Supporting Information

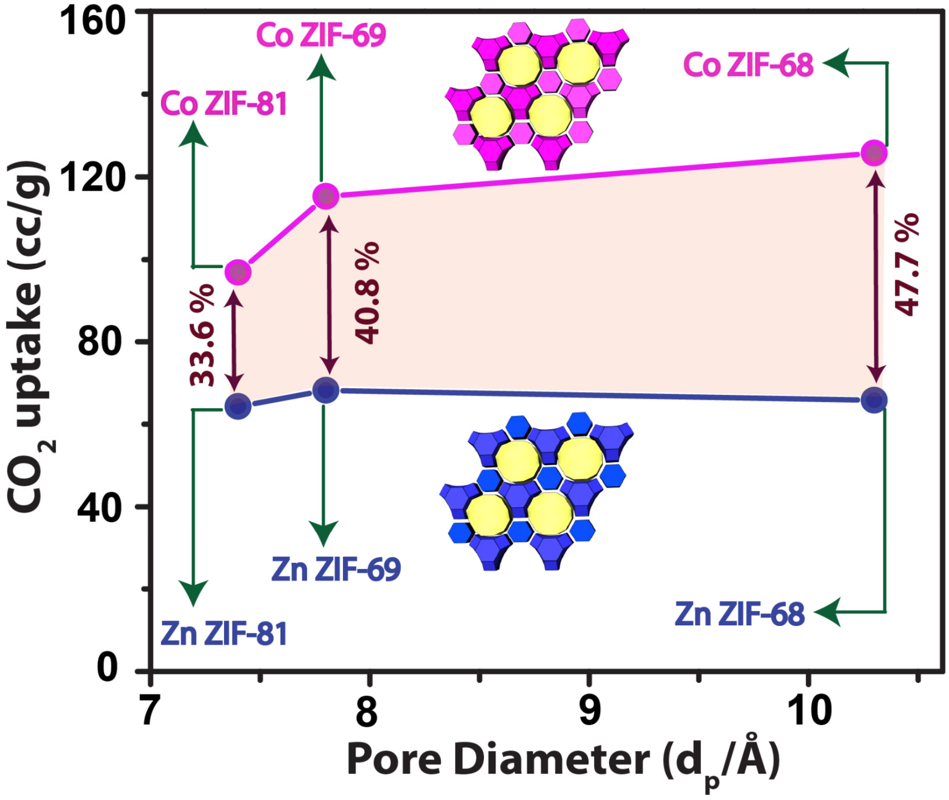
Enhancement of CO_2 Uptake in Iso-reticular Zeolitic Imidazolate Frameworks via Metal Substitution

Tamas Panda[a], Krishna M. Gupta[b], Jianwen Jiang[b] and Rahul Banerjee*[a]

[a] *Physical/Materials Chemistry Division, CSIR National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.*

[b] *Department of Chemical & Biomolecular Engineering, National University of Singapore, 117576, Singapore.*

E-mail: r.banerjee@ncl.res.in Fax: + 91-20-25902636; Tel: + 91-20-25902535



CONTENT

Section S1. Experimental measurements and methods used. **3**

Section S2. Detailed synthetic procedures, PXRD patterns and IR spectra for Co-ZIF-68, -69 and -81. **4-9**

Section S3. Single crystal X-ray diffraction data collection, structure solution and refinement procedures. **10-20**

Section S4. TGA data and the thermal stability Co-ZIF-68, -69 and -81. **21-22**

Section S5. Water stability of ZIF- 68, -69 and -81. **22-23**

Section S6. Single crystal structures of ZIF- 68, -69 and -81. **24-25**

Section S7. Gas adsorptions of Co-ZIF-68, -69 and -81. **25-33**

Section S8. *Ab initio* calculations of CO_2 binding energies. **34-35**

Section 1: Experimental measurements and methods used:

General Remarks: 2-nitroimidazole (2-nIM) was purchased from 3B Scientific Corporation, $Co(NO_3)_2.6H_2O$, benzimidazole, 5-chloro bezimidazole, 6-bromo benzimidazole and methanol were purchased from Sigma Aldrich Chemicals. *N, N*-dimethylformamide (DMF) was purchased from Rankem Chemicals. All starting materials were used without further purification. All experimental operations were performed in 5 mL glass vial inside a programmed oven for Co-nIM based Zeolitic Imidazolate Frameworks synthesis.

PXRD, TGA and FT-IR Experiments: The powder X-ray diffraction patterns were recorded using PANalytical X'PERT PRO instrument using iron-filtered Cu Kα radiation (λ=1.5406 Å) in the 2θ range of 5°-50° with a step size of 0.02° and a time of 0.3 second per step. Thermo gravimetric analysis (TGA) experiments were carried out in the temperature range of 25–800 °C on a SDT Q600 TG-DTA analyzer under N_2 and air atmosphere at a heating rate of 10 °C min-1. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal ZnSe ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR (Golden Gate).

Section S2. Detailed synthesis procedures of Co-ZIF-68, -69, and -81 and their experimental and simulated PXRD patterns:

Synthesis of Co-ZIF-68 [$C_{10}H_7CoN_5O_2$. DMF]: 1 ml 0.2(M) DMF solution of $Co(NO_3)_2.6H_2O$ was added to 1.5 ml 0.2(M) DMF solution of 2 nitro imidazole and 1 ml 0.2(M) DMF solution of benzimidazole in a 5 ml culture tube and heated 120 °C temperature for 24h. Plate like pink crystals were collected by filtration (75% yield by Co) and washed with DMF and dry acetone then dried in air.

FT-IR: (KBr 4000-600 cm^{-1}): 1670(w), 1660(m), 1461(s), 1354(s), 1273(m), 1237(s), 1171(s), 1110(m) , 901 (m), 825(m), 733 (s), 647 (m) cm^{-1}

Elemental analysis (%) of as synthesized Co-ZIF-68. [$C_{10}H_7CoN_5O_2$. DMF] calcd: C (43.21%), H (3.80%), N (23.26%); Found: C (43.32%), H (3.85%), N (23.02%)

Elemental analysis (%) of vacuum dried sample of Co-ZIF-68 [$C_{10}H_7CoN_5O_2$] calcd: C=41.67%, H=2.43 % and N=24.31%; Found: C=41.22%, H=2.45% and N=24.15%

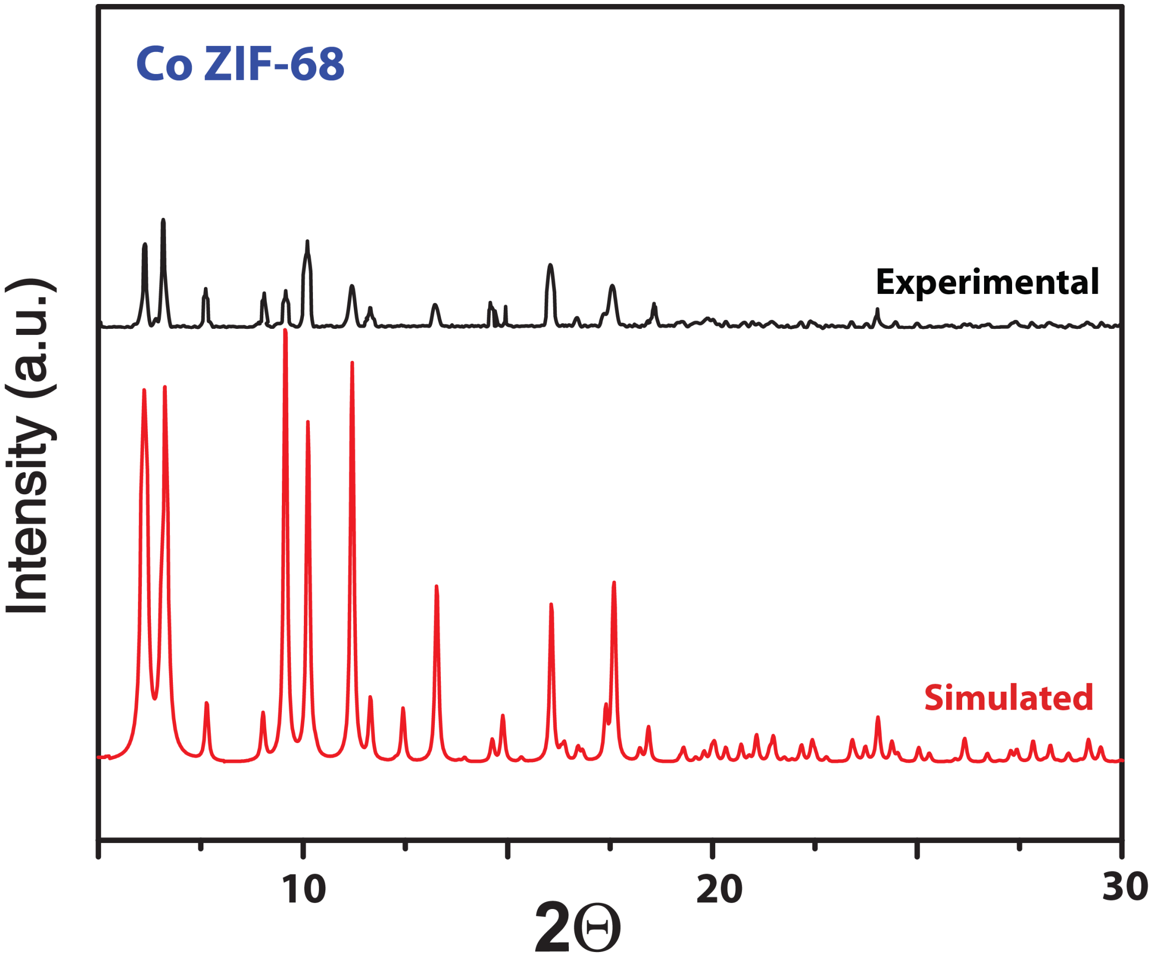


Figure S1. Comparison of the experimental PXRD pattern of as-synthesized Co-ZIF-68 (top) with the simulated single crystal structure (bottom).

Synthesis of Co-ZIF-69 [$C_{10}H_5Cl_2CoN_5O_2$. DMF]: 1 ml 0.2(M) DMF solution of $Co(NO_3)_2.6H_2O$ was added to 1.0 ml 0.2(M) DMF solution of 2 nitro imidazole and 3 ml 0.2(M) DMF solution of 5-chlorobenzimidazole in a 5 ml culture tube and heated 120 °C temperature for 12h. pink crystals were collected by filtration (77% yield by Co) and washed with DMF and dry acetone then dried in air.

FT-IR: (KBr 4000-600 cm^{-1}): 1660(s), 1456(s), 1360 (s), 1283(m), 1237(m), 1156(s), 1095(s) , 1059 (m), 953 (m), 795 (s), 718(m), 647(s) cm^{-1}

Elemental analysis (%) of as synthesized Co-ZIF-69. [$C_{10}H_5Cl_2CoN_5O_2$. DMF] calcd: C (36.28%), H (2.79%), N (19.53%); Found C (35.98%), H (2.67%), N (19.55%).

Elemental analysis (%) of vacuum dried sample of Co-ZIF-69 [$C_{10}H_5Cl_2CoN_5O_2$] calcd: C (33.62%), H (1.40%), N (19.61%); Found C (33.48%), H (1.50%), N (19.55%).

