Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic supporting information

Characterization and properties of Zn/Co zeolitic imidazolate frameworks *vs.* ZIF-8 and ZIF-67

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Contents

Experimental

All sample were synthesized at room temperature method. Two metal salts were dissolved in methanol followed by addition of the adequate amount of ligand. The amount of metal salt, ligand and methanol are provided in Table S1.

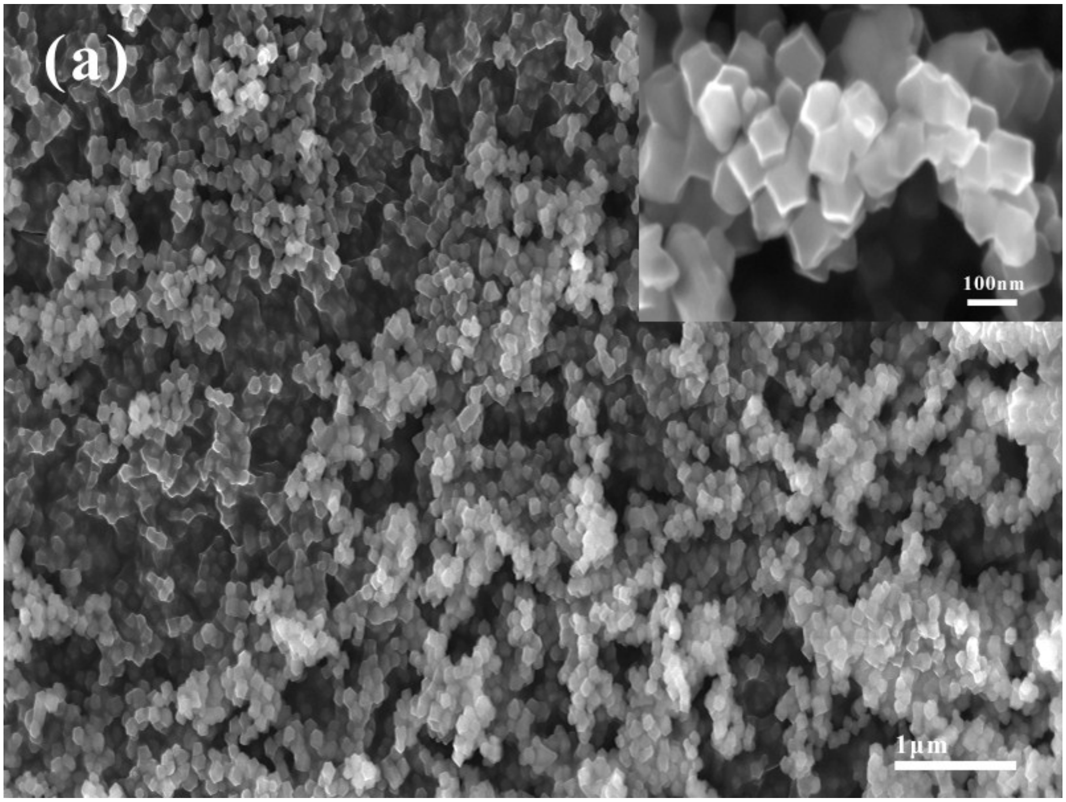
Table S1 Mol and mass/volume of reagent used to synthesize ZIF-8, ZIF-67 and dual metal Zn/Co-ZIF.

Sample	Metal source		Ligand	Total solvent
	$Zn(NO_3)_2{\cdot}6H_2O$	$Co(NO_3)_2{\cdot}6H_2O$	2-IMI	Methanol
ZIF-8	1 mmol, 0.297g	-	8 mmol, 0.66g	30 ml
ZIF-67	-	1 mmol, 0.291g	8 mmol, 0.66g	30 ml
Zn/Co-ZIF	0.5 mmol, 0.1485	0.5 mmol, 0.145g	8 mmol, 0.66g	30 ml

Characterization

- Scanning Electron Microscope

The morphology studies were conducted on Scanning Electron Microscopy (SEM) from JEOL (JSM-5610LV, 0.5–35 kV)



