Electronic Supplementary Information

Metal imidazolate sulphate frameworks as a variation of zeolitic imidazolate frameworks

Kyungkyou Noh,[a] Jaeung Sim,[b] Jonghoon Kim[c] and Jaheon Kim*[c]

[a] Department of Information Communication Convergence Technology, Soongsil University, Seoul 06978, Republic of Korea.

[b] Department of Fire Safety Research, Korea Institute of Civil Engineering and Building Technology, Hwaseong-Si, Gyeonggi-Do 18544, Republic of Korea.

[c] Department of Chemistry, Soongsil University, Seoul 06978, Republic of Korea; E-mail: jaheon@ssu.ac.kr

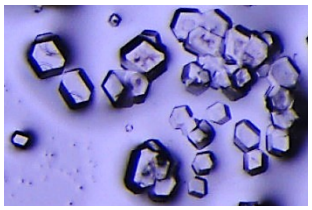
General Methods

Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), benzimidazole, and 2-methylimidazole were purchased from Sigma-Aldrich. 2-Ethylimidazole, 2-nitroimidazole, 2-mercaptobenzimidazole, and 1,3-dimethyl-2-imidazolidinone were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), *N*,*N*-dimethylformamide (DMF), acetonitrile, and dichloromethane were purchased from Daejung Chemicals & Metals Co., Ltd. Before experiments, $Zn(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dried under vacuum at ambient temperature for 1 day, and all other reagents were used without further purification.

Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex diffractometer with CuKα radiation (λ = 1.5418 Å). Single crystal X-ray diffraction (SCXRD) data were collected at 100 or 173 K with synchrotron radiation on a Rayonix MX225HS CCD area detector at BL2D-SMC beamline at Pohang Accelerator laboratory (PAL). Thermogravimetric analyses (TGA) were carried out using a PerkinElmer Pyris 1 in air at a heating rate of 5 °C/min. Fourier transform infrared (FT-IR) spectra were measured employing a JASCO FT/IR-7400 spectrophotometer and a PerkinElmer FT/IR Spectrum Two spectrometer on samples prepared as KBr pellets. ^{1}H-NMR spectra were recorded with a JEOL ECZ500/S1 spectrometer (500 MHz, Jeol, Tokyo, Japan). The N_2, H_2 and CO_2 adsorption-desorption isotherms were measured using the standard volumetric procedure on a BELSORP-mini instrument (BEL-Japan, INC.). Methanol adsorption-desorption isotherms were measured using the standard volumetric procedure on a BELSORP-max instrument (BEL-Japan, INC.). Elemental analysis was performed with a Thermo Scientific Flash 2000 HT analyzer. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was carried out employing PerkinElmer Optima 7300DV & Avio500. Field emission-scanning electron microscope (FE-SEM) images were obtained using the Carl Zeiss GeminiSEM 300 at 10 kV.

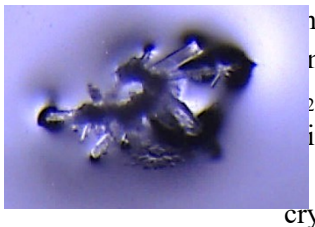
Synthesis of Compounds

Synthesis of $[Zn(SO_4)_2(HmIm)_2][NH_2(CH_3)_2]_2$ (1).



$Zn(SO_4)\cdot 7H_2O$ (347 mg, 1.2 mmol) and 2-methylimidazole (mImH, 197 mg, 2.4 mmol) were placed in a 30 mL vial, and then 15 mL of DMF and 0.5 mL of H_2O were added. After stirring the reaction mixture at room temperature for 30 minutes, the vial was capped and sealed with Teflon tape, and heated in an oven at 120°C for 4 days to give colourless block crystals. The collected crystals were washed sequentially with DMF (3 × 10 mL) and 15 mL of dichloromethane, and dried in air. Yield was 15 % (46 mg) based on 1 mole of zinc sulphate. Elemental microanalysis for $C_{12}H_{28}N_6O_8S_2Zn$, calculated (%): C, 28.05; H, 5.49; N, 16.35; S, 12.48. Found (%): C, 26.02; H, 4.63; N, 15.11; S, 11.24.

Synthesis of $[Zn(SO_4)_2(eImH)_2][NH_2(CH_3)_2]_2$ (2).

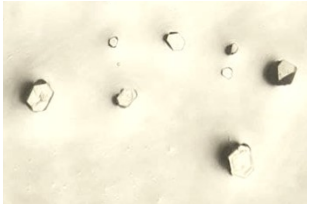


n(SO4)·7H2O (347 mg, 1.2 mmol) and 2-ethylimidazole (eImH, 231 mg, 2.4 mol) were placed in a 30 mL vial, and then 15 mL of DMF and 0.5 mL of 2O were added. After stirring the reaction mixture at room temperature for 30 inutes, the vial was capped and sealed with Teflon tape, and heated in an oven 120 °C for 4 days to give colourless rectangular crystals. The collected crystals were washed sequentially with DMF (3 × 10 mL) and 15 mL of dichloromethane, and dried in air (317 mg, yield 97 %). Elemental analysis for $C_{14}H_{32}N_6O_8S_2Zn$, calculated (%): C, 31.03; H, 5.95; N, 15.51; S, 11.83. Found (%): C, 29.74; H, 5.05; N, 14.20; S, 11.20. FT-IR spectrum is given in Fig. S23.

Synthesis of $[Zn_2(SO_4)_2(BIm)_2][NH_2(CH_3)_2]_2$ (MISF-1).

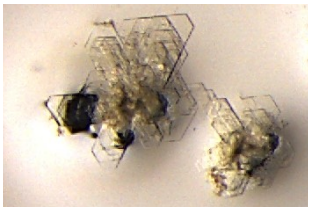
n(SO4)·7H2O (347 mg, 1.2 mmol) and benzimidazole (BImH, 284 mg, 2.4 mol) were placed in a 30 mL vial, and then 15 mL of DMF and 0.5 mL of H_2O re added. After stirring the reaction mixture at room temperature for 30 inutes, the vial was capped and sealed with Teflon tape, and heated in an oven 120 °C for 4 days to give colourless needle crystals. The collected crystals were washed sequentially with DMF (3 × 10 mL) and 15 mL of dichloromethane, and dried in air (340 mg, yield 91 %). Elemental analysis for $C_{18}H_{26}N_6O_8S_2Zn_2$, calculated (%): C, 33.30; H, 4.04; N, 12.94; S, 9.87. Found (%): C, 34.21; H, 3.98; N, 12.76; S, 9.97. FT-IR spectrum is given in Fig. S23.

Synthesis of $[Zn(SO_4)(nIm)][NH_2(CH_3)_2]$ (MISF-2).



$Zn(SO_4)\cdot 7H_2O$ (144 mg, 0.5 mmol) and 2-nitroimidazole (nImH, 226 mg, 2.0 mmol) were placed in a 30 mL vial, and then 20 mL of DMF and 1.0 mL of H_2O were added. After stirring the reaction mixture at room temperature for 30 minutes, the vial was capped and sealed with Teflon tape, and heated in an oven at 120 °C for 3 days to give yellow block crystals. The collected crystals were washed sequentially with DMF (3 × 10 mL) and acetonitrile (3 × 10 mL), and dried in vacuum for 1 h (46 mg, yield 29 %). Elemental analysis for $C_8H_{12}N_5O_6SZn$, calculated (%): C, 25.85; H, 3.25; N, 18.84; S, 8.63. Found (%):C, 18.25; H, 3.59; N, 16.10; S, 10.05. FT-IR spectrum is given in Fig. S23.

Synthesis of $[Zn_{0.5}(H_2O)(DMI)][Zn_3(nIm)_3(SO_4)_2]$ (MISF-3).



$Zn(NO_3)\cdot 6H_2O$ (75 mg, 0.25 mmol), nImH (57 mg, 0.5 mmol), and 2-mercaptobenzimidazole (150 mg, 1.0 mmol) were placed in a 30 mL vial, and then dissolved completely in 10 mL of 1,3-dimethyl-2-imidazolidinone (DMI). After adding 0.75 mL of H_2O in the solution, the vial was capped and sealed with Teflon tape, and heated in an oven at 120 °C for 4 days to give yellow plate crystals. Due to a low yield (ca. 8 %), the crystals were collected from a total of 10 batches, and washed with DMI (3 × 10 mL), and dried at 60 °C in vacuum for 10 h. Elemental analysis for evacuated **MISF-3**, $C_{14}H_{18}N_{11}O_{16}S_2Zn_{3.5}$, calculated (%): C, 18.91; H, 2.04; N, 17.33; S, 7.21. Found (%): C, 17.45; H, 2.13; N, 15.87; S, 7.07. FT-IR spectrum is given in Fig. S23.

Preparation of MISF-3-Ni.

