

## Supporting Information

# A Series of Cation-Modified Zirconium-Based Metal-Organic Frameworks for Carbon Dioxide Capture

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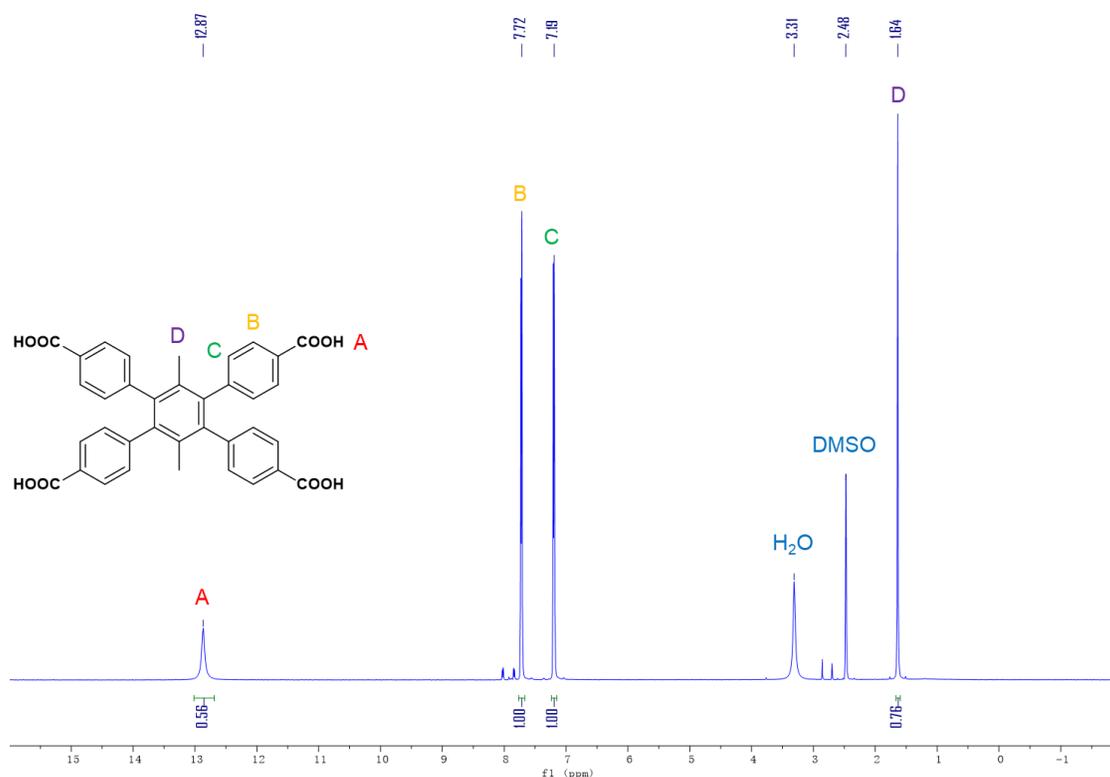
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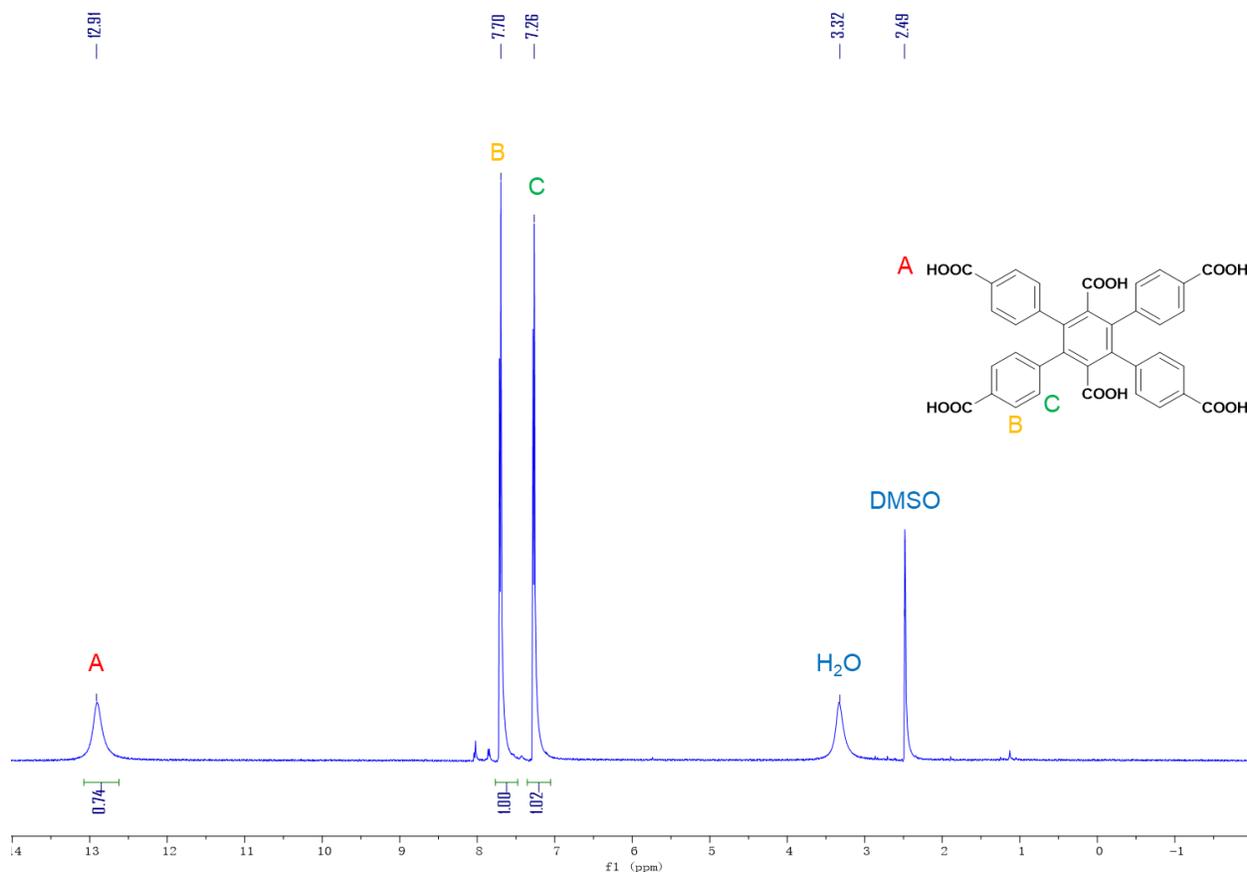
## S1. Materials

