Solution Mediated Phase Transformation (RHO to SOD) in Porous Co-Imidazolate based Zeolitic Framework with High Water Stability

(Supporting Information: 20 pages)

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Content

Page

Section 1: Experimental measurements and methods used:

General Remarks: 2-nitroimidazole (2-NIm) was purchased from 3B Scientific Corporation, $Co(NO_3)_2.6H_2O$, Methanol, *N*, *N*-diethylformamide (DEF) and DCM 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 CoNIm Zeolitic Imidazolate Frameworks synthesis.

PXRD, TGA, SEM, 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}. SEM images were obtained with a FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union as well as by sprinkling the powder on carbon tape. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm^{-1} region or using a Diamond ATR (Golden Gate). Leica M-80 optical microscope with hot stage and camera attachment was used for collecting photographs of ZIF crystals.

Section 2: Detailed synthesis procedure of CoNIm (SOD) and CoNIm (RHO) ZIF

Synthesis of CoNIm (RHO): 0.056 g of 2-nitroimidazole (2-NIm) in 2.5 mL of DEF (0.20 M, 0.49 mmol) and 0.072 g of $Co(NO_3)_2.6H_2O$ in 1.25 mL DEF solution (0.20 M, 0.24 mmol) were mixed together in a 5 mL glass vial. Then the resulting solution was heated in an oven at 120 °C and allowed to react solvothermally for 12 to 15 h. The resulting product was in the form of pink rhombic dodecahedron shaped single crystals. Then washed with DEF and dried in air to get ~10-15 mg of pure crystals of CoNIm (RHO). (Yield: 22%). ***FT-IR*****: (4000–600 cm^{-1}):** 2926(w), 1651(s), 1527(w), 1476(m), 1253(w),1157(m), 1093(w), 946(w), 827(w), 792(s), 657(w). ***Elemental analysis (activated)*****:** Calcd. (%) C, 24.24; H, 1.3; N, 29.67; Found (%): C, 24.16; H, 1.41; N, 27.87.

Synthesis of CoNIm (SOD): 0.056 gm of 2-NIm in 2.5 mL of DMF (0.20 M, 0.49 mmol) and 0.072 gm of $Co(NO_3)_2.6H_2O$ in 1.25 mL DMF solution (0.20 M, 0.24 mmol) were mixed together in a 5 mL glass vial. Then the resulting solution was heated in an oven at 120 °C and allowed to react solvothermally up to 24-27 h. The resulting product was in the form of pink cube shaped single crystals, was washed with DMF and dried in air to get ~10-15 mg of pure crystals of CoNIm (SOD). (Yield: 22%). ***FT-IR*****: (4000– 600 cm^{-1}):** 2926(w), 1651(s), 1527(w), 1476(m), 1253(w),1157(m), 1093(w), 946(w), 827(w), 792(s), 657(w). ***Elemental analysis (activated)*****:** Calcd. (%) C, 25.43; H, 1.4; N, 29.67; Found (%): C, 25.09; H, 1.45; N, 28.07.

Section 3: Powder X-ray diffraction (PXRD) demonstrating the phase transformation from CoNIm (RHO) to CoNIm (SOD) ZIF:

From the powder X-ray pattern of synthesized CoNIm frameworks shows that up to 15 h aging of synthesis there was pure CoNIm (RHO) phase but as reaction progress, beyond 15 h, in between 15 to 18 h small nuclei of CoNIm (SOD) starts forming which can be seen as mixed [CoNIm (RHO+SOD)] equally intense peaks in the PXRD pattern. Again at 21 h we could found that the CoNIm (RHO) characteristic peaks intensities were gradually decreases [still mixture of CoNIm (RHO) and CoNIm (SOD)], finally at 24 h aging extensively CoNIm (RHO) has been converted into CoNIm (SOD) ZIF.

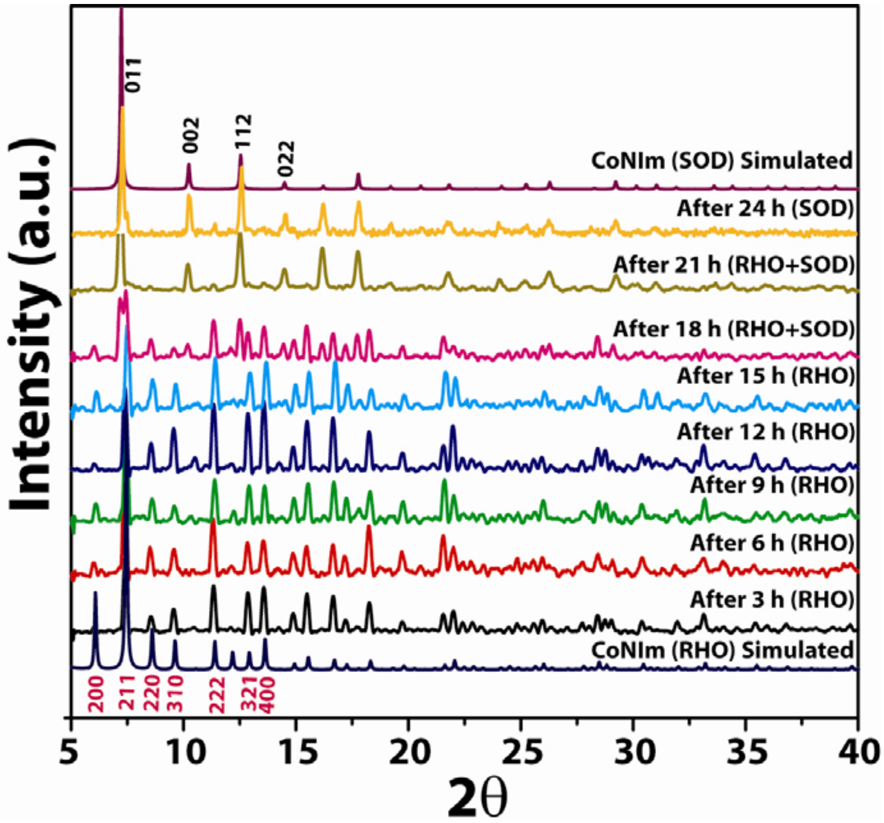

Figure S1: *Ex*perimental PXRD pattern demonstrating phase transformation at different stages (each 3 h interval) from CoNIm (RHO) 3h (black) to CoNIm (SOD) ZIF; 24 h (golden yellow), comparison with simulated CoNIm (RHO) (blue, bottom) and CoNIm (SOD) (brown, top) from its single crystal structure. Red (bottom) and black (top), three digit numbers represent the planes correspond to the characteristic peaks of CoNIm (RHO) and CoNIm (SOD) ZIF.

