Electronic Supplementary Material (ESI) for Dalton Transactions.

Modulating the basicity of Zn-MOF-74 via cation exchange with calcium-ions

Zhuxiu Zhang,[a] Yue Xiao,[a] Mifen Cui,[a] Jihai Tang,*[ab] Zhaoyang Fei,[ab] Qing Liu,[a] Xian Chen[a] and Xu Qiao*[a]

[a]State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, No. 30 Puzhunan Road, Nanjing 211816, China.

[b]Jiangsu National Synergetic Innovation Centre for Advanced Materials (SICAM), No. 5 Xinmofan Road, Nanjing 210009, China.

Material

All reagents and solvents were purchased from commercial sources and used without further purification.

Synthesis of Zn-MOF-74

1.00 g of 2,5-dihydroxyterephthalic acid (DHTA) and 4.52 g of $Zn(NO_3)_2$ $4H_2O$ were dissolved in 100 mL of DMF by ultrasound applied for 10 min. Then 5 mL of water was added and the solution was decanted into 4 100 mL vials, which were capped tightly and placed in a 110℃ oven for 21.5 h. After cooling down to room temperature, the yellow crystals were harvested and washed with methanol, then immersed in methanol. The products were combined and exchanged into fresh methanol daily for 3 days. They were then evacuated to dryness and heated under vacuum at 150 °C, after 10 hours at 150 °C, the heat was increased to 265 °C for another 10h. The sample was cooled to room temperature and stored.

Post-synthetic cation exchange of Zn-MOF-74

Zn-MOF-74 (60 mg) and calcium chloride (263 mg) were immersed in 10 mL DMF and dispersed via bath sonication. This mixture was placed at 25/50/75/100 °C for 1/3/5/7 d. After cooling down to room temperature the supernatant was collected and the precipitate was washed three times by redispersion in 10 mL DMF, followed by re-collection via centrifugation. The product was then washed a further three times with 10 mL portions of MeOH by the same process daily for 3 days. The final solid product was collected by centrifugation and evacuated to dryness and heated under vacuum at 150 °C for 10h. Ni/Zn-MOF-74 was synthesized via a similar synthetic procedure using nickel chloride hexahydrate as the metal source.

Characterizations

N_2 isotherms and pore size distribution were measured with a Micromeritics 3 Flex instrument. Measurements were performed at 77 K with the temperature held constant

with a liquid nitrogen bath. Zn and Ca molar ratios were determined by the inductively coupled plasma atomic emission spectrometer (ICP-AES) method on a Jarrell-Ash 1100 instrument. Thermal gravimetric analysis (TGA) was performed on Mettler Toledo TGA/DSC at 10 °C/min^{-1} under O_2 and N_2 with a flow rate of 40 mL/min, respectively. X-ray photoelectron spectroscopy (XPS) measurement was performed using a PHI 5000 VersaProbe spectrometer equipped with a monochromatic Al Kα anode. The charging e□ects were corrected by using C 1s band at the binding energy of 284.8 eV. Temperature programmed desorption of CO_2 (CO_2-TPD) experiments were conducted on a Micromeritics AutoChem 2920 apparatus. The sample was activated at 200 ℃ for 2 h prior to the adsorption of CO_2 (99.999%) at room temperature. After the physical adsorbed CO_2 was purged by a He flow (99.999%) at room temperature, the sample was heated to 400 ℃ at the rate of 5 ℃·min^{-1}, and the CO_2 liberated was detected by TCD.

Knoevenagel Condensation Reaction

The catalytic performance of Zn-MOF-74, Ni/Zn-MOF-74 and Ca/Zn-MOF-74 was evaluated by Knoevenagel condensation reaction. Before using, the catalysts are activated at 250 °C for 10 hours. Catalyst (50 mg) and toluene (2 mL) was placed in a 10 mL two-necked glass flask containing a water-cooled condenser. The equimolar quantities of malononitrile (1 mmol) and other six benzaldehyde derivatives were added to the flask subsequently. After the reaction mixtures were stirred at 70 °C for 12 hours, the product was cooled to room temperature and the n-dodecane (0.5 g) as an internal standard was injected. A centrifuge separates the supernatant, which was tested by means of a gas chromatograph (GC, SP-6800A) equipped with a capillary 0.32 mm × 30 m × 0.25 μm SE-54 column and a flame ionization detector (FID).

