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# Supporting Information

# A Zirconium-based Microporous Metal-Organic Framework for Molecular Sieving CO₂ Separation

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Materials and Methods

All chemical reagents, solvents and gases were commercially available and directly used without further purification unless further noticed.

*Powder X-ray diffraction analysis*: Powder X-ray diffraction patterns were collected by a Panalytical X'Pert powder diffractometer equipped with a Cu sealed tube ($\lambda$ = 1.54184 Å) at 40 kV and 40 mA over the $2\theta$ range of 5−30°.

**Scanning Electron microscopy (SEM)** images were obtained using Hitachi S5500 device at an accelerating voltage of 30 kV.

**Thermogravimetric analyses (TGA)** were performed on a TGA/DCS system (Mettler-Toledo, Columbus, OH) with STARe software. Samples were heated from 25 to 800 °C at a rate of 5 °C/min under $N_2$ with flow rate 20 mL/min.

**Synthesis of Zr-FA**

$ZrCl_4$ (58 mg, 0.25 mmol and 2,3-Dimethylmaleic anhydride (40 mg, 0.25 mmol) was added into a 21 mL glass vial, which was charged with. 4 mL N,N'-dimethylformamide (4 mL; > 99.8%) and formic acid (1.5 mL) were introduced. Single crystals were formed after following heating at 100 °C for 72 h. While powdered **Zr-FA** was synthesized through directly adding $ZrCl_4$ (58 mg, 0.25 mmol), DMF (4 mL) and formic acid (2.5 mL) were introduced. After sonication for 10 min, the obtained clear solution was heated at 100 °C for 24 h to obtain a microcrystalline powder of **Zr-FA** samples.

**Gas Sorption Measurements**

The gas sorption isotherms were collected on an automatic volumetric adsorption apparatus (Micromeritics ASAP 2020 surface area analyzer). Prior to the gas sorption analyses, the samples were washed with water several times and activated under dynamic vacuum overnight

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at 60 °C (333K) for 24h. The sorption measurements of **Zr-FA** were kept at 273, and 298 K by using ice–water bath, and water bath in an air-conditioned laboratory (25 °C), respectively.

***Isosteric heat of adsorption:*** The binding energy of $CO_2$ is reflected in the isosteric heat of adsorption, $Q_{st}$. The virial equation was employed to calculate the enthalpies of $CO_2$ adsorption:[1]

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

where P is pressure (mmHg), N is the adsorbed quantity (mmol g$^{-1}$), T is the temperature (K), $a_i$ and $b_i$ are virial coefficients, R is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), and m and n determine the number of coefficients required to adequately describe the isotherm. Isotherms of **Zr-FA** for $CO_2$ reported here are estimated using pure-component collected at 273 and 298 K.

**Calculation Details:**

All the calculations were performed in the Material Studio 2019 package (BIOVIA, Dassault Systèmes, Materials Studio 2019, Dassault Systems, San Diego, 2018.). The single crystal structure of **Zr-FA** was taken as initial geometry for further computational calculations and considered as rigid in the simulations. The partial charge of framework was taken from Mulliken charge obtained from single point energy calculations using first-principle density funtional theory (DFT) in the CASTEP code, using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and on-the-fly generated ultrasoft

pseudopotentials. A cutoff energy of 450 eV and a $1 \times 1 \times 1$ $k$-point mesh were found to be enough for the total energy to converge within $1 \times 10^{-5}$ eV atom$^{-1}$. The simulated annealing (SA) calculations were performed to find the most energetically favorable binding site for $CO_2$ molecule, using universal forcefield. The interaction energy between gas and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. The equilibration steps and the production steps were set as $1 \times 10^6$ and $5 \times 10^6$, respectively, to ensure the equilibration. The cut-off radius was chosen as 15.5 Å for the LJ potential and the long-range electrostatic interactions were handled by the Ewald summation method, with a Buffer width of 0.5 Å and accuracy of $1 \times 10^{-5}$ kcal mol$^{-1}$.

**Ideal Absorbed Solution Theory (IAST) Calculation**

The adsorption selectivity for $CO_2/CH_4$ or $CO_2/N_2$ separation is defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

$q_1$ and $q_2$ are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures $p_1$ and $p_2$.