Water stability of CoNIm (RHO):

The powder X-ray pattern of synthesized CoNIm (RHO) indicates the framework stability in deionised water for 7 days, boiling water (100 °C) for 1 day and in hot water (7 days at 85 °C). But in hydrothermal (85 °C) condition the framework is stable up to 1 day, beyond that; it goes to a different crystalline phase.

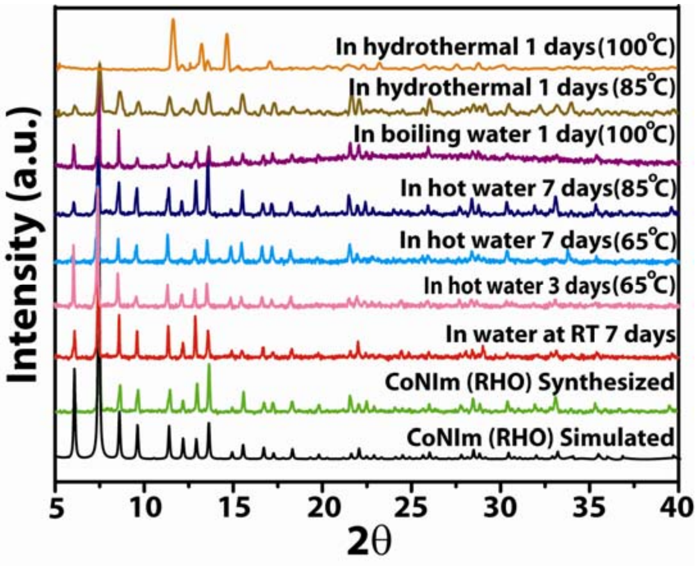

Figure S2: Experimental PXRD pattern to show the water stability and phase purity of CoNIm (RHO) ZIF in deionised water at different temperature for 1 to 7 days time period.

Water stability of CoNIm (SOD):

The framework of CoNIm (SOD) decomposes even in deionised water within 24 h that could be due to the narrow pore aperture, diameter and hydrophilic environment around the Co(II) centre. Water molecule can frequently reach at metal centre (Co) which facilitates hydrolysis of the Co(II) centre; as a result the framework decomposes so early.

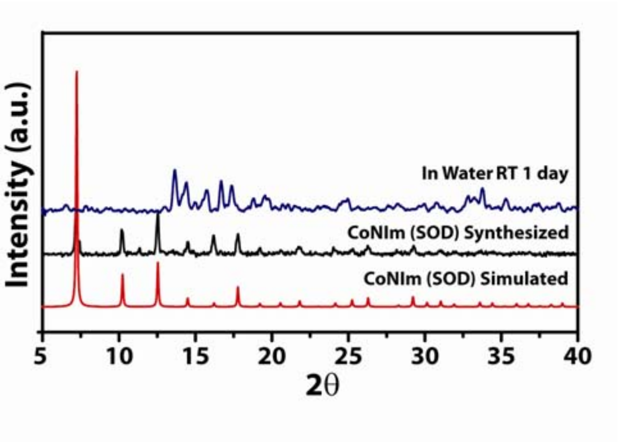

Figure S3: Experimental PXRD patterns to show the water instability of CoNIm (SOD) ZIF.

Section 4: VT-PXRD and Thermal stability (TGA):

To understand the crystallinity and phase change at different temperature we performed VT-PXRD. Which infers that CoNIm (RHO) framework is stable for a wide range of temperature (up to 300 °C). There was no phase change observed within 25 °C-300 °C range and all the characteristic PXRD peaks are matched well with the simulated one from single crystal XRD of CoNIm (RHO).

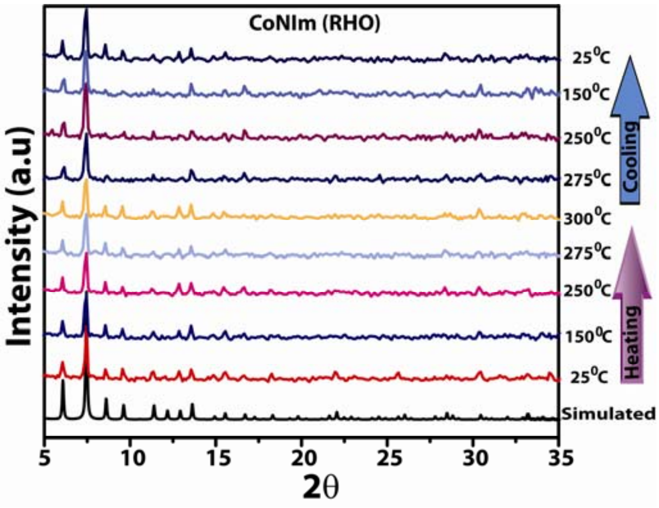

Figure S4: Experimental VT- PXRD patterns of CoNIm (RHO) ZIF from 25 °C to 300 °C.

From VT-PXRD clearly seen that CoNIm (SOD) framework is not fully stable for the range of temperature (25 to 300 °C), there is an additional peak seen at 7 degree (2θ) after in situ heating the sample to 150 °C (indicated by red arrow). Also some characteristic peaks broadened and some were missed from the PXRD pattern. The phase change occurs within (150 °C-300 °C) range may be due to the solvent molecules (DEF) escape out from the framework.