The activated **MISF-3** crystals (100 mg) at 60 °C for 10 h were immersed in 0.5 M DMI solution of $Ni(NO_3)_2\cdot 6H_2O$ at room temperature for 1 day. The collected crystals were immersed again in the same but fresh DMI solution for 1 day. The filtered crystals were washed with neat DMI (3 × 15 mL), and further soaked in 15 mL of dichloromethane for 1 day to replace the solvent, and then washed with dichloromethane (3 × 10 mL) to obtain **MISF-3-Ni**. Finally, **MISF-3-Ni** was heated at 60°C for 10 hours under vacuum for further analysis. As a result of ICP-AES analysis, Zn was measured to be 322.997 ppm and Ni was measured to be 48.663 ppm, which corresponds to a molar ratio of Zn : Ni = 5.91 : 1. FT-IR spectrum is given in Fig. S23.

X-Ray Crystallography

A single crystal was attached to an oil-covered CryoLoop on a goniometer head. Under liquid nitrogen stream, the crystal was mounted on a Bruker diffractometer with an ADSC Q210 CCD area detector at 2D SMC with a silicon (111) double-crystal monochromator at Pohang Accelerator laboratory (PAL). The wavelength of the X-ray generated by PLSII 2D bending magnets was adjusted to λ = 0.630 Å (**MISF-1**) or 0.700 Å (**1**, **2**, **MISF-2**, and **MISF-3**). Data collection was conducted by an omega-scan method at 100 K except for **MISF-3** (173 K). Over the range of the omega angle, 180°, diffraction images were collected with a step increase of 1° and an exposure time of 1 sec per frame at a detector distance 90.00 mm, which was controlled using the PAL ADSC Quantum-210 ADX Program.[S1] The HKL3000sm (Ver. 703r) software package[S2] was used for the refinement of unit cell parameters, and data reduction with a higher symmetric unit cell. Absorption corrections were applied to all crystal data but seemed not to be effective for **MISF-1** that has thin needle morphology; thus, the eight large residual peaks (2.06 ~ 2.65 eÅ^{-3}) around two Zn atoms in **MISF-1** are ascribed to the insufficient absorption correction. The structure was solved by direct methods using the SHELX-S program and further developed with difference Fourier syntheses and subsequent refinement processes using the SHELX-L Version 2018/3.[S3] All non-H atoms were refined anisotropically except for those of the dimethylammonium cation of **MISF-2**. Hydrogen atoms were generated and included at ideal positions using the AIFX command in SHELX-L. Due to severe disorder of the dimethylammonium ion in **MISF-2**, a proper disordered model was not able to be applied and thus its N and C atoms were refined

isotropically under geometry restraints using DFIX. In contrast, the disorder of the coordinated sulphate ion to a Zn atom could be resolved and its atoms were refined anisotropically. In addition, the structural refinement of **MISF-2** could be conducted smoothly using TWIN and BASF instructions. In the case of **MISF-3**, a DMI solvent molecule was found in pores and refined anisotropically but with many SHELX restraints instructions (DFIX, SADI, ISOR) because of a large thermal motion. Additionally, one of the coordinated DMI to Zn4 had large and elongated thermal ellipsoids, but its possible disorder model was not further investigated to make a simpler structural model.

The CIF files for **1**, **2**, **MISF-1**, **MISF-2**, and **MISF-3** were deposited as CCDC 2128435-2128439 which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/?.

References

S1. A. J. Arvai, C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation; Poway, CA, USA, **1983**.

S2. Z. Otwinowski, W. Minor, *Methods in Enzymology*, ed. C. W. Carter, Jr., R. M. Sweet, Academic Press, New York, 1997, vol. 276, part A, pp. 307.

S3. Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112.

Table S1. Crystal data and refinement results for **1**

Empirical formula	$C_{12}\ H_{28}\ N_6\ O_8\ S_2\ Zn$	
Formula weight	513.89	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$ (No. 29)	
Unit cell dimensions	a = 14.426(3) Å	α = 90°
	b = 10.493(2) Å	β = 90°
	c = 14.810(3) Å	γ = 90°
Volume	2241.8(8) $Å^3$	
Z	4	
Density (calculated)	1.523 g/cm^3	
Absorption coefficient	1.280 mm^{-1}	
F(000)	1072	
Crystal size	0.050 x 0.016 x 0.006 mm^3	
Theta range for data collection	2.364 to 27.816.	
Index ranges	-19<=h<=19, -13<=k<=13, -19<=l<=19	
Reflections collected	15716	
Independent reflections	5404 [R(int) = 0.0849]	
Completeness to theta = 24.835	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5404 / 1 / 268	
Goodness-of-fit on F2	1.146	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1327	
R indices (all data)	R1 = 0.0469, wR2 = 0.1341	
Absolute structure parameter	0.022(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.456 and -1.558 $e.Å^{-3}$	

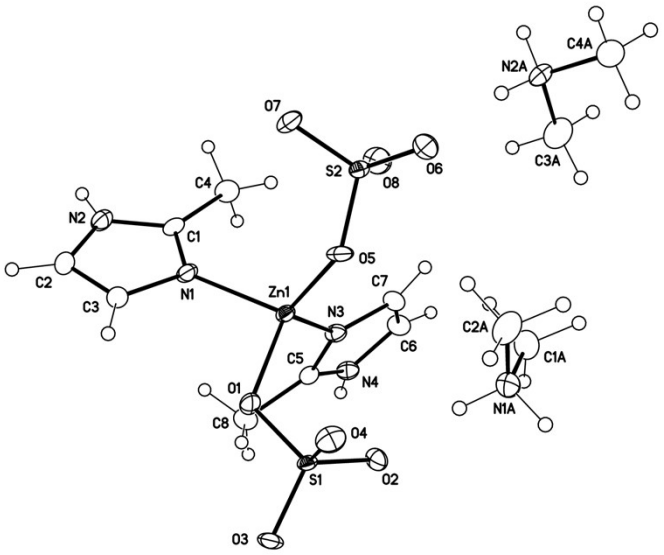


Figure S1. An ORTEP drawing of the asymmetric unit of **1**. The thermal ellipsoids are displayed with 50% probability level.

Table S2. Crystal data and refinement results for **2**

Empirical formula	$C_{14}\ H_{32}\ N_6\ O_8\ S_2\ Zn$	
Formula weight	541.94	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Orthorhombic	
Space group	*Pca*2$_1$ (No. 29)	
Unit cell dimensions	*a* = 14.624(3) Å	α = 90°
	b = 10.424(2) Å	β = 90°
	c = 15.046(3) Å	γ = 90°
Volume	2293.6(8) Å^3	
Z	4	
Density (calculated)	1.569 g/cm^3	
Absorption coefficient	0.938 mm^{-1}	
F(000)	1136	
Crystal size	0.090 x 0.070 x 0.030 mm^3	
Theta range for data collection	1.732 to 24.826.	
Index ranges	-19<=h<=19, -13<=k<=13, -19<=l<=19	
Reflections collected	16686	
Independent reflections	5516 [R(int) = 0.0654]	
Completeness to theta = 22.210	99.4 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.476	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5516 / 1 / 287	
Goodness-of-fit on F2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0836	
R indices (all data)	R1 = 0.0309, wR2 = 0.0837	
Absolute structure parameter	0.014(6)	
Extinction coefficient	0.0050(9)	
Largest diff. peak and hole	0.629 and -0.553 e.Å^{-3}	

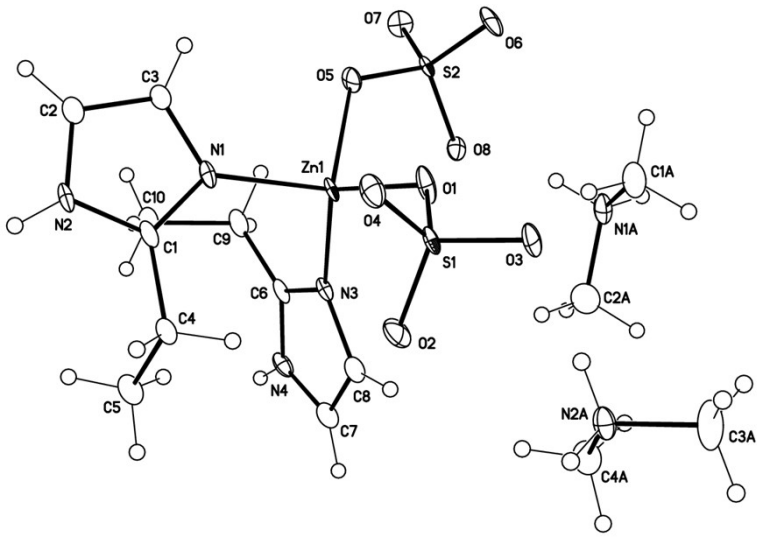


Figure S2. An ORTEP drawing of the asymmetric unit of **2**. The thermal ellipsoids are displayed at 50% probability level.