X-ray Structure Determination

Powder X-ray diffraction (PXRD) patterns were recorded on SmartLab X-ray diffractionmeter (Rigaku, Japan) using Cu Kα radiation as X-ray source. Measurements were made over a range of $3° < 2\theta < 50°$ in 0.02° steps at a scanning rate of 10 ℃/min.

The tube voltage and current were 40 kV and 40 mA, respectively. The crystal structure of Ca/Zn-MOF-74 was determined by using *TOPAS*[1] program for the indexing and the Rietveld refinement. The crystal structure of the Zn-MOF-74 was used as starting model for the Rietveld refinement. The Ca atoms were refined at the same position as Zn atoms with 1/3 occupancies based on the result from ICP-AES. Other atoms were freely refined with one uniform temperature factor.

(1) Coelho Software, 4.2; Topas Academics, 2007.

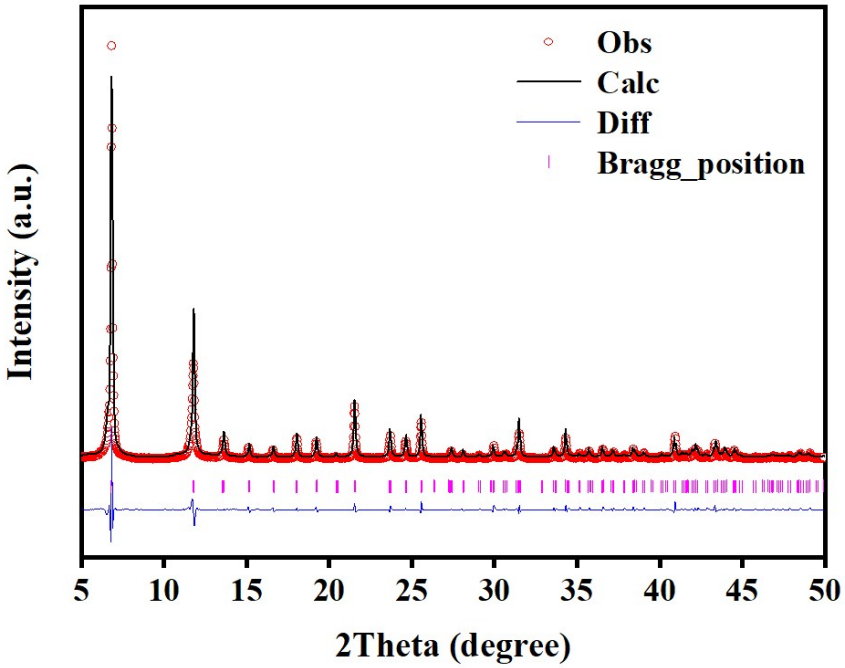

Figure S1. Rietveld plot of Ca/Zn-MOF-74 (75℃).

Table S1. Structure Data of Zn-MOF-74 and Ca/Zn-MOF-74

compound	Zn-MOF-74	Ca/Zn-MOF-74
formula		
crystal system	trigonal	trigonal
space group	$R\bar{3}$	$R\bar{3}$
a (Å)	25.9322(15)	26.0556(27)
b (Å)	25.9322(15)	26.0556(27)
c (Å)	6.8365(4)	6.8505(8)
V (Å^3)	3981.47(40)	4027.68(62)

R_p (%)	—	7.8
R_{wp} (%)	—	11.2
R_{exp} (%)	—	4.18

Table S2. Atomic coordinates for Ca/Zn-MOF-74

Atom	S.O.F.	x/a	y/b	z/c
Zn1	0.67	0.38659	0.3511	0.14623
Ca1	0.33	0.38659	0.3511	0.14623
O1		0.3212	0.29406	0.3566
O2		0.30167	0.22886	0.5956
O3		0.35522	0.27349	-0.0007
C1		0.316	0.24606	0.4216
C2		0.32706	0.20744	0.2846
C3		0.34369	0.22211	0.0857
C4		0.34884	0.18004	-0.0259
H4		0.3592	0.1886	-0.16
O11		0.45785	0.34629	0.2783
N11		0.5092	0.3533	0.5524
C11	0.76	0.4609	0.333	0.4466
C21	0.7	0.5664	0.4013	0.4692
C31	0.76	0.5081	0.3362	0.7586
C11	0.24	0.519	0.381	0.324
C21	0.24	0.4566	0.2975	0.695
C31	0.24	0.544	0.382	0.741
O12	0.24	0.6313	0.4024	0.325
O22	0.5	2/3	1/3	0.61
O33	0.5	2/3	1/3	0.41667