Reagents and solvents were used as received from: *Alfa-Aesar*: Formic acid (97%), zirconium dichloride oxide octahydrate (98%), potassium phosphate (97%), 1,2,4,5-tetrabromo-3,6-dimethyl-benzene (99%+), lithium hydroxide (97%), potassium hydroxide (98%), calcium hydroxide (99.5%), dichloromethane (99.5%), methanol (99.9%), DMF (99%) ethyl acetate (99%); *Acros Organics*: 2,4-methoxycarbonylphenylboronic acid (98%), sodium hydroxide (99%); *Oakwood Chemical*: Sodium sulfate anhydrous (99%); tert-butyl alcohol (99%) *Merk*: Potassium permanganate (99%); *VWR*: hydrochloric acid (36.5%-38%), nitric acid (concentrated), acetic acid (99%); *Strem Chemical*: Pd(PPh<sub>3</sub>)<sub>4</sub>; *PraxAir*: N<sub>2</sub> (99.99%), CO<sub>2</sub> (99.9%)

## S2. Characterizations of Ligands



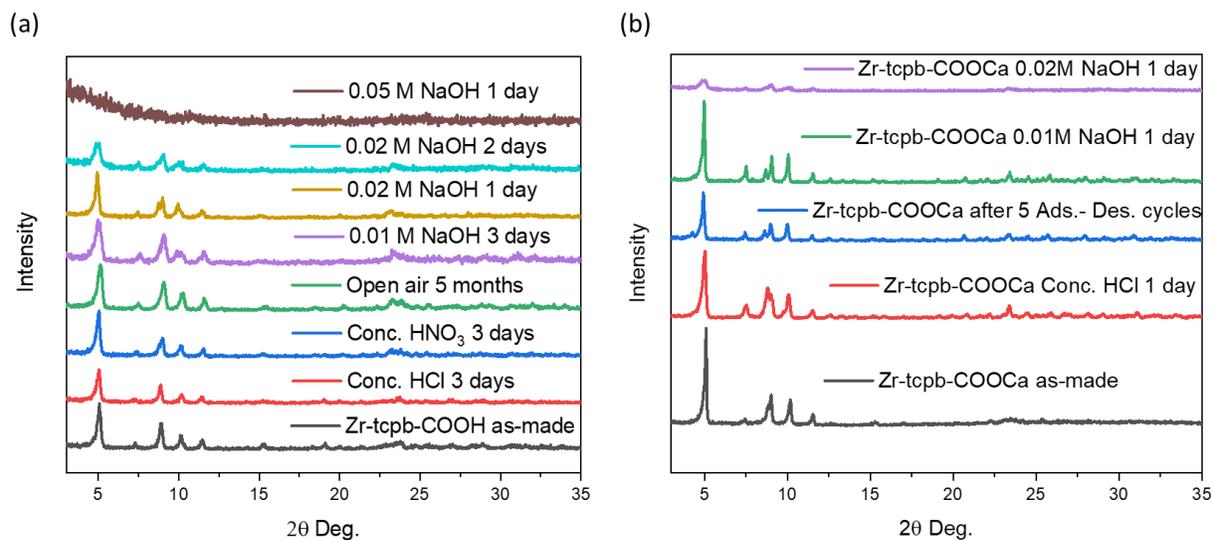
**Figure S1.** <sup>1</sup>H-500hz-DMSO NMR of 1,2,4,5-tetrakis(4-carboxyphenyl)-3,6-dimethyl-benzene (H<sub>4</sub>tcpb-(Me)<sub>2</sub>).