Table S3. Crystal data and refinement results for **MISF-1**

Empirical formula	$C_{36}\,H_{52}\,N_{12}\,O_{16}\,S_4\,Zn_4$	
Formula weight	1298.61	
Temperature	100(2) K	
Wavelength	0.630 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$ (No. 29)	
Unit cell dimensions	a = 9.7390(19) Å	α = 90°
	b = 22.092(4) Å	β = 90°
	c = 11.364(2) Å	γ = 90°
Volume	2445.0(8) $Å^3$	
Z	2	
Density (calculated)	1.764 g/cm^3	
Absorption coefficient	1.573 mm^{-1}	
F(000)	1328	
Crystal size	0.140 x 0.031 x 0.009 mm^3	
Theta range for data collection	1.634 to 24.834°.	
Index ranges	-12<=h<=12, -29<=k<=29, -15<=l<=14	
Reflections collected	18075	
Independent reflections	5901 [R(int) = 0.0958]	
Completeness to theta = 22.210°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.670	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5901 / 1 / 355	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1468	
R indices (all data)	R1 = 0.0582, wR2 = 0.1487	
Absolute structure parameter	0.011(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.653 and -1.836 $e.Å^{-3}$	

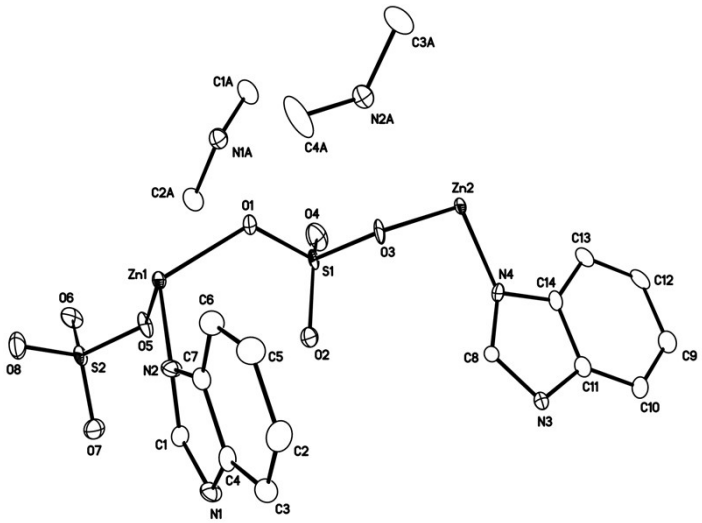


Figure S3. An ORTEP drawing of the asymmetric unit of **MISF-1**. The thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are not shown for simplicity.

Table S4. Crystal data and refinement results for **MISF-2**

Empirical formula	$C_5 H_{10} N_4 O_6 S Zn$	
Formula weight	319.62	
Temperature	100 (2) K	
Wavelength	0.700 Å	
Crystal system	Tetragonal	
Space group	$I4_1/a$ (No. 88)	
Unit cell dimensions	a = 15.217(2) Å	α = 90°
	b = 15.217(2) Å	β = 90°
	c = 20.632(4) Å	γ = 90°
Volume	4777.5(14) $Å^3$	
Z	16	
Density (calculated)	1.777 g/cm^3	
Absorption coefficient	2.168 mm^{-1}	
F(000)	2592	
Crystal size	0.070 x 0.060 x 0.030 mm^3	
Theta range for data collection	1.638 to 29.992°.	
Index ranges	-21<=h<=21, -15<=k<=15, -29<=l<=29	
Reflections collected	6972	
Independent reflections	3646 [R(int) = 0.0165]	
Completeness to theta = 24.835°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.388	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3646 / 14 / 167	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1543	
R indices (all data)	R1 = 0.0566, wR2 = 0.1556	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.168 and -1.147 $e.Å^{-3}$	

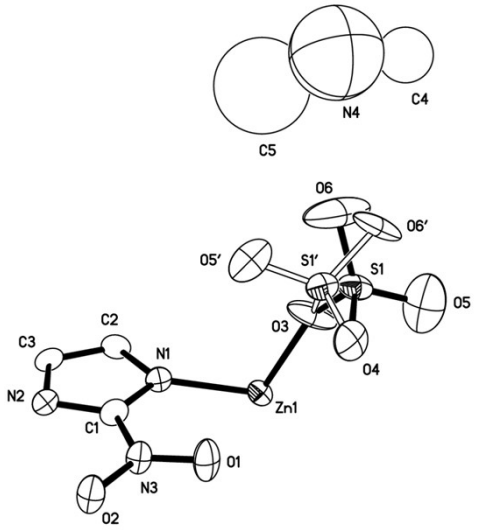


Figure S4. An ORTEP drawing of the asymmetric unit of **MISF-2**. The thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are not shown for simplicity. The sulphate ion is disordered over two sites with equal probability, respectively. The dimethyl ammonium cation was severely disordered and a proper disordered model could not be applied. Therefore, the thermal parameters of the C and N atoms of the dimethylammonium ion were refined isotropically.

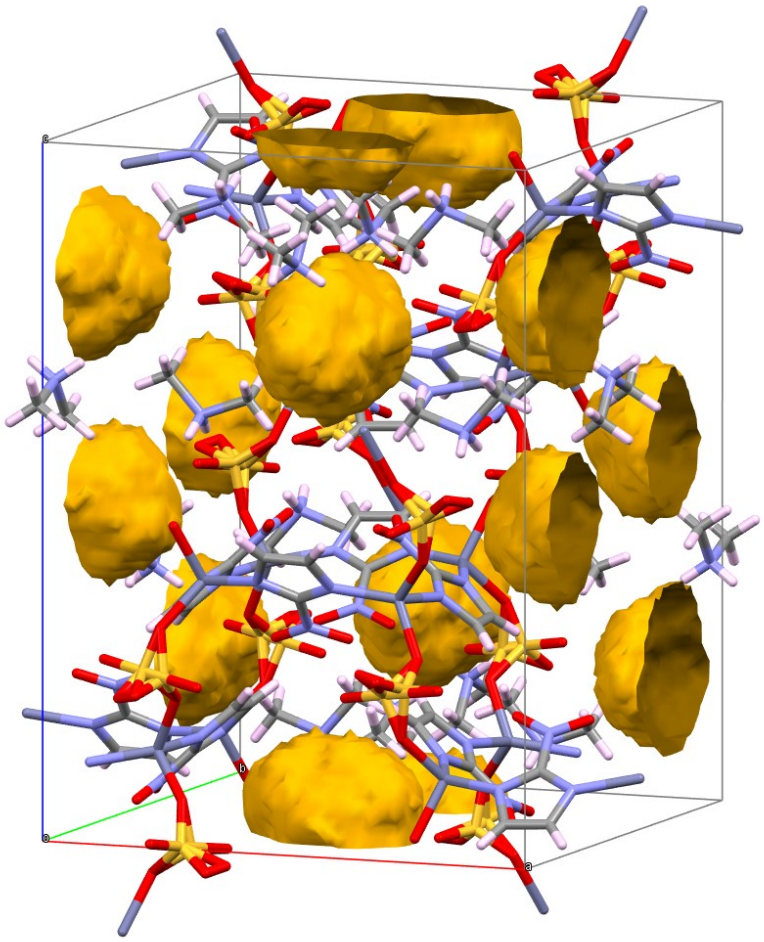


Figure S5. The isolate small pores in the unit cell of **MISF-2** calculated and drawn by Mercury 2020.2.0 (Build 290188).