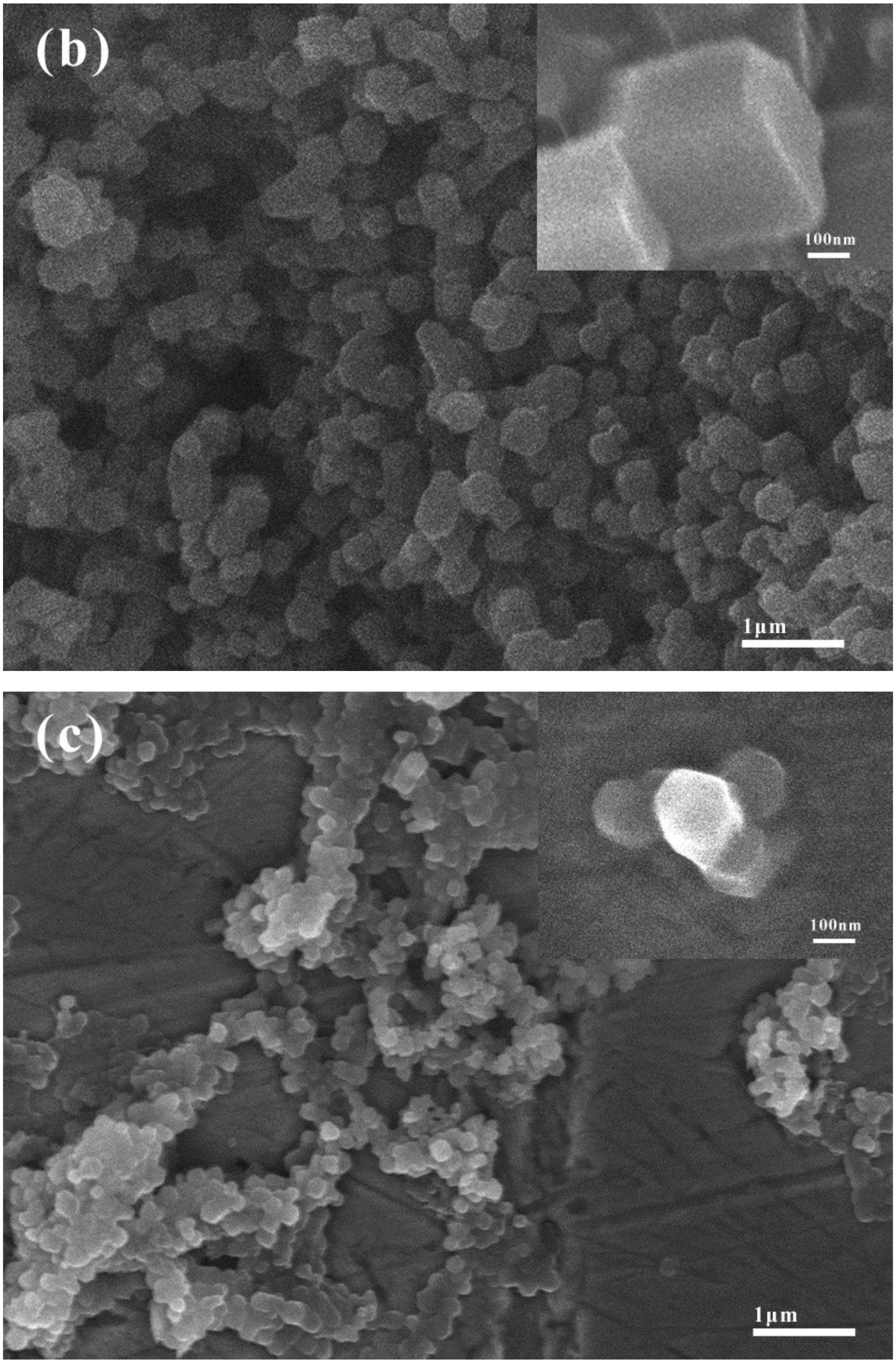
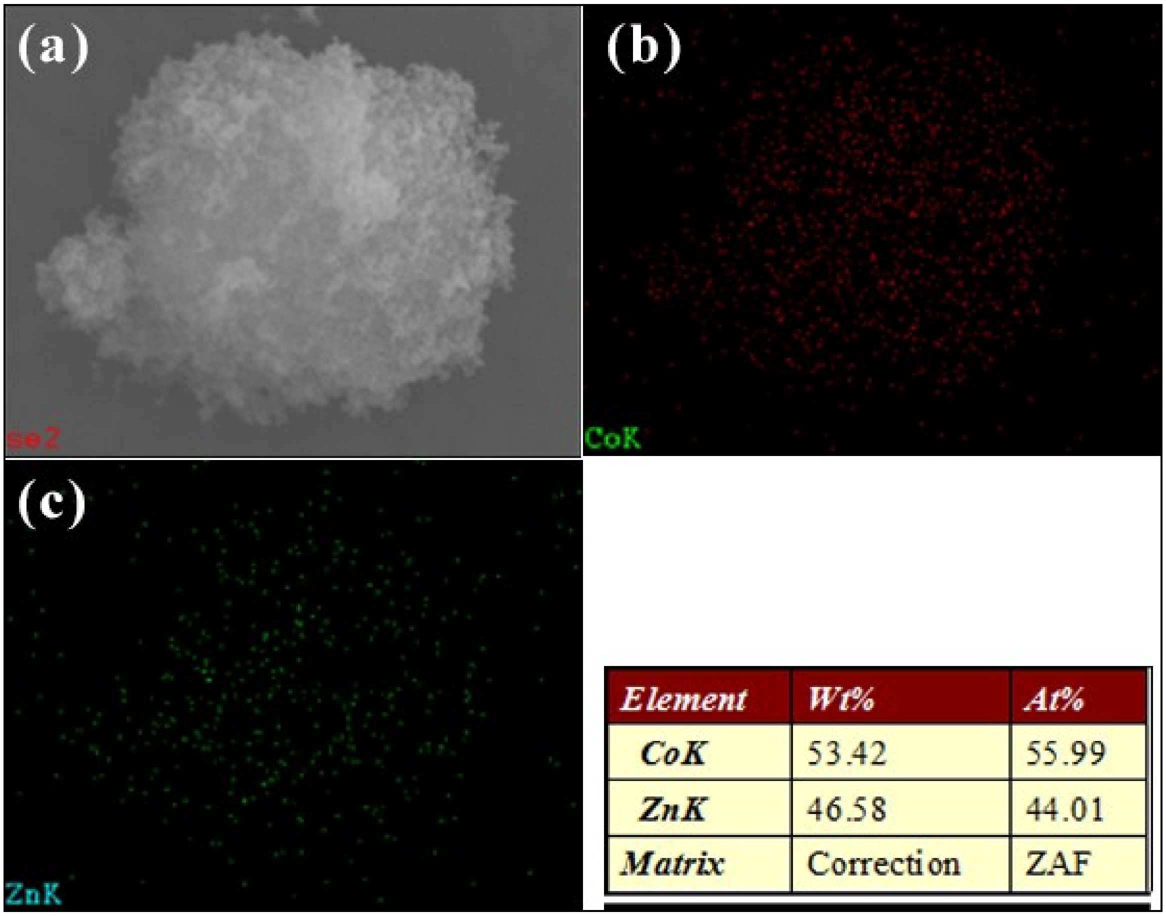


Figure S1. SEM images of a) ZIF-8, b) ZIF-67 and c) Zn/Co-ZIF; The small inserts display the morphology of the samples.



Element	Wt%	At%
CoK	53.42	55.99
ZnK	46.58	44.01
Matrix	Correction	ZAF

Figure S2. The metal dispersion of Zn and Co in Zn/Co-ZIF investigated by SEM-EDX mapping technique: a) The selected crystal, b) The dispersion of Co metal, c) The dispersion of Zn metal and table presenting the metal content in the sample.

- Single crystal X-ray diffraction

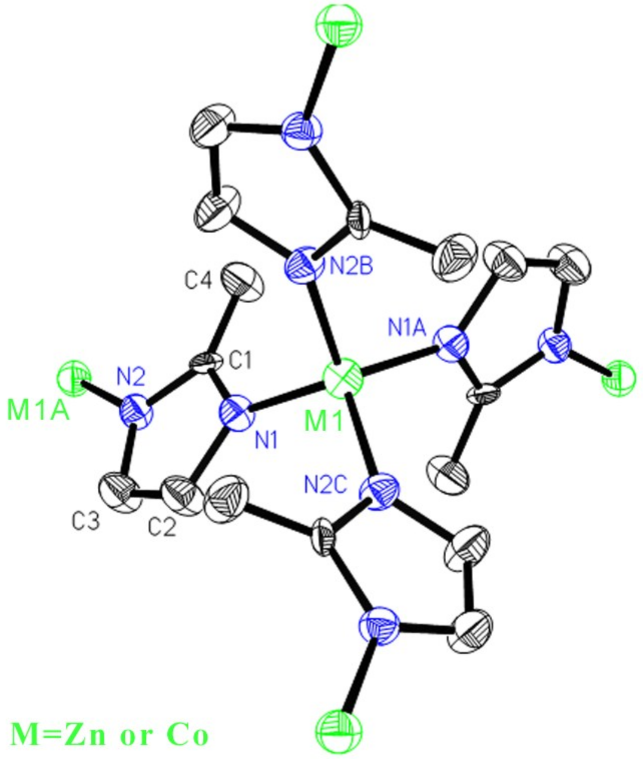


Figure S3. ORTEP diagram of the asymmetric unit of Zn/Co-ZIF

Table S2. Crystal data and structure refinement for Zn/Co-ZIF

Formula sum	$C_{16} H_{20} Co N_8 Zn$
Formula weight	448.7 g/mol
Crystal system	cubic
Space-group	I -4 3 m (217)
Cell parameters	a=17.099(4) Å=b=c; α=β=γ=90°
Cell volume	4999.33(200) Å^3
Z	6
Calc. density	0.894166 g/cm^3
Meas. density	0 g/cm^3
Melting point	
RAll	0.0539
RObs	
Pearson code	cI1068
Formula type	NO8P16Q20
Wyckoff sequence	h22d

