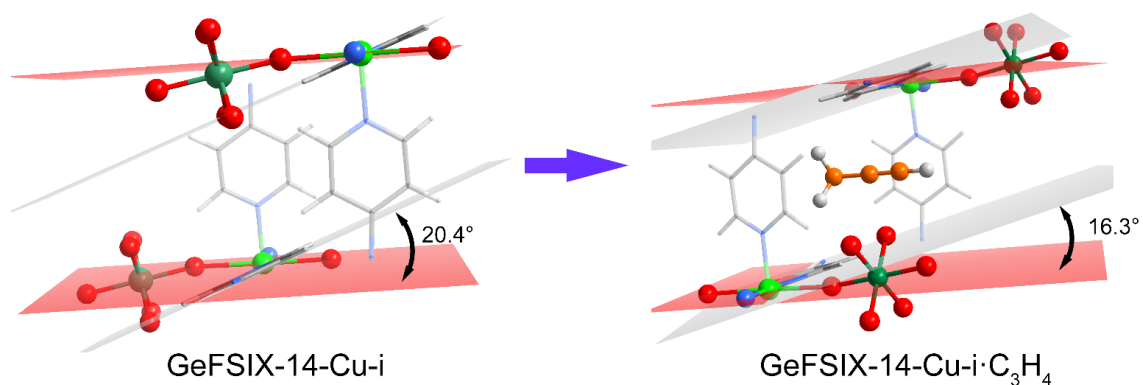


Figure S7. The adsorption isotherms of  $C_3H_6$  on TIFSIX-14-Cu-i at temperature from 273 to 313 K.

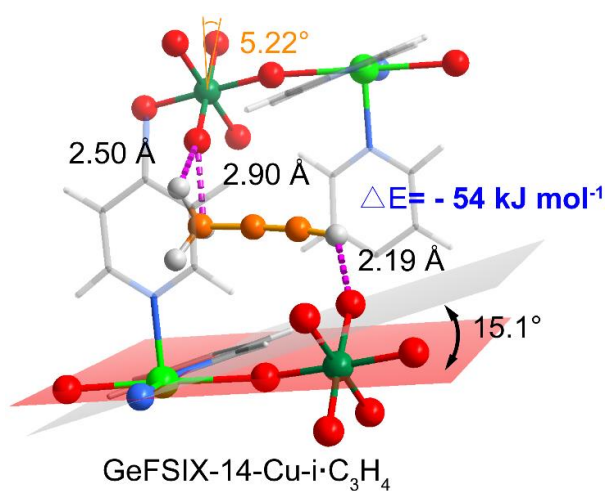


**Figure S8. The adsorption isotherms of C<sub>3</sub>H<sub>6</sub> on GeFSIX-14-Cu-i at temperature from 273 to 313 K.**





**Figure S9.** The DFT calculated configuration of bare GeFSIX-14-Cu-i and after the C<sub>3</sub>H<sub>4</sub> molecule entry. (Color code: F, red; Ge, green; C, gray-40%; H, gray-25%, Cu, bright green; N, light blue).



**Figure S10.** The DFT calculated configuration of GeFSIX-14-Cu-i with loaded C<sub>3</sub>H<sub>4</sub>. (Color code: F, red; Ge, green; C, gray-40%; H, gray-25%, Cu, bright green; N, light blue).

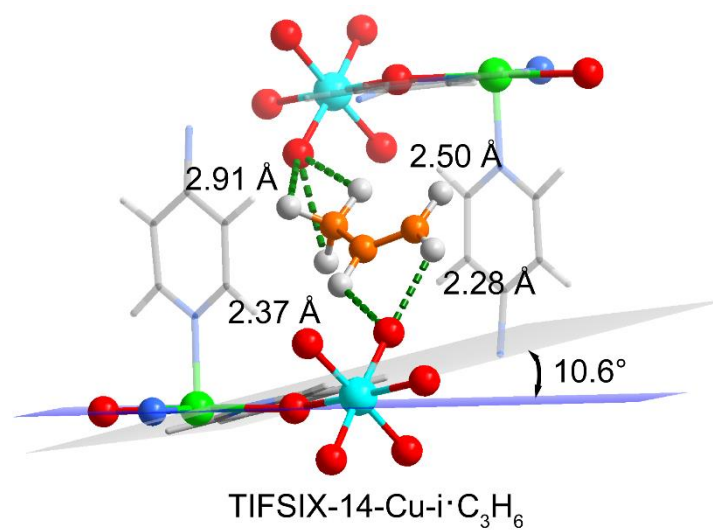


Figure S11. The DFT calculated configuration of TIFSIX-14-Cu-i with loaded C<sub>3</sub>H<sub>6</sub>. (Color code: F, red; Ti, turquoise; C, gray-40%; H, gray-25%, Cu, bright green; N, light blue).