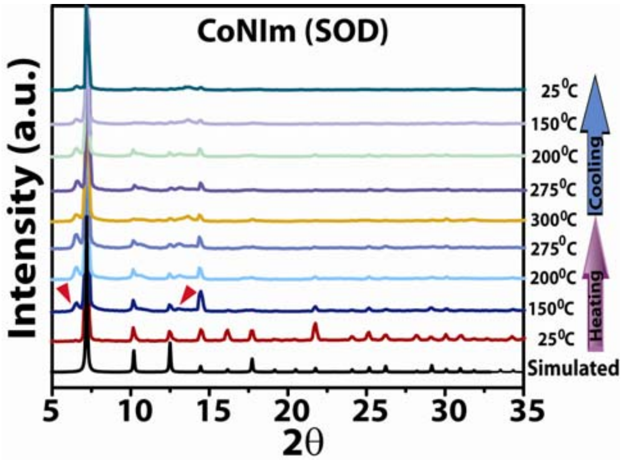

Figure S5: Experimental VT- PXRD pattern of CoNIm (SOD) ZIF from 25 °C to 300 °C.

TGA were performed on both as-synthesized and activated samples (after solvent exchange and strong evacuation at 150 °C) of CoNIm (RHO) and CoNIm (SOD) respectively under N_2 atmosphere. The TGA for CoNIm (RHO) (black) shows that there were weight loss of almost 32-35 wt% up to 150 °C which indicates that the solvent molecules (DEF) escape out from the pore and then the framework is stable up to 310 °C, after this temperature complete framework decomposes. Large pore opening in CoNIm (RHO) allows the bulky DEF molecule to escape easily from the framework, which shows straight plateau from 30 to 310 °C for the activated (AE) sample. There was huge weight loss after 310 °C, which indicates that sublimation may take place and 95-97% weight loss occurs in the form of vapour. The red curve is for activated sample at 150 °C.

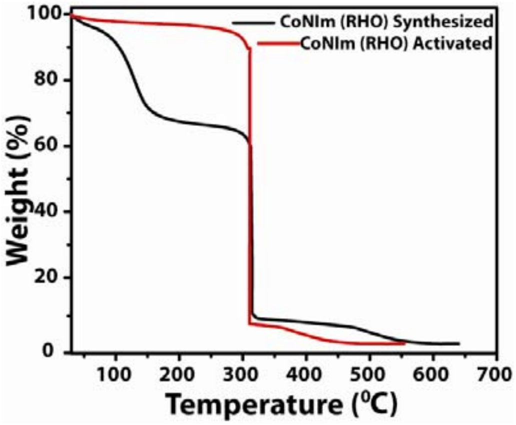

Figure S6**:** Thermal stability and the thermal gravimetric analysis (TGA) of CoNIm (RHO) ZIF under N_2 atmosphere.

TGA for CoNIm (SOD) as synthesised (black) shows that weight loss up to 20-22% at 150 °C. Which indicates that the solvent molecules (DEF) escape out from the pore and then the framework is stable up to 350 °C (next 40% weight loss), after this temperature complete framework starts decomposing. The red curve is for activated sample at 150 °C, which is not fully activated because of smaller pore aperture. Therefore the solvent molecule (DEF) does not fully leaving the framework easily.

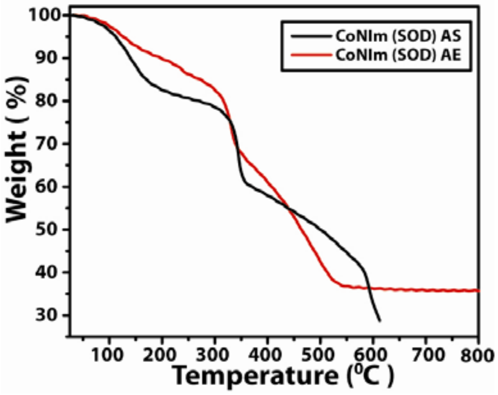

Figure S7**:** Thermal stability and the thermal gravimetric analysis (TGA) of CoNIm (SOD) ZIF under N_2 atmosphere.

Section 5: Detailed SEM image of important stages of synthesis; from CoNIm (RHO) to CoNIm (SOD) ZIF phase transformation and crystal morphology.

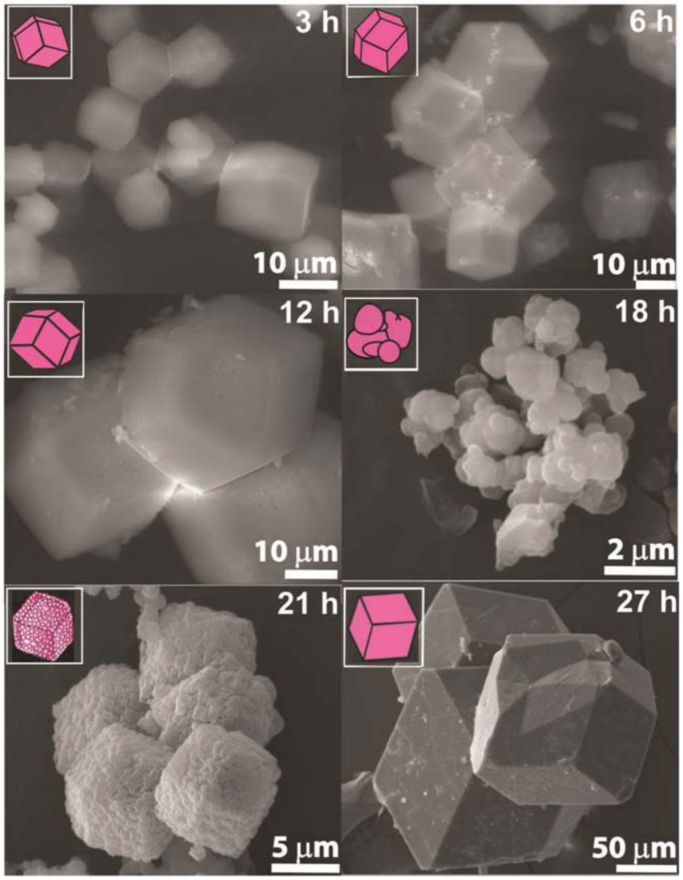

Figure S8: SEM images at different time interval of synthesis; 3 h, 6 h and 12 h for CoNIm (RHO) ZIF, 18 h and 21 h for CoNIm (RHO+SOD) and 27 h for CoNIm (SOD) respectively; demonstrating the crystal morphology while phase transformation from CoNIm (RHO) to CoNIm (SOD) ZIF. (Hour abbreviated as h).

