Supplementary Information

“Supramolecular Cu(II)–dipyridyl frameworks featuring weakly coordinating dodecaborate dianions for selective gas separation”

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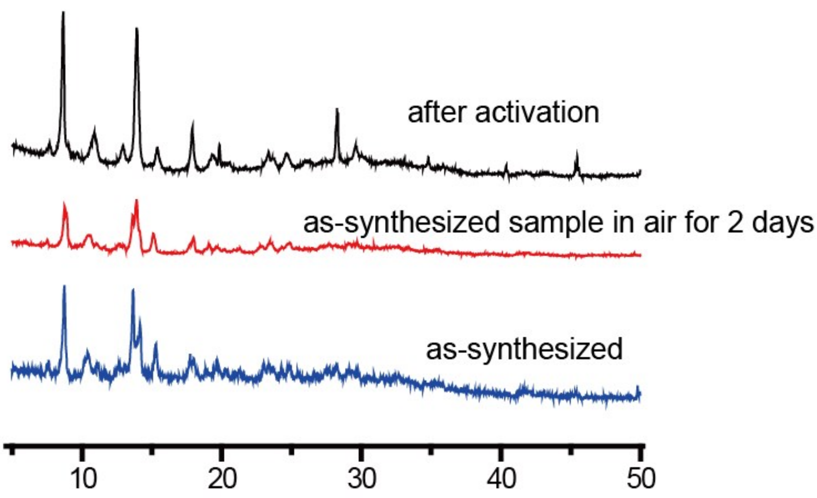

Fig. S1 PXRD patterns of BSF-74b. It is different from the predicted PXRD patterns from the crystal structure of BSF-74.

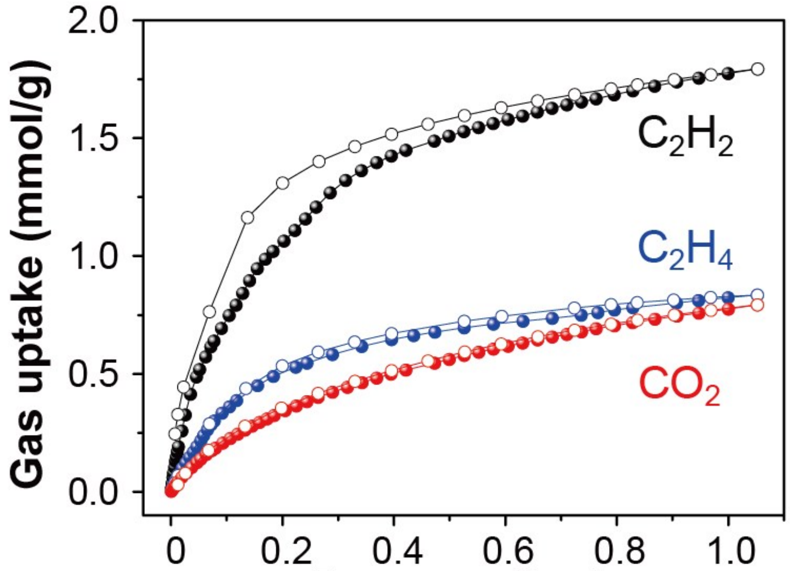

Fig. S2 C_2H_2, CO_2 and C_2H_4 adsorption and desorption isotherms on activated BSF-74b at 273 K

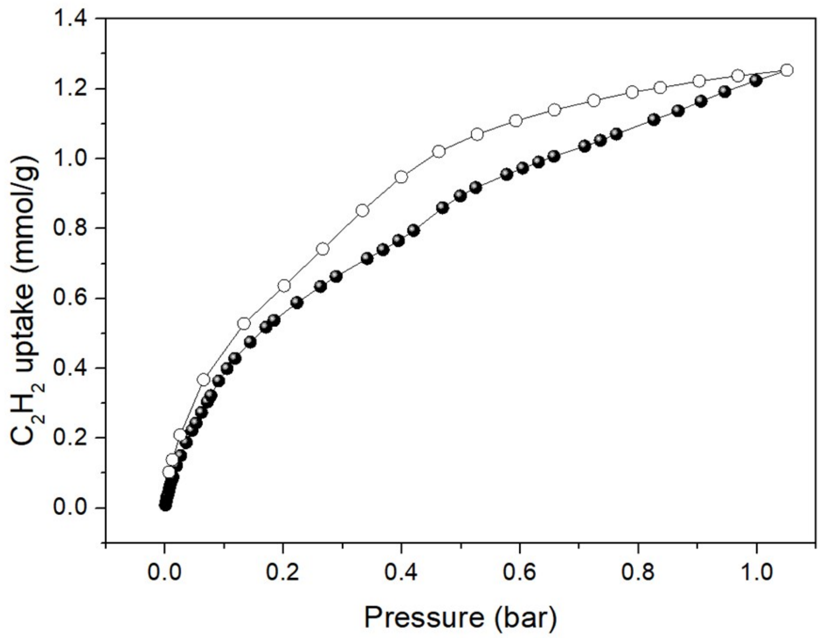

Fig. S3 C_2H_2 adsorption and desorption isotherms on activated BSF-74b at 298 K after exposure in humid air for 1 day