- Fourier Transform Infrared Resonance (FTIR)

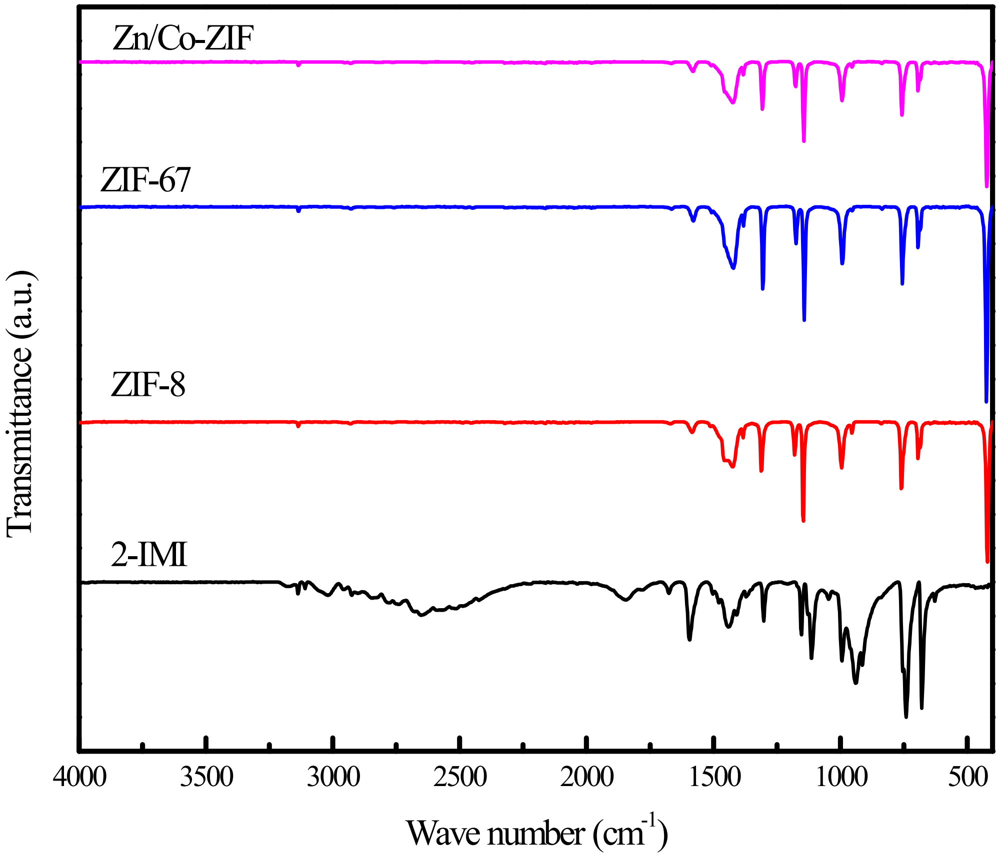


Figure S4. FT-IR spectra of zeolitic imidazolate framework series compared with 2-methylimidazole (2-MIM), the applied ligand.

- X-ray diffraction (XRD)

The crystallinity was analyzed using powder X-ray diffraction (XRD) applying a Cu K_α radiation source (Bruker D8-Discover).

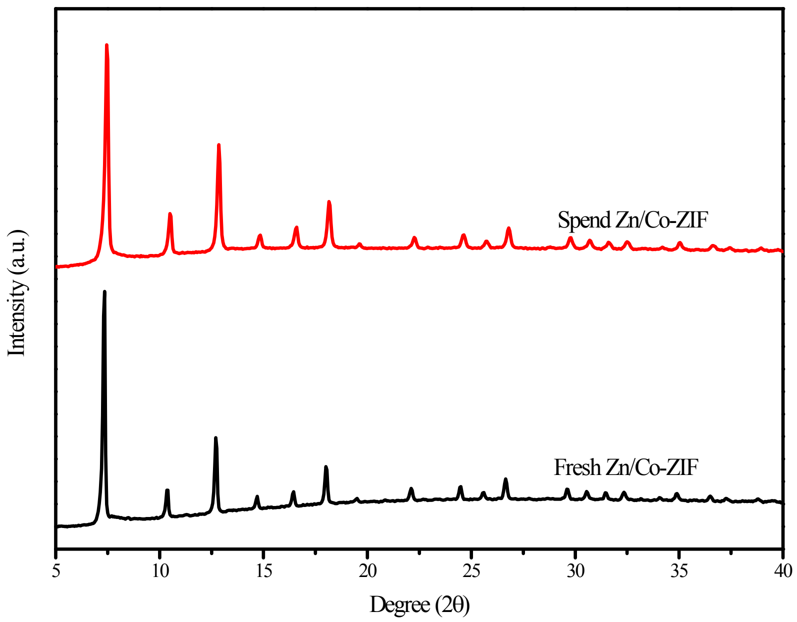
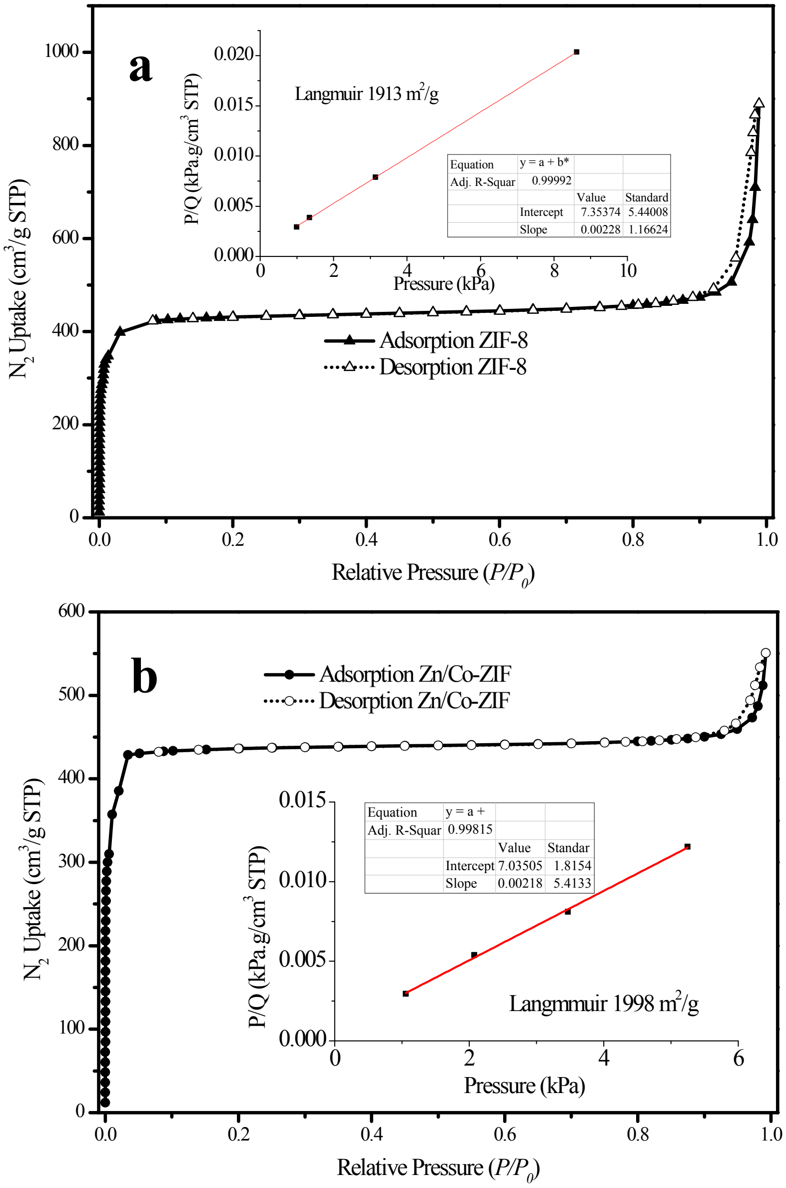