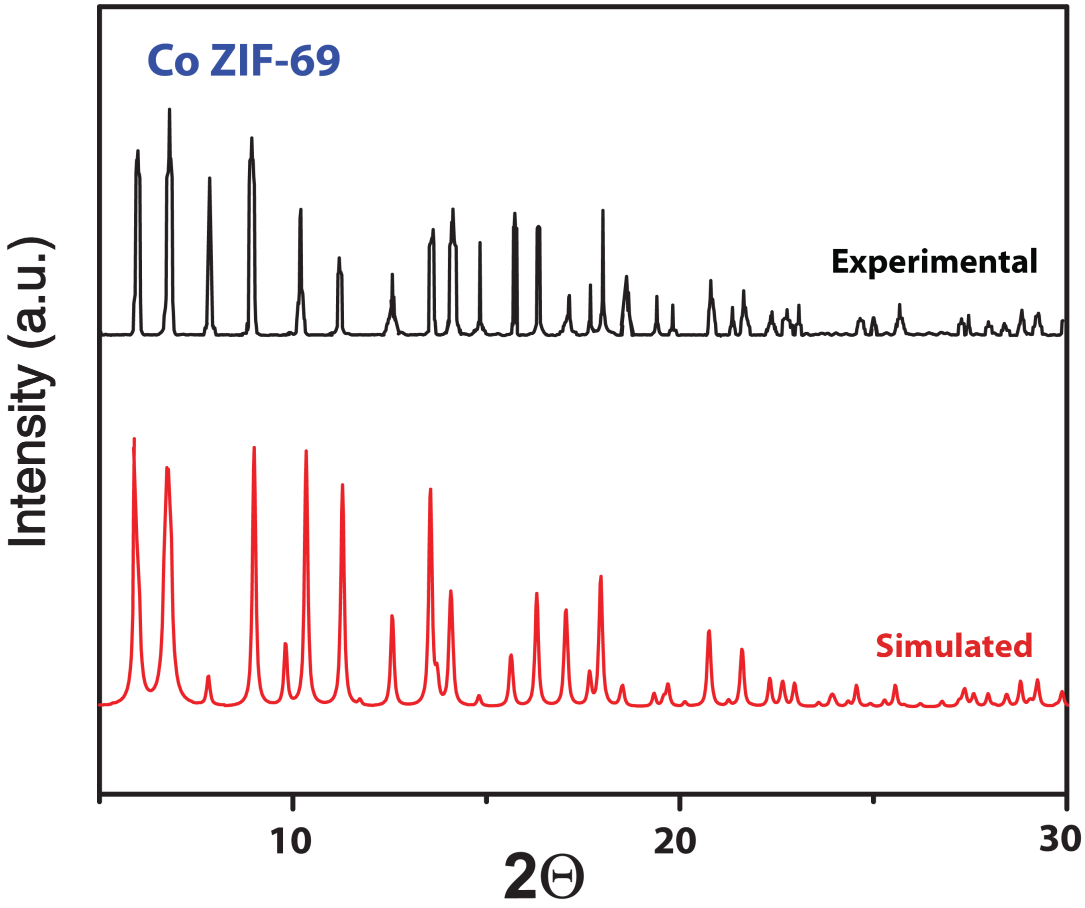


Figure S2. Comparison of the experimental PXRD pattern of as-synthesized Co-ZIF-69 (top) with the simulated from its single crystal structure (bottom).

Synthesis of Co-ZIF-81 [$C_{10}H_5Br_2CoN_5O_2$. DMF]: 1 ml 0.2(M) DMF solution of $Co(NO_3)_2.6H_2O$ was added to 1.0 ml 0.2(M) DMF solution of 2 nitro imidazole and 2 ml 0.2(M) DMF solution of 5-bromobenzimidazole in a 5 ml culture tube and heated 120 °C temperature for 12h. pink crystals were collected by filtration (60% yield by Co) and washed with DMF and dry acetone then dried in air.

FT-IR: (KBr 4000-600 cm^{-1}): 1644(w), 1456(s), 1349 (s), 1283(m), 1237(m), 1151(s), 1100(m), 1049 (m), 947 (m), 795 (s), 698(m), 647(s) cm^{-1}.

Elemental analysis (%) of as synthesized Co-ZIF-81. [$C_{10}H_5Br_2CoN_5O_2$. DMF] calcd: C (30.06%), H (2.31%), N (16.19%); Found C (30.15%), H (2.28%), N (16.17%).

Elemental analysis (%) of vacuum dried sample of Co-ZIF-81 [$C_{10}H_5Br_2CoN_5O_2$] calcd: C (26.92%), H (1.12%), N (15.70%); Found C (26.8 8%), H (1.05%), N (15.61%).

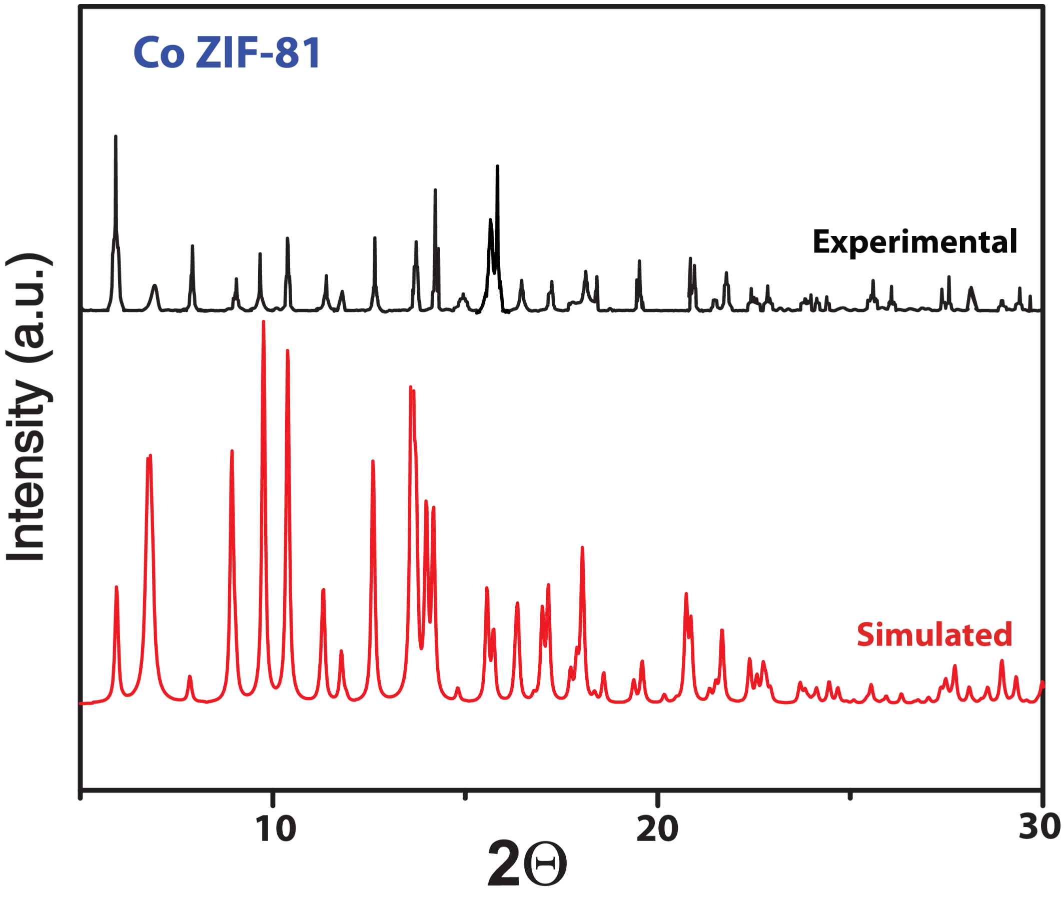


Figure S3. Comparison of the experimental PXRD pattern of as-synthesized Co-ZIF-81 (top) with the simulated from its single crystal structure (bottom).

IR spectrums:

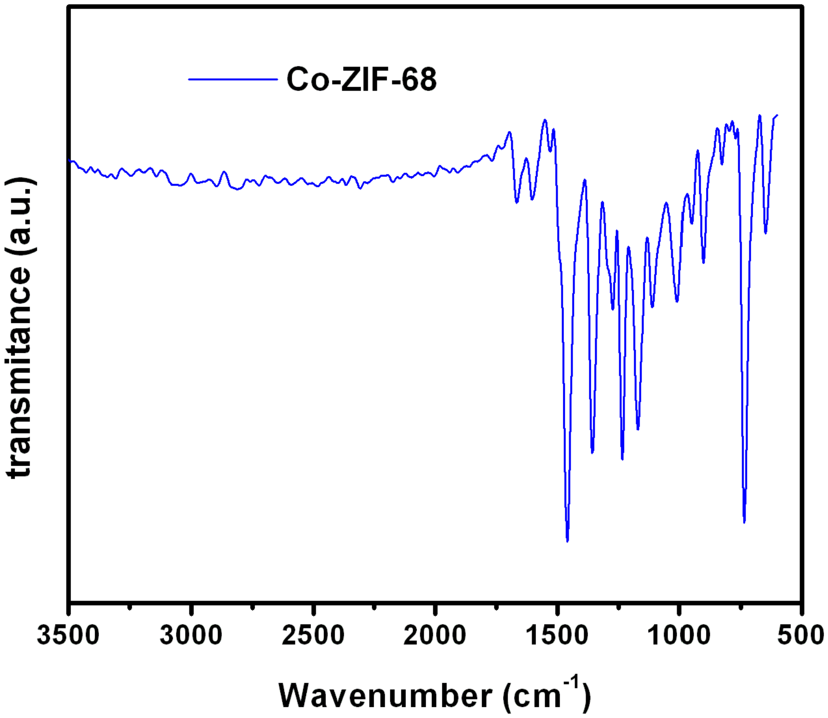


Figure S4. IR spectrums of Co-ZIF-68

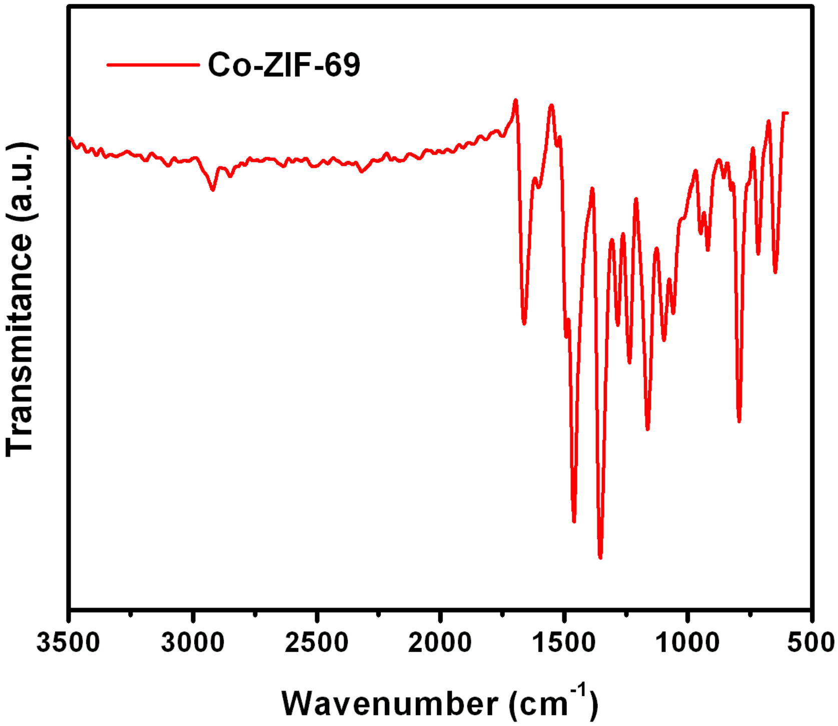


Figure S5. IR spectrums of Co-ZIF-69

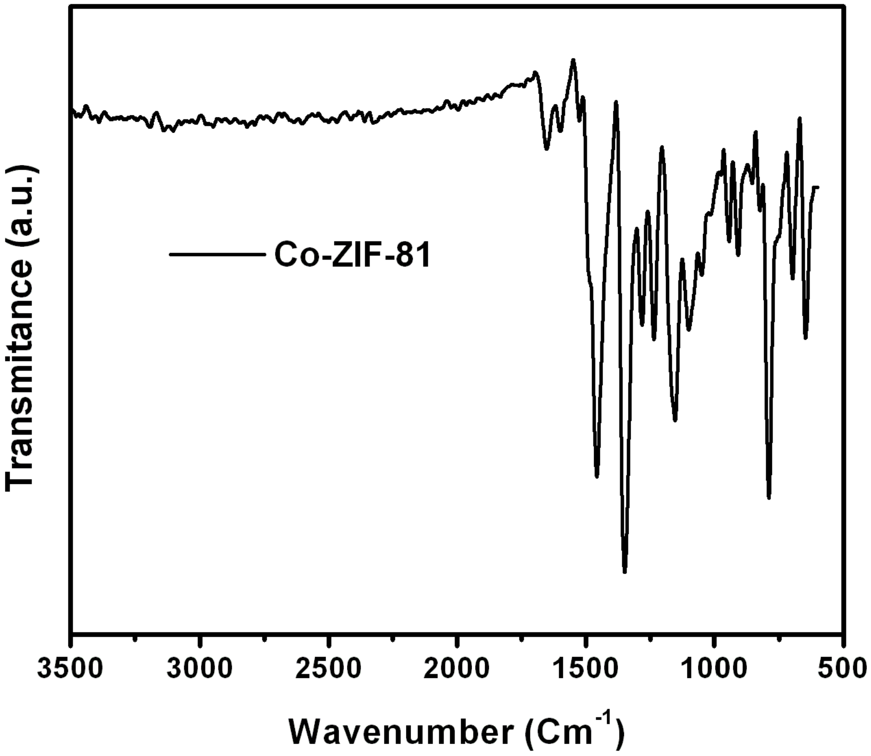


Figure S6. IR spectrums of Co-ZIF-81

Section S3. Single crystal X-ray diffraction data collection, structure solution and refinement procedures:

General data collection and refinement procedures:

Data were collected on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W (50 kV, 0.8 mA) to generate Mo Kα radiation (λ = 0.71073 Å). The crystal reported in this paper was mounted on Nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. CrysAlis^{Pro} program software was used to carry out overlapping φ and ω scans at detector (2θ) settings ($2\theta = 28°$). Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration. In no data collection was evidence for crystal decay encountered. Following exhaustive review of collected frames the resolution of the dataset was judged. Data were integrated using CrysAlis^{Pro} software with a narrow frame algorithm. Data were subsequently corrected for absorption by the program SCALE3 ABSPACK[1] scaling algorithm.These structures were solved by direct method and refined using the SHELXTL 97[2] software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times Ueq of the attached C atoms. Data were collected at 100(2) K for the Co-ZIFs presented in this paper. This lower temperature was considered to be optimal for obtaining the best data. The structure was examined using the Addsym subroutine of PLATON[3] to assure that no additional symmetry could be applied to the models. The ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. For all structures we note that elevated R-values are commonly encountered in MOF crystallography (specially in ZIFs) for the reasons expressed above by us and by other research groups.[4-13] Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited in CCDC as deposition No. CCDC 952993 –952995. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 lEZ, U.K. [fax: þ 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk].