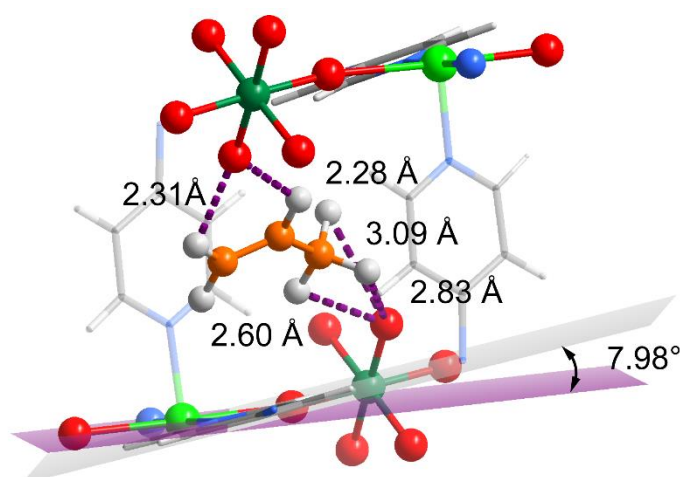


Figure S12. The DFT calculated configuration of GeFSIX-14-Cu-i with loaded C<sub>3</sub>H<sub>6</sub>. (Color code: F, red; Ge, green; C, gray-40%; H, gray-25%, Cu, bright green; N, light blue).

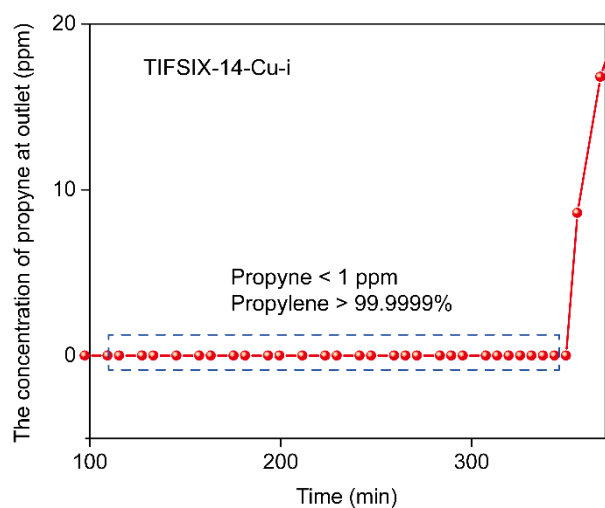


Figure S13. The concentration of  $C_3H_4$  in the outlet gas of TIFSIX-14-Cu-i.

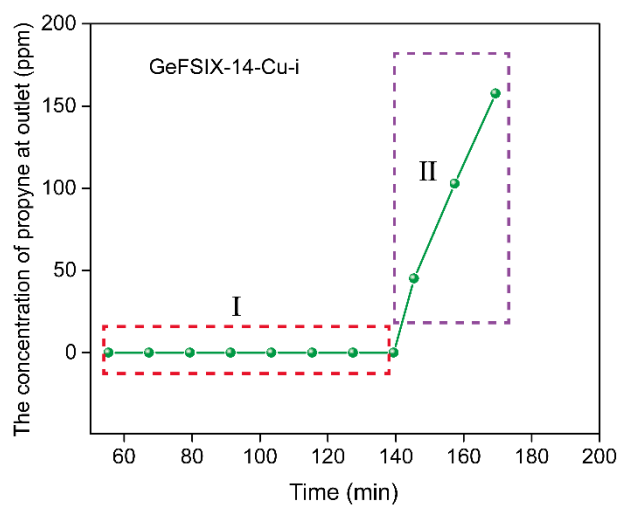


Figure S14. The concentration of  $C_3H_4$  in the outlet gas of GeFSIX-14-Cu-i.

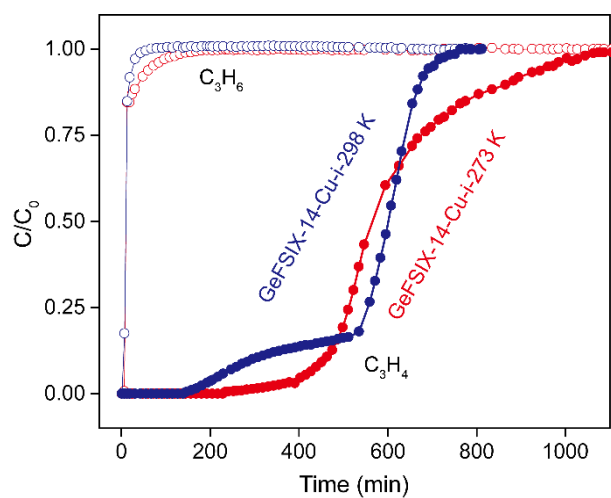


Figure S15. The  $C_3H_4/C_3H_6$  (1/99) breakthrough experiment results of GeFSIX-14-Cu-i at the temperature of 273 K and 298 K.

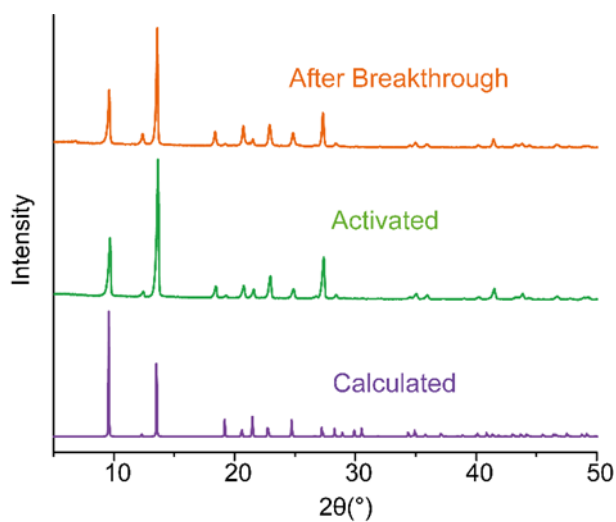


Figure S16. The XRD results of TIFSIX-14-Cu-i sample after breakthrough experiment.