*Breakthrough separation experiments*: The breakthrough experiments were conducted in a dynamic gas breakthrough set-up. A stainless-steel column with inner dimensions of 4 mm and a length of 81 mm was used for sample packing. The activated sample (0.982 g **Zr-FA**) was then packed into the column. The flow and pressure of binary gas ($CO_2/N_2$ at 15/85, v/v, $CO_2/CH_4$ at 50/50, v/v) were controlled by using a pressure control valve and a mass flow controller. The outlet effluent from the column was continuously monitored by gas chromatography (GC-2014, Shimadzu) with a thermal conductivity detector. The column packed with activated sample was first purged with helium gas flow for 1 h at room temperature. The gas mixtures flow rate is 2 mL/min at 1 bar for $CO_2/CH_4$ at 50/50 (6 mL/min at 1 bar for

$CO_2/N_2$ at 15/85, v/v) during the breakthrough process. After the breakthrough experiment, the sample was regenerated with helium gas flow (80 mL/min) for about 50 min at 298 K.

**Table S1.** Physical properties of $CO_2$, $CH_4$ and $N_2$.[2]

| Compounds | Carbon dioxide ($CO_2$) | Methane ($CH_4$) | Nitrogen ($N_2$) |
|---|---|---|---|
| Polarizability ($cm^3$) | $29.11 \times 10^{25}$ | $25.93 \times 10^{25}$ | $17.40 \times 10^{25}$ |
| Kinetic Diameter (Å) | 3.30 | 3.76 | 3.64 |
| Boiling point (K) | 194.7 | 111.7 | 77.35 |
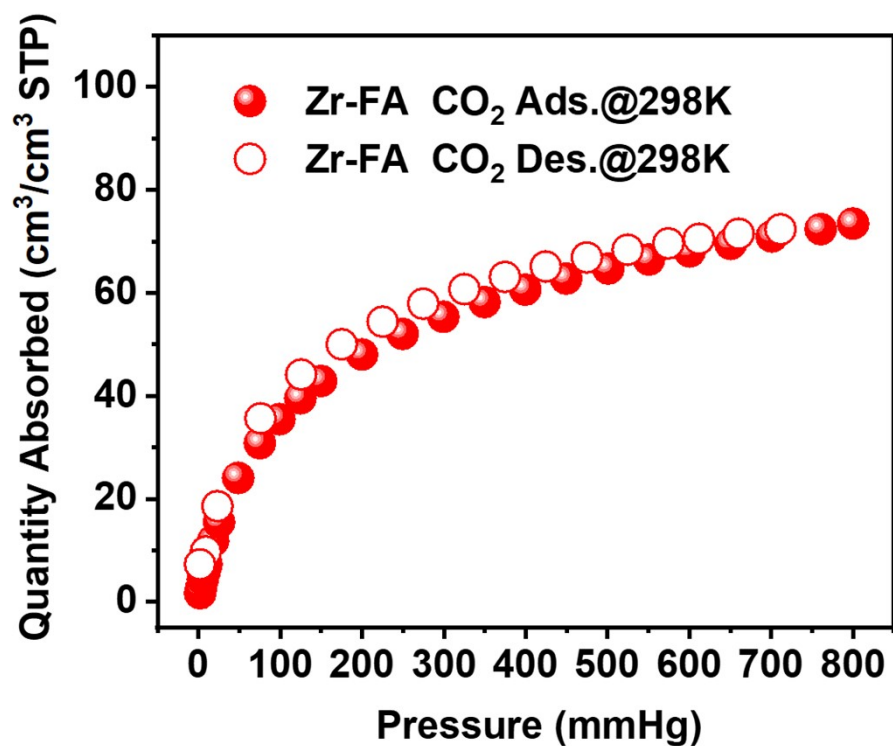
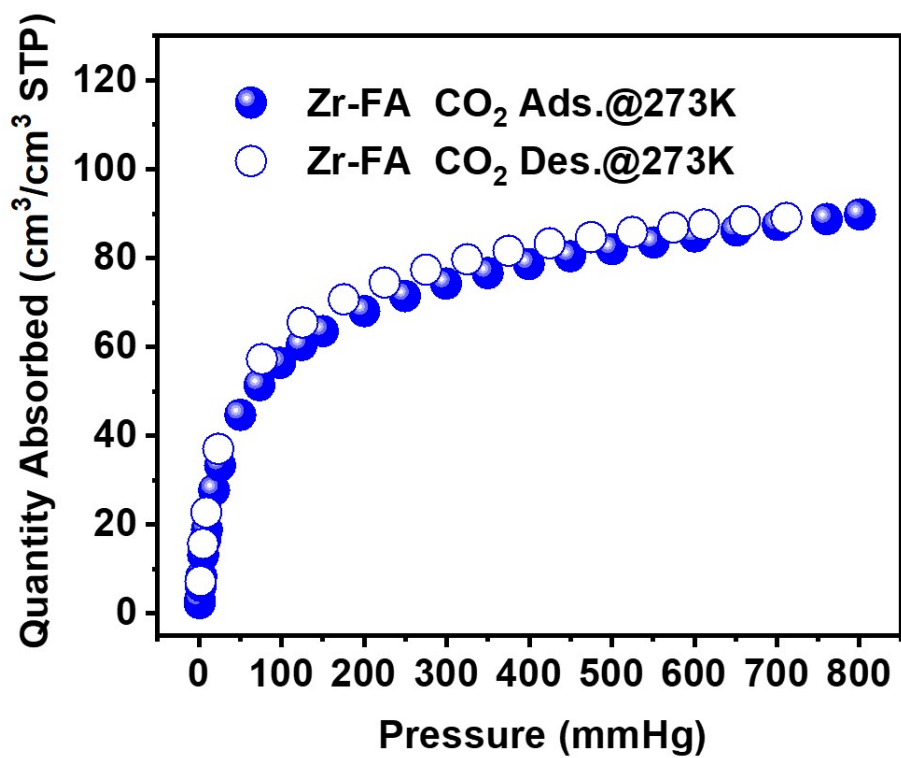**Fig. S1.** CO$_2$ sorption isotherms for **Zr-FA** at 298 K.