1. CrysAlisPro, Version 1.171.33.66; Oxford Diffraction Ltd.: Abingdon, U.K., 2010.
2. G. M. Sheldrick, (1997). SHELXS ‘97 and SHELXL ‘97. University of Göttingen, Germany.
3. A. L. Spek (2005) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
4. L. A. Dakin, P. C. Ong, J. S. Panek, R. J. Staples, and P. Stavropoulos, Organometallics, 2000, **19**, 2896.
5. S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, and M. Yamashita, J. Am. Chem. Soc. 2002, **124**, 2568.
6. M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O’Keeffe, and O. M. Yaghi, Proc. Natl. Acad. Sci. USA, 2002, **99**, 4900.
7. R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, and K. R. Dunbar, Inorg. Chem. 1999, **38**, 144.
8. K. Biradha, Y. Hongo, and M. Fujita, Angew. Chem. Int. Ed. 2000, **39**, 3843.
9. P. Grosshans, A. Jouaiti, M. W. Hosseini, and N. Kyritsakas, New J. Chem, (Nouv. J. Chim,) 2003, **27**, 793.
10. N. Takeda, K. Umemoto, K. Yamaguchi, and M. Fujita, Nature (London) 1999, **398**, 794.
11. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, and O. M. Yaghi, Science, 2002, **295**, 469.
12. B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, and W. Lin, Angew. Chem. Int. Ed. 2005, **44**, 72.
13. F. A. Cotton, C. Lin, and C. A. Murillo, Inorg. Chem. 2001, **40**, 478.

Co-ZIF-68 (Hexagonal)

Experimental and refinement details for Co-ZIF-68:

A pink colored plate like crystal ($0.31\times 0.26 \times 0.15$ mm^3) of **Co-ZIF-68** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation ($\lambda = 0.71073$ Å) at 100(2) K in a liquid N_2 cooled stream of nitrogen. A total of 5153 reflections were collected of which 2116 were unique. The range of θ was from 3.05 to 29.26. Analysis of the data showed negligible decay during collection. The structure was solved in the Hexagonal $P6_3/mmc$ space group, with Z = 24, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. we have repeatedly collected the single crystal XRD data of Co-ZIF-68 at different temperature (100, 120, 150K). We would like to mention that each time during the refinement of crystal structure we encountered electron densities within the framework cavity. However, assigning these electron densities with isolated O, N and C atoms, leads to highly distorted atoms, although the refinement become stable with decreased R factor and goodness of fit. Hence, we believe that one DMF molecule reside inside the asymmetric unit of Co-ZIF-68, however, these atoms of DMF molecule have very high thermal parameters apart from Co-ZIF frameworks with several IUCr checkcif errors. Hence we have decided to use the SQUEEZE routine to remove these unstable and highly distorted DMF molecules from the pores of Co-ZIF-68. It should be noted that SQUEEZE structure is very stable with minimal IUCr checkcif problems, less R factor and goodness of fit. In this manuscript we have provided the SQUEEZE applied cif file of Co-ZIF-68. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0992$($F > 2\sigma F$) and $wR_2 = 0.2938$ (all data) with GOF = 0.884. CCDC 952993.

Refine_special_details: We believe anisotropic distortion in the aromatic ring in Co-ZIF-68 structure appears due to static or dynamic disorder. As a result despite lowering the data collection temperature to 100 K this distortion remains persistent. There is disorder by symmetry in the structure of Co-ZIF-68.

Table S1: Crystal data and structure refinement for Co-ZIF-68 (squeezed):

Empirical formula	$C_{10}H_7CoN_5O_2$
Formula weight	288.14
Temperature	100(2) K
Wavelength	0.71073
Crystal system	Hexagonal
Space group	*P*6$_3$/mmc
Unit cell dimensions	a = 26.674(2) Å α = 90°
	b = 26.674(2) Å β = 90°
	c = 18.4694(20)Å γ = 90°
Volume	11380.5(19)
Z	24
Density (calculated)	1.009
Absorption coefficient	0.905
F(000)	3480
Crystal size	0.31× 0.26 × 0.15mm^3
Theta range for data collection	3.05– 29.26
Index ranges	-26= h <= 36, -32<= k <= 36, -25<= l <= 25
Reflections collected	5153
Independent reflections	2116
Completeness to theta	98.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5153/0/165
Goodness-of-fit on F^2	0.884
Final R indices [I>2sigma(I)]	R_1 = 0.0992, wR_2 = 0.2938
R indices (all data)	R_1 = 0.1630, wR_2 = 0.3300
Largest diff. peak and hole	0.916 and -0.565 eÅ^{-3}

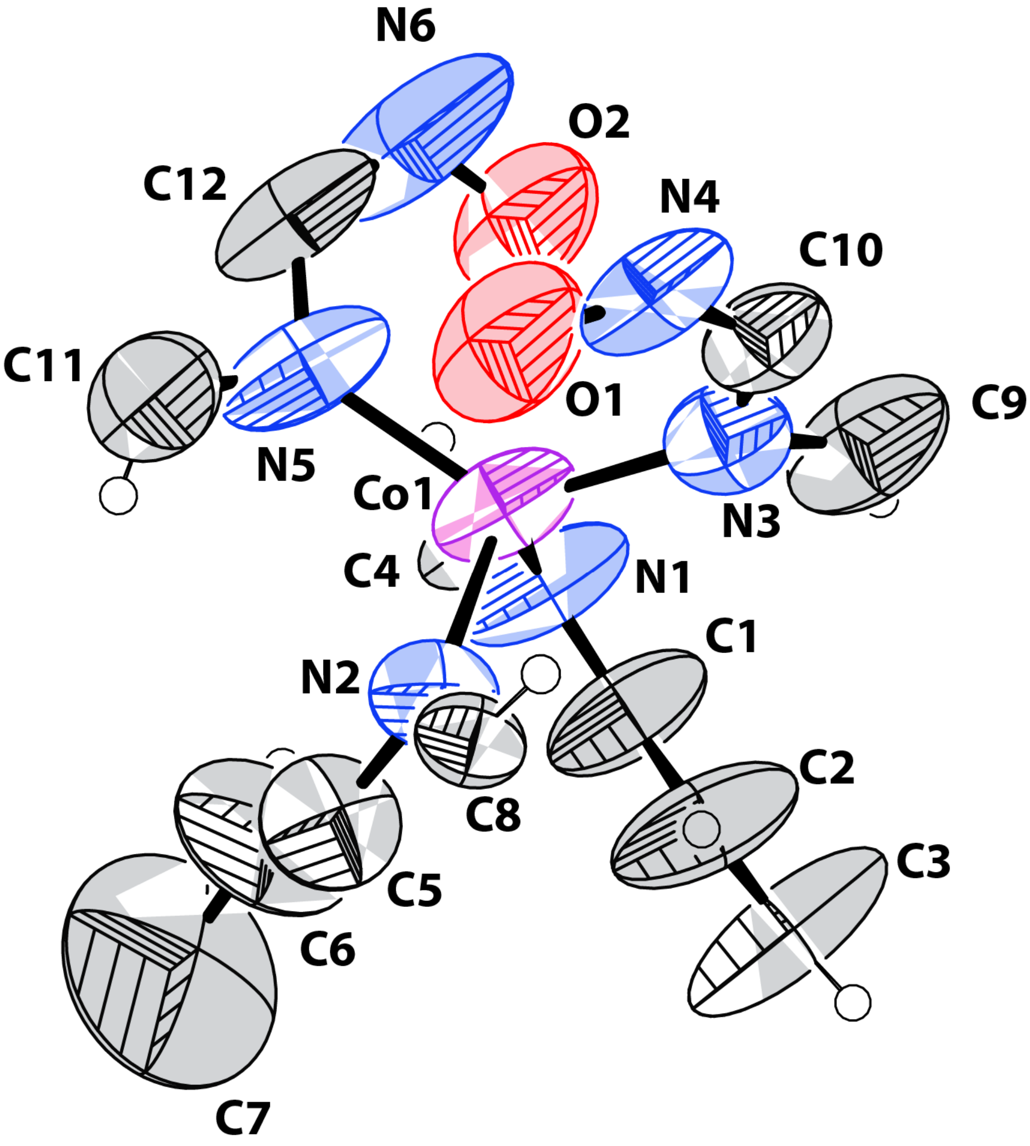


Figure S7. ORTEP diagram (50% probability) of the asymmetric unit of Co-ZIF-68.

Co-ZIF-69 (Hexagonal)

Experimental and refinement details for Co-ZIF-69:

A colorless block like crystal (0.33× 0.23× 0.16 mm^3) of **Co-ZIF-69** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation (λ = 0.71073 Å) at 100(2) K in a liquid N_2 cooled stream of nitrogen. A total of 5174 reflections were collected of which 2364 were unique. The range of θ was from 3.16 to 29.17. Analysis of the data showed negligible decay during collection. The structure was solved in the Hexagonal $P6_3$/mmc space group, with Z = 24, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. we have repeatedly collected the single crystal XRD data of Co-ZIF-69 at different temperature (100, 120, 150K). We would like to mention that each time during the refinement of crystal structure we encountered electron densities within the framework cavity. However, assigning these electron densities with isolated O, N and C atoms, leads to highly distorted atoms, although the refinement become stable with decreased R factor and goodness of fit. Hence, we believe that one DMF molecule reside inside the asymmetric unit of Co-ZIF-69, however, these atoms of DMF molecule have very high thermal parameters apart from Co-ZIF-69 frameworks with several IUCr checkcif errors. Hence we have decided to use the SQUEEZE routine to remove these unstable and highly distorted DMF molecules from the pores of Co-ZIF-69. It should be noted that SQUEEZE structure is very stable with minimal IUCr checkcif problems, less R factor and goodness of fit. In this manuscript we have provided the SQUEEZE applied cif file of Co-ZIF-69. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0997$ ($F > 2\sigma F$) and $wR_2 = 0.2862$(all data) with GOF = 0.979. CCDC 952994.

Refine_special_details:

We believe anisotropic distortion in the aromatic ring in Co-ZIF-69 structure appears due to static or dynamic disorder. As a result despite lowering the data collection temperature to 100 K this distortion remains persistent. Moreover, there is disorder by symmetry in the crystal structure of Co-ZIF-69.

NB: There is only one Cl atom per cobalt metal center in the crystal structure Co-ZIF-69. However, due to crystallographic disorder of chlorine atom Co-ZIF-69 shows two chlorine atoms with ½ occupancy factor per cobalt center. Hence, the formula used (C10H5Cl2CoN5O2) in the cif and crystallographic tables is the original one, generated from crystallographically.