**Figure S2.** <sup>1</sup>H-500hz-DMSO NMR of 1,2,4,5-tetrakis(4-carboxyphenyl)-3,6-dicarboxyl-benzene (H<sub>4</sub>tcpb-(COOH)<sub>2</sub>).

### S3. Powder X-Ray Diffraction (PXRD) Patterns

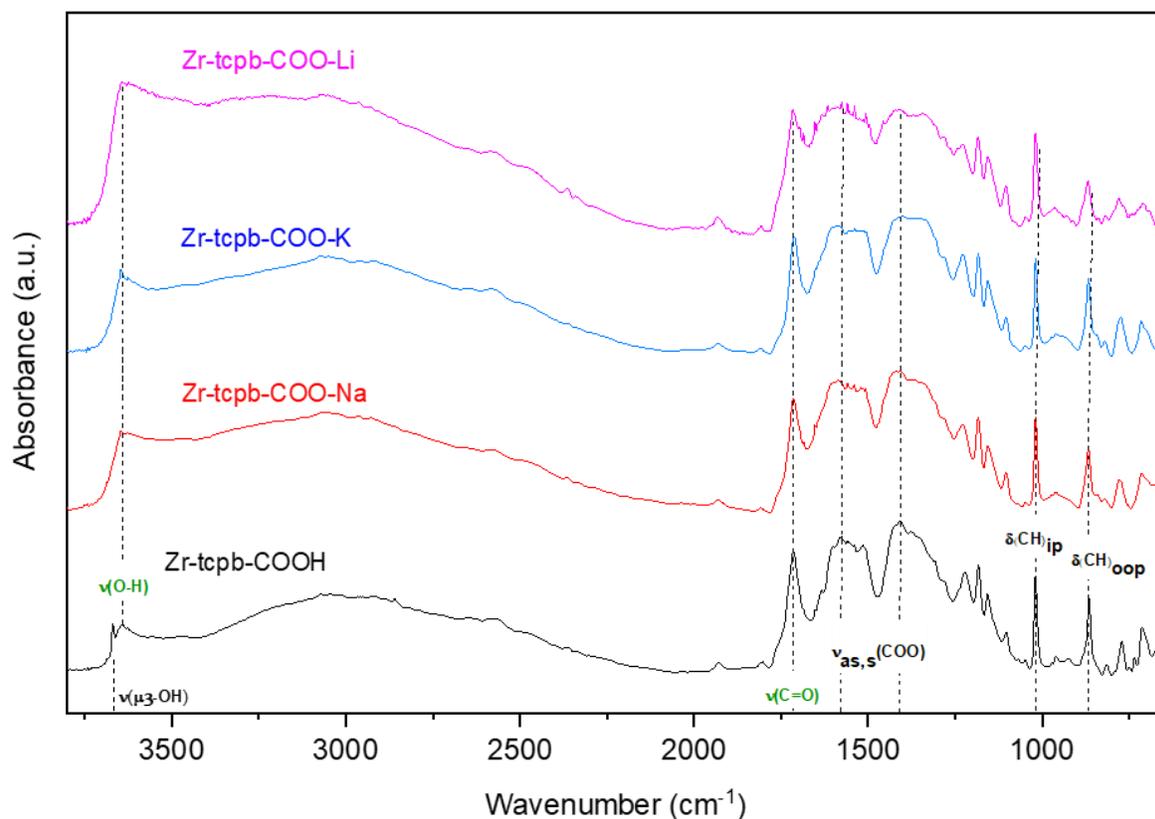
Powder X-ray diffraction (PXRD) analyses were performed using a Rigaku Ultima-IV-diffractometer at room temperature under Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Data were collected at room temperature in a  $2\theta$  range of  $3\text{-}40^\circ$ , with the operating power set to 40 kV/44 mA. The scan rate was  $2^\circ/\text{min}$ , with a step size of  $0.2^\circ$ .