Table S5. Crystal data and refinement results for **MISF-3**

Empirical formula	$C_{19}\ H_{26}\ N_{13}\ O_{17}\ S_2\ Zn_{3.5}$	
Formula weight	1001.44	
Temperature	173 (2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c* (No. 15)	
Unit cell dimensions	*a* = 24.841(5) Å	α = 90°.
	b = 14.724(3) Å	β = 102.79(3)°
	c = 20.723(4) Å	γ = 90°.
Volume	7392(3) $Å^3$	
Z	8	
Density (calculated)	1.803 g/cm^3	
Absorption coefficient	2.440 mm^{-1}	
F(000)	4048	
Crystal size	0.099 x 0.094 x 0.094 mm^3	
Theta range for data collection	1.594 to 27.817°.	
Index ranges	-33<=h<=33, -18<=k<=18, -27<=l<=27	
Reflections collected	17368	
Independent reflections	8885 [R(int) = 0.0320]	
Completeness to theta = 24.835°	97.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.452	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8885 / 33 / 496	
Goodness-of-fit on F2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0750, wR2 = 0.2241	
R indices (all data)	R1 = 0.1090, wR2 = 0.2467	
Extinction coefficient	0.00152(18)	
Largest diff. peak and hole	1.685 and -1.366 $e.Å^{-3}$	

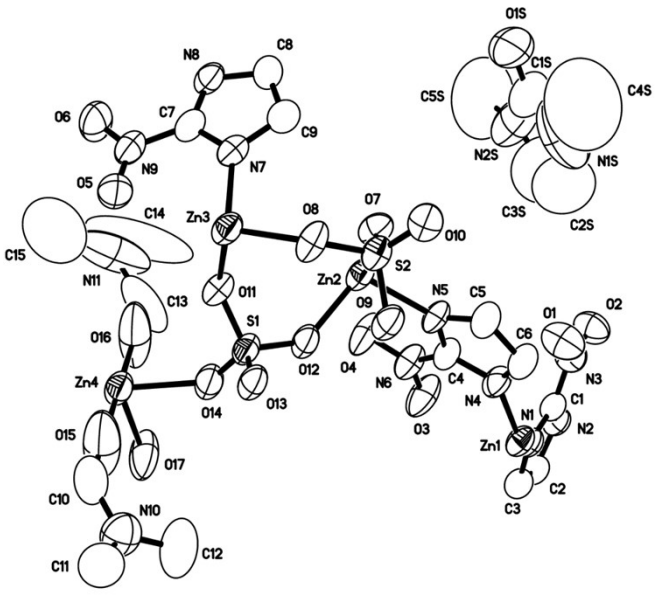


Figure S6. An ORTEP drawing of the asymmetric unit of **MISF-3**. The thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are not shown for simplicity. The two DMI molecules coordinated to Zn4 sit on a special position and thus half of them are shown in the asymmetric unit.

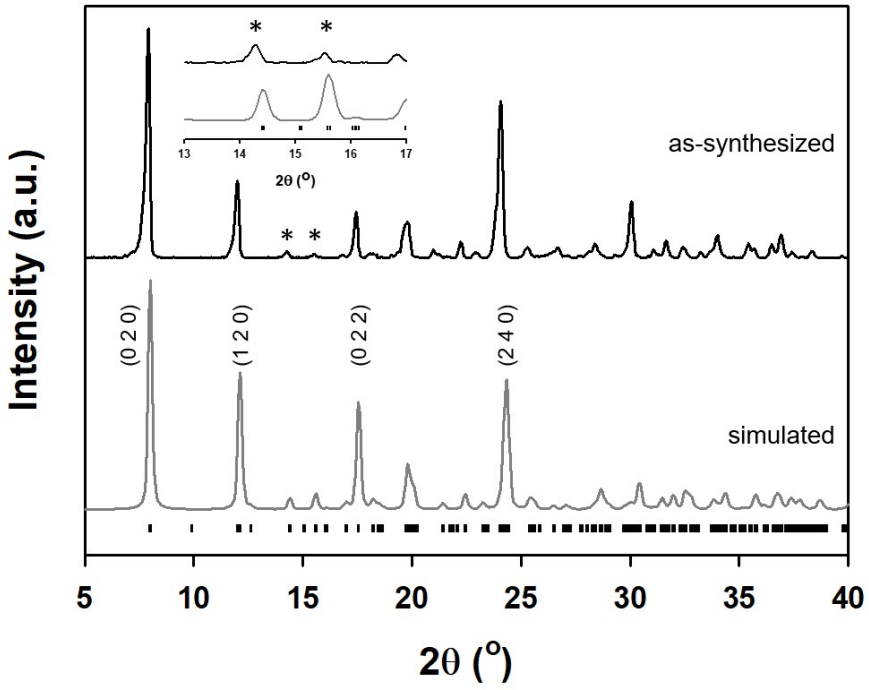


Figure S7. The measured and simulated PXRD patterns for **MISF-1**. The inset is enlarged display for the as-synthesized (top) and simulated (bottom) patterns between 13° and 17°.

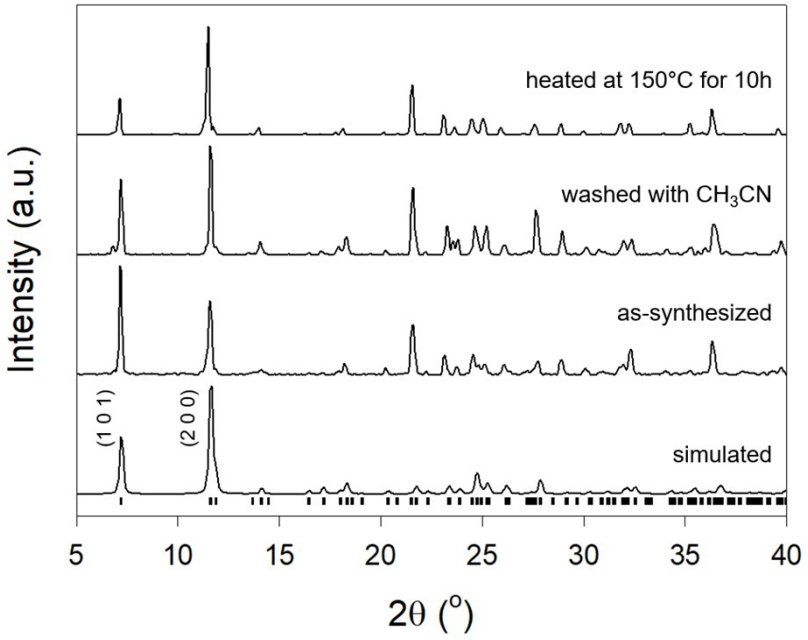


Figure S8. The measured and simulated PXRD patterns for **MISF-2**.

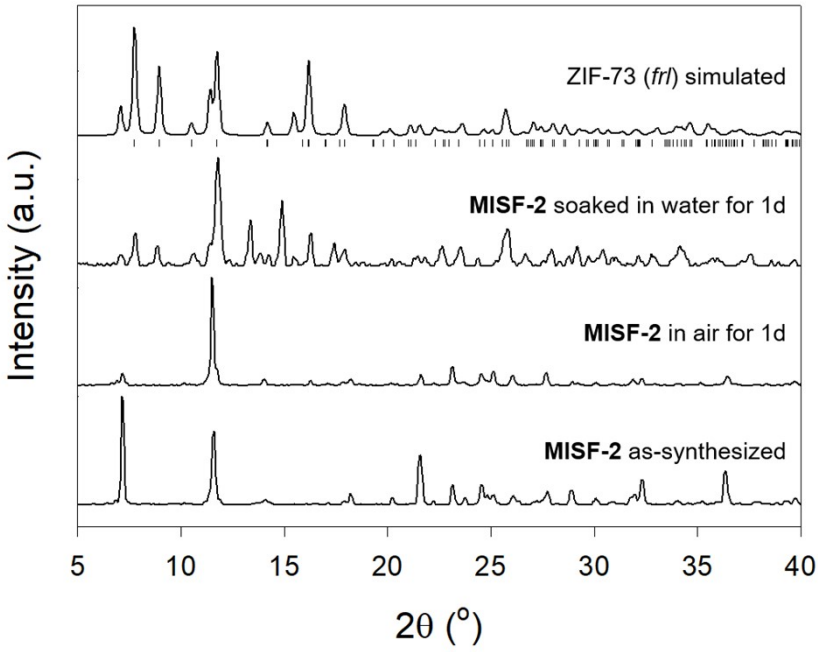
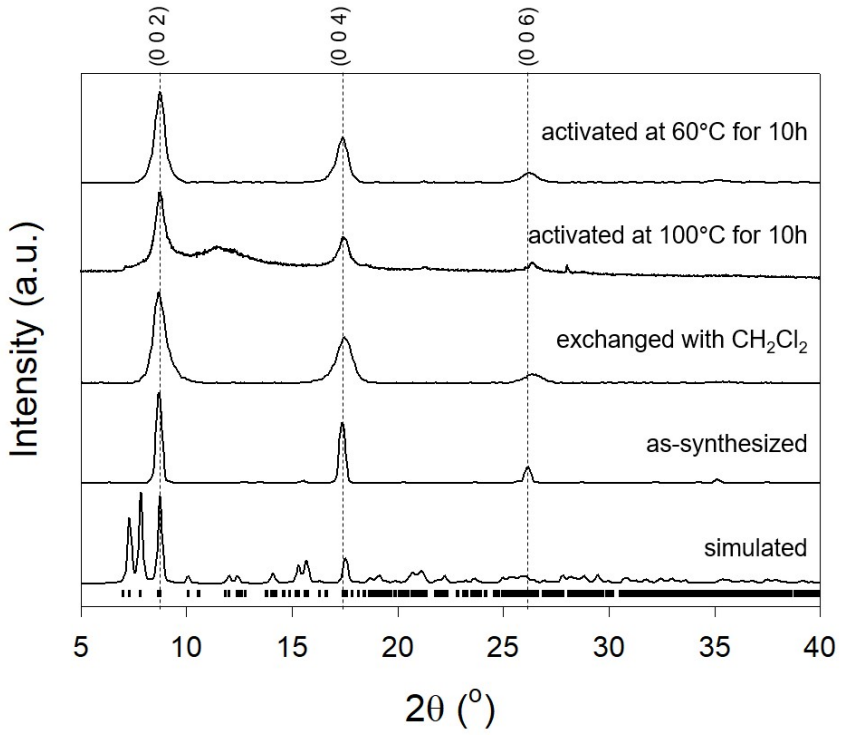
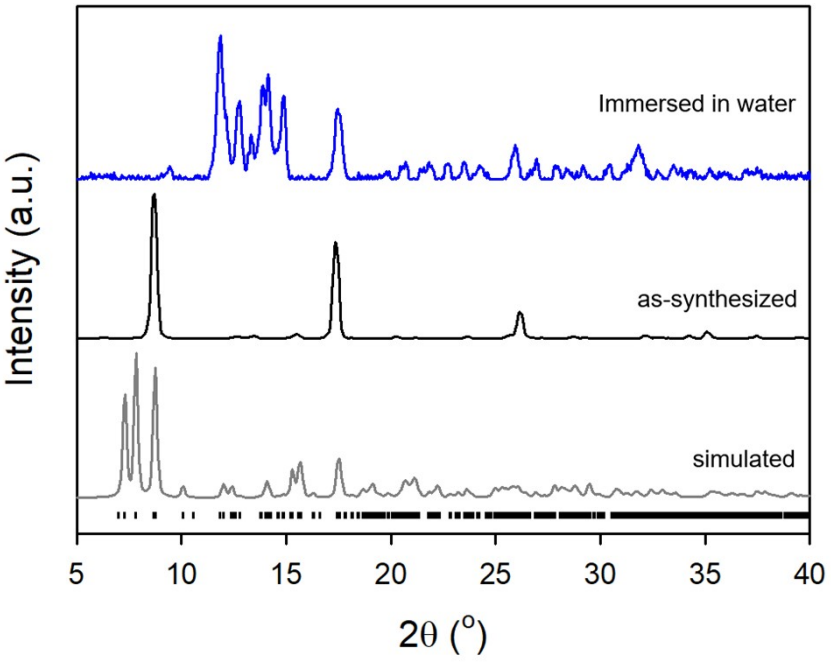