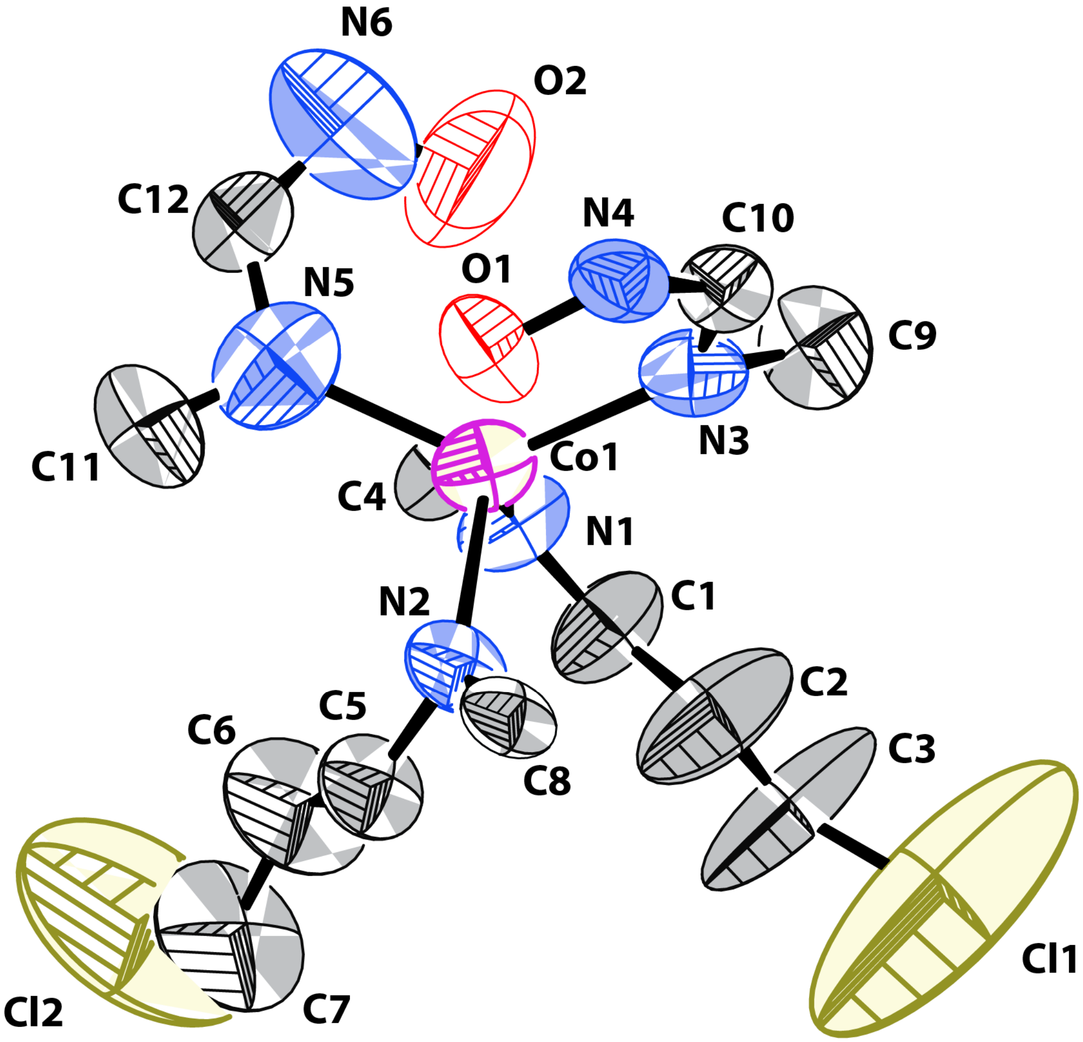


Figure S8. ORTEP diagram (50% probability) of the asymmetric unit of Co-ZIF-69.

Table S2: Crystal data and structure refinement for Co-ZIF-69 (squeezed):

Empirical formula	C10H5Cl2CoN5O2
Formula weight	357.02
Temperature	100(2) K
Wavelength	0.71073Å
Crystal system	Hexagonal
Space group	$P6_3$/mmc
Unit cell dimensions	a = 26.113(2) Å α = 90°
	b = 26.113(2) Å β = 90°
	c = 19.6459(14) Å γ = 120°
Volume	11601.2(16)
Z	24
Density (calculated)	1.226
Absorption coefficient	1.168
F(000)	4248
Crystal size	0.33× 0.23× 0.16 mm^3
Theta range for data collection	3.16– 29.17
Index ranges	-34= h <= 31, -35<= k <= 35, -21<= l <= 25
Reflections collected	5174
Independent reflections	2364
Completeness to theta	99.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5174 /0/191
Goodness-of-fit on F^2	0.979
Final R indices [I>2sigma(I)]	R_1 = 0.0997, wR_2 = 0.2862
R indices (all data)	R_1 = 0.1765, wR_2 = 0.3340
Largest diff. peak and hole	0.733 and – 0.566 $eÅ^{-3}$

Co-ZIF-81 (Hexagonal)

Experimental and refinement details for Co-ZIF-81:

A colorless block like crystal (0.31× 0.26× 0.17 mm^3) of **Co-ZIF-81** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation (λ = 0.71073 Å) at 100(2) K in a liquid N_2 cooled stream of nitrogen. A total of 4947 reflections were collected of which 1471 were unique. The range of θ was from 3.13 to 29.14. Analysis of the data showed negligible decay during collection. The structure was solved in the Hexagonal $P6_3/mmc$ space group, with Z = 24, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. we have repeatedly collected the single crystal XRD data of Co-ZIF-81 at different temperature (100, 120, 150K). We would like to mention that each time during the refinement of crystal structure we encountered electron densities within the framework cavity. However, assigning these electron densities with isolated O, N and C atoms, leads to highly distorted atoms, although the refinement become stable with decreased R factor and goodness of fit. Hence, we believe that one DMF molecule reside inside the asymmetric unit of Co-ZIF-81, however, these atoms of DMF molecule have very high thermal parameters apart from Co-ZIF-81 frameworks with several IUCr checkcif errors. Hence we have decided to use the SQUEEZE routine to remove these unstable and highly distorted DMF molecules from the pores of Co-ZIF-81. It should be noted that SQUEEZE structure is very stable with minimal IUCr checkcif problems, less R factor and goodness of fit. In this manuscript we have provided the SQUEEZE applied cif file of Co-ZIF-81. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0995$ ($F > 2\sigma F$) and $wR_2 = 0.2545$(all data) with GOF = 0.702. CCDC 952995.

Refine_special_details:

We believe anisotropic distortion in the aromatic ring in Co-ZIF-81 structure appears due to static or dynamic disorder. As a result despite lowering the data collection temperature to 100 K this distortion remains persistent. Moreover, there is disorder by symmetry in the crystal structure of Co-ZIF-81.

NB: There is only one Br atom per cobalt metal center in the crystal structure Co-ZIF-81. However, due to crystallographic disorder of bromine atom Co-ZIF-81 shows two bromine atoms with ½ occupancy factor per cobalt center. Hence, the formula used (C10H5Br2CoN5O2) in the cif and crystallographic tables is the original one, generated from crystallographically.

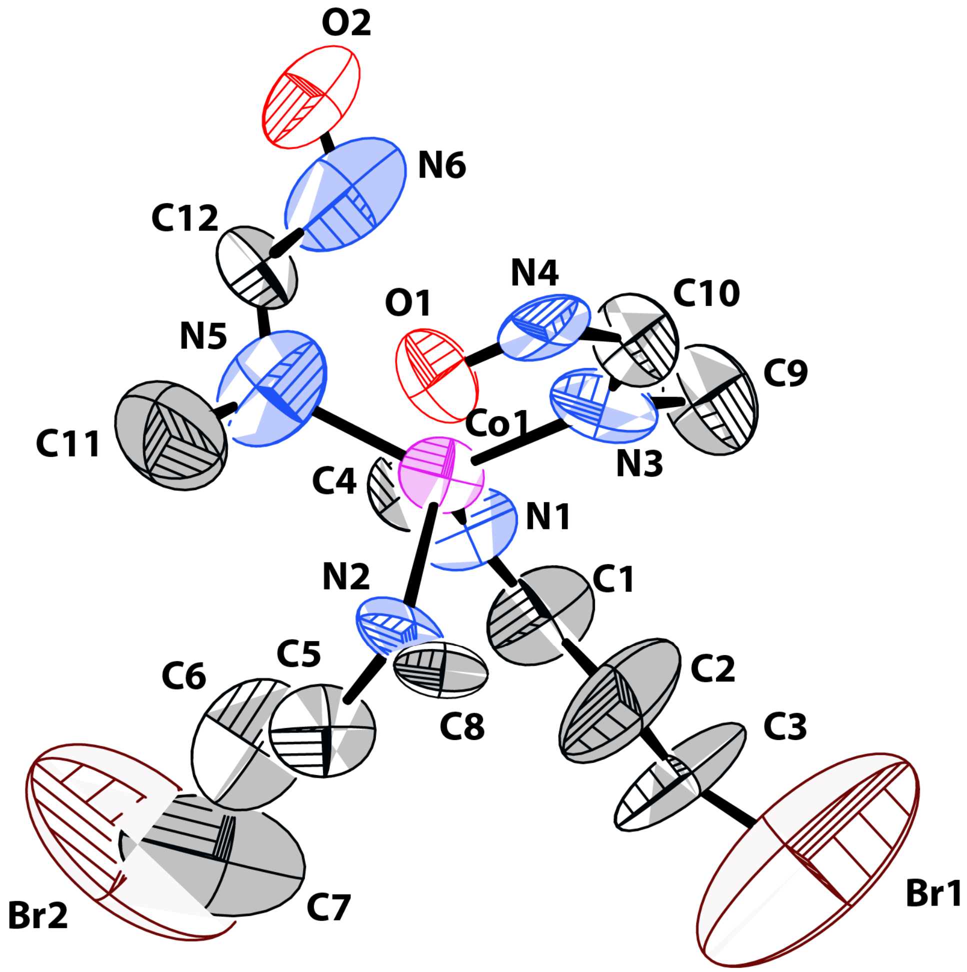


Figure S9. ORTEP diagram (50% probability) of the asymmetric unit of Co-ZIF-81.

Table S3: Crystal data and structure refinement for Co-ZIF-81 (squeezed):

Empirical formula	$C_{10}H_5Br_2CoN_5O_2$
Formula weight	445.92
Temperature	100(2) K
Wavelength	0.71073Å
Crystal system	Hexagonal
Space group	$P6_3$/mmc
Unit cell dimensions	a = 25.9949(12) Å α = 90°
	b = 25.9949(12) Å β = 90°
	c = 19.7757(11) Å γ = 120°
Volume	11572.9(10)
Z	24
Density (calculated)	1.536
Absorption coefficient	5.038
F(000)	5112
Crystal size	0.31× 0.26× 0.17 mm^3
Theta range for data collection	3.13– 29.14
Index ranges	-19= h <= 35, -20<= k <= 35, -18<= l <= 27
Reflections collected	4947
Independent reflections	1471
Completeness to theta	94.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4947 /0/191
Goodness-of-fit on F^2	0.702
Final R indices [I>2sigma(I)]	R_1 = 0.0995, wR_2 = 0.2545
R indices (all data)	R_1 = 0.1975, wR_2 = 0. 3115
Largest diff. peak and hole	0.657 and – 0.537 eÅ^{-3}

Section S4. TGA data and the thermal stability of Co-ZIF-68, -69 and -81:

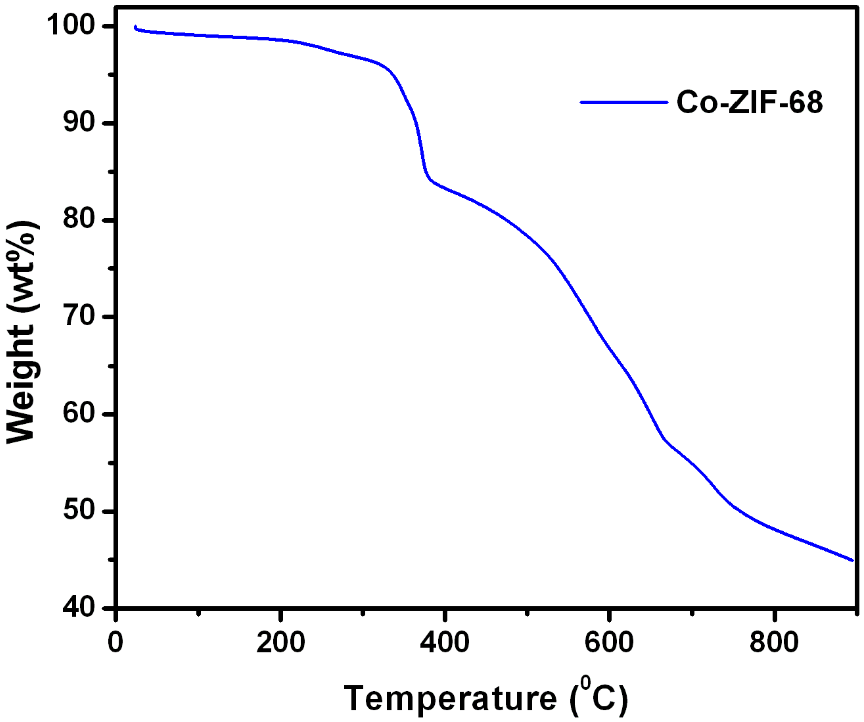


Figure S10. Thermo gravimetric analysis (TGA) data of Co-ZIF-68.