**Figure S3.** PXRD patterns of Zr-tcpb-COOH (a) and Zr-tcpb-COOCa (b) taken after being treated under various chemical conditions along with those of as-made samples.

#### S4. FT-IR Measurements

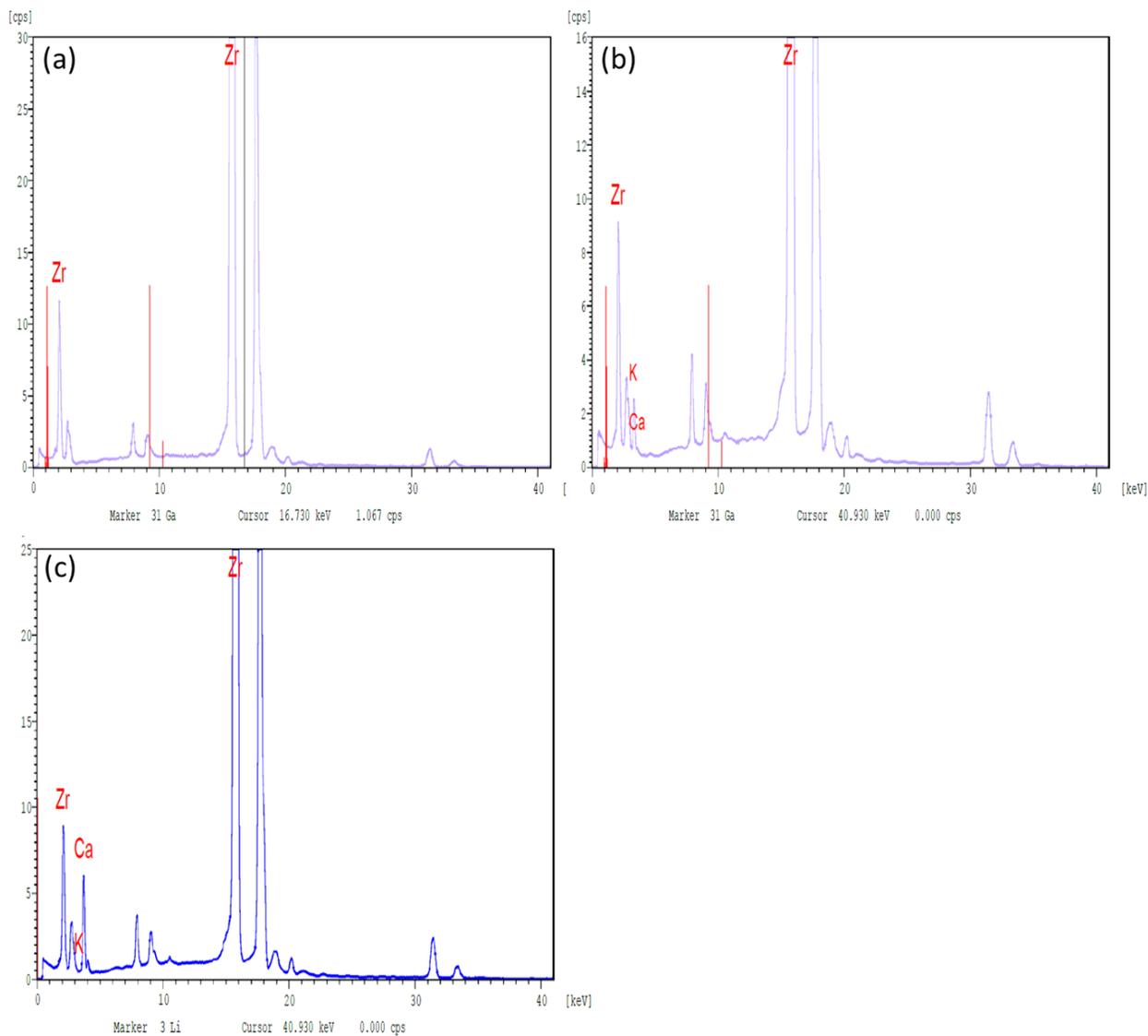
IR measurements were performed on a Nicolet 6700 FTIR spectrometer equipped with a liquid N<sub>2</sub>-cooled mercury cadmium telluride MCT-A detector. The sample of MOF compound (~2 mg) was pressed onto a KBr pellet and placed into a vacuum cell placed at the focal point of the sample compartment of the infrared spectrometer. The cell was connected to a vacuum line for evacuation. All spectra were recorded under vacuum (base pressure < 20 mTorr) in transmission mode with a frequency range of 600–4000 cm<sup>-1</sup> (4 cm<sup>-1</sup> spectral resolution).