Table S2. Representative Bond distances of Ca/Zn-MOF-74

Atom1	Atom2	Length (Å)
Zn/Ca	O1	2.1578(3)
Zn/Ca	O3	2.0291(4)
Zn/Ca	O11	2.1248(6)
Zn/Ca	O1	2.1935(4)
Zn/Ca	O2	2.0347(4)
Zn/Ca	O3	2.0376(4)

Table S2. Representative Bond distances of Zn-MOF-74

Atom1	Atom2	Length (Å)
Zn	O1	2.150(2)
Zn	O3	2.021(3)
Zn	O11	2.116(4)
Zn	O1	2.184(4)
Zn	O2	2.028(3)
Zn	O3	2.030(4)

Quantitative Analysis of Thermal Gravimetric Curve

Aiming to verify the accuracy of the exchange rate calculated by ICP-AES, quantitative analysis of thermal gravimetric curve (under O_2 flow) was carried out. According to the molecular formula of MOF-74 ($Zn_2C_8H_2O_6$), the reaction for the complete oxidation of Ca/Zn-MOF-74 is shown below:

$$2Zn_{2-x}Ca_xC_8H_2O_6\,(s) + 13O_2\,(g) \longrightarrow 2Zn_{2-x}Ca_xO_2 + 2H_2O\,(g) + 16CO_2\,(g)$$

Where x represents the quantity of calcium ions in the sample.

The molecular weights of $Zn_2C_8H_2O_6$ and ZnO are 324.82 and 81.38 g mol^{-1}, respectively. According the weight of ZnO after complete oxidation, the ideal weight of parent Zn-MOF-74 ($Zn_2C_8H_2O_6$) could be calculated according to the following equation:

$$W_{ideal} = \frac{M_{MOF}}{M_{oxide}} \times W_{end} \quad (1)$$

Where M_{MOF} is the molecular weight of MOF-74; M_{oxide} is the molecular weight of equivalent MOF-74 derived metal oxide; W_{end} is the end weight percentage of TGA curve, which is considered as the residual weight percentage of metal oxide; Note: For Ca/Zn-MOF-74, M_{MOF} and M_{oxide} are calculated according to the exchange ratio calculated by ICP-AES.

As shown in Fig. S2, the ideal weight percent of $Zn_2C_8H_2O_6$ (83.05%) is calculated from the weight percent of residual ZnO (41.61%), which is consistent with the actual value of the TGA (82.84%). The same method is used to analyze Ca/Zn-MOF-74 (25-100 ℃) (Fig. S2-S5). For Ca/Zn-MOF-74 (25-75 ℃), the calculated weight percentages of bimetallic MOFs are consistent with the actual values in TGA curves. This can prove that the molar ratios of Ca:Zn measured by ICP-AES are accurate and there is no Ca^{2+} on the surface or channel of the framework. It is worth noting that for the sample exchanged at 100 ℃, the calculated weight (%) of ideal Ca/Zn-MOF-74 ($Zn_{0.65}Ca_{1.35}C_8H_2O_6$) is much higher than the actual value (Fig. S5). Combined with the results of N_2 sorption and SEM, there is no doubt that cation exchange under 100 ℃ will collapse the structure of Zn-MOF-74.

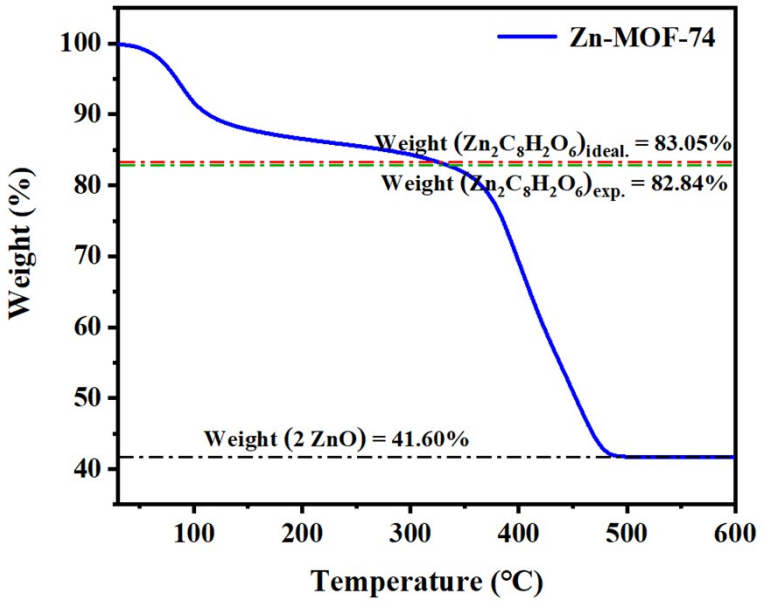

Fig S2. TGA curve of Zn-MOF-74 in O_2 atmosphere.