Figure S5. XRD spectra of fresh (top) and spend (down) catalyst of dual metal Zn/Co-ZIF.

- Gas adsorption (N_2, CO_2 and CH_4)

The surface area/porosity measurements and adsorption-desorption isotherm were performed on ASAP 2020 instrument (Micromeritics) with N_2 (99.999%), CO_2 (99.999%) and CH_4 (99.999%). The characterization samples were pretreatment at 200°C under vacuum for 200 min before analysis (activation).



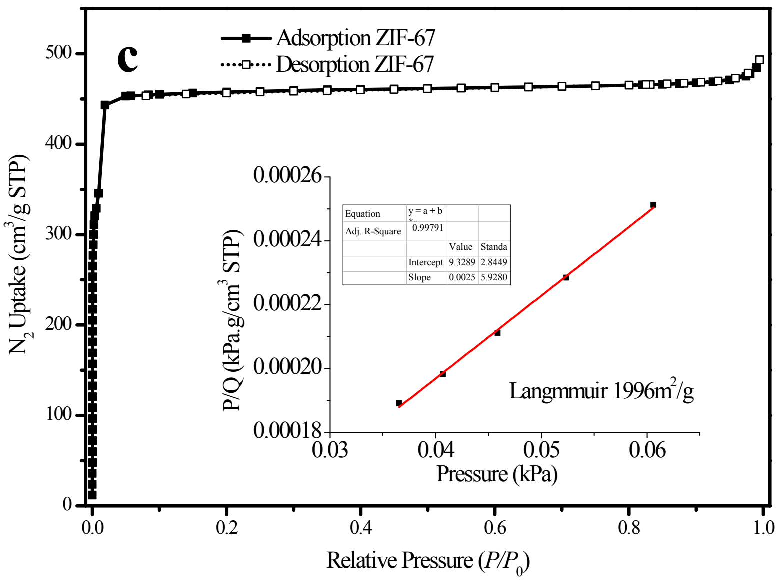


Figure S6. N_2 adsorption isotherm at 77K and Langmuir surface area plot (insert): a) ZIF-8, b) Zn/Co-ZIF, c) ZIF-67.

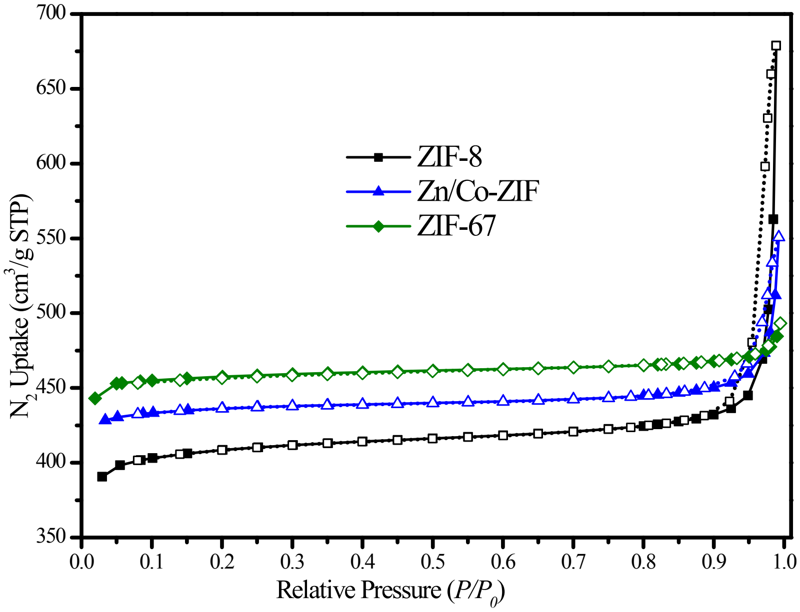
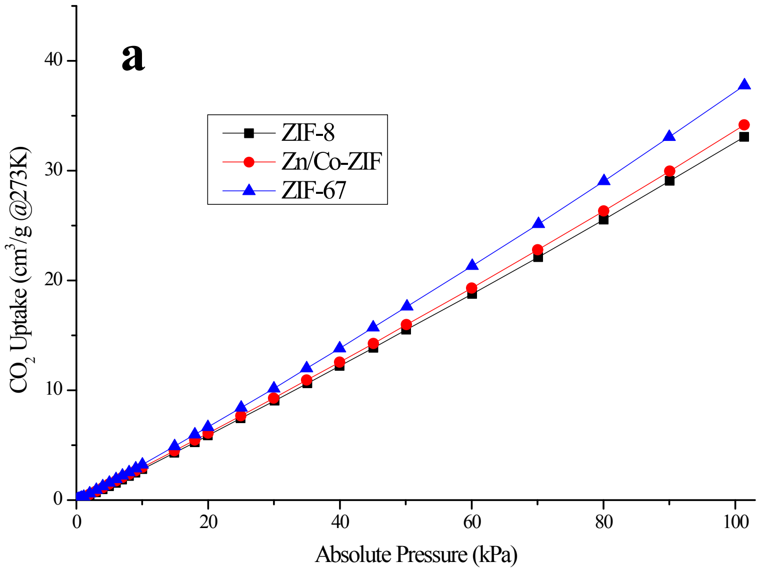
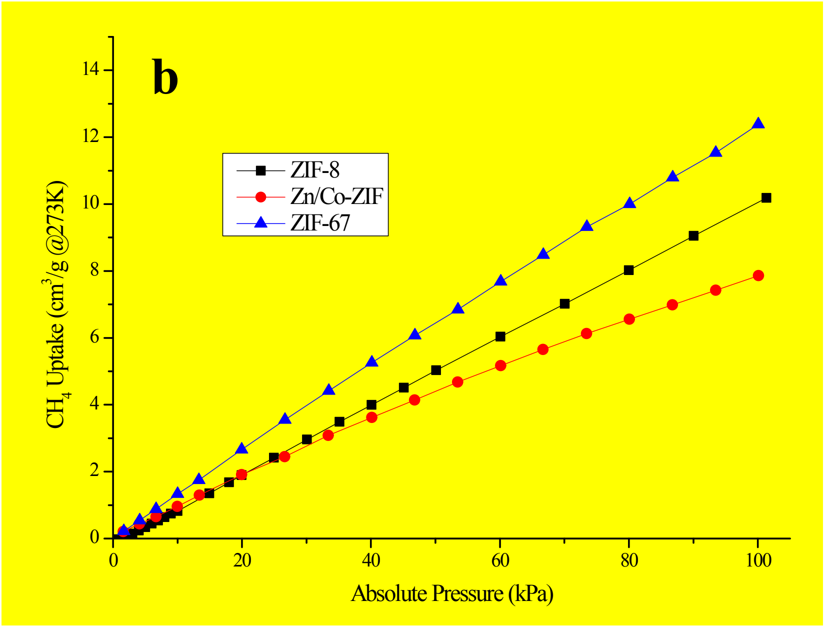