SEM images shows that CoNIm (RHO) having rhombic dodecahedron shape starts forming after 3 h of synthesis, the crystal size is very small (10-15 μm) and subsequently the size becomes larger up to 12 h (50±5 μm). As we going further with time the crystals starts breaking down and change its original shape, the CoNIm (SOD) nuclei forming at 18 h of synthesis. The crystal shape become semi-spherical, then after these small nuclei are aggregating to form crystalline island and further takes complete cube shaped single crystals at 24-27 h. At this condition the crystal phase changes from CoNIm (RHO) to CoNIm (SOD). The shape of both crystal phases is almost identical but distinguishable by close visual examination, again from PXRD we could identify the pure phase of the individual specimens.

Section 6: FT-IR

As shown in Figure S9 the complete disappearance of the strong and broad —NH band between 3350-2500 cm^{-1} and the associated weak band near 1651 cm^{-1} indicates that the 2-nitroimidazolate links in CoNIm (RHO) and CoNIm (SOD) ZIF has been fully deprotonated.

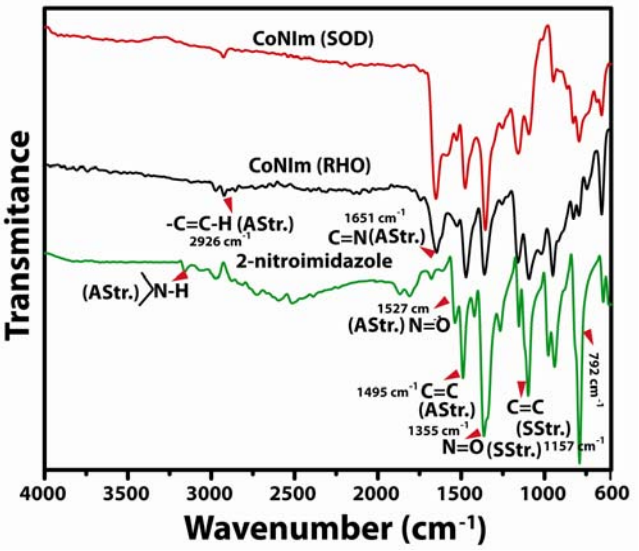

Figure S9: Comparison of the FT-IR spectra of as-synthesized CoNIm (RHO) and CoNIm (SOD) ZIFs with 2-nitroimidazole (2-NIm).

Section 7: Gas Adsorption analysis of CoNIm (RHO) and CoNIm (SOD) ZIFs.

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 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 CoNIm zeolitic framework were soaked in dried CH_2Cl_2 (DCM):MeOH (v/v 1:1) mixture for 12 h. Freshly dried CH_2Cl_2: MeOH (v/v 1:1) mixture was subsequently added and the crystals were kept for additional 48 h to remove free solvates presented in the framework. The so-obtained material was dried under dynamic vacuum (< 10^{-3} Torr) at RT overnight. The sample were heated under dynamic 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 (DEF and DMF). Apparent surface areas of 2087 m^2g^{-1} (Langmuir model) and 1864 m^2g^{-1} (Brunauer– Emmett–Teller (BET) model [K. S. Walton, R. Q. Snurr, *JACS* 129, 8552 (2007)] for CoNIm (RHO) and CoNIm (RHO) ZIF has apparent surface areas of 1235 m^2g^{-1} (Langmuir model) and 1097 m^2g^{-1} (Brunauer– Emmett–Teller (BET) were obtained by using the data points (P/P_o= 0.01-0.1) on the adsorption branch.

Water Adsorption Measurements of CoNIm (RHO): Low-pressure volumetric water adsorption measurements were performed at 293K, with pressure ranging from 0 to 0.9 [relative pressure (P/P_o)] on a Quantachrome Autosorb-iQ-MP automatic volumetric instrument. The pink coloured crystals of CoNIm (RHO) were soaked in dried CH_2Cl_2: MeOH (v/v 1:1) mixture for 12 h. Freshly dried CH_2Cl_2: MeOH (v/v 1:1) mixture was subsequently exchanged and the crystals were kept for additional 48 h to remove free solvates presented in the framework. The so-obtained material was dried under dynamic vacuum ($< 10^{-3}$ Torr) at RT overnight. The samples were heated under dynamic at 80 ºC (12 h) to remove the solvent present on the surface and then further heated to 150 ºC (12 h) to remove further solvent molecule (DEF) floating inside the framework. CoNIm (RHO) shows water vapour uptake 200 $cm^3(STP)g^{-1}$, at a relative pressure (P/P_o) of 0.9.

This high water uptake could be due to the partial hydrophilic environment created by polar nitro group (2-NIm) and the large pore aperture as well as super cage in CoNIm (RHO) ZIF. Although the 8 member ring windows are hydrophobic due to the nitro group directing away from the pore but at high pressure water molecules are going inside the cage and hence the high water uptake.

N_2 adsorption isotherm for CoNIm (RHO) and CoNIm (SOD) ZIFs:

Apparent surface areas 2087 m^2g^{-1} (Langmuir) and 1,858 m^2g^{-1} (BET) for CoNIm (RHO) ZIF were obtained by using the data points on the adsorption branch in the range of $P/P_0 = 0.01$-0.1, and a micropore volume of 0.827 cm^3/g was obtained based on a single data point at $P/P_o = 0.1$. The linearity of fitting to BET equation is 0.999494. For CoNIm (SOD) the surface area 1235 m^2g^{-1} (Langmuir) and 1097 m^2g^{-1} (BET) were obtained by using the data points on the adsorption branch in the range of $P/P_o = 0.01$-0.1, and a micropore volume of 0.477 cm^3/g for CoNIm (SOD) ZIF was obtained based on a single data point at $P/P_o = 0.1$.