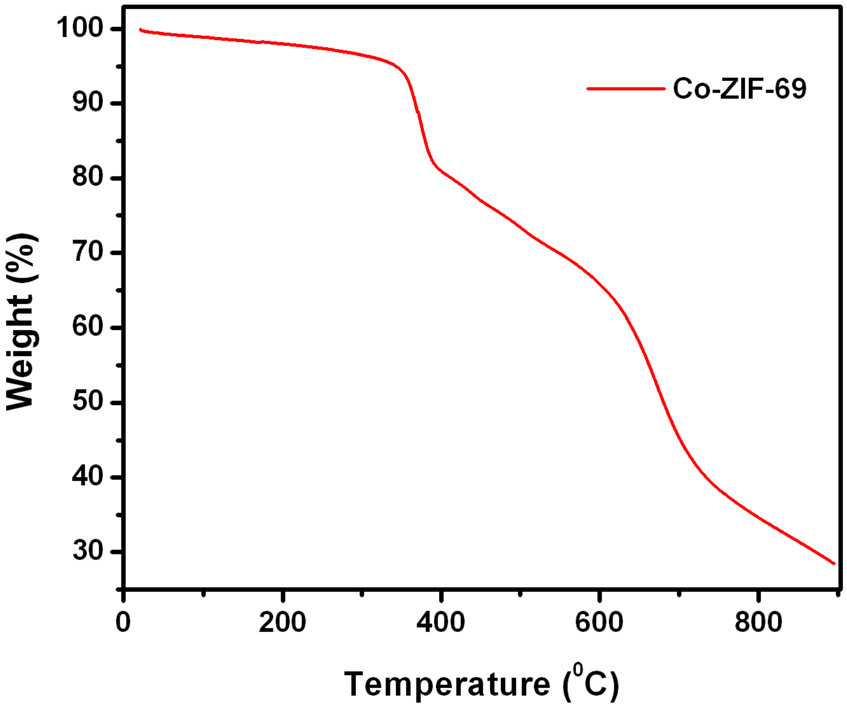


Figure S11. Thermo gravimetric analysis (TGA) data of Co-ZIF-69.

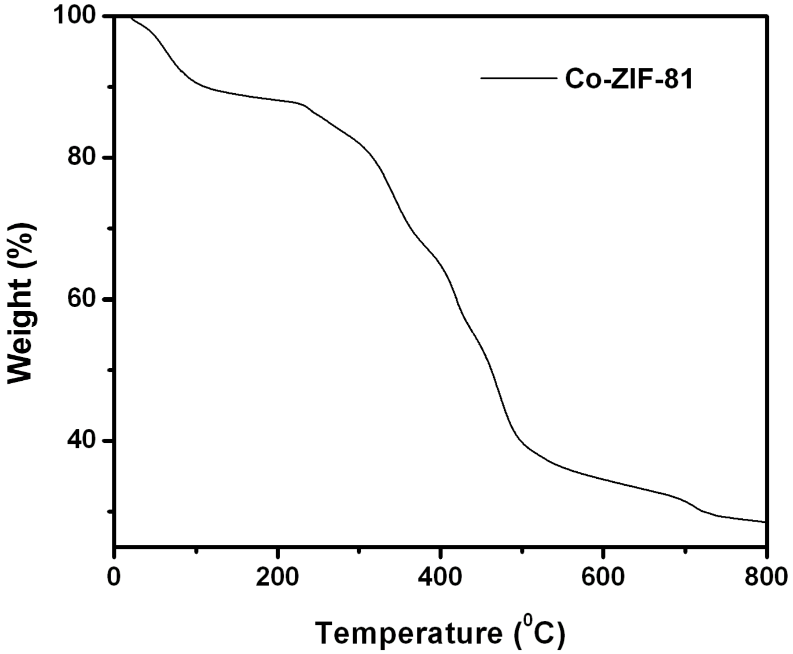


Figure S12. Thermo gravimetric analysis (TGA) data of Co-ZIF-81.

Section S5. Water stability of Co-ZIF-68, -69 and -81:

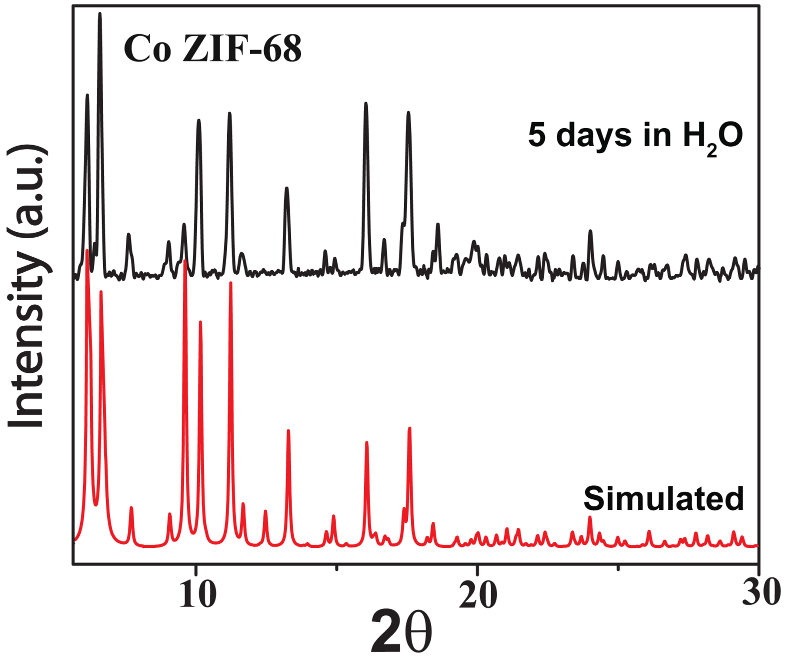


Figure S13. PXRD patterns of Co-ZIF-68 performed during stability test in water. The framework structure of Co-ZIF-68 was unchanged after 5 days and matches well with simulated PXRD.

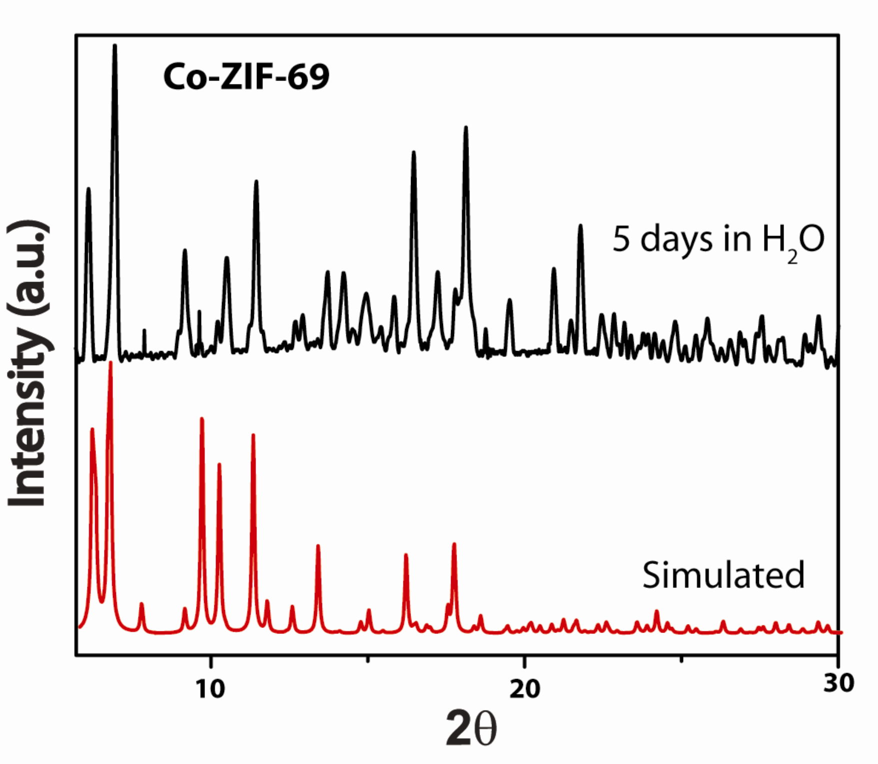


Figure S14. PXRD patterns of Co-ZIF-69 performed during stability test in water. The framework structure of Co ZIF-69 was unchanged after 5 days and matches well with simulated PXRD.

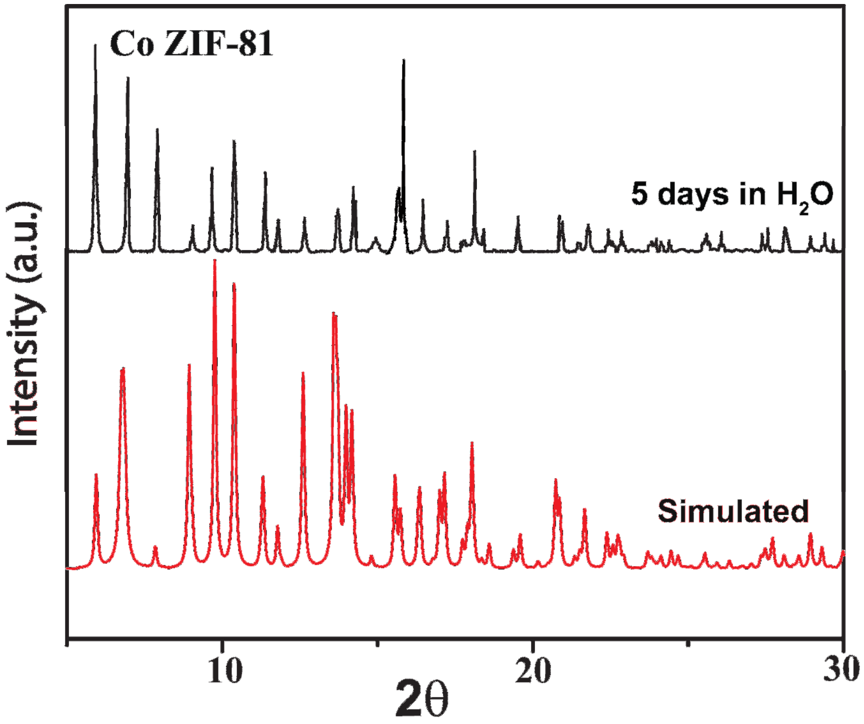


Figure S15. PXRD patterns of Co-ZIF-81 performed during stability test in water. The framework structure of Co-ZIF-81 was unchanged after 5 days and matches well with simulated PXRD.

Section S6. Single crystal structures of MOFs:

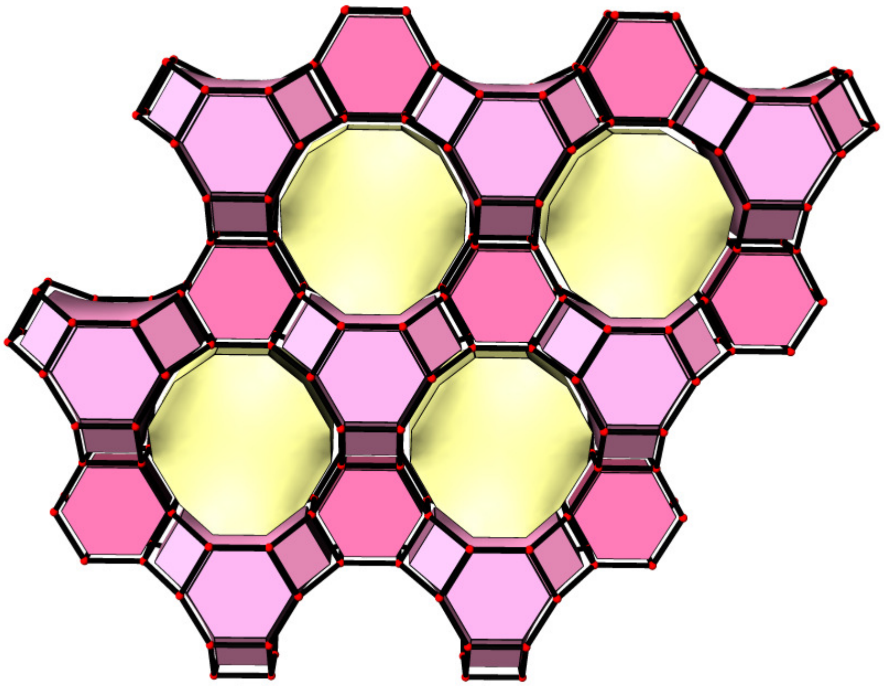


Figure S16. Co-ZIF-68, -69 and -81 adopts GME topology. The structure is shown as an exploded tiling (pink) with all the tetrahedral Co(II) atoms (red) linked.