**Figure S4.** IR spectra of Zr-tcpb-COOH and samples upon treatment with alkali hydroxide solutions. All spectra are referenced to the blank KBr under vacuum. Notation and acronym:  $\nu$ , stretching;  $\delta$ , deformation; *ip*, in plane; *as*, asymmetric; and *s*, symmetric.

### S5. X-Ray Fluorescence (XRF) Spectra

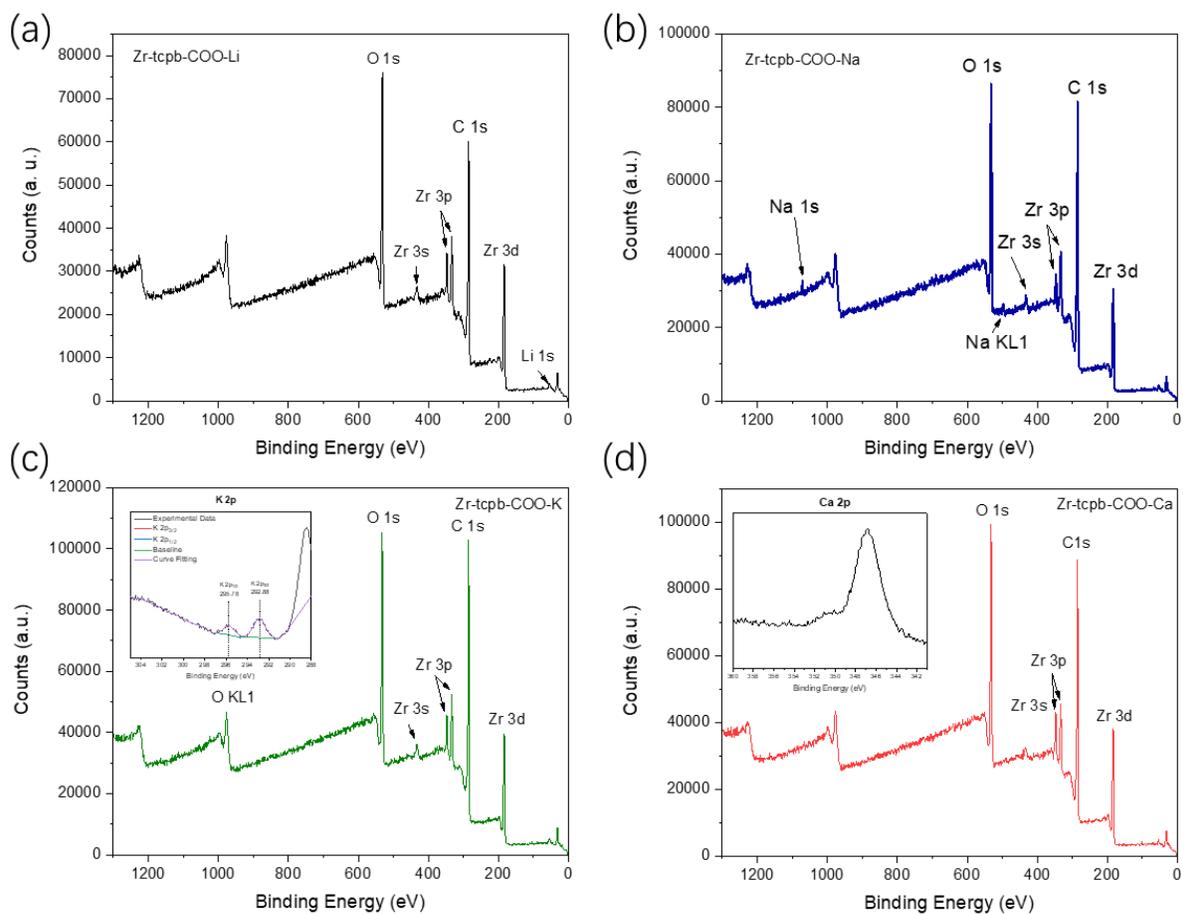
X-ray fluorescence (XRF) spectroscopic measurements were performed on a Horiba X-ray Analytical Micro-scope XGT-1000WR, with operational voltage and current at 50 kV and 60  $\mu$ A, respectively. The loading percentage of cations was determined by calculating the relative amounts of  $Zr^{4+}$  and  $M^+/M^{2+}$ . In Zr-tcpb-COO-K sample, the loading percentage is calculated 0.66 K per ligand, while Zr-tcpb-COO-Ca is calculated 0.71 Ca per ligand.