**Fig. S2.** CO$_2$ sorption isotherms for **Zr-FA** at 273 K.
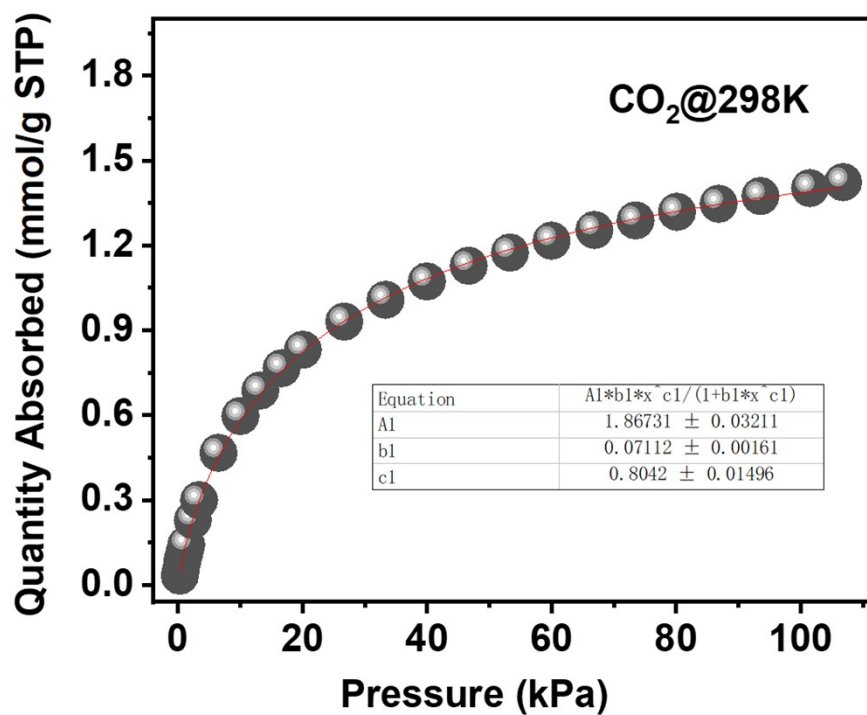
**Fig. S3.** The graphs of the single-site Langmuir-Freundlich equation fitting for CO$_2$ isotherms of **Zr-FA** at 298 K.
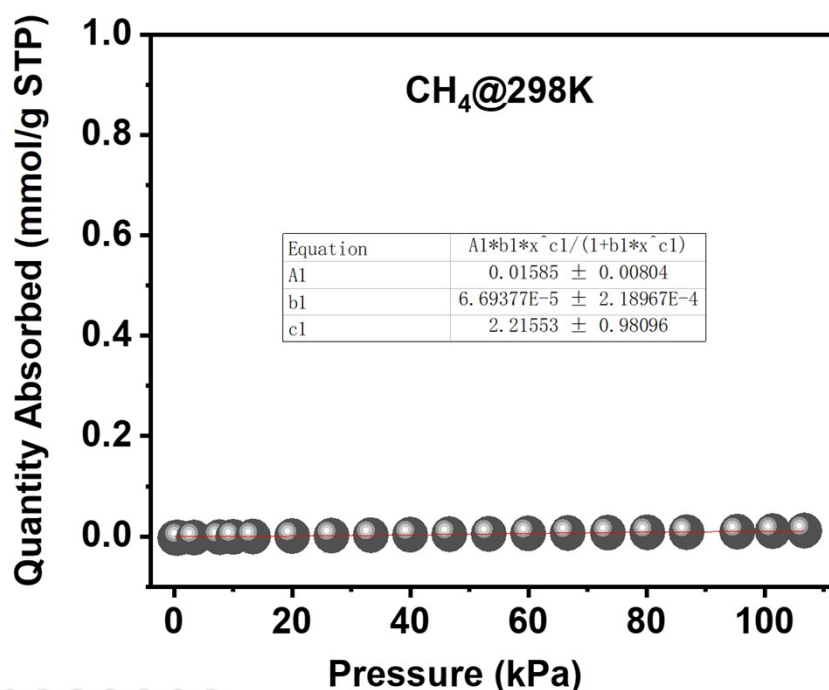