Figure S7. Comparison of the N_2 adsorption isotherms at 77K of the ZIF series


a
CO$_2$ Uptake (cm^3/g @273K)
0
10
20
30
40
ZIF-8
Zn/Co-ZIF
ZIF-67
0
20
40
60
80
100
Absolute Pressure (kPa)


b
CH$_4$ Uptake (cm^3/g @273K)
0
2
4
6
8
10
12
14
ZIF-8
Zn/Co-ZIF
ZIF-67
0
20
40
60
80
100
Absolute Pressure (kPa)

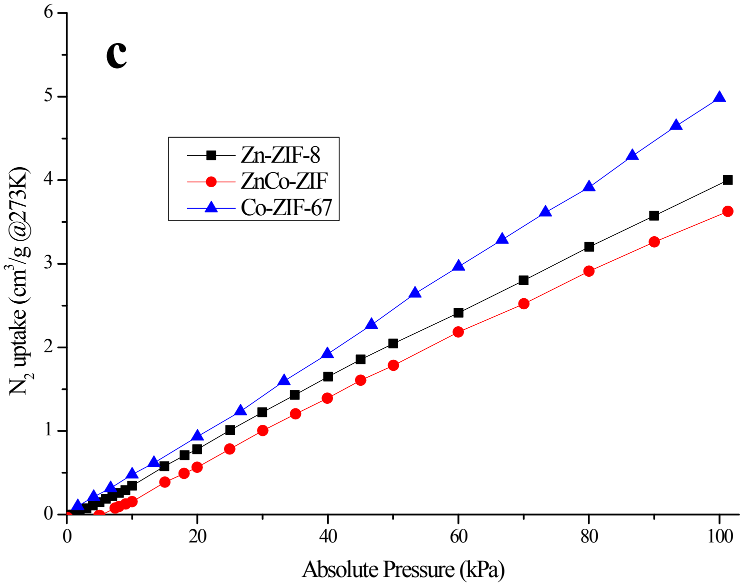


Figure S8. Gas adsorption comparison of CO_2 (a), CH_4 (b) and N_2 (c) at 273K and pressure up to 1 atm (101.3 kPa) for the ZIF series.

- Temperature Program Desorption (TPD)

The temperature programmed desorption (TPD), was performed for all samples using a Micromeritics Chemisorb 2750 automated system with ChemiSoft TPx software. The samples were pretreated at 250°C under carrier He gas for 1h, then cooled down to the adsorption temperature at 25 °C. NH_3 and CO_2 as probe gases were introduced to the sample by continuous flow. The probe gas was adsorbed to saturation at adsorption temperature of 25 °C which can be observed from the stable TCD detector signal. The physically adsorbed gas on the samples was then removed by flushing the samples with He gas till a stable TCD signal was obtained. The temperature programmed desorption was measured using a TCD detector, temperature rising to 270 °C at a rate of 10 °C/min. Investigation of the defects in MOFs using temperature programmed desorption of CO as a probe gas (CO-TPD) was used in this study too. The samples were pretreated at 250°C under carrier He gas for 1h, then cooled to 25 °C, the adsorption temperature. The CO probe gas was introduced to the sample using a continuous flow. The probe gas was adsorbed to saturation at the adsorption temperature of 25 °C which was observed from the stable signal of the TCD detector. Thereafter, the physically adsorbed probe gas was removed by flushing the samples with He gas till a stable TCD signal was obtained. The temperature programmed desorption was measured with a TCD detector, temperature rising to 270 °C at a rate of 10 °C/min.

- Calculation of acidity

Calculation of total acidity was calculated from the NH_3-TPD profiles.

The NH_3-TPD profiles:

- Area under the NH_3-TPD profile of a sample = A
- The number of moles of NH_3 was calculated from the calibration curve made for NH_3 using the following formula:

  The number of moles of $NH_3 = 0.294 \times A$ mmol.

- Catalyst mass = B g.

$$\text{The total acidity of a sample} = \text{mmol of } NH_3/\text{dry catalyst mass}$$
$$= (0.294 \times A/B)\ \text{mmol } NH_3/\text{g catalyst}$$

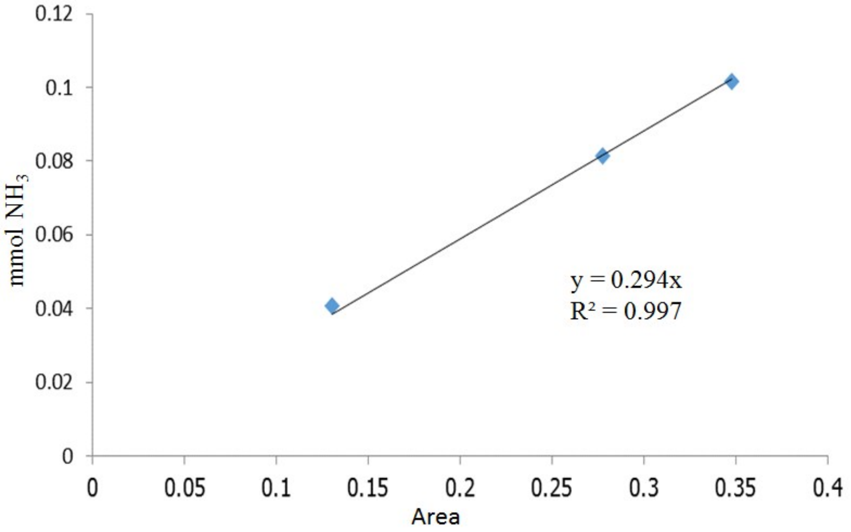


Figure S9. The calibration curve for ammonia using Micromeritics Chemisorp 2750

- Calculation of basicity

Calculation of total basicity from the CO_2-TPD profiles.

The CO_2-TPD profiles:

- Area under the CO_2-TPD profile of a sample = A
- The number of moles of CO_2 was calculated from the calibration curve made for CO_2 using the following formula:

The number of moles of CO_2 = 0.0176×A mmol.

- Catalyst mass = B g.