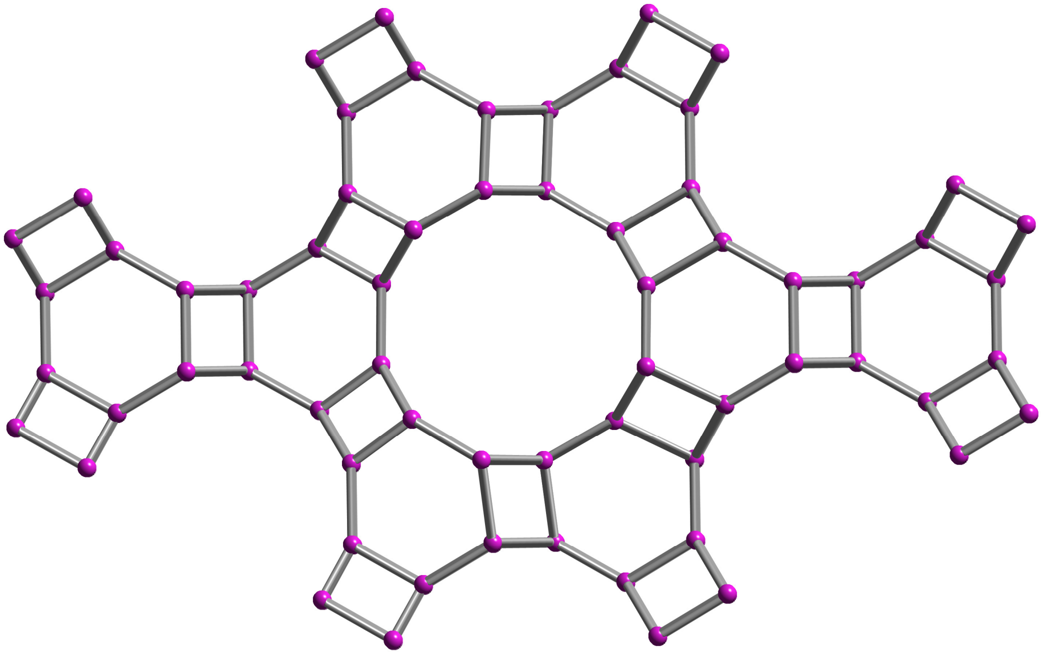


Figure S17. GME topology framework build by Co metal center connection of Co-ZIF-68, -69 and -81 .

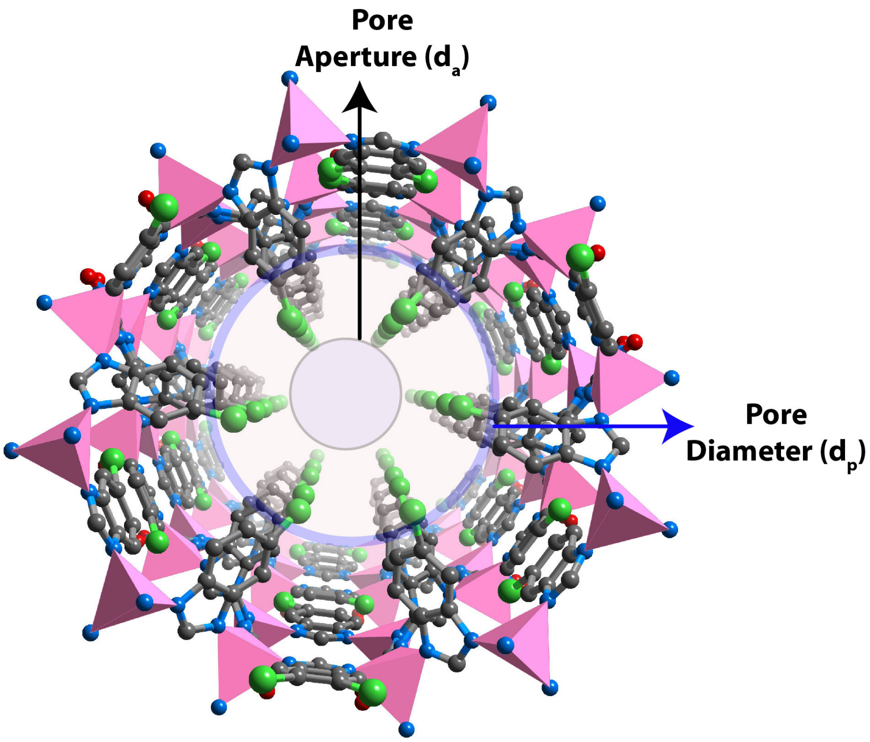


Figure S18: Pictorial definition of pore aperture (d_a) and pore diameter (d_p) of Zn and Co based GME ZIFs.

Table S4: Pore diameters (d_p) and Pore Apertures (d_a) of Zn and Co-ZIFs:

S.N	Zn and Co ZIFs	Pore diameter (d_p)	Pore Aperture (d_a)
1	Zn-ZIF-68	10.3 Å	7.5 Å
2	Co-ZIF-68	10.5 Å	7.7 Å
3	Zn-ZIF-69	7.8 Å	4.4 Å
4	Co-ZIF-69	8.0 Å	4.6 Å
5	Zn-ZIF-81	7.4 Å	3.9 Å
6	Co-ZIF-81	7.7 Å	4.1 Å

Section S7. Gas Adsorption analysis of Co-ZIF-68, -69 and -81:

Gas Adsorption Measurements: Low-pressure volumetric gas adsorption measurements were performed at 77 K for N_2, maintained by a liquid nitrogen bath, with pressures ranging from 0 to 760 Torr on a Quantachrome, Quadrasorb automatic volumetric instrument. CO_2 adsorption measurements were carried out at 273 K and 298K within the same pressure range. Ultra high-purity H_2 was obtained by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the volumetric system. The pink coloured micro crystals of Co-ZIF-68, -69 and -81 were soaked in dried Methanol for 12 h. Freshly dried MeOH was subsequently added and the crystals were kept for additional 48 h to remove free solvates presented in the framework. The so-obtained materials were dried under dynamic vacuum (< 10^{-3} Torr) at RT overnight. The sample were heated under at 60 ºC (12 h) to remove the solvent present on the surface and then further heated to 120 ºC (24 h) to remove the non coordinated solvent molecule (DMF). Co-ZIF-68 has apparent surface area 791.13 m^2g^{-1} (Brunauer–Emmett–Teller (BET) model [K. S. Walton, R. Q. Snurr, JACS 129, 8552 (2007)]. Co-ZIF-69 has apparent surface area of 700.71 m^2g^{-1} (Brunauer– Emmett–Teller (BET) were obtained by using the data points (P/Po= 0.01-0.1) on the adsorption branch. However, for Co-ZIF-81 has apparent surface areas of 661.23 m^2g^{-1} (Brunauer– Emmett–Teller (BET) were obtained by using the data points (P/Po= 0.01-0.1) on the adsorption branch.

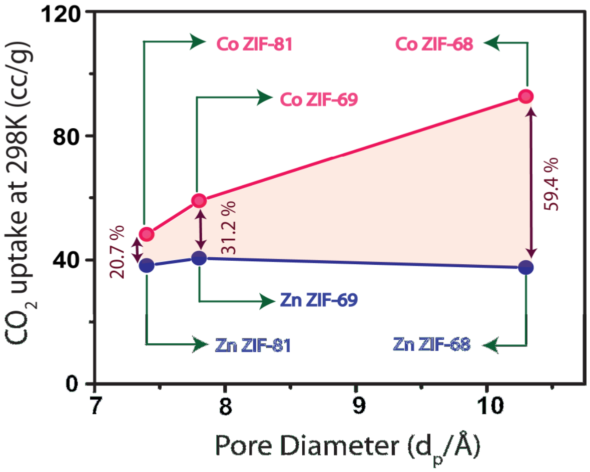


Figure S19. Pore diameter (d_p) vs CO_2 uptake at 298K for Co and Zn based GME ZIFs. It is clearly indicate that Co based GME ZIFs analogue has much higher CO_2 uptake than Zn based GME ZIFs.

We would like to mention that, Although, different metal doped iso-structural MOFs can exhibit different properties but it is limited to only few MOFs within a particular short range. For example, Zn/DOBDC shows CO2 uptake 120 cc/gm at 1 bar pressure, however changing the metal from Zn to Co enhances the CO2 uptake to 152 cc/gm [*J. Am. Chem. Soc.,* 2008, 130, 10870]. The CO$_2$ uptake increases 21.05 % from Zn/DOBDC to isostructural Co/DOBDC which is a small enhancement. On the other hand, in our contribution, changing of metal center (Zn to Co) in a series of isoreticular imidazolate frameworks (ZIF-68, -69 and -81) drastically enhances the CO$_2$ uptake. For Co-ZIF-68, -69 and-81 the increment of CO$_2$ from its Zn analogues are 33.6, 40.8, 47.7 % at 273K and 20.7, 31.2, 59.4 % at 298K respectively (see Figure S20)

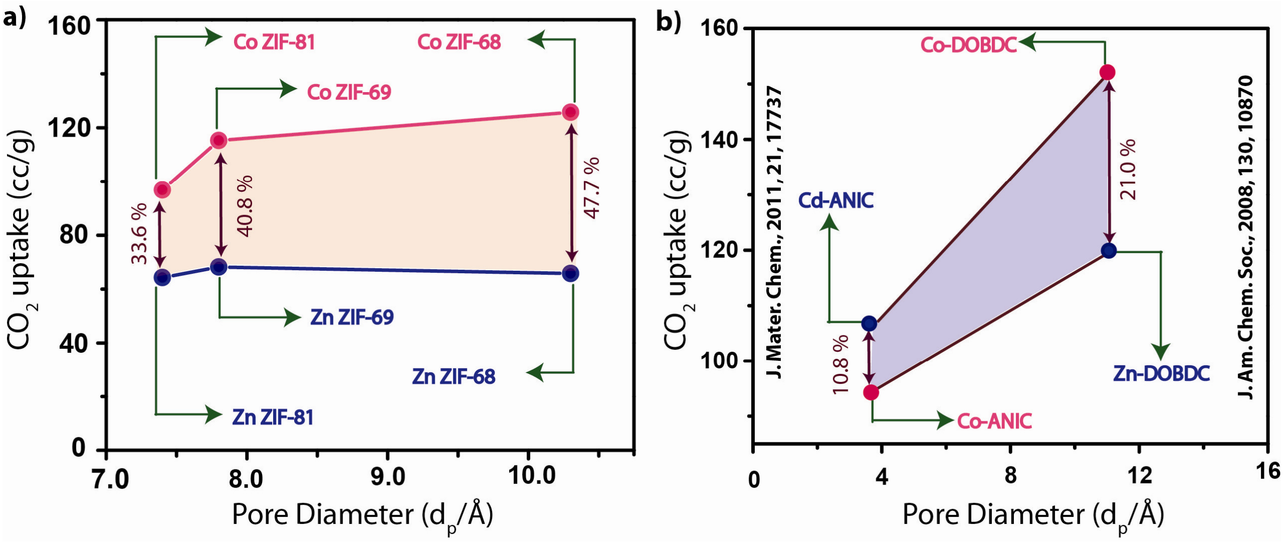


Figure S20: a) Drastic CO$_2$ uptake enhancement of Co ZIF-68, -69 and -81 from their Zn based analogues at 273K b) Small CO$_2$ uptake enhancement of reported MOFs by changing metal center.

