Supporting Information

High Hydroxide Conductivity in a Chemically Stable Crystalline Metal-Organic Framework Containing Water-Hydroxide Supramolecular Chain

Sanjog S. Nagarkar,[a] Bihag Anothumakkool,[b,c] Aamod V. Desai,[a] Mandar M. Shirolkar,[d] Sreekumar Kurungot,[b,c] and Sujit K. Ghosh[*a]

[a] *Indian Institute of Science Education and Research (IISER) Pune, Maharashtra 411 008, (India).*
[b] *Physical and Materials Chemistry Division, National Chemical Laboratory (NCL), Pune, Maharashtra 411 008, India.*
[c] *Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhawan, 2 Rafi Marg, 110 001 New Delhi, India.*
[d] *Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China.*

Fax: *+91-20-25908022* ***Tel:*** *+91-20- 25908076* ***E-mail:*** ***sghosh@iiserpune.ac.in***

Experimental Section:-

Physical Measurements: Thermogravimetric analyses (TGA) were recorded on Perkin-Elmer STA 6000 TGA analyzer under N_2 atmosphere (10 °C min^{-1}). The IR spectra were recorded on NICOLET 6700 FT-IR spectrophotometer using KBr pellet. CHNO analysis was done using VarioELcube. BELCAT-A and BELMass (BEL Japan, Inc.) instruments were used to perform temperature-programmed desorption mass spectrometry. The heating rate of was 3 °C/min under helium gas flow (30 ml/min). The EDX analysis SEM image was obtained using FEI Quanta 3D dual beam ESEM at 30KV.

Synthesis of pymcaH ligand:[1] To a suspension of 2-cyanopyrimidine (1 g, 8.5 mmol) in 25 mL of water was added KOH (1.12 g, 20 mmol) and the mixture refluxed for 2 h. After cooling, the solution was neutralized with dil. HCl at 0 °C, and the solvent was then removed in a vacuum. The crude solid was dissolved with CH_2Cl_2 and the solid KCl was filtered off. The filtrate concentrated to afford the pymcaH acid in a yield of 45%. ^1H NMR (δ): H3 and H5 (9.12, doublet), H4 (7.54, triplet). ^{13}C NMR (δ): C4 (122.8), C3 and C5 (158.5), C1 (161.2), C7OOH (172.3).

Synthesis of [Ni_2(μ-pymca)$_3$]OH·nH_2O: MOF was synthesized using modified synthetic procedure. Then 2-pyrimidinecarboxylic acid (pymcaH, 38 mg, 0.3 mM) and $NiCl_2$ (74 mg, 0.3 mM) were added to Teflon lined vessel containing 7 mL H_2O. The vessel was heated at 160 °C for 20 h and then cooled to room temperature slowly over the period of 48 h. MOF **1** was obtained as greenish crystalline powder which was then filtered and washed with water to get **1** in 45 % yield. $C_{15}H_{20}N_6Ni_2O_{12}$ Theoretical: C 30.34, H 3.40; N 14.15, O 32.34; Observed C 30.10, H 3.01; N 13.97, O 32.02. C/N Theoretical = 2.14; Found = 2.15 and C/O Theoretical = 0.93; Found = 0.94.

X-ray Crystal Structure Analysis: The powder X-ray diffraction patterns (PXRD) was recorded using Bruker D8 Advanced X-Ray diffractometer (Cu Kα, λ=1.5406 Å). The PXRD measurement was carried out using a zero background sample holder. The structure of product **1** was obtained by Rietveld refinement. Fullprof suit (Version March 2014) was used to carry out Rietveld refinement.[2] GFourier and Bond_Str packages available with Fullprof suite were employed to extract information about the bond length. The refinement was carried out by following the procedure described previously.[3] The lattice parameters and the various structural parameters have been estimated during the refinement. The electron density was visualized through maximum entropy method (MEM) analysis derived through Rietveld analysis. The MEM analysis was performed using Dysnomai package integrated with Visualization for Electronic and Structural Analysis (VESTA) software (Version 3.1.8).[4]

Chemical Stability Studies of 1: The water stability of **1** was ascertained by dipping 50 mg of **1** in 25 mL boiling water for 24 h. Similarly the base stability of **1** was determined by immersing 50 mg of **1** in 25 mL solutions of NaOH (1N) and with required pH for 8 h. The time dependence of base stability for compound **1** was monitored by dipping 2 mg of **1** in 5 mL aqueous NaOH (1N) solution and the small fraction of the supernatant solution was collected at different time intervals and analyzed for Ni(II) content using ICP analysis.