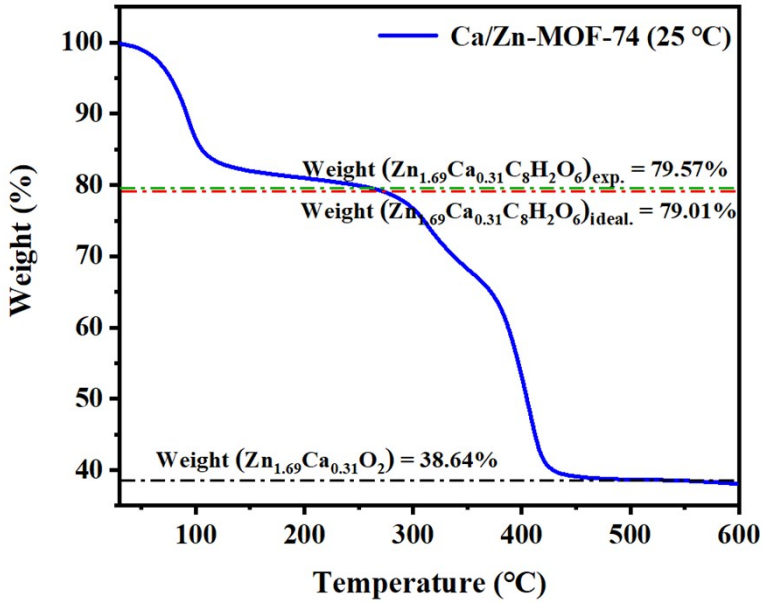

Fig S3. TGA curve of Zn-MOF-74 (25 ℃) in O_2 atmosphere.

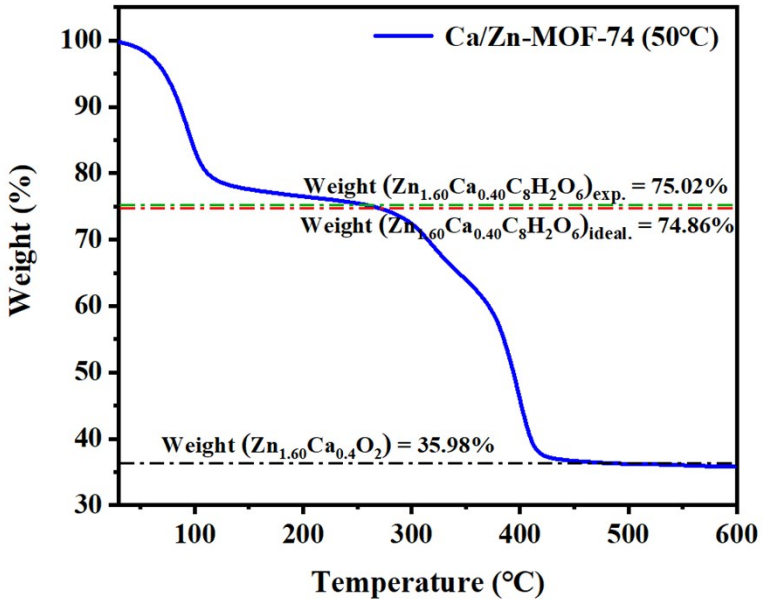

Fig S4. TGA curve of Zn-MOF-74 (50 ℃) in O_2 atmosphere.