Figure S9. The PXRD patterns of **MISF-2** samples. The chemical composition of the solid obtained when **MISF-2** is soaked in water for 1 d gave elemental analysis results as follows. Found (%):C, 24.95; H, 1.35; N, 36.35; S, 0.

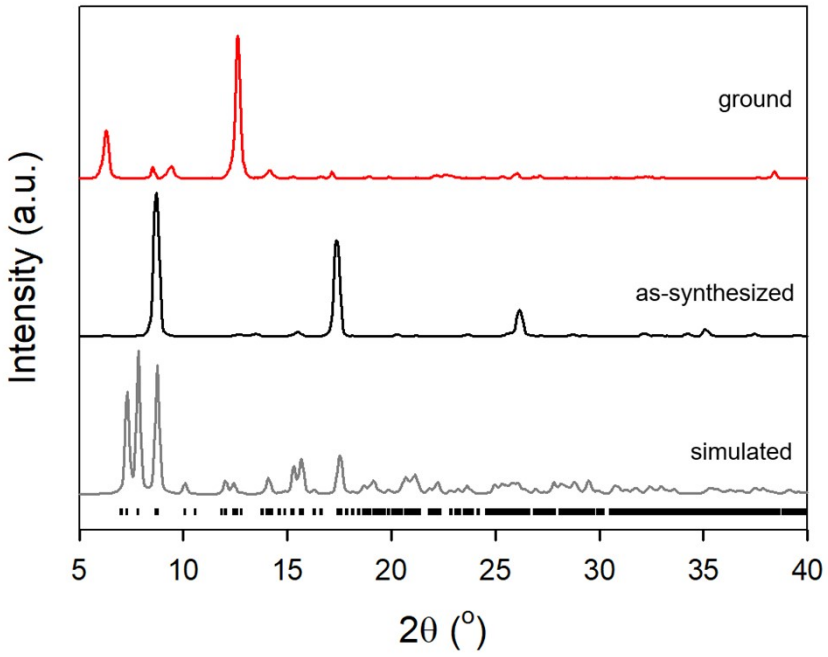


(a)

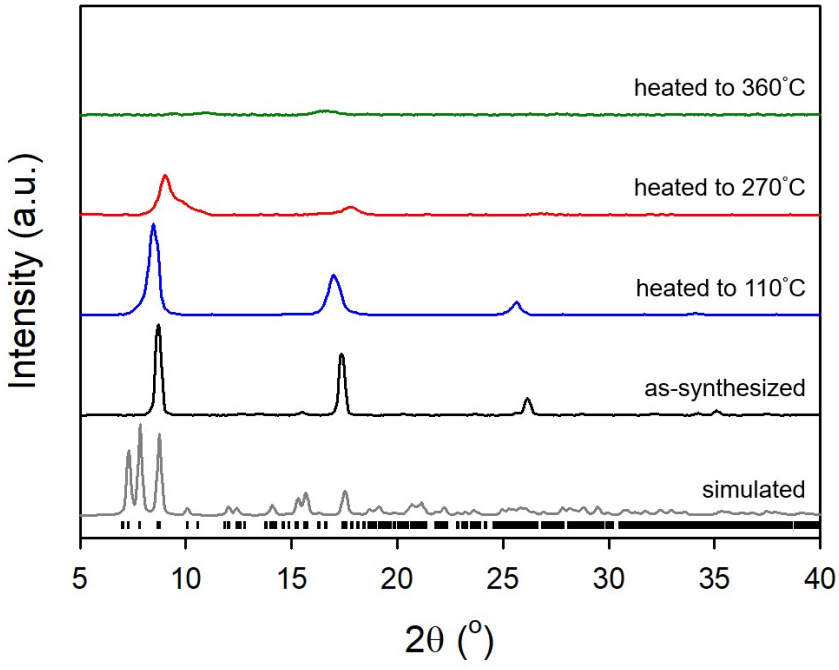


(b)

Figure S10. The PXRD patterns for **MISF-3** samples: (a) the activated samples are compared to the as-synthesized one, where the simulated pattern was generated using the X-ray structure.



(c)



(d)

Figure S10. The PXRD patterns for **MISF-3** samples (c) ground in air for about 5 min, and (d) heated at a TGA apparatus at ambient atmosphere up to 110 °C, 270 °C, and 360 °C, respectively. Elemental analysis results are as follows. Found (%) for the 110 °C sample: C, 25.76; H, 3.2; N, 22.79; S, 5.63. For the 270 °C sample, found (%): C, 19.91; H, 2.2; N, 21.07; S, 7.11. For the 360 °C sample, found (%):C, 15.93; H, 1.58; N, 19.85; S, 8.82.

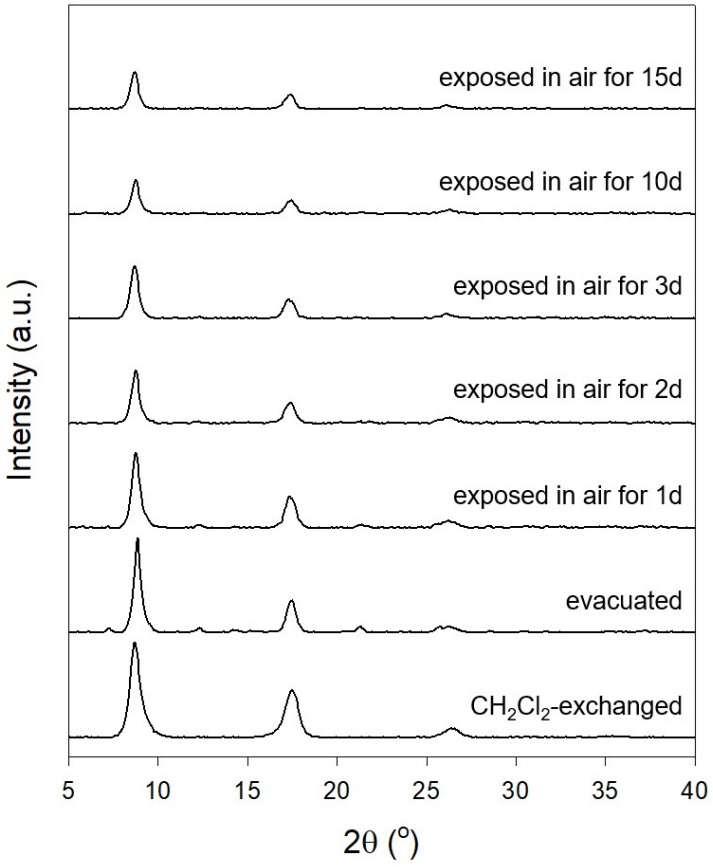


Figure S11. The PXRD patterns for **MISF-3** when evacuated samples are exposed in air up to 15 days. Each PXRD pattern was measured with almost the same quantity of samples to monitor the decrease in peak intensity.