**Fig. S4.** The graphs of the single-site Langmuir-Freundlich equation fitting for CH$_4$ isotherm of **Zr-FA** at 298 K.
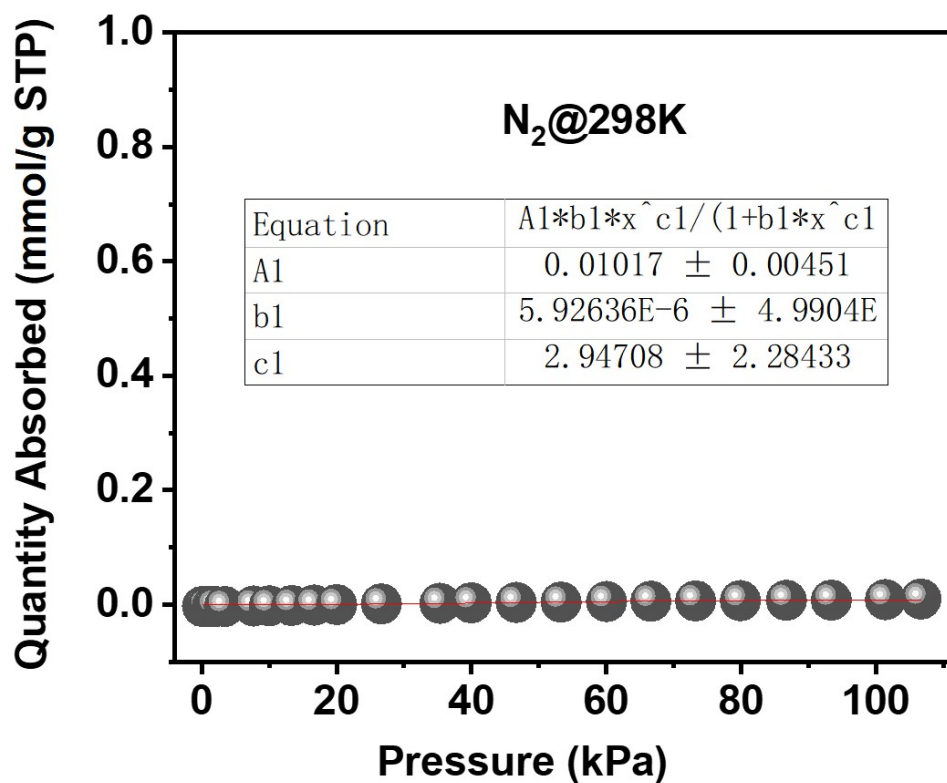
**Fig. S5.** The graphs of the single-site Langmuir-Freundlich equation fitting for
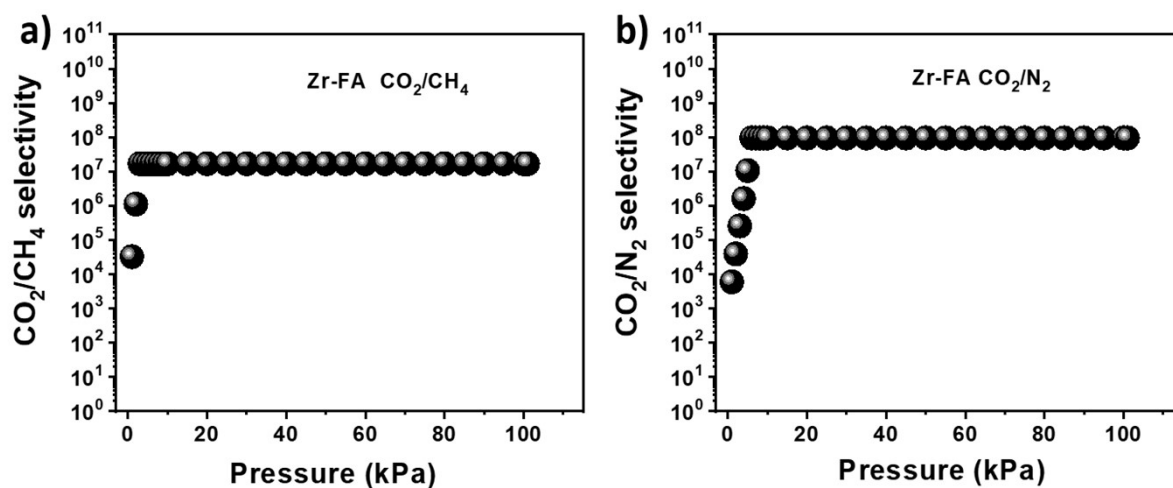
$N_2$ isotherm of **Zr-FA** at 298 K.