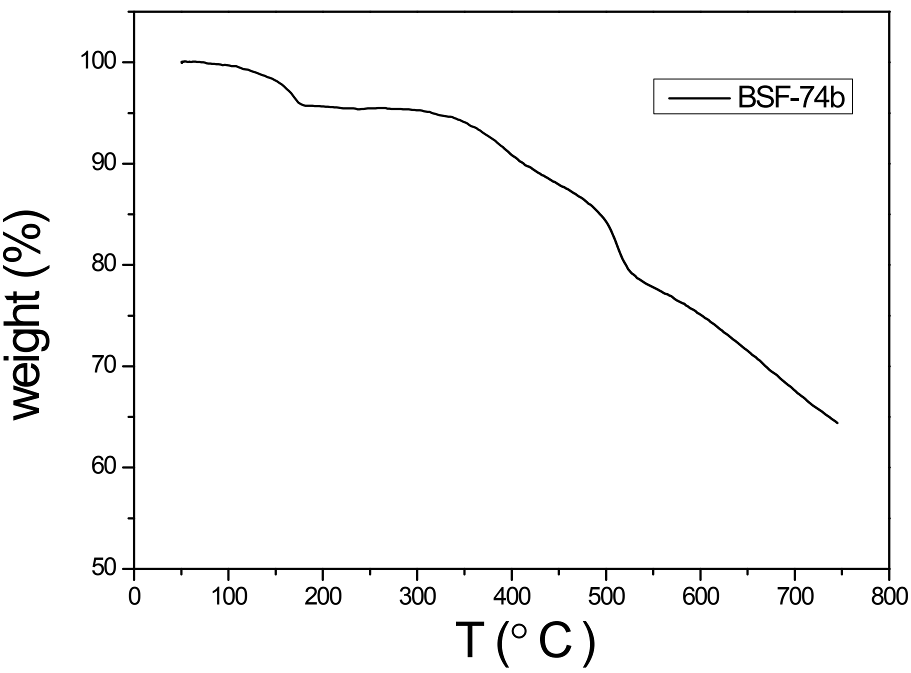

Fig. S4 TGA curves of BSF-74b

Table S1 Summary of gas adsorption properties and C_2H_2/CO_2 selectivities of the reported MOFs.[a]

Materials	C_2H_2 (mmol/g)	CO_2 (mmol/g)	$V_{C_2H_2/CO_2}$	S	Ref
UTSA-300a	3.08	0.15	20.53	743	*J. Am. Chem. Soc.* **2017**, *139*, 8022-8028
Cu-CPAH	5.88	3.93	1.50	3.6	*ACS Appl. Mater. Inter.* **2020**, *12*, 5999-6006
ZJNU-13	5.29	3.92	1.35	5.6	*ACS Appl. Nano Mater.* **2020**, *3*, 2911-2919.
FeNi-M'MOF	4.29	2.72	1.58	24	*Angew. Chem.* **2020**, *59*, 4396-4400
JCM-1	3.35	1.7	1.97	13.7	*Angew. Chem.* **2018**, *57*, 7869-7873
SNNU-45	5.98	4.35	1.37	10.8	*Angew. Chem.* **2019**, *58*, 13590-13595
TIFSIX-2-Ni-i [b]	4.21	4.54	0.93	6.2	*Chem. Eng. J.* **2018**, *352*, 803-810
TIFSIX-2-Cu-i [b]	4.1	4.3	0.95	6.5	*Chem* **2016**, *1*, 753-765
NKMOF-1-Ni	2.72	2.28	1.19	25	*Angew. Chem.* **2018**, *130*, 11137-11141
ZJUT-2a	3.39	2.19	1.55	10	*Chem. Commun.* **2019**, *55*, 11354-11357
FJU-89a	4.53	2.73	1.66	4.3	*ACS Appl. Mater. Inter.* **2018**, *10*, 30912-30918
TCuI	2.2	1.6	1.38	5.3	*Chem. Eur. J.* **2020**, *26*, 43923-4929.
TCuBr	2.8	2	1.40	9.5	
TCuCl	3	2	1.50	16.9	