**Figure S5.** XRF spectra of (a) as-made Zr-tcpb-COOH: Zirconium Mass(%): 99.87 3Sigma(%): 1.61 Intensity(cps/mA): 91658.48; Calcium Mass(%): 0.08 3Sigma(%): 0.99 Intensity(cps/mA): 18.66; Potassium Mass(%): 0.05 3Sigma(%): 1.28 Intensity(cps/mA): 6.51 ; (b) Zr-tcpb-COO-K: Zirconium Mass(%): 91.29 3Sigma(%): 1.20 Intensity(cps/mA): 133281.25; Calcium Mass(%): 0.00 3Sigma(%): 0.00 Intensity(cps/mA): 0.00 ; Potassium Mass(%): 8.71 3Sigma(%): 1.07 Intensity(cps/mA): 544.94 ; (c) Zr-tcpb-COO-Ca: Zirconium Mass(%): 90.59 3Sigma(%): 0.99 Intensity(cps/mA): 118623.16 ; Calcium Mass(%): 9.41 3Sigma(%): 0.79 Intensity(cps/mA): 1286.52 ; Potassium Mass(%): 0.00 3Sigma(%): 0.00 Intensity(cps/mA): 0.00

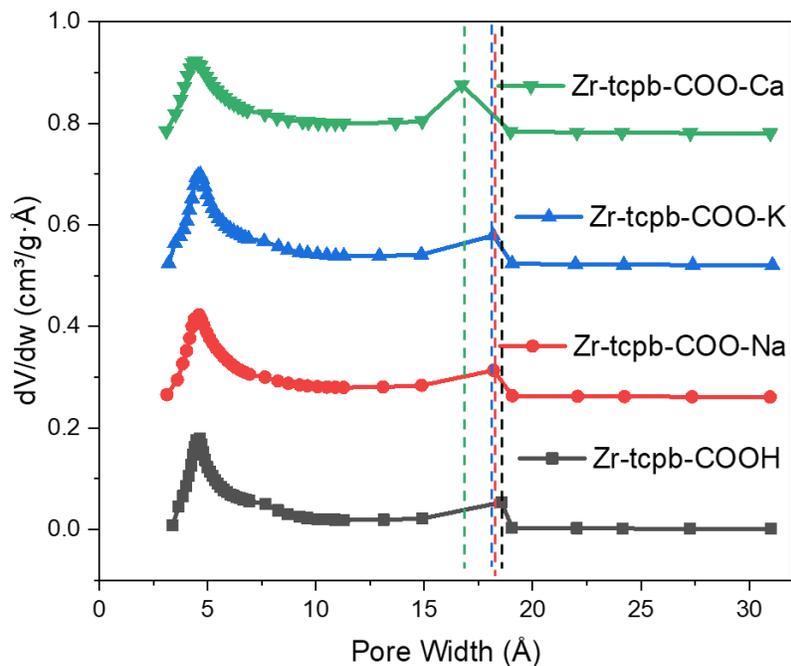
## S6. X-ray Photoelectron Spectroscopy (XPS) Data

The powdered samples were placed on carbon tape, and spectra X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatic Al K $\alpha$  source (1486.6 eV), hemispherical analyzer, and multichannel detector.