**Fig. S6. a)** IAST selectivity of **Zr-FA** for a) an equimolar $CO_2/CH_4$ mixture at 298 K; **b)**

$CO_2/N_2$ (15:85) mixture at 298 K.

The chart contains a legend:
- CO₂ at 298K
- CO₂ at 273K
- Virial Fitting

Y-axis: LnP, X-axis: n(mg/g)

Embedded table:

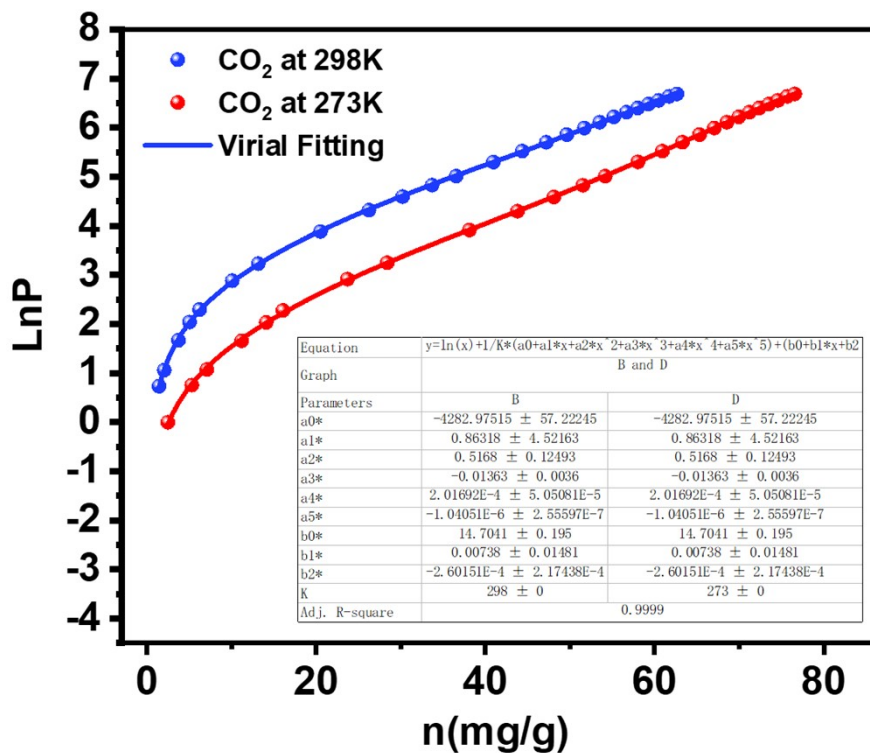| Equation | $y=\ln(x)+1/K*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)+(b0+b1*x+b2$ | |
|---|---|---|
| Graph | B and D | |
| Parameters | B | D |
| a0* | −4282.97515 ± 57.22245 | −4282.97515 ± 57.22245 |
| a1* | 0.86318 ± 4.52163 | 0.86318 ± 4.52163 |
| a2* | 0.5168 ± 0.12493 | 0.5168 ± 0.12493 |
| a3* | −0.01363 ± 0.0036 | −0.01363 ± 0.0036 |
| a4* | 2.01692E-4 ± 5.05081E-5 | 2.01692E-4 ± 5.05081E-5 |
| a5* | −1.04051E-6 ± 2.55597E-7 | −1.04051E-6 ± 2.55597E-7 |
| b0* | 14.7041 ± 0.195 | 14.7041 ± 0.195 |
| b1* | 0.00738 ± 0.01481 | 0.00738 ± 0.01481 |
| b2* | −2.60151E-4 ± 2.17438E-4 | −2.60151E-4 ± 2.17438E-4 |
| K | 298 ± 0 | 273 ± 0 |
| Adj. R-square | 0.9999 | |