The total basicity of sample = mmol of CO_2/dry catalyst mass

= (0.0176×A/B) mmol CO_2/g catalyst

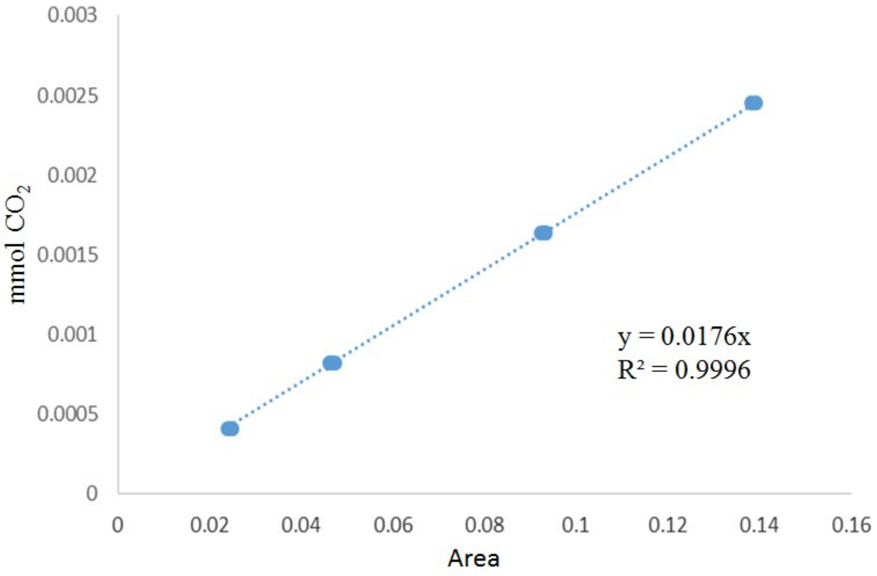


Figure S10. The calibration curve for carbon dioxide using Micromeritics Chemisorp 2750

The stability testing

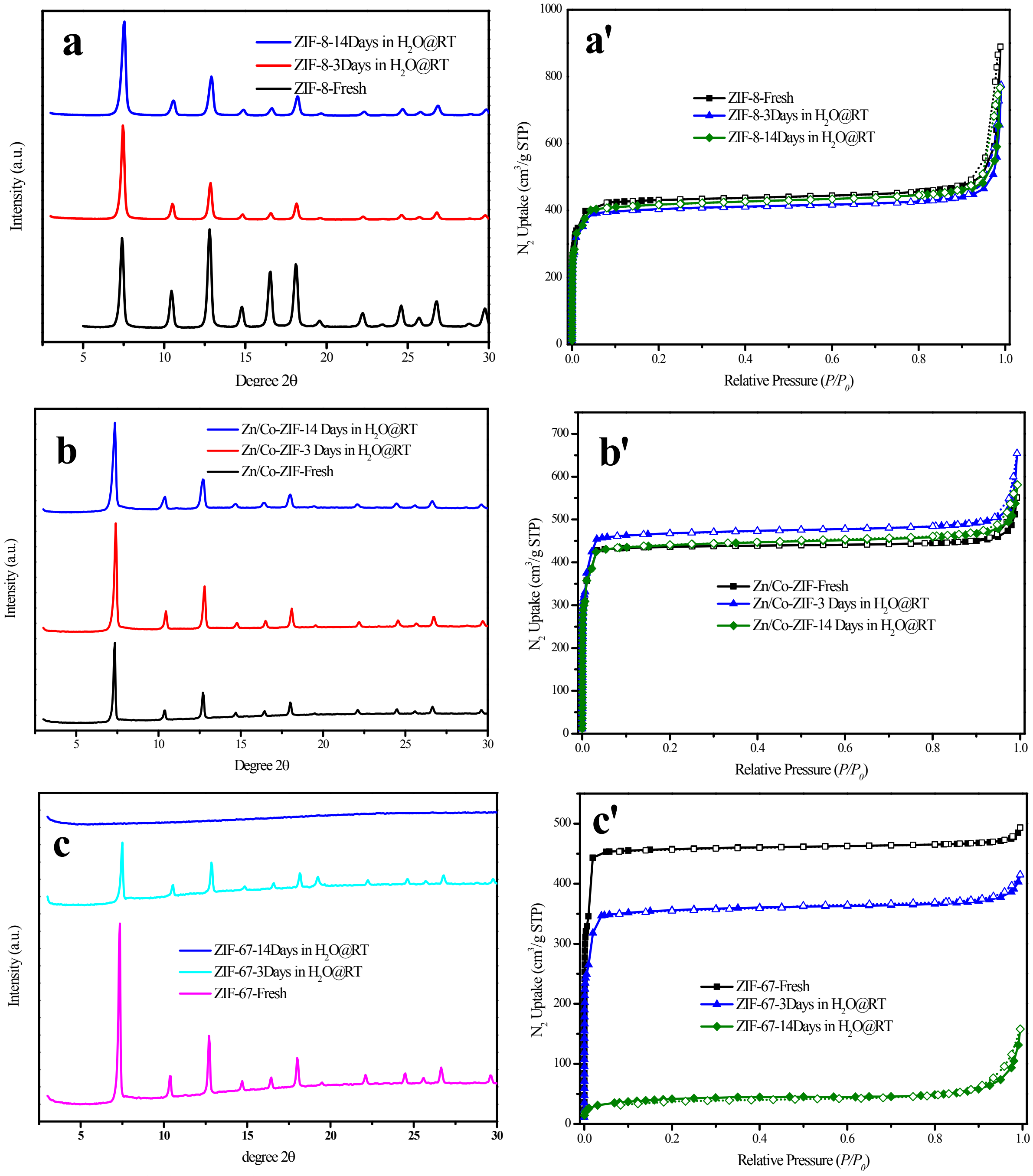


Figure S11. Stability study using XRD spectra of ZIF-8(a), Zn/Co-ZIF(b), ZIF-67(c) and the isotherm of N_2 adsorption of ZIF-8(a') Zn/Co-ZIF(b') and ZIF-67(c') for varies conditions.

Notes: M-ZIF-X-Fresh: The sample after synthesis and activated at 200 ^{o}C under vacuum for 200 min
M-ZIF-X-3DaysH_2O@RT: The sample after immersed in water for 3 days at room temperature (25^{o}C) and activation
M-ZIF-X-14DaysH_2O@RT: The sample after immersed in water for 14 days at room temperature (25^{o}C) and activation