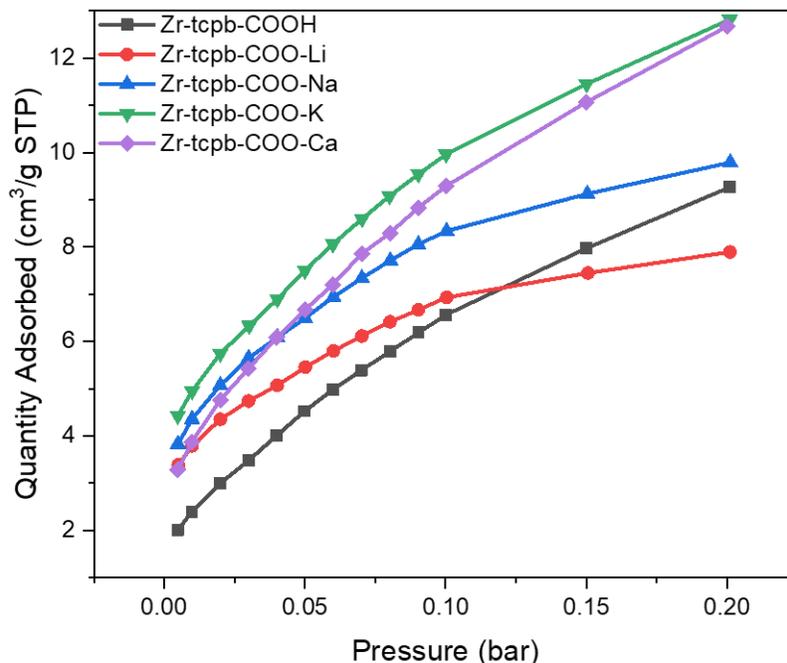


**Figure S6.** XPS spectra of (a) Zr-tcpb-COO-Li, (b) Zr-tcpb-COO-Na, (c) Zr-tcpb-COO-K (K 2p) and (d) Zr-tcpb-COO-Ca (Ca 2p).

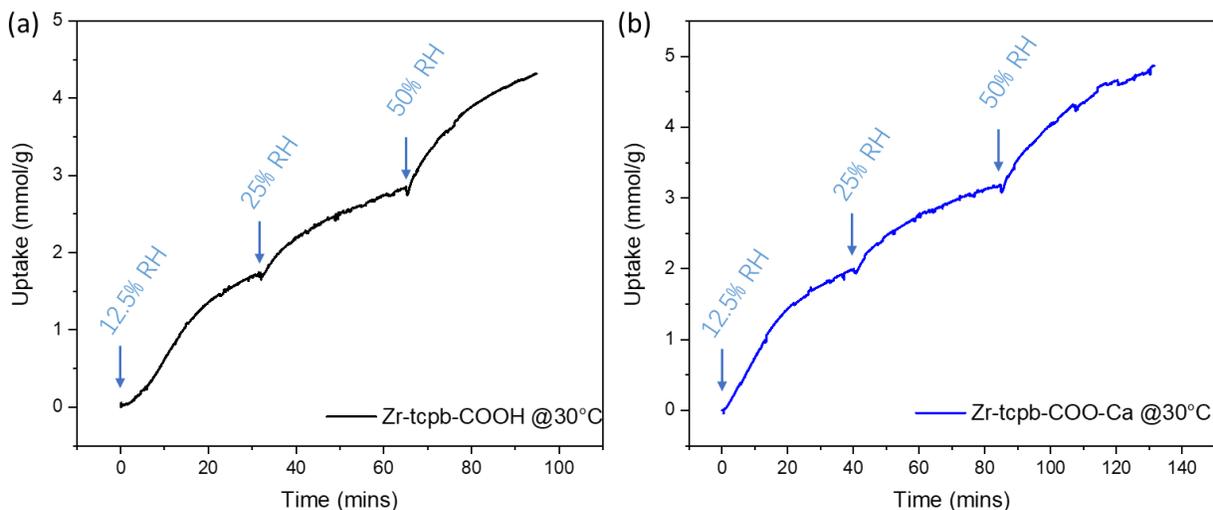
## S7. Gas Adsorption Measurements



**Figure S7.** The pore size distribution calculated by Horvath-Kawazoe model using N<sub>2</sub> 77 K isotherms data. Pore size for Zr-tcpb-COOH: (4.49 Å & 18.5 Å), Zr-tcpb-COO-Na: (4.61 Å & 18.2 Å), Zr-tcpb-COO-K: (4.66 Å & 18.18 Å), and Zr-tcpb-COO-Ca: (4.44 Å & 16.73 Å)