**Fig. S8.** Virial fitting for $CO_2$ isotherms of **Zr-FA** at 273K and 298K.
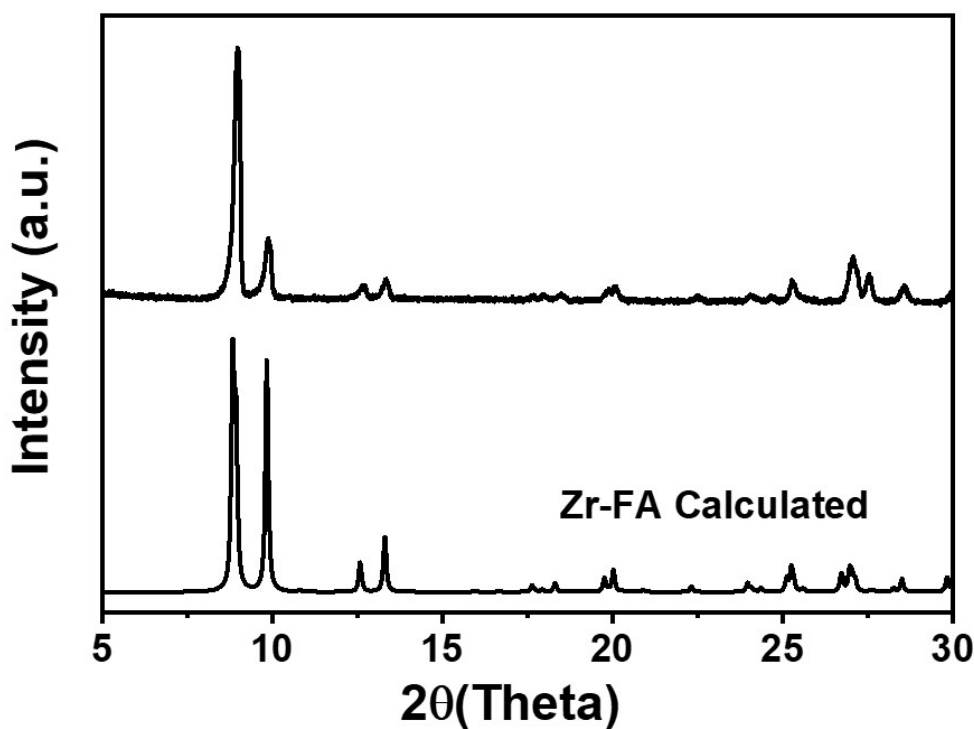


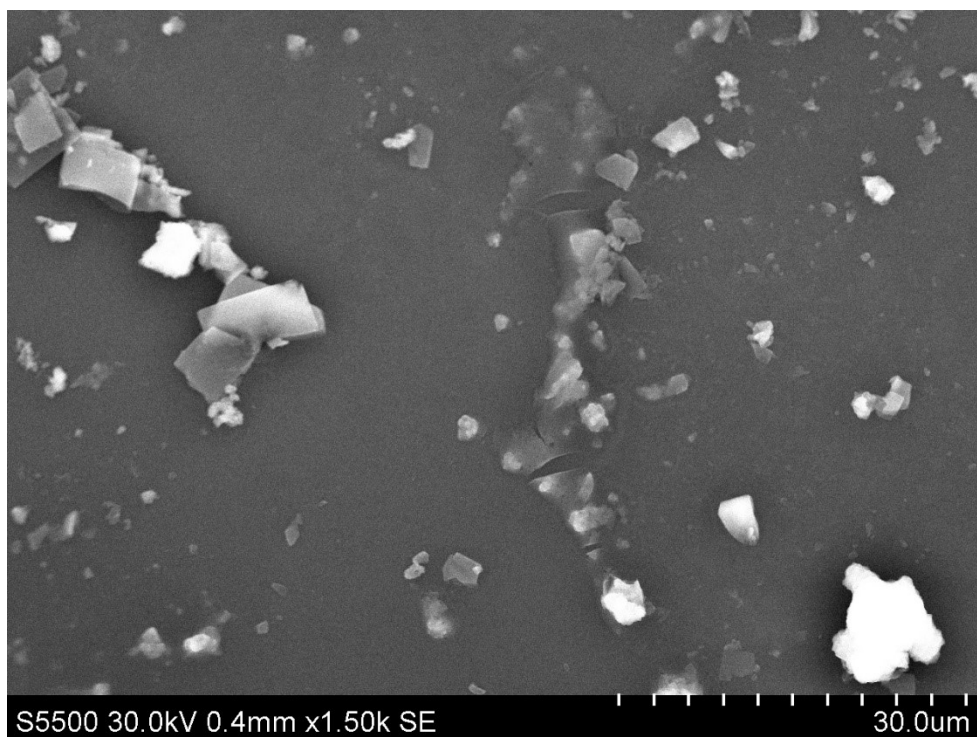**Fig. S9.** PXRD patterns for as-synthesized **Zr-FA**.
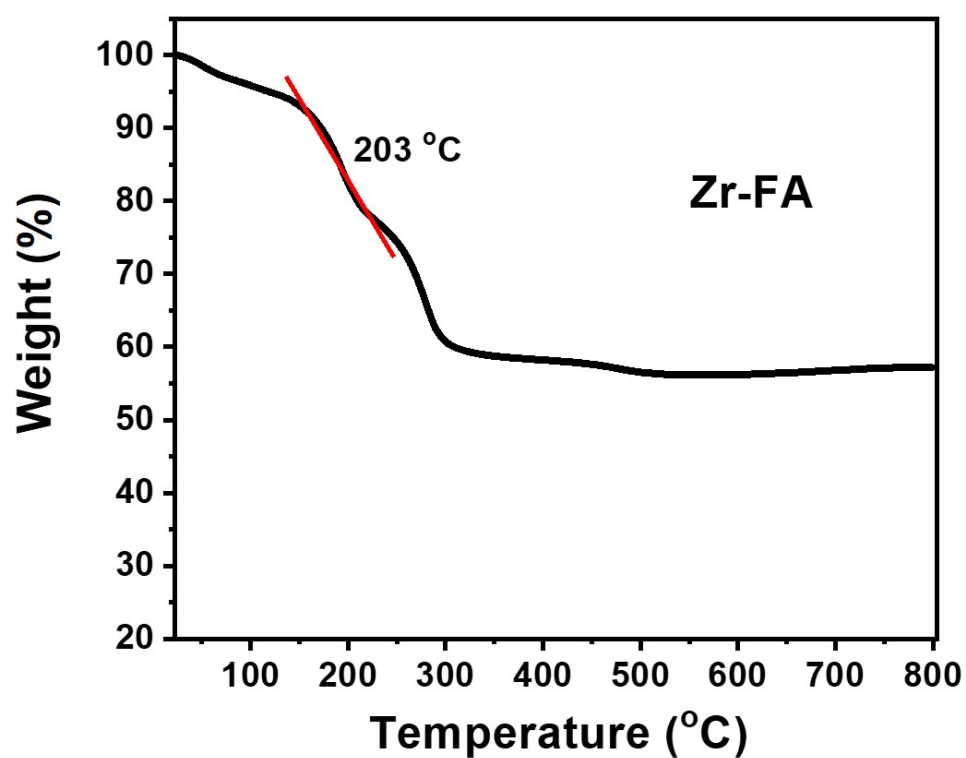
**Fig. S10.** SEM images of **Zr-FA**.



**Fig. S11.** TGA curve of as-synthesized **Zr-FA**.

References
[1] J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* 2006, **128**, 1304–1315.
[2] C. E. Webster, R. S. Drago, M. C. Zerner, *J. Am. Chem. Soc.* 1998, **120**, 5509-5516.