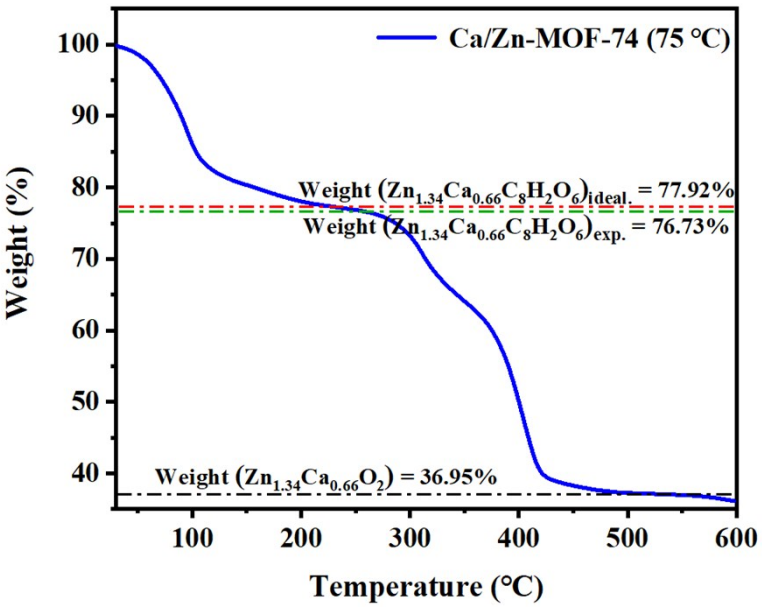

Fig S5. TGA curve of Zn-MOF-74 (75 ℃) in O_2 atmosphere.

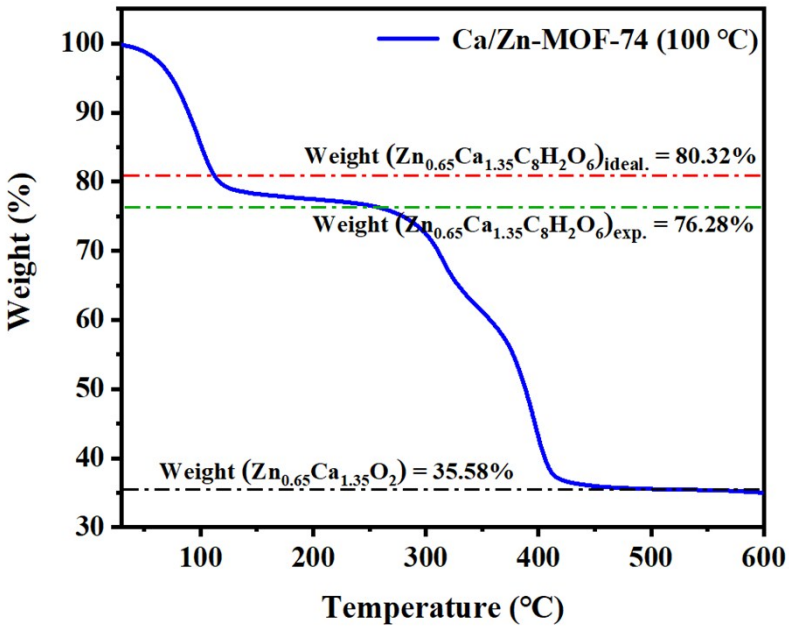

Fig S6. TGA curve of Zn-MOF-74 (100 ℃) in O_2 atmosphere.

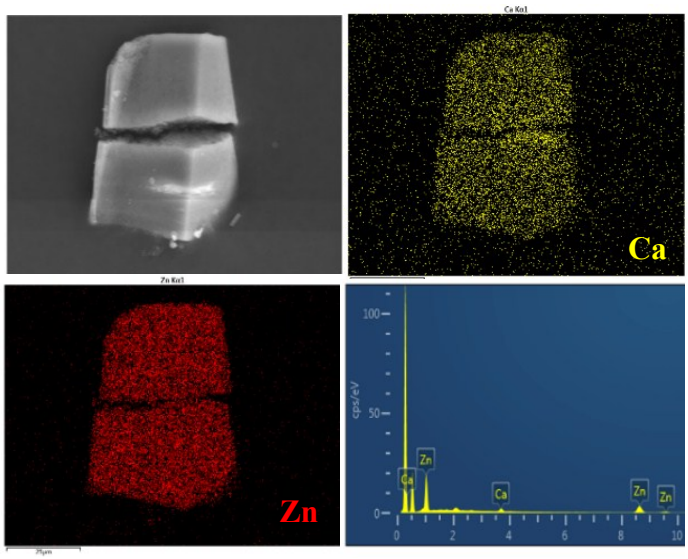

Fig S7. elemental mapping and EDX spectrum of Ca/Zn-MOF-74.