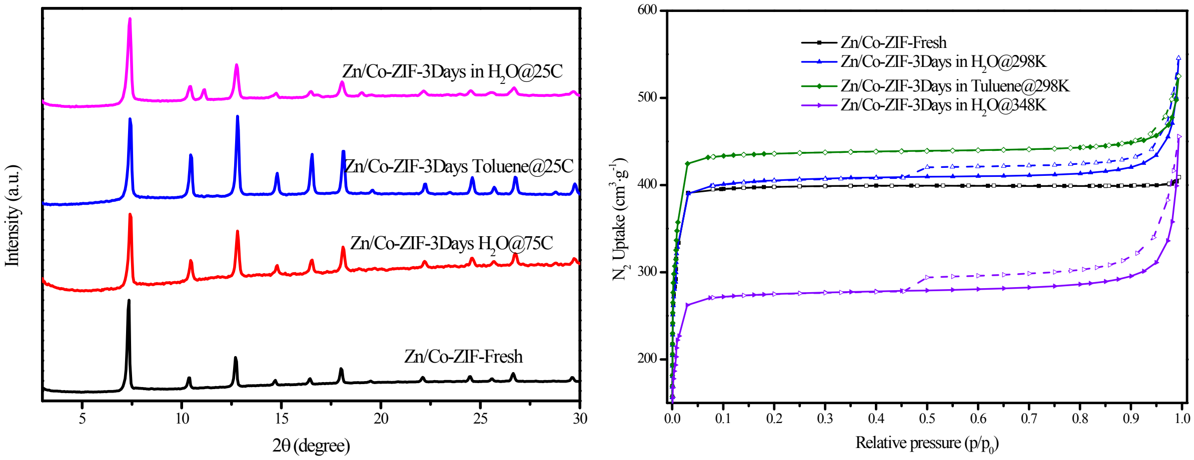


Figure S12. Zn/Co-ZIF stability study using XRD spectra (a), and N_2 adsorption isotherm (b) for varies stability conditions.

The normalized XRD spectra obtained for the Zn/Co-ZIF samples from the stability study are similar to the fresh sample, however, an unstable base line of Zn/Co-ZIF was observed after immersion in water at 75 °C (Zn/Co-ZIF-3Days in H_2O@75C) which might play role in phase transition in the crystal structure (Fig.S12a). The N_2 adsorption isotherm represents the surface area and porosity of the materials (Fig.S12b). The meso-porous (hysteresis lope at high pressure, $P/P_o > 0.5$) was found in the samples after immersion in water and toluene. A higher N_2 adsorption was observed for the sample immersed in toluene for 3 days which might be related to removal of residuals from the pores (solved in toluene). Whereas, the N_2 adsorption was significantly decreased for the sample immersed in water at 75°C for 3 days, this result confirmed the transition of the crystal phase as observed in XRD.

Catalytic activity

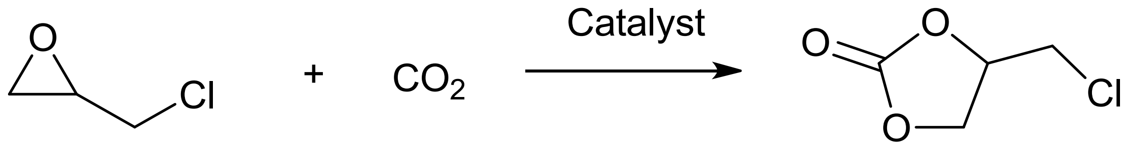


Figure S13. CO_2 conversion to chloropropene carbonate. The reaction progression was identified using ^1H-NMR in $CDCL_3$ 500 MHz:

Epichlorohydrin: δ 3.57-3.63 (m, 2H), **3.23 (m, 1H)**, 2.68 (m, 1H), 2.88 (m, 1H);

Chloropropene carbonate: 1H NMR (500 MHz, CDCl3): δ **4.90-5.02 (m, 1H)**, 4.61 (t, J = 8.6 Hz, 1H), 4.45 (dd, J = 8.9, 5.7 Hz, 1H), 3.68-3.78 (m, 1H). 13C NMR (100 MHz, $CDCl_3$): δ 154.5, 74.5, 67.0, 44.1.

The catalytic performance was calculated using the peak ratio (3.23 (m, 1H) of epichlorohydrin to 4.90-5.02 (m, 1H) of chloropropene carbonate).

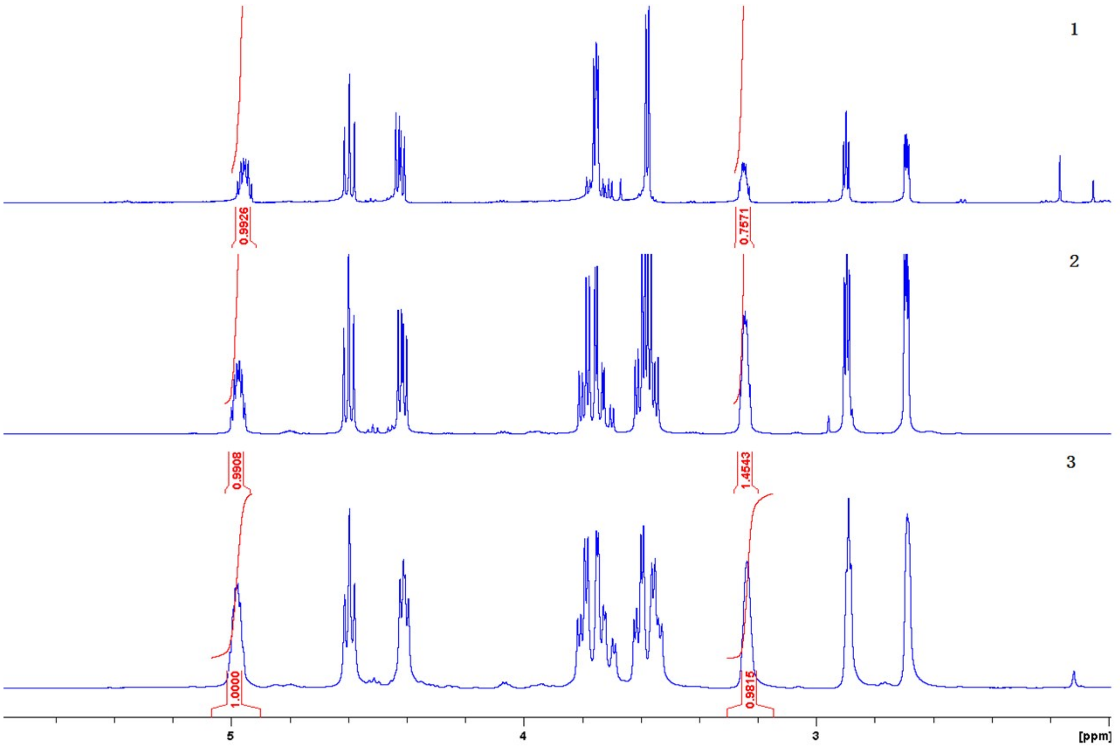


Figure S14. The comparable of Catalytic performance of Zn/Co-ZIF (1), ZIF-8 (2) and ZIF-67 (3) of CO_2 conversion to Chloropropene carbonate. (Reaction conditions: 100^{o}C for 4h, 7 bar)