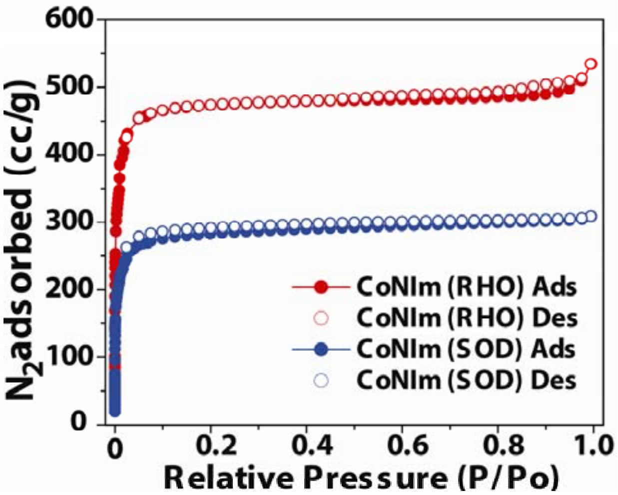

Figure S10. The N_2 gas-sorption isotherms for CoNIm (RHO) and CoNIm (SOD) ZIFs measured at 77 K. The filled and open circle represents adsorption and desorption branches, respectively.

Table S1: Lists of all ZIFs with RHO topology reported in the literature and pore aperture, pore diameter as well as their surface area.

SL. No.	ZIFs (RHO)	Pore aperture (d_a) in Å	Pore diameter (d_p) in Å	Surface area (Langmuir) in m^2g^{-1}	Surface area (BET) in m^2g^{-1}	References
1	CdIF-9	9.0	23	3010	—	*Chem. Euro. J.,* 2010, **16**, 1137
2	CdIF-4	6.8	21.6	2420	—	*Chem. Euro. J.,* 2010, **16**, 1137
3	**CoNIm (RHO)**	**7.1**	**22.3**	**2087**	**1858**	**This work**
4	BIF-9-Li	4.2	—	1818	1523	*J. Am. Chem. Soc.*, 2009, **131**, 6111
5	Rho-ZMOF	5.7	18.2	1067	—	*Chem. Commun.*, 2006**,** 1488
6	BIF-9-Cu	3.3	—	1524	1287	*J. Am. Chem. Soc.*, 2009, **131**, 6111
7	ZIF-25	—	—	—	1110	*J. Am. Chem. Soc.,* 2010, **132**, 11006
8	ZIF-96	—	—	—	960	*J. Am. Chem. Soc.,* 2010**, 132**, 11006
9	Zn (nIm)(pur)	9	—	—	897	*Chem. Commun*., 2012**, 48**, 6690
10	ZIF-93	—	—	—	864	*J. Am. Chem. Soc.,* 2010, **132**, 11006
11	ZIF-71	4.2	16.5	—	652	*J. Am. Chem. Soc.,* 2010, **132**, 11006
12	ZIF-97	—	—	—	564	*J. Am. Chem. Soc.,* 2010, **132**, 11006
13	ZIF-11	3	14.6	—	—	*Proc. Natl. Acad. Sci*. U. S. A, 2006, **103**, 10186
14	ZIF-12	3	14.6	—	—	*Science*, 2008**, 319**, 939

Table S2: Lists of most highlighted ZIFs (except CdIF) and their (BET) surface area.

SL. No.	ZIFs	Topology	Surface area (BET) in m^2g^{-1}	References
1	**CoNIm (RHO)**	**RHO**	**1858**	**This work**
2	**ZIF-70**	**GME**	**1730**	*J. Am. Chem. Soc*., 2009, **131,** 3875
3	**ZIF-8**	**SOD**	**1630**	*Proc. Natl. Acad. Sci*. U. S. A, 2006, **103,** 10186
4	**BIF-9-Li**	**RHO**	**1523**	*J. Am. Chem. Soc*., 2009, **131,** 6111
5	**ZIF-82**	**GME**	**1300**	*J. Am. Chem. Soc*., 2009, **131,** 3875
6	**BIF-9-Cu**	**RHO**	**1287**	*J. Am. Chem. Soc*., 2009, **131,** 6111
7	**ZIF-90**	**SOD**	**1270**	*J. Am. Chem. Soc*., 2008, **130,** 12626
8	**ZIF-25**	**RHO**	**1110**	*J. Am. Chem. Soc.,* 2010, **132,** 11006
9	**CoNIm (SOD)**	**SOD**	**1097**	*Science*, 2008**, 319,** 939/ **This work**
10	**ZIF-68**	**GME**	**1090**	*J. Am. Chem. Soc*., 2009, **131,** 3875
11	**ZIF-91**	**SOD**	**1070**	*J. Am. Chem. Soc*., 2008, **130,** 12626
12	**ZIF-95**	**POZ**	**1050**	*Nature,* 2008, **453,** 207
13	**ZIF-96**	**RHO**	**960**	*J. Am. Chem. Soc.,* 2010**, 132**, 11006
14	**ZIF-69**	**GME**	**950**	*J. Am. Chem. Soc*., 2009, **131,** 3875
15	**Zn(nIm)(pur)**	**RHO**	**897**	*Chem. Commun*., 2012**, 48**, 6690
16	**ZIF-93**	**RHO**	**864**	*J. Am. Chem. Soc.,* 2010, **132**, 11006
17	**ZIF-79**	**GME**	**810**	*J. Am. Chem. Soc*., 2009, **131,** 3875
18	**ZIF-81**	**GME**	**760**	*J. Am. Chem. Soc*., 2009, **131,** 3875
19	**ZIF-71**	**RHO**	**652**	*J. Am. Chem. Soc.,* 2010, **132,** 11006
20	**ZIF-78**	**GME**	**620**	*J. Am. Chem. Soc*., 2009, **131,** 3875
21	**ZIF-100**	**MOZ**	**595**	*Nature,* 2008, **453,** 207

Section 8: Single crystal X-ray diffraction; data collection, structure solution and refinement procedures.