Gas and Water Uptake: The sample was pretreated at 130 °C overnight under reduced pressure to get dehydrated phase which then subjected to sorption studies. The gas adsorption isotherms were collected using a BEL-max and water adsorption was collected using a BEL-aqua from (BEL-Japan).

Conductivity Measurements: The ionic conductivity of **1** was determined using impedance analysis. The powder of **1** (ca. 90 mg) was pressed (8 ton) to pellet using 13 mm standard die. The thickness of pellet was measured by thickness gauge (Absolute, Mitutoyo Co. Ltd., Japan, accuracy 0.01 mm). The pellet was then sandwiched between the electrodes and subjected to impedance analysis. AC impedance measurements were carried out using Bio-Logic SP-300. The temperature and humidity conditions were controlled by an incubator SH-221, ESPEC Co. Ltd., Japan. Applied frequency range for the measurement was from 106 to 0.01 Hz against the open circuit potential with sinus amplitude of 10 mV.

Impedance Data Fitting: All the EIS data were fitted using an EC-Lab Software V10.19 and the conductivity of material was determined from the resistance obtained by impedance spectra fitting using equivalent circuit elements.

[CCDC 1057104 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Figures:-

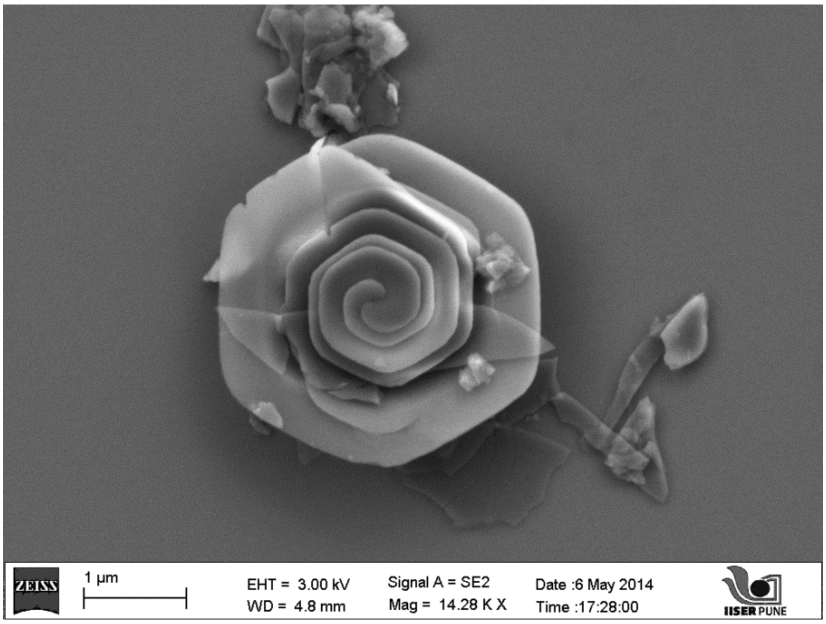


Figure S1: SEM image of compound **1** demonstrating thehexagonal structure.