MUF-17 [c]	2.73	2.28	1.20	6.01	*Chem. Mater.* **2019**, *31*, 4919-4926
JXNU-5a	2.5	1.55	1.61	5	*Inorg. Chem.* **2019**, *58*, 5089-5095
SNNU-150-Al	4.33	1.98	2.19	7.27	*Inorg. Chem.* **2020**, *59*, 4825-4834
SNNU-150-Ga	1.78	1.19	1.50	4.93	
SNNU-150-In	1.56	1.03	1.51	5.57	
UTSA-50a [d]	5.08	2.88	1.76	13.3	*J. Mater. Chem. A* **2013**, *1*, 77-81.
UTSA-74a [d]	4.83	3.17	1.52	9	*J. Am. Chem. Soc.* **2016**, *138*, 5678-5684.
FJU-90	8.03	4.6	1.75	4.3	*J. Am. Chem. Soc.* **2019**, *141*, 4130-4136.
SNNU-65-Cu-Sc	7.99	3.14	2.54	13.5	*Chem. Commun.* **2018**, *54*, 2012-2015.
SNNU-65-Cu-Fe	7.25	2.9	2.50	6.7	
SNNU-65-Cu-Ga	6.32	2.62	2.41	18.7	
SNNU-65-Cu-In	6.84	2.5	2.74	7	
FJU-6-TATB [d]	4.91	2.59	1.90	3.1	*J. Am. Chem. Soc.* **2020**, *142*, 9258-9266
UPC-110	3.28	1.08	3.04	5.1	*ACS Sustainable Chem. Eng.* **2019**, *7*, 2134-2140
CPM-107op	4.35	1.56	2.79	5.7	*Angew. Chem.* **2019**, *58*, 11757-11762
PCM-48 [d]	1.14	0.97	1.18	4.3	*Chem. Commun.* **2018**, *54*, 9937-9940.
$[Ni_3(HCOO)_6]$	2.38	1.73	1.38	22	*ACS Sustainable Chem. Eng.* **2019**, *7*, 1667-

					1672
UTSA-83	0.53	0.17	3.12	6.2	*Inorg. Chim. Acta* **2019**, *495*, 118938
BSF-1	2.35	1.77	1.33	3.4	
BSF-2	1.85	1.33	1.39	5.1	*Angew. Chem.* **2020**, *59*, 17664-17669
BSF-3	3.65	2.11	1.73	16.3	
HOF-3a [d]	2.1	0.94	2.23	21	*Angew. Chem.* **2015**, *54*, 574-577
DICRO-4-Ni-i	1.92	1.03	1.86	13.9	*ACS Appl. Mater. Inter.* **2017**, *9*, 33395-33400
ECUT-HOF-30 [d]	1.95	0.4	4.88	9	*Chem. Eng. J.* **2019**, 123117
BSF-74b	1.58	0.5	3.16	9.7	*This work*

[a] all conditions are under 298 K and 1 bar, equimolar selectivity unless stated; [b] C_2H_2/CO_2 = 2:1; [c] 293 K; [d] 296 K.

Table S2 Summary of gas adsorption properties and C_2H_2/C_2H_4 selectivities of the reported MOFs.[a]

Materials	C_2H_2 (mmol/g)	C_2H_4 (mmol/g)	$V_{C_2H_2/C_2H_4}$	S	Ref
M'-MOF-3a[b]	1.88	0.4	4.73	24.03	*Nat Commun* **2011**, *2*, 204
UTSA-100a[b]	4.27	1.66	2.57	10.7	*Nat. Commun* **2015**, *6*, 7328
NOTT-300[c]	6.34	4.28	1.48	2.2	*Nat. Chem.* **2014**, *7*, 121–129
MOF-74-Co[b]	8.17	7.02	1.16	1.70	*Energ. Environ. Sci.* **2012**, *5*, 9107
JCM-1	3.35	1.56	2.15	13.2	*Angew. Chem. Int. Ed.* **2018**, *57*, 7869–7873
FJU-22a[b]	5.13	3.83	1.34		*Chem. - Eur. J.* **2016**, *22*, 5676–5683
NKMOF-1-Ni	2.72	2.11	1.29	~20[d]	*Angew. Chem. Int. Ed.* **2018**,