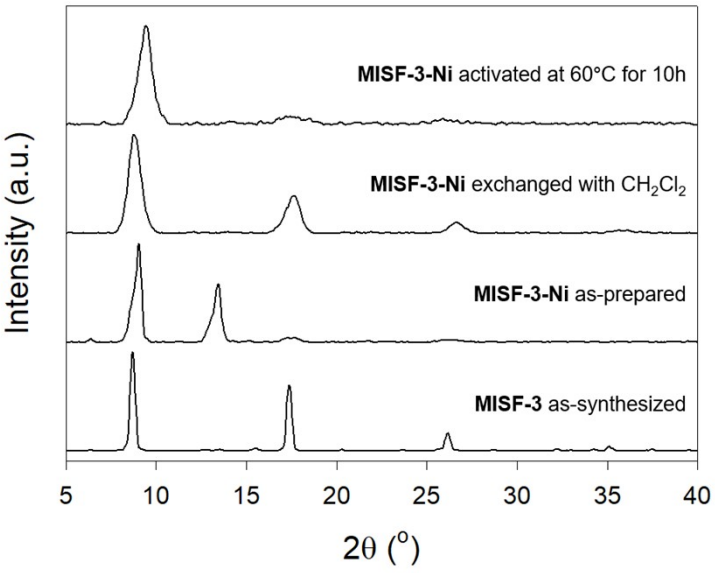
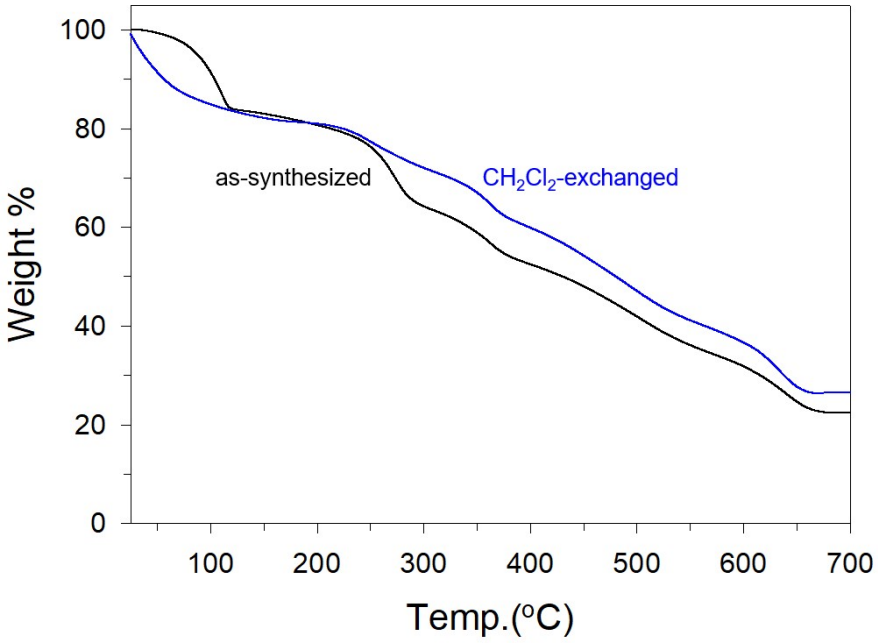
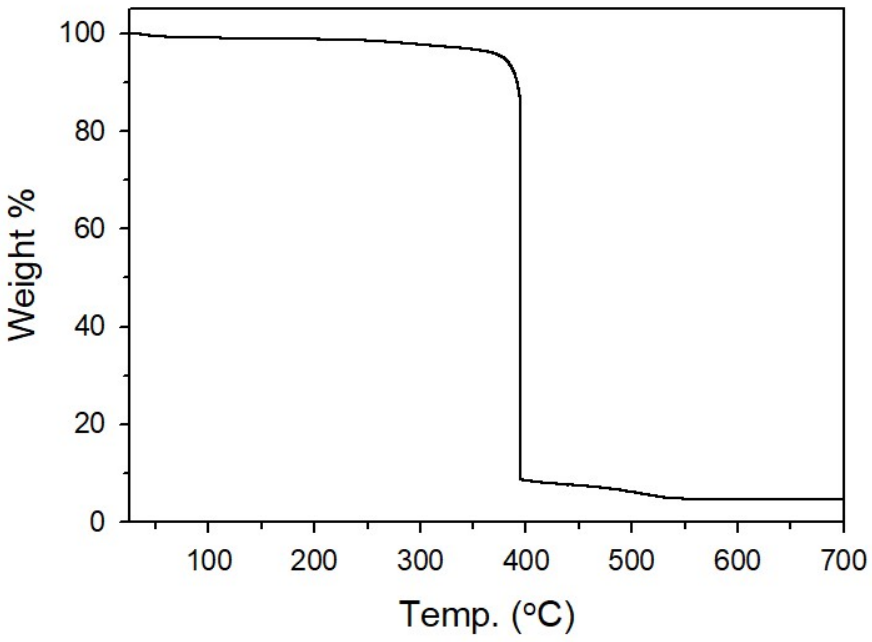


Figure S12. The PXRD patterns for **MISF-3-Ni** samples.



(a)



(b)

Figure S13. The TGA curves for **MISF-3** samples: (a) as-synthesized and solvent-exchanged samples and (b) a pale-yellow powder produced immediately when MISF-3 is immersed in water. The elemental analysis for the pale-yellow powder: found(%): C, 24.99; H, 1.40; N, 36.19; S, 0.

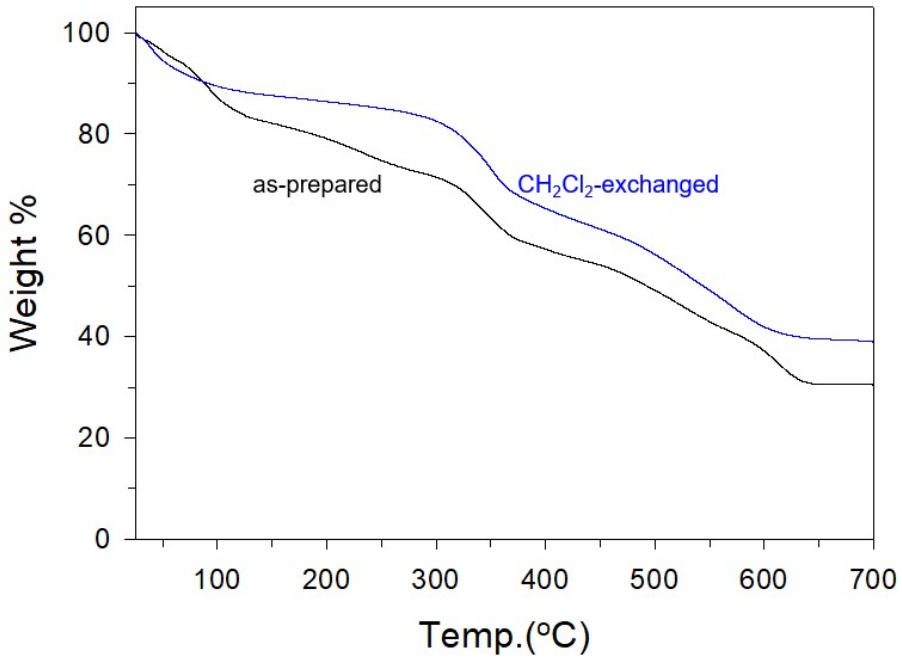


Figure S14. The TGA curves for **MISF-3-Ni** samples.

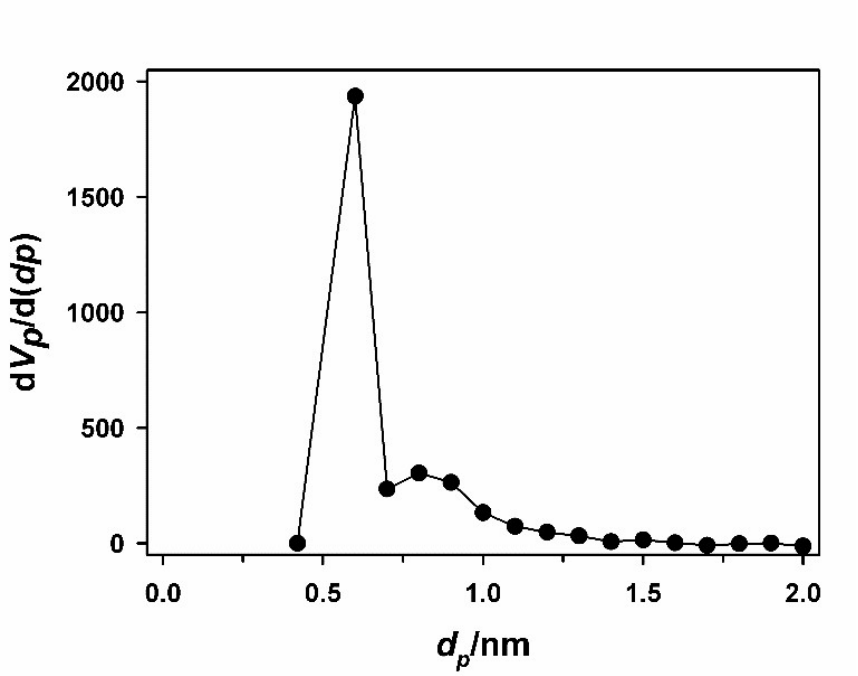


Figure S15. The pore size distribution of **MIS-3**.