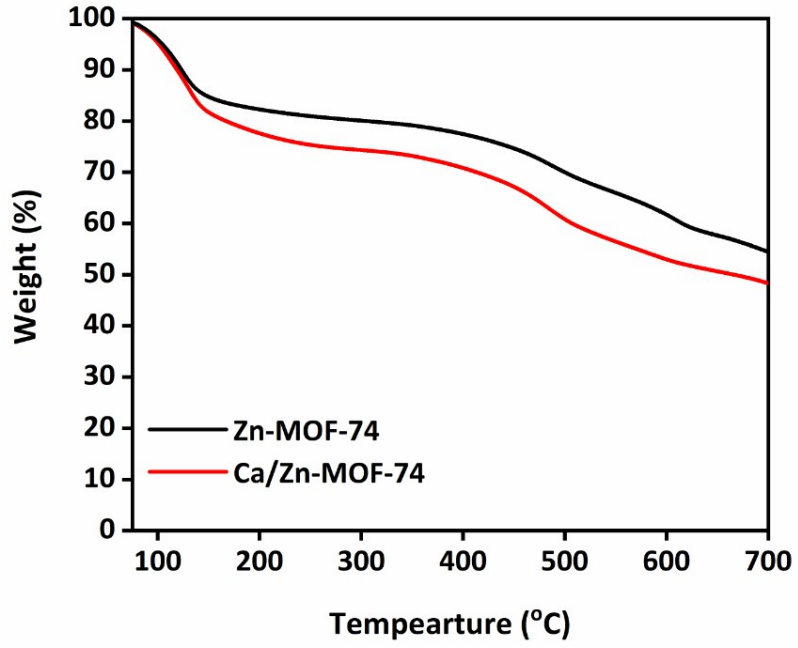

Fig S8. TGA curves of Zn-MOF-74 and Zn/Ca-MOF-74 in N_2 atmosphere.

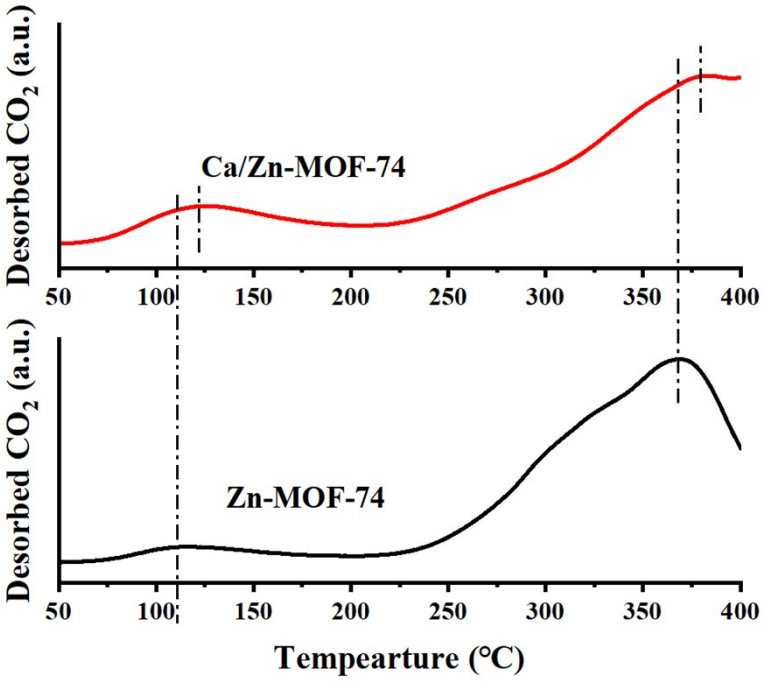

Fig S9. CO_2-TPD profiles of Zn-MOF-74 and Ca/Zn -MOF-74.