					57, 10971–10975
PCP-33	5.44	3.88	1.40	~1.2	*Inorg. Chem.* **2015**, *54*, 4279–4284.
SIFSIX-1-Cu	8.5	3.67	2.07	10.6[e]	
SIFSIX-2-Cu-i	4.02	2.19	1.84	44.8[e]	*Science* **2016**, *353*, 141–144.
SIFSIX-3-Zn	3.64	2.24	1.62	8.8[e]	
UTSA-200a	3.65	0.63	5.79	>6k[e]	*Adv. Mater.* **2017**, 29, 1704210
UTSA-300a	3.08	0.04	74.9	$>10^6$	*J. Am. Chem. Soc.* **2017**, *139*, 8022–8028
MUF-17[c]	2.74	1.96	1.40	6.01	*Chem. Mater.* **2019**, *31*, 4919–4926
BSF-1	2.35	1.63	1.44	2.4	
BSF-2	1.85	1.32	1.40	2.9	*Angew. Chem.* **2020**, *59*, 17664–17669
BSF-3	3.59	2.37	1.51	8.0	
BSF-3-Co	3.85	2.51	1.53	10.2	
BSF-74b	1.58	0.68	2.21	5.3	This work

[a] all conditions are under 298 K and1 bar, equimolar selectivity unless stated; [b]296 K； [c] 293 K; [d] selectivity for C_2H_2/C_2H_4 (1/9); [e] selectivity for C_2H_2/C_2H_4 (1/99).

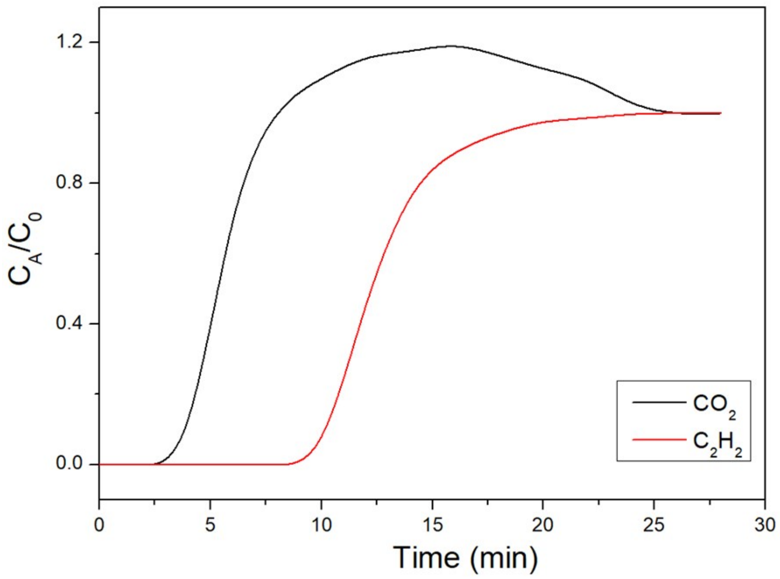

Fig. S5 Experimental column breakthrough curves for equimolar C_2H_2/CO_2 mixtures (298 K, 1 bar, gas flow: 1 mL/min) in an adsorber bed packed with BSF-74b

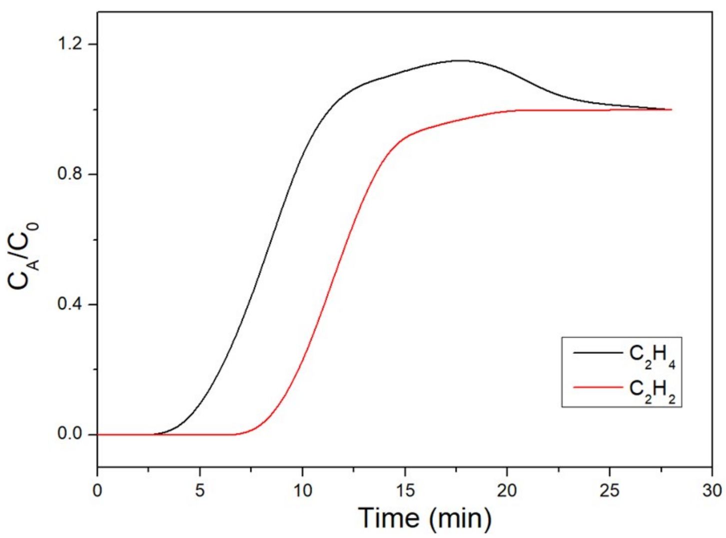

Fig. S6 Experimental column breakthrough curves for equimolar

C_2H_2/C_2H_4mixtures (298 K, 1 bar, gas flow: 1 mL/min) in an

adsorber bed packed with BSF-74b