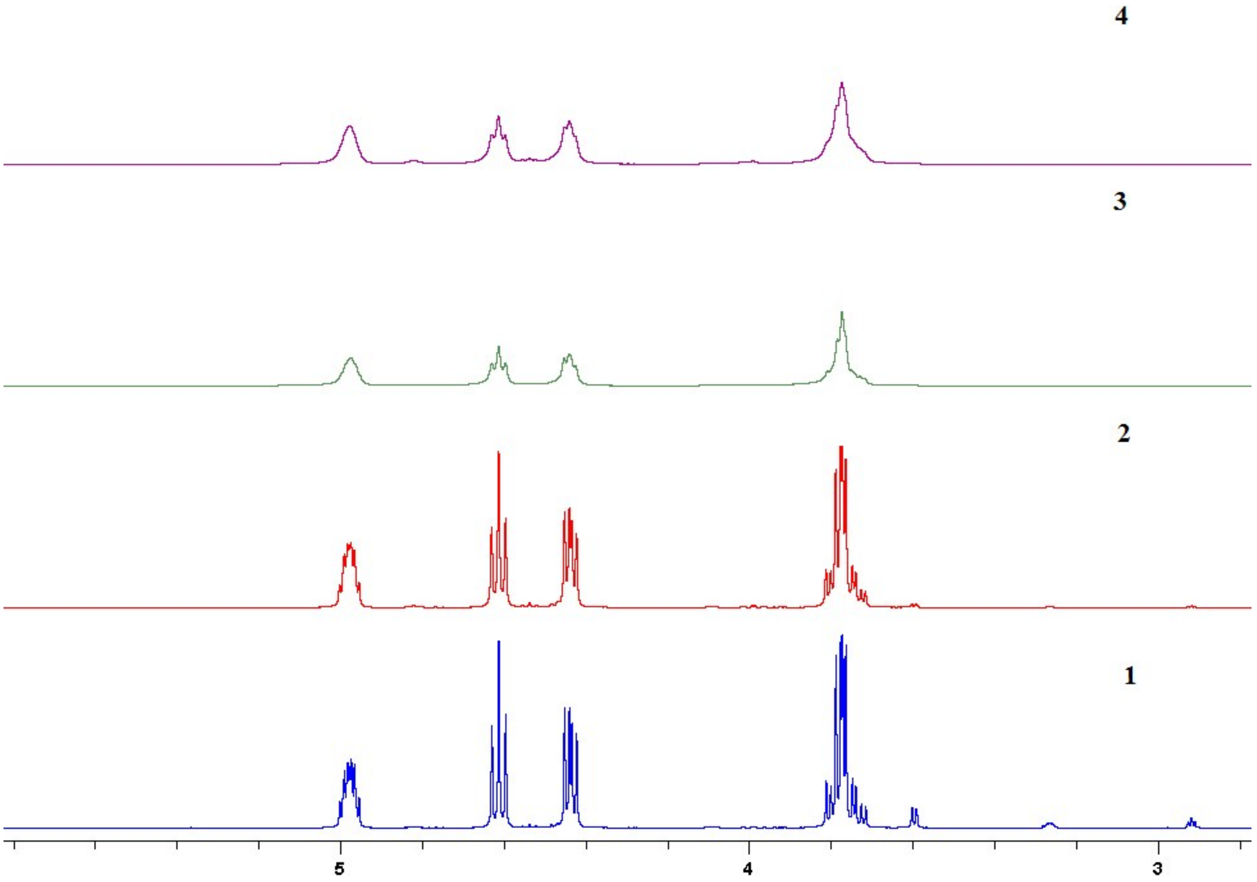


Figure S15. Catalytic performance of recycled Zn/Co-ZIF: First run (1), Second run (2), Third run (3) and forth run (4). (Reaction conditions: 100^{o}C for 16h, 7 bar)

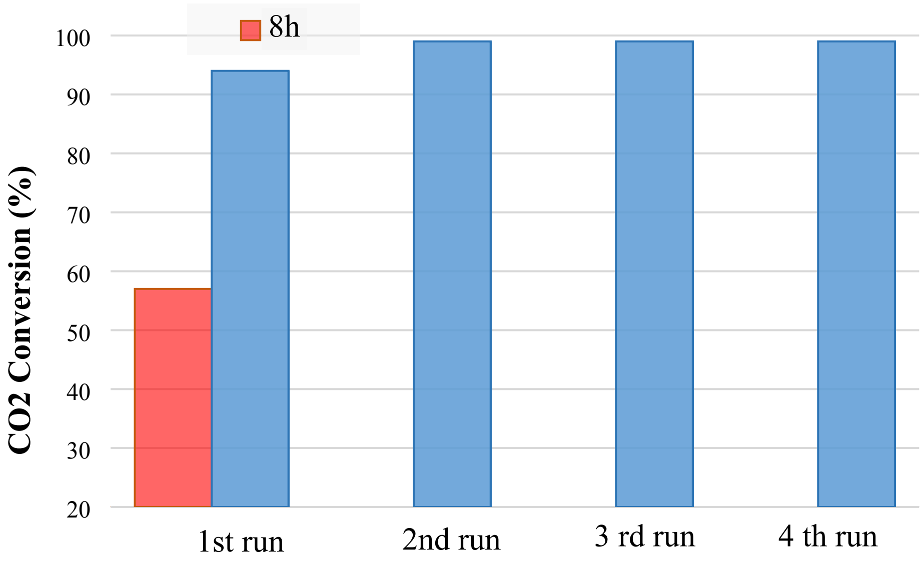


Figure S16. Recyclability of Zn/Co-ZIF (reused for 4 cycles); reaction conditions: 100^{o}C at 7 bar, reaction time 8h (red bar) and 16 h (blue bar).

Thermal stability (TGA)

The thermal stabilities of the MOFs were tested by thermal gravimetric analysis (TGA) from room temperature up to 800°C using a heating rate of 10°C/min under Ar atmosphere (20 cc/min). All ZIF-8 samples were activated at 200°C under vacuum for 3h before TGA analysis.

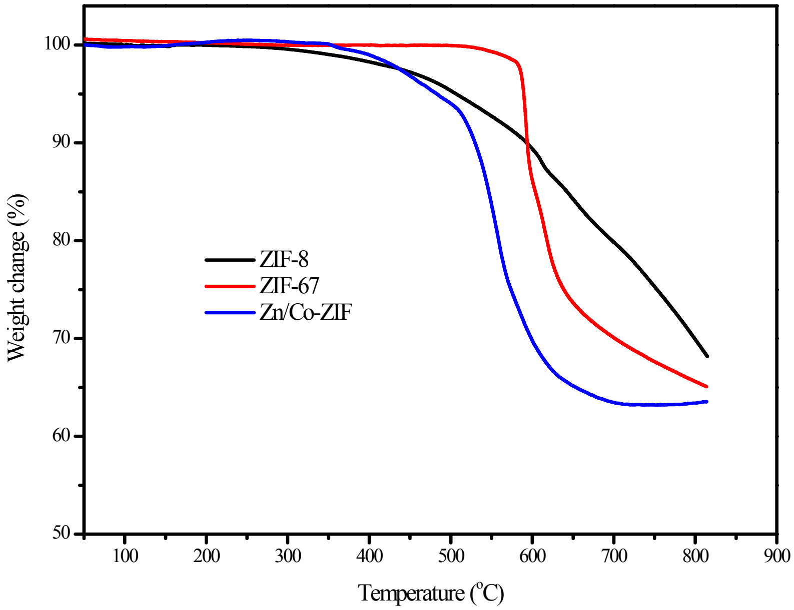


Figure S17. TGA analysis of the ZIF series.