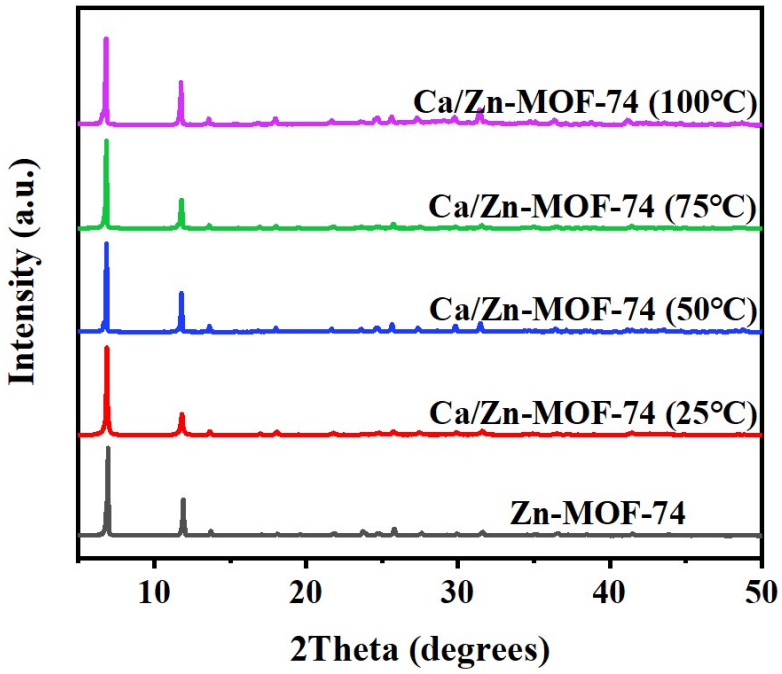

Fig S10. PXRD patterns of Zn-MOF-74 and Ca/Zn-MOF-74 exchanged at 25, 50, 75 and 100℃.

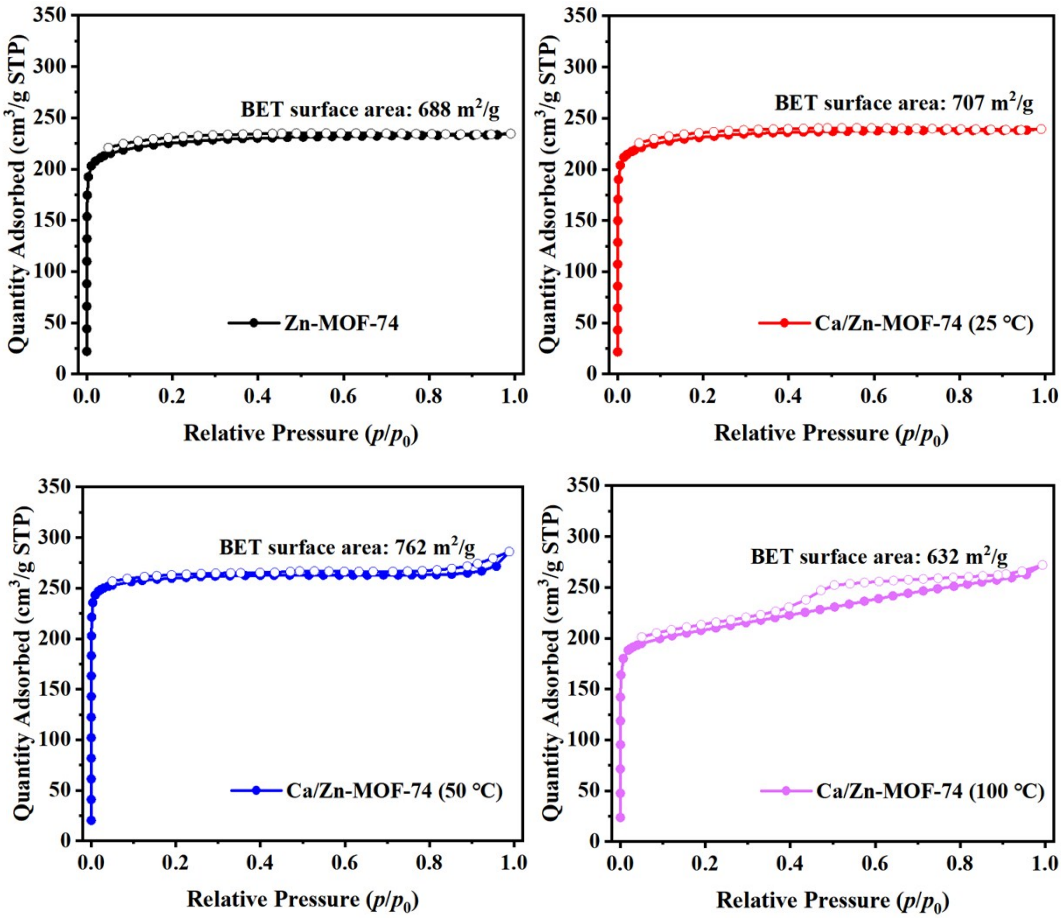

Fig S11. N_2 sorption isotherms of Zn-MOF-74 and Ca/Zn-MOF-74 exchanged at 25, 50, and 100℃.