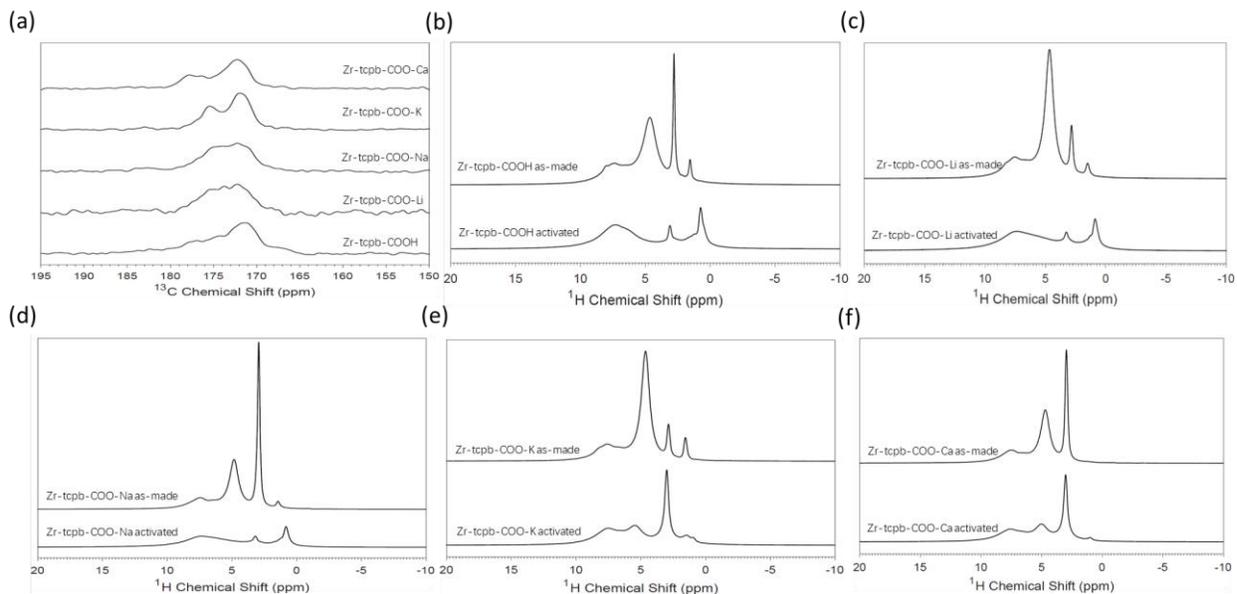


**Figure S8.** Room temperature (298 K) single component CO<sub>2</sub> adsorption isotherms at low-pressure region for the Zr-tcpb-COOM series.



**Figure S9.** Water adsorption isotherms measured on a gravimetric adsorption analyzer. (a) water uptake in activated Zr-tcpb-COOH at relative humidity (RH) of 12.5%, 25%, and 50% at 303 K; (b) water uptake in activated Zr-tcpb-COO-Ca at relative humidity (RH) of 12.5%, 25%, and 50% at 303 K.

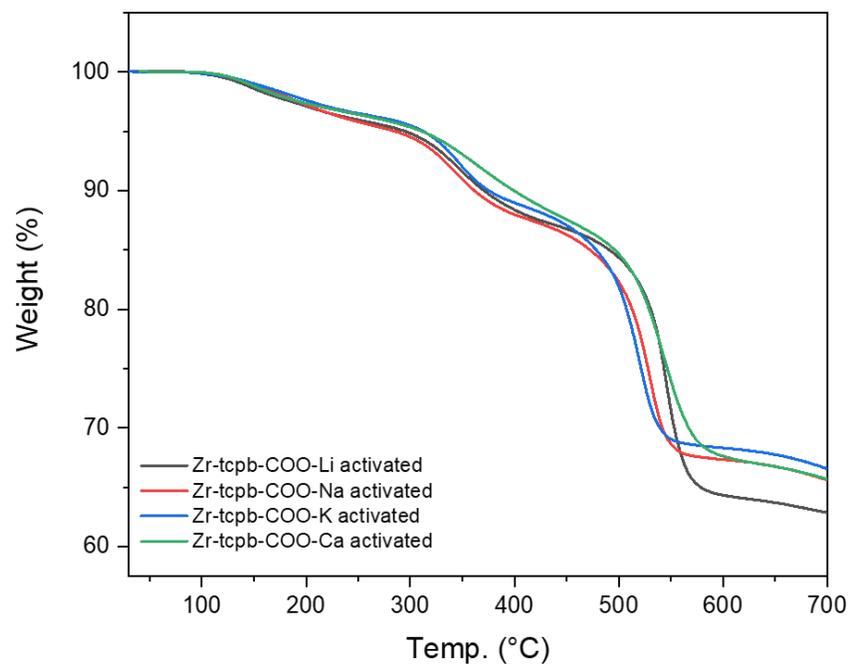
## S8. Solid-State NMR Analysis



**Figure S10.** Solid-State  $^{13}\text{C}$  CP-MAS NMR of (a) as-made and modified samples and  $^1\text{H}$  NMR of activated and as-made sample of (b) Zr-tcpb-COO-Li; (c) Zr-tcpb-COO-Na; (d) Zr-tcpb-COO-K; and (e) Zr-tcpb-COO-Ca.

## S9. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was completed via a TA Instruments Q5000 under constant  $\text{N}_2$  flow (20 mL/min). Approximately 10 mg of MOFs samples were placed into a platinum pan, which was then heated from 30-700  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C}/\text{min}$ . The weight loss from MOFs were monitored over the temperature increase.



**Figure S11.** The thermogravimetric plot of activated Zr-tcpb-COOM series. Samples were activated under a constant N<sub>2</sub> flow for 30 mins at 373 K.