Single Crystal X-Ray Diffraction:
Data was collected 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) and Cu Kα radiation (λ = 1.54178 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 suite to carry out overlapping φ and ω scans at detector (2θ) settings (2θ = 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. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. Highly porous crystals that contain solvent-filled pores often yield raw data where observed strong (high intensity) scattering becomes limited to ~1.0 Å at best, with higher resolution data present at low intensity. A common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays, did not improve the quality of the high angle data in this case, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffused scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal contributes to the background and the 'washing out' of the weaker data. The only optimal crystals suitable for analysis were generally small and weakly diffracting. Unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens have not yet been fruitful. Data were collected at 293(2) K for the CoNIm (RHO) ZIF presented in this paper. Electron density within void spaces has not been assigned to any guest entity but has been modeled as isolated oxygen and/or carbon atoms. The foremost errors in all the models are thought to lie in the assignment of guest electron density. The structure was examined using the Adsym subroutine of PLATON[3] to assure that no additional symmetry could be applied to the

models. SQUEEZE on PLATON has been used to remove highly disordered solvent molecules floating inside the cage. The ellipsoids in ORTEP diagrams are displayed at the 50% probability. For all structures we note that elevated R-values are commonly encountered in MOF crystallography 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 with the CCDC as deposition No. CCDC 886561. 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].

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Experimental and Refinement Details for CoNIm (RHO):

A pink rhombic dodecahedron crystal (0.28× 0.15× 0.12 mm^3) of CoNIm (RHO) 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) and Cu Kα radiation (λ = 1.54178 Å) at 293(2) K. A total of 8985 reflections were collected of which 2308 were unique. The range of θ was from 3.73 to 71.42°. Analysis of the data showed negligible decay during collection. CoNIm (RHO) ZIF structure was solved in Im-3m (cubic) space group with 48 (Z=48) Co atoms with a unit cell [a, b, c ~ 29.0302(5) and α, β, γ ~ 90°], using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. The tetrahedrally coordinated Co is surrounded by four 2-nitroimidazole linkers with mirror symmetry. However, Co1 atom lies on a 2-fold symmetry axis and the two (N2—C1 and N4—C3) bonds of either 2-nitroimidazole (as shown in the asymmetric unit, Figure S11) lies on mirror planes. As a result the asymmetric unit contains only 0.5 Co atoms and two 0.5 2-nitroimidazole unit. The attempts made to model the guests (solvent molecules) did not lead to identification of guest entities in any of the structures due to the limited periodicity of the solvent molecules in the crystals. Since the solvent is neither bonded to the framework nor tightly packed into the voids, solvent disorder can be expected for the MOF structures. Thus, electron density within void spaces which could not be assigned to any definite guest entity was modeled as isolated carbon atoms, and the foremost errors in all the models lie with the assignment of guest electron density. "Solvent" is 1 atom refined as nitrogen atoms of undefined solvent, located in a void of the framework. To assess the correctness of the atomic positions in the framework, the application of the SQUEEZE routine of A. Spek has been performed. However, atomic co-ordinates for the "non-SQUEEZE" structures are also presented. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0875 [I>2σ (I)] and wR2 = 0.2688 (all data) with GOF = 0.871. For the structure where the SQUEEZE program has not been employed, final full matrix least-squares refinement on F^2 converged to $R1$ = 0.1222 [I>2σ (I)] and $wR2$ = 0.3995 (all data) with GOF = 1.032.

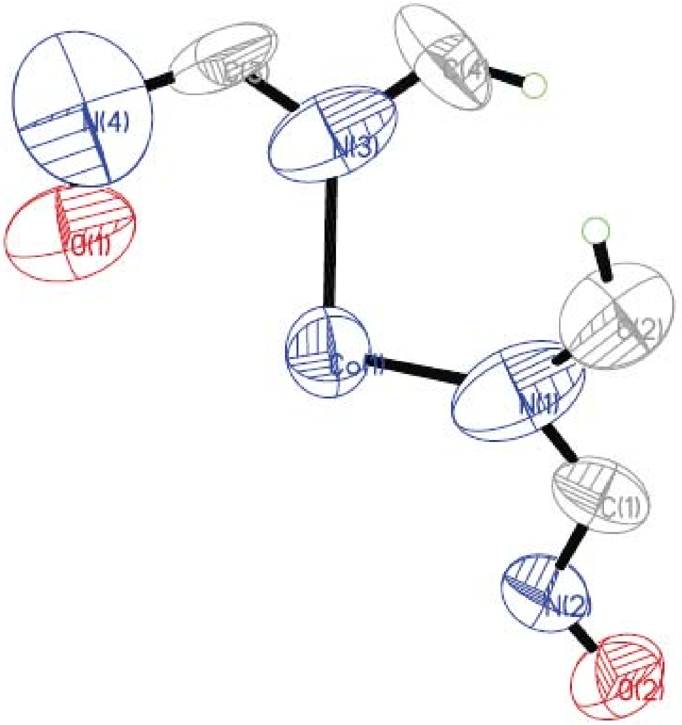

Figure S11. ORTEP drawing of an asymmetric unit of CoNIm (RHO) ZIF generated from SHELXTL 97[2] software with 50% probability, excluding the guest entities.

Table S3. Crystal data and structure refinement for **CoNIm (RHO)**

Empirical formula	C6 H4 Co N7 O4
Formula weight	297.09
Temperature	293(2)
Wavelength	1.54184 Å
Crystal system	Cubic
Space group	Im-3m
Unit cell dimensions	*a* = 29.0302(5) Å, α = 90°
	b = 29.0302(5) Å, β = 90°
	c = 29.0302(5) Å, γ = 90°
Volume	24465.3(7)
Z	48
Density (calculated)	0.968
Absorption coefficient	6.743
F (000)	7104
Crystal size	0.28× 0.15× 0.12 mm^3
Theta range for data collection	3.73 to 71.42°
Index ranges	-19 <= h <= 35, -19 <= k <= 35, -11 <= l <= 35
Reflections collected	9069
Independent reflections	2308
Completeness to theta = 71.42°	98.4%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2308/0/89
Goodness-of-fit on F2	1.032
Final R indices [I>2σ(I)]	R1 = 0.1222, wR2 = 0.3445
R indices (all data)	R1 = 0.2231, wR2 = 0.3995
Largest diff. peak and hole	0.121 and -0.419 e.$Å^{-3}$