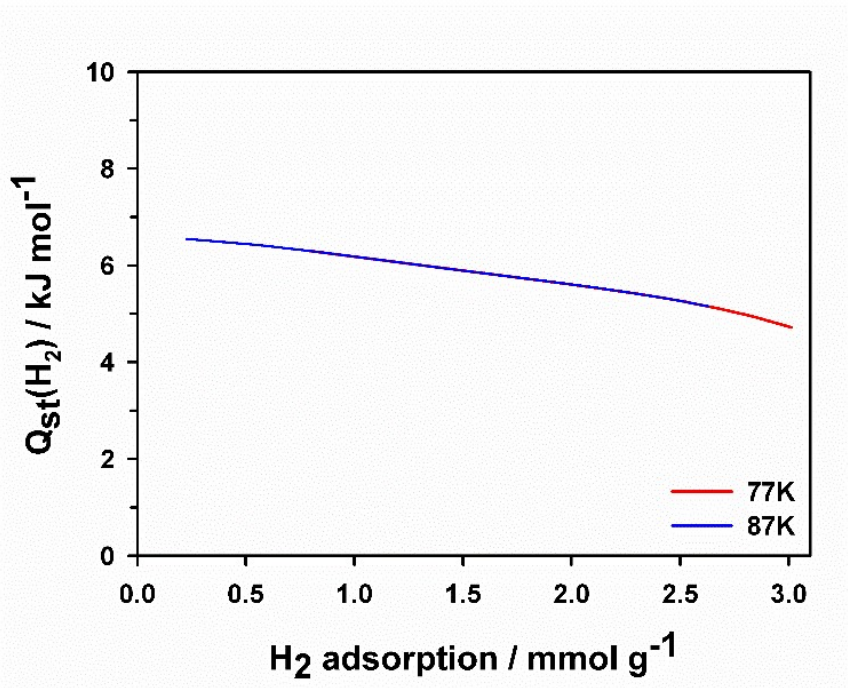


Figure S16. The isosteric heat of H_2 adsorption for **MISF-3**.

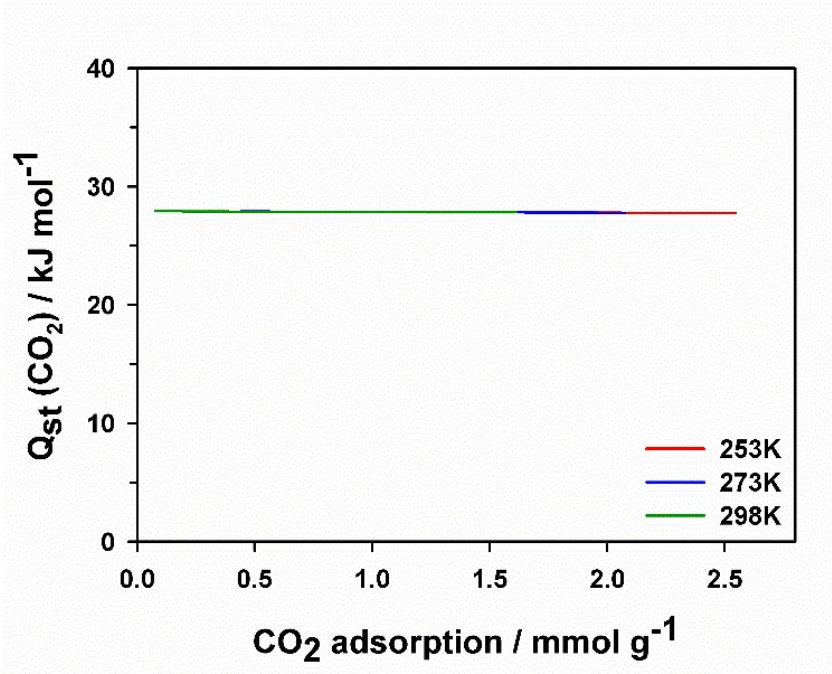


Figure S17. The isosteric heat of CO_2 adsorption for **MISF-3**.

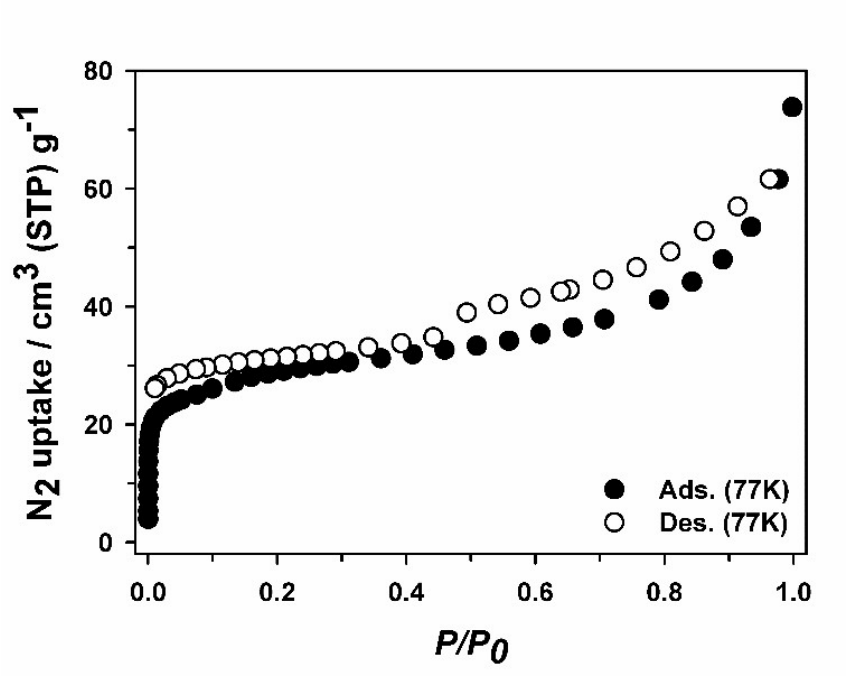


Figure S18. The N_2 adsorption-desorption isotherm of **MISF-3-Ni** measured at 77 K.

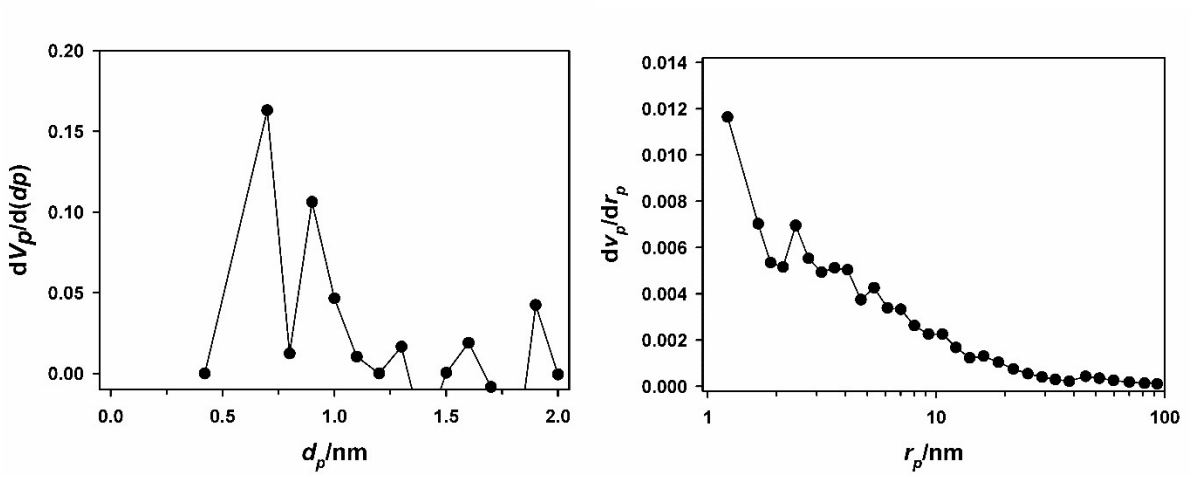


Figure S19. The pore size distribution of **MISF-3-Ni**.