H_2 adsorption isotherm of Co-ZIF-68, -69 and -81:

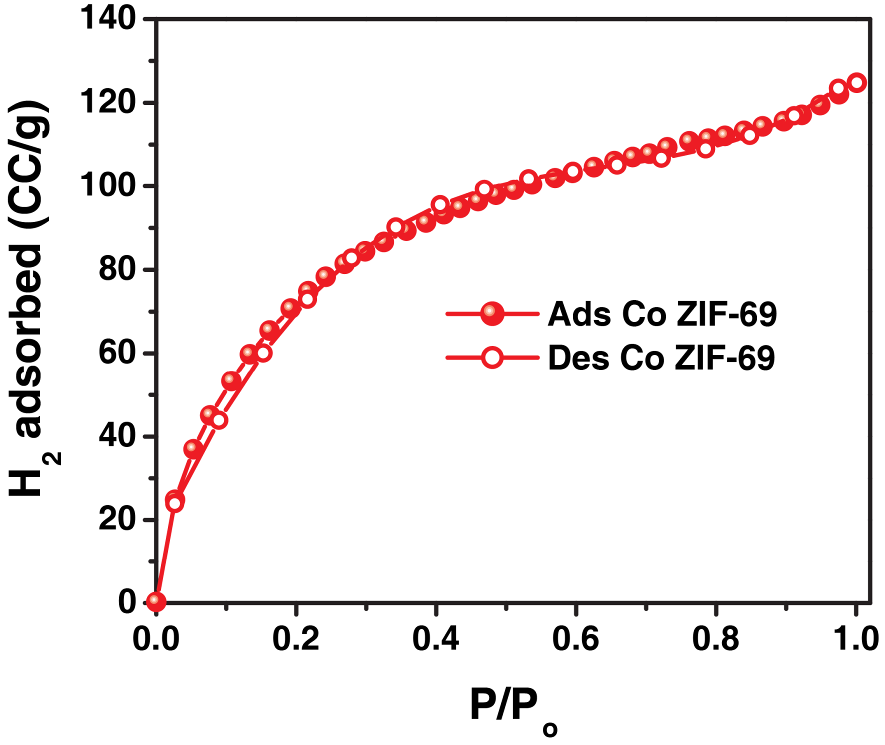


Figure S21. H_2 adsorption isotherm of Co-ZIF-69 taken at 77 K (red). Filled and open symbols represent adsorption and desorption branches.

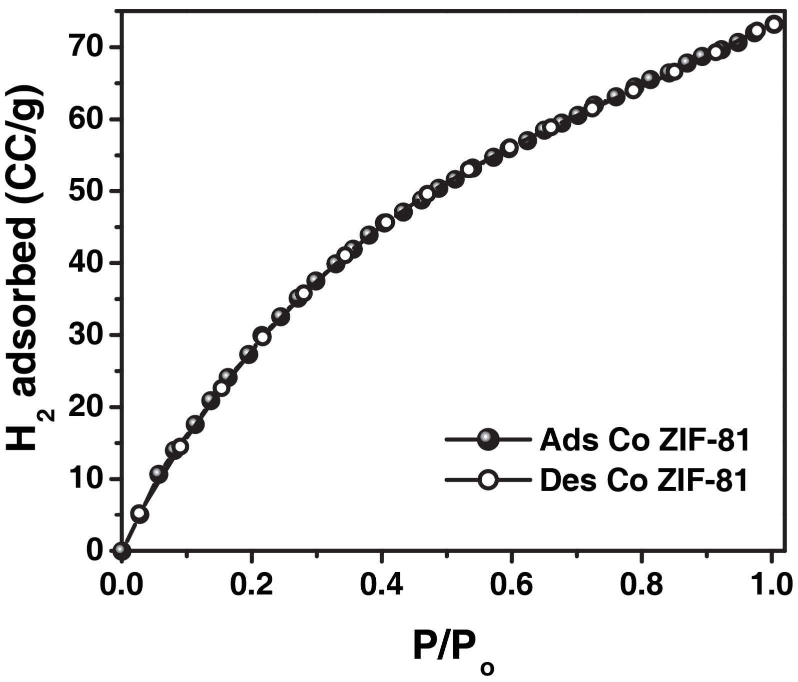


Figure S22. H_2 adsorption isotherm of Co-ZIF-81 taken at 77 K. Filled and open symbols represent adsorption and desorption branches.

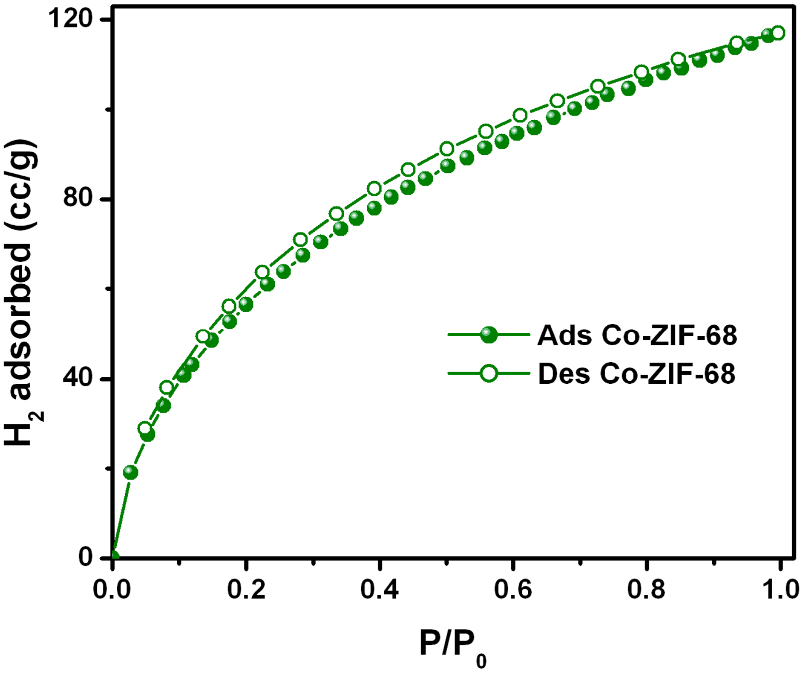


Figure S23. H$_2$ adsorption isotherm of Co-ZIF-81 taken at 77 K. Filled and open symbols represent adsorption and desorption branches.

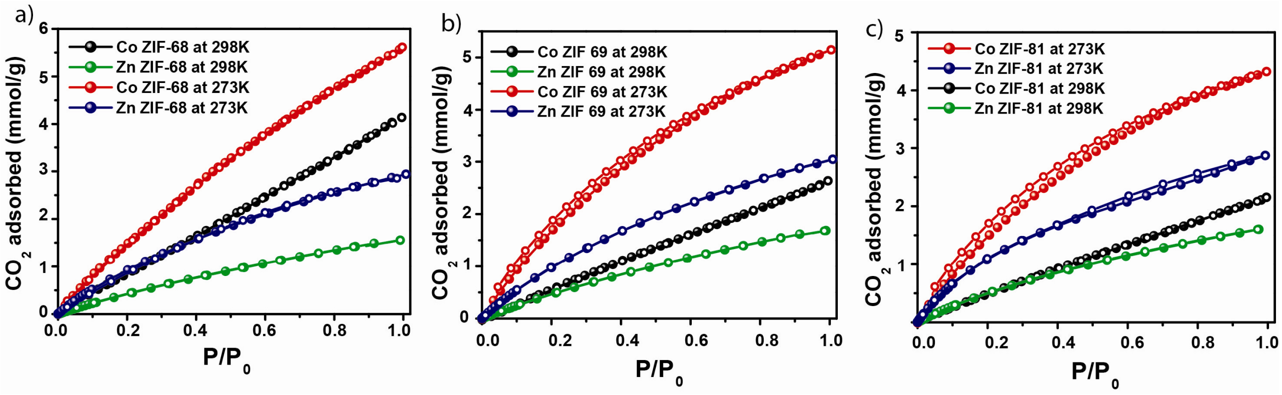


Figure S24: Gravimetric CO$_2$ Gas adsorption isotherms (1 bar) of ZIF-68, 69 and 81 at 273K and 298K. (b) Zn and Co-ZIF-68 (c) Zn and Co-ZIF-69 (d) Zn and Co-ZIF-81. The filled and open circles represent adsorption and desorption, respectively. Zn ZIF-68, 69 and 81 (*J. Am. Chem. Soc.*, 2009, **131**, 3875) isotherm has been reproduced for comparison.

Selectivity of CO_2 in compair with N_2 of Co-ZIF-68, -69 and -81 at 273K:

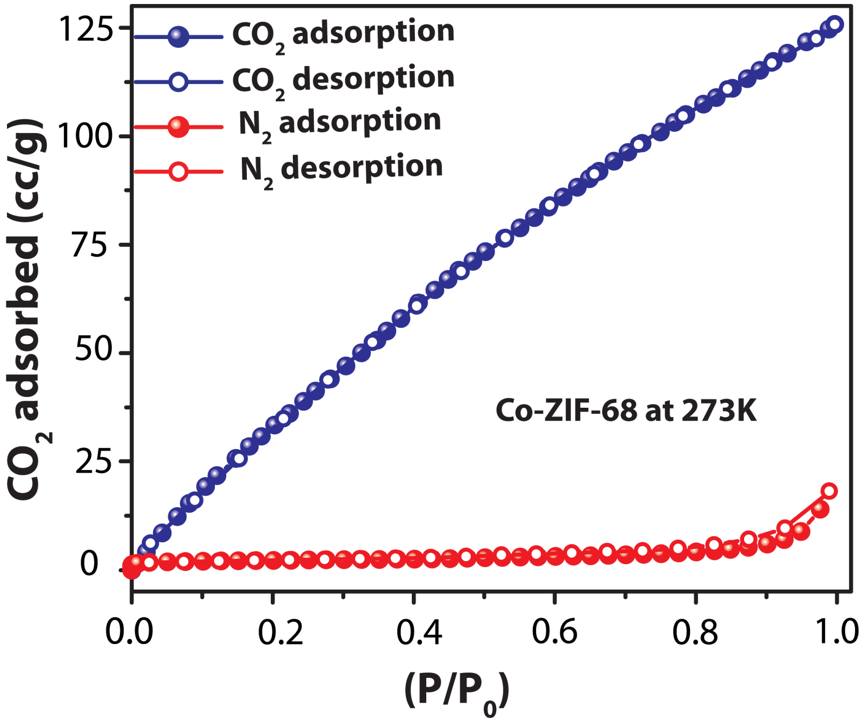


Figure S25. Selectivity of CO_2 uptake in compare with its N_2 uptake at 273K of Co-ZIF-68.

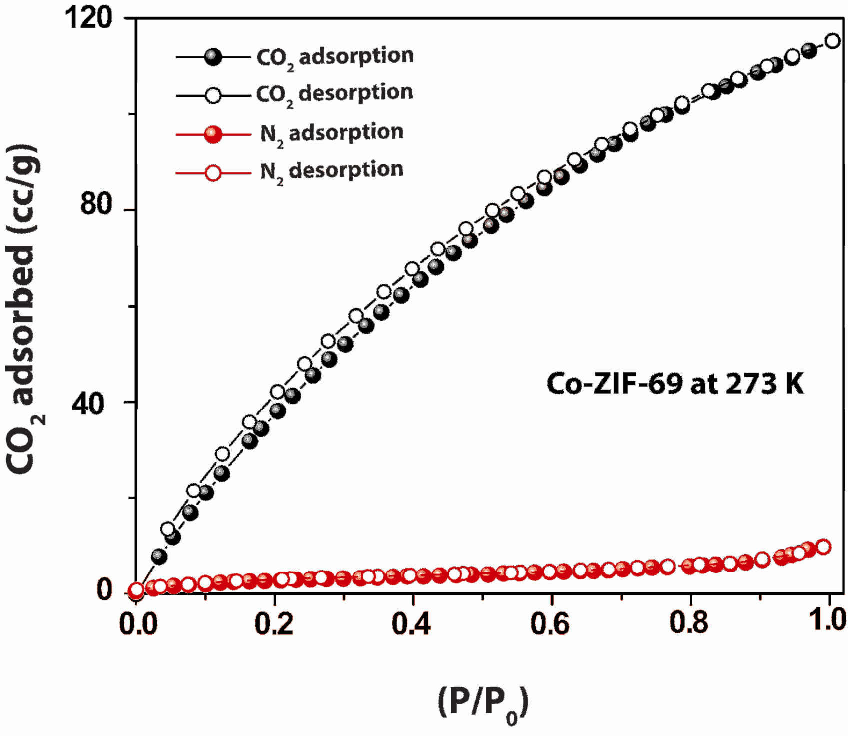


Figure S26. Selectivity of CO_2 uptake in compare with its N_2 uptake at 273K of Co-ZIF-69.