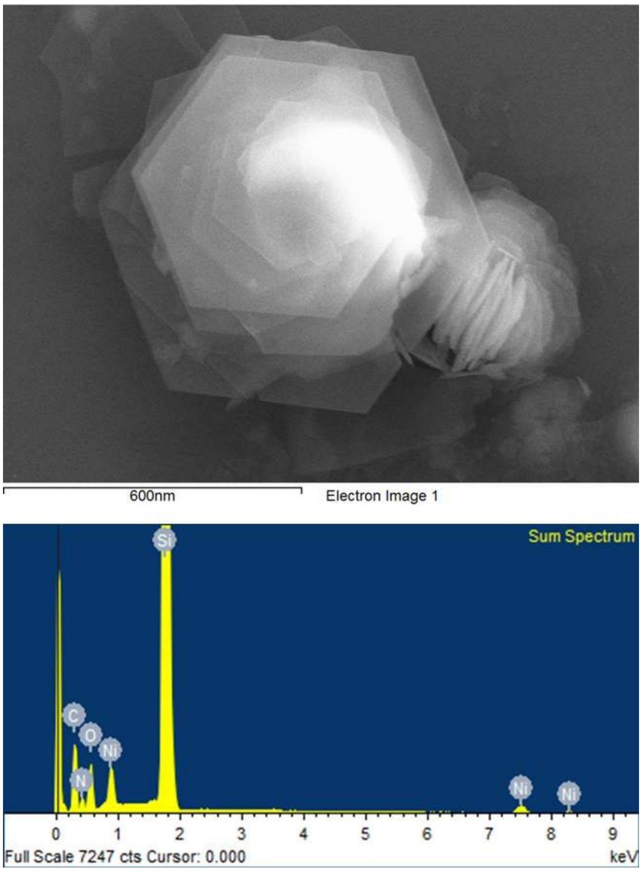


Figure 2: SEM image of hexagonal particle of compound **1** and corresponding EDX spectrum of compound **1**.

Multiple particle wide area EDX analysis of compound 1

Batch-A:

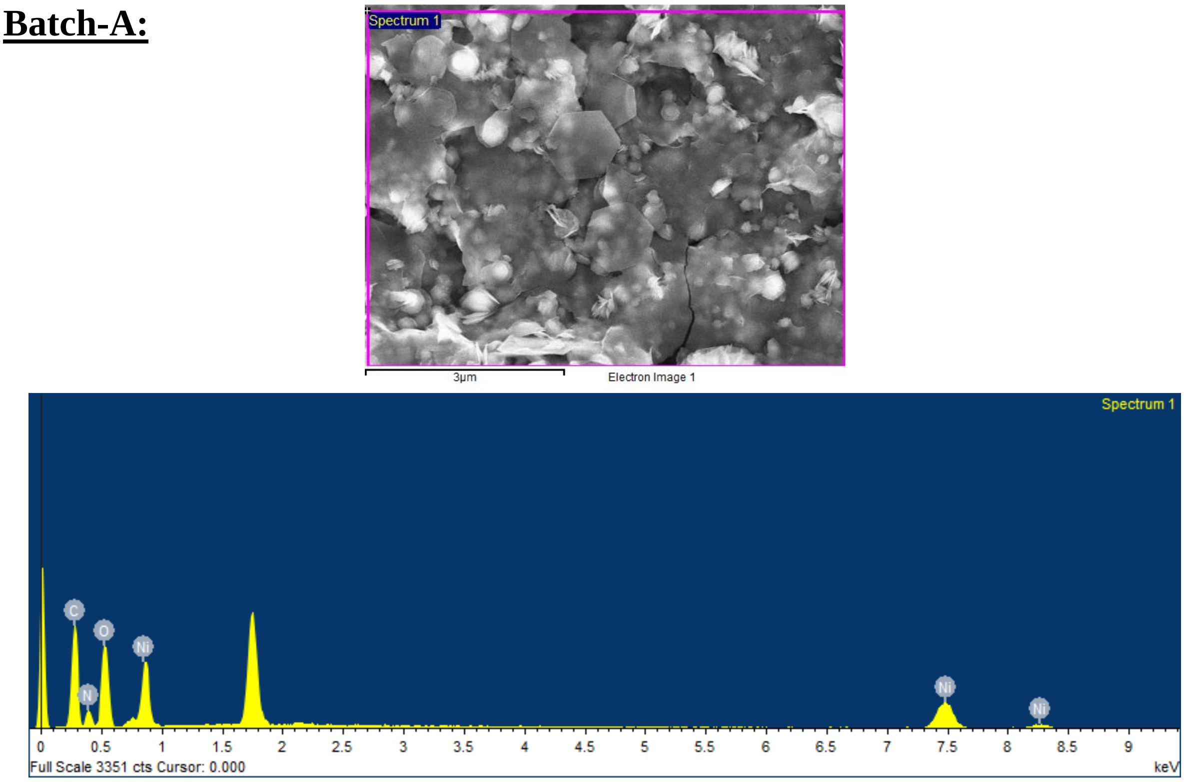


Figure S3.A1: Multiple particles wide area EDX spectrum of compound