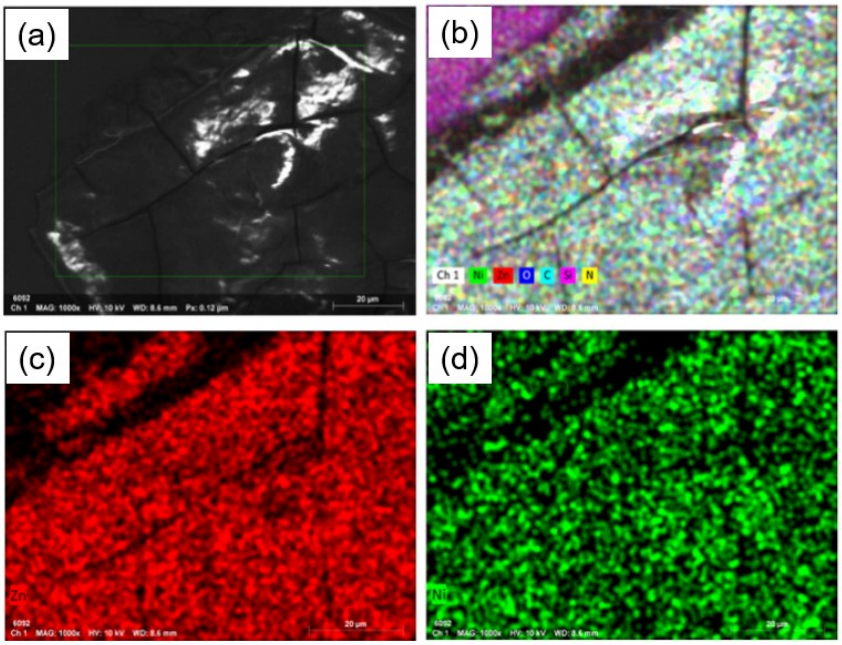


Figure S20. The SEM and energy dispersive X-ray elemental mapping images of a **MISF-3-Ni** crystal: (a) the mapping area on a crystal surface, the mapping of Ni, Zn, O, C, Si, and N, (c) Zn, and (d) Ni.

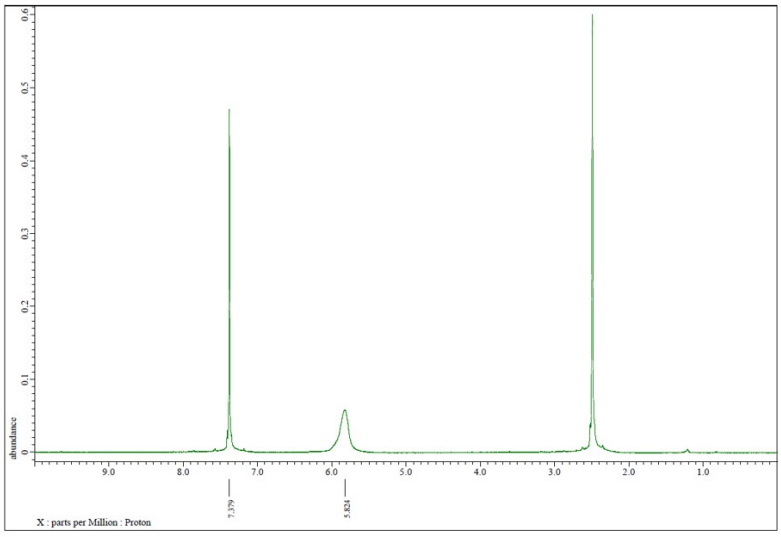


Figure S21. ^{1}H-NMR spectrum for the pale-yellow solid obtained by immersing **MISF-3** in water. The solid was dissolved in DCl/DMSO-d_6. Only the 2-methylimidazole at 7.339 ppm was observed except for the water and DMSO signals.

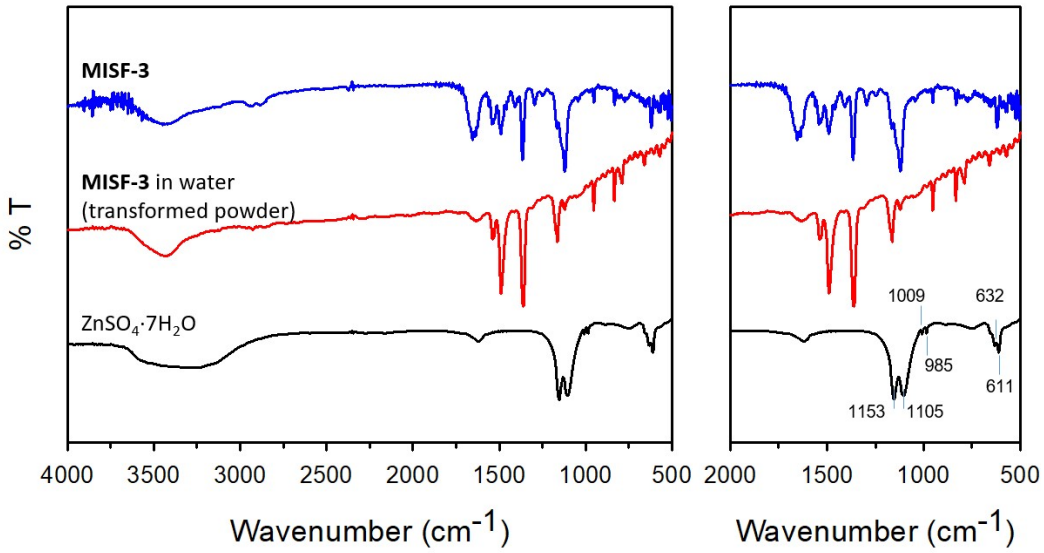


Figure S22. FT-IR spectrum for the pale-yellow solid (or transformed powder) obtained by immersing **MISF-3** in water, **MISF-3**, and $ZnSO_4 \cdot 7H_2O$ (reference). The wavenumbers in the spectrum are given for the sulphate bands.

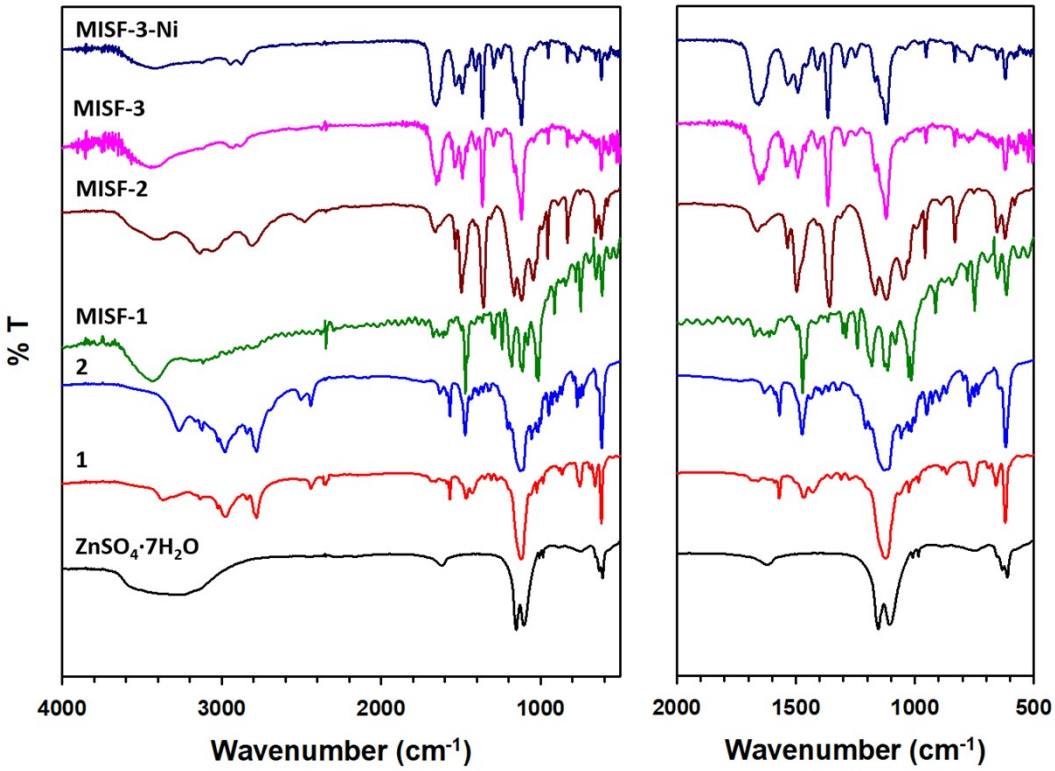


Figure S23. FT-IR spectra for the compounds in this work and $ZnSO_4 \cdot 7H_2O$ (reference).