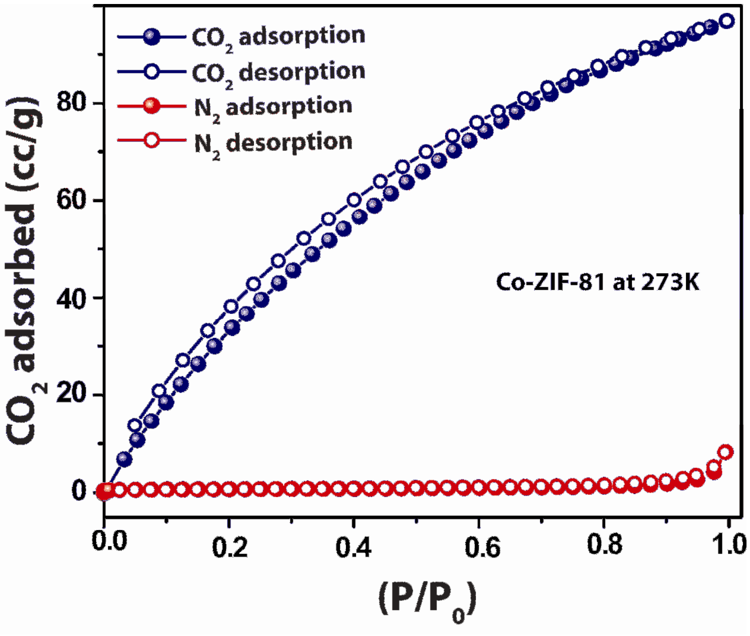


Figure S27. Selectivity of CO_2 uptake in compare with its N_2 uptake at 273K of Co-ZIF-81.

Table S5: Ranking of low pressure (1 bar) CO_2 Adsorption Capacities in Metal Organic Frameworks at 273K and 298K:

SL. No.**	MOFs	CO_2 uptake Gravimetrically (mmol/g at 1 bar)		CO_2 uptake Volumetrically (cc/g at 1 bar)		Reference
		273K	298K	273K	298K	
1	Mg\DOBDC	NA	8.08		180.99	*J. Am. Chem. Soc.* 2008, *130*, 10870.
2	Co\DOBDC	NA	7.11		159.26	, *J. Am. Chem. Soc.* 2008, *130*, 10870.
3	Ni\DOBDC	NA	5.80		129.92	*J. Am. Chem. Soc.* 2008, *130*, 10870.
4	Zn\DOBDC	NA	5.51		123.42	*J. Am. Chem. Soc.* 2008, *130*, 10870.
5	UTSA-20	NA	5.01		112.22	*Angew. Chem. Int. Ed.* 2011, *50*, 3178.
6	HKUST-1	NA	4.72		105.72	*Microporous and Mesoporous Materials*. 2002, *55*, 217.
7	Zn + 4,4' bipy + (BTA-TBA)	NA	4.10		91.84	*J. Am. Chem. Soc.* 2010, *132*, 950.

8	Bio-MOF-11	6.0	4.01	134.4	89.82	*J. Am. Chem. Soc.* 2010, *132*, 38.
9	$[Zn_2(1)(DMF)_2]_n(DMF)_m$ [MOF(4)]	5.80	NA	129.92		*J. Mater. Chem.*, 2009, *19*, 213.
10	$[Zn_3(OH)(p\text{-}CDC)_{2.5}]_n$	NA	4.00		89.6	*Chem. Commun*., 2008, 4135.
11	Co-ZIF-68	5.61	4.1	125.66	91.84	This work
12	ZTF-1	5.35	3.79	119.84	84.89	*Chem. Commun*., 2011, 2011.
13	Co-ZIF-69	5.14	2.63	115.13	58.91	This work
14	Cd-ANIC-1	4.72	3.84	105.72	86.01	*J. Mater. Chem.*, 2011, 21, 17737.
15	Co-ZIF-81	4.32	2.15	96.76	48.16	This work
16	$Zn_2(C_2O_4)(C_2N_4H_3)_2.(H_2O)_{0.5}$	4.30	3.78	96.32	84.67	*Chem. Commun*., 2009, 5230.
17	Co-ANIC-1	4.22	3.48	94.52	77.95	*J. Mater. Chem.*, 2011, 21, 17737.
18	CUK-1	NA	3.48	NA	77.95	*Adv. Mater.* 2007, *19*, 1830.
19	YO-MOF	NA	3.39	NA	75.93	*Chem. Eur. J.* 2010, *16*, 276.
20	SNU-M10	NA	3.30	NA	73.92	, *Angew. Chem*. 2009, *121*, 6997.
21	MOF-505	NA	3.27	NA	73.24	*Angew. Chem. Int. Ed.* 2005, *44*, 4745.
22	$H_3[(Cu_4Cl)_3\text{-}(BTTri)_8]$	NA	3.25	NA	72.8	*J. Am. Chem. Soc.* 2009, *131*, 8784.
23	$(In_3O)(OH)(ADC)_2(NH_2IN)_2 \bullet 2.67\ H_2O$	NA	3.21	NA	71.9	*Chem. Commun.,* 2010, *46*, 7400.
24	CPM-6	4.76	2.90	106.62	64.96	*J. Am. Chem. Soc.* 2010, *132*, 17062.
25	TMA@ Bio-MOF-1,	4.5	NA	100.8	NA	*J. Am. Chem. Soc.* 2010, *132*, 5578.
26	TEA@ Bio-MOF-1	4.2	NA	94.08	NA	*J. Am. Chem. Soc.* 2010, *132*, 5578.
27	TBA@ Bio-MOF-1	3.5	NA	78.4	NA	*J. Am. Chem. Soc.* 2010, *132*, 5578.

28	**UMCM-150**	**NA**	**2.80**	**NA**	**67.72**	***J. Am. Chem. Soc.* 2007, *129*, 15740.**
29	**$Zn_2(BDC)_2$ (DABCO)**	**NA**	**2.71**	**NA**	**60.7**	***Chem. Eur. J.* 2005, *11*, 3521.**
30	**CPM-5**	**3.62**	**2.43**	**81.08**	**54.43**	***J. Am. Chem. Soc.* 2010, *132*, 17062.**
31	**ZIF-78**	**3.348**	**2.23**	**75**	**49.95**	***J. Am. Chem. Soc.* 2009, *131*, 3875.**
32	**ZIF-96**	**NA**	**2.16**	**NA**	**48.384**	***J. Am. Chem. Soc.*, 2010, *132*, 11006.**
33	**IRMOF-3**	**NA**	**2.14**	**NA**	**47.93**	***Angew. Chem. Int. Ed.* 2010, *49*, 1258**
34	**$(In_3O)(OH)(ADC)_2(IN)_2 \bullet 4.67\ H_2O$**	**NA**	**2.08**	**NA**	**46.592**	***Chem. Commun.*, 2010, *46*, 7400.**
35	**MOF-177**	**NA**	**1.72**	**NA**	**38.52**	***J. Am. Chem. Soc.* 2004, *126*, 5666.**
36	**Zn-ZIF-69**	**3.03**	**1.69**	**67.87**	**37.85**	***J. Am. Chem. Soc.* 2009, *131*, 3875.**
37	**MOF-5**	**NA**	**0.92**	**NA**	**20.608**	***J. Am. Chem. Soc.* 2004, *126*, 5666.**

Table S6: Pore volume surface area and CO_2 uptake of all Co and Zn-ZIFs:

S.N	**Zn and Co ZIFs**	**Pore diameter (d_p)**	**Pore Aperture (d_a)**	**Pore Volume**	**Surface Area (m^2g^{-1})**	**CO_2 uptake (cc/g)**	
						273K	**298K**
1	**Zn-ZIF-68**	**10.3 Å**	**7.5 Å**	**571.81**	**1090**	**65.80**	**37.57**
2	**Co-ZIF-68**	**10.5 Å**	**7.7 Å**	**605.81**	**792**	**125.73**	**92.66**
3	**Zn-ZIF-69**	**7.8 Å**	**4.4 Å**	**248.34**	**950**	**68.18**	**40.02**
4	**Co-ZIF-69**	**8.0 Å**	**4.6 Å**	**267.94**	**700**	**115.25**	**59.01**
5	**Zn-ZIF-81**	**7.4 Å**	**3.9 Å**	**212.06**	**760**	**64.27**	**38.01**
6	**Co-ZIF-81**	**7.7 Å**	**4.1 Å**	**238.91**	**661**	**96.81**	**48.21**

Section S8. *Ab initio* calculations of CO_2 binding energies

To elucidate the difference in experimentally measured adsorption isotherms of CO_2 in Zn- and Co-ZIFs, we calculated CO_2 binding energies with Zn- and Co-ZIF-68 clusters from first-principles method. Two representative clusters constructed on the basis of experimental crystallographic data, as shown in **Figure S25**, were used in *ab intio* calculations. For each cluster, CO_2 position was optimized using the Becke exchange plus the Lee-Yang-Parr functional and 6-31g(d,p) basis set; interaction energy was evaluated from the 2nd Møller-Plesset method and 6-311++g(d,p) basis set. The basis set superposition errors were corrected by counterpoise method.[1] All the *ab intio* calculations were performed using Gaussian 09.[2]

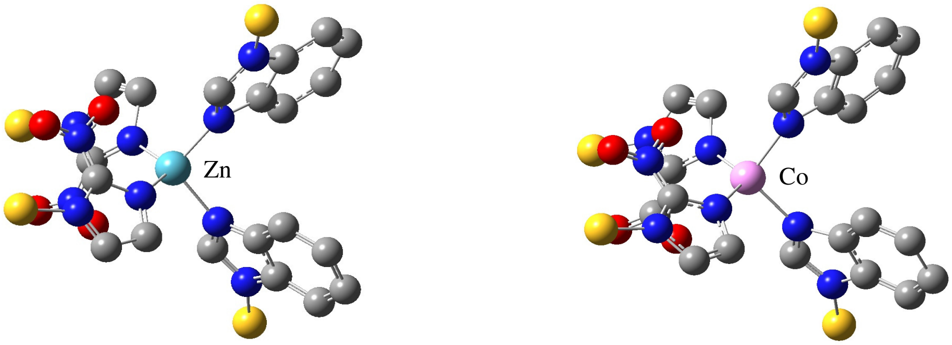


Figure S28. Zn-ZIF-68 and Co-ZIF-68 clusters. The clusters are terminated by Li atoms (yellow); H atoms are omitted for clarity.

Figure S26 illustrates the optimized CO_2 positions around Zn-ZIF-68 and Co-ZIF-68 clusters. The binding energies are −16.37 and −19.89 kJ/mol, respectively. That is, CO_2 binding energy around Co-ZIF-68 cluster is stronger. The difference of binding energy (~ 3 kJ/mol) is for one cluster only and seems to be small. In the crystalline structures, however, the difference would be significantly enhanced and lead to distinctly different adsorption isotherms as experimentally observed.

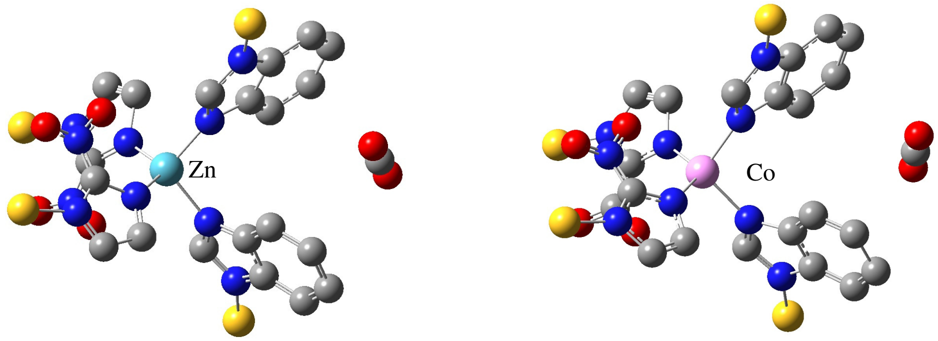


Figure S29. Optimized CO_2 positions around Zn-ZIF-68 and Co-ZIF-68 clusters.

1. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A.D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 09*, Revision D.01 ed. Gaussian Inc., Wallingford CT, **2009**.