Table S4. Crystal data and structure refinement for **CoNIm (RHO) (SQUEEZE)**

Empirical formula	C6 H4 Co N6 O4
Formula weight	283.08
Temperature	293(2)
Wavelength	1.54184 Å
Crystal system	Cubic
Space group	Im-3m
Unit cell dimensions	*a* = 29.0302(5) Å, α = 90°
	b = 29.0302(5) Å, β = 90°
	c = 29.0302(5) Å, γ = 90°
Volume	24465.3(7)
Z	48
Density (calculated)	0.922
Absorption coefficient	6.709
F (000)	6768
Crystal size	0.28× 0.15× 0.12 mm^3
Theta range for data collection	3.73 to 71.42°
Index ranges	-19 <= h <= 35, -19 <= k <= 35, -11 <= l <= 35
Reflections collected	8985
Independent reflections	2308
Completeness to theta = 71.42°	97.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2308/0/80
Goodness-of-fit on F2	0.871
Final R indices [I>2σ(I)]	R1 = 0.0875, wR2 = 0.2338
R indices (all data)	R1 = 0.1648, wR2 = 0.2688
Largest diff. peak and hole	0.082 and -0.379 e.$Å^{-3}$

Section 9: Different Models of CoNIm (RHO) and CoNIm (SOD) ZIFs from single crystal data.

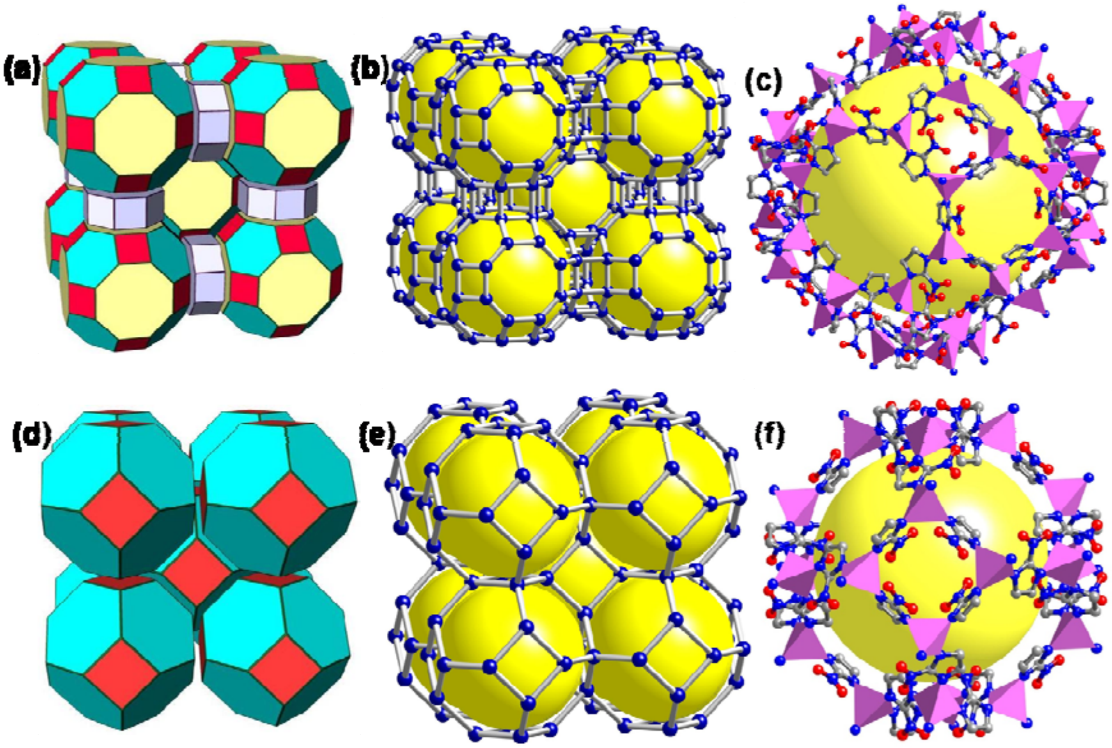

Figure S12: (a, d) tiling shows subdivision of space in RHO/SOD topologies **(b, e)** nets (grey line and deep blue dots) representing 2-NIm linker and Co centre, yellow ball inside indicates the free space inside the framework. **(c, f)** a cut away view of one of the [CoNIm (RHO)/CoNIm (SOD) ZIFs] Ziolitic Framework cage from single crystal XRD structure, CoN_4 pink tetrahedral with ball and stick links (yellow ball represents the empty space inside the framework). H atoms have been omitted for clarity. C, grey; N, blue; O, red; Co, pink.

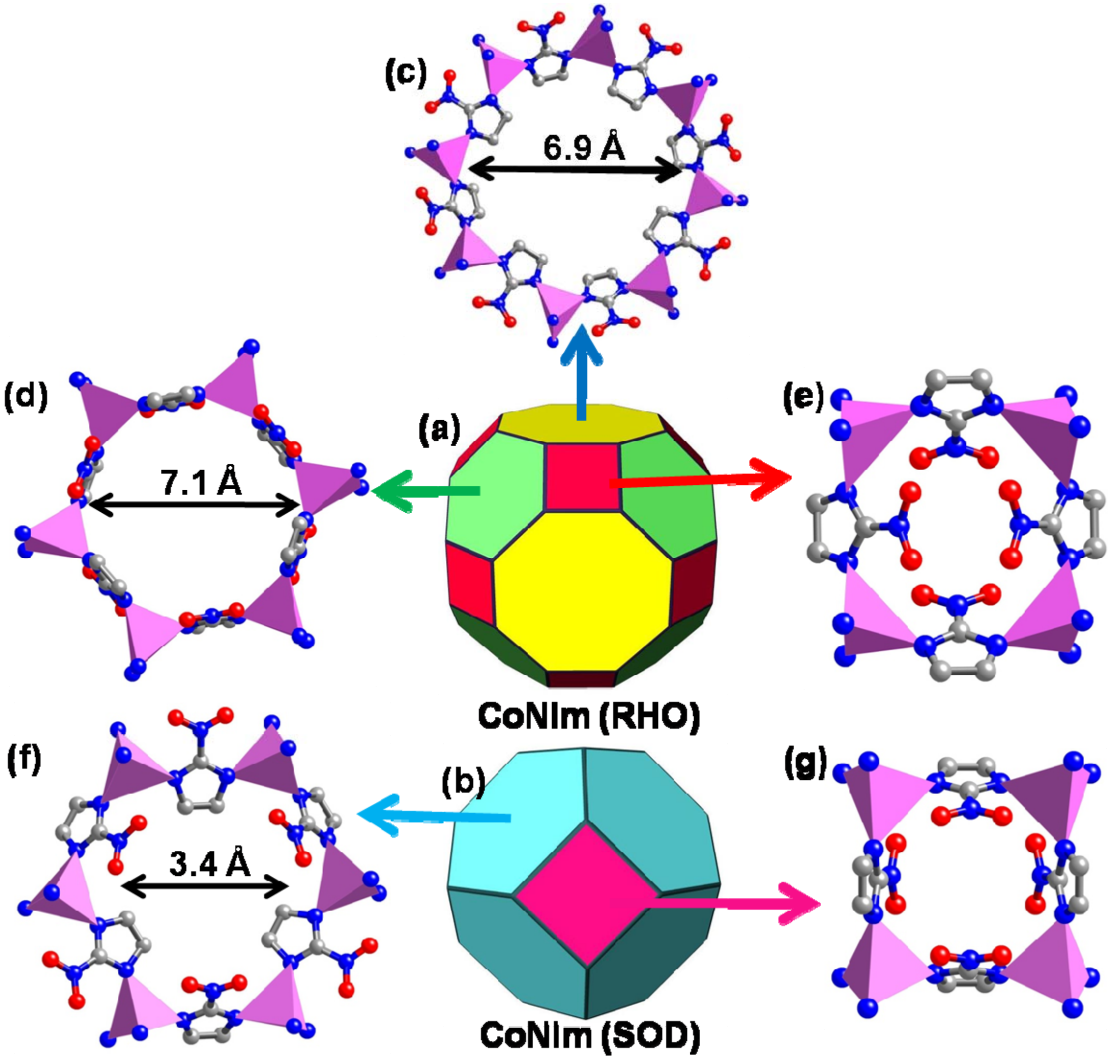

Figure S13: **(a)** tiling shows subdivision of space in CoNIm (RHO) ZIF cage **(b)** tiling shows subdivision of space in CoNIm (SOD) ZIF cage **(c)** a side view of 8 member ring face (yellow) of CoNIm (RHO), from SCXRD data, showing the hydrophobic pore with aperture 6.95 Å **(d)** a side view of 6 member ring face (green) of CoNIm (RHO) ZIF cage, showing the large pore aperture 7.13 Å **(e)** a side view of 4 member ring face (red) of CoNIm (RHO) ZIF, showing the hydrophilic pore environment (pore aperture negligible) **(f)** a side view of 6 member ring face (cyano) of CoNIm (SOD) ZIF cage from SCXRD data, showing the hydrophilic pore with narrow aperture of 3.4 Å **(g)** a side view of 4 member ring face (dark red) of CoNIm (SOD) ZIF, showing the hydrophilic pore environment (pore aperture negligible); H atoms have been omitted for clarity. C, grey; N, blue; O, red; Co, pink tetrahedra.

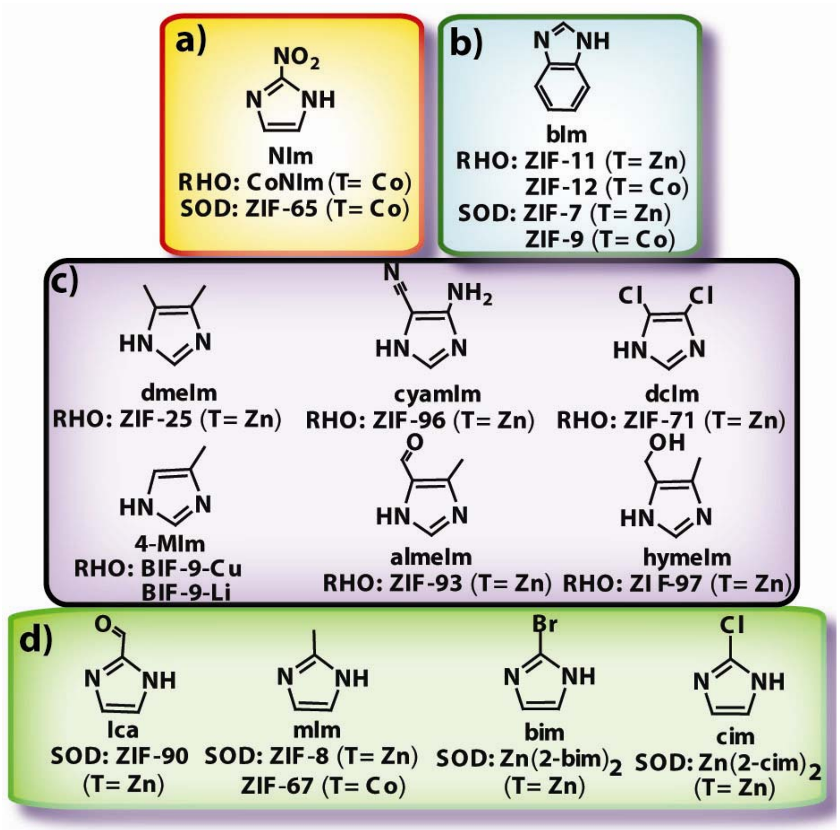

Figure S14: Imidazolate-type links used for the synthesis of ZIFs with RHO and SOD topology. **a) 2-NIm** is the only 2-substituted linker adopts both RHO and SOD topology. **b)** bIm is the only 4, 5 substituted linker which adopts RHO as well as SOD topology. **c)** Series of 4, 5 substituted imidazolate links which gives only RHO topology. **d)** Series of 2 substituted imidazolate links which forms only SOD topology. (Each category of linkers is enclosed; ‘T’ represents the metal atom used for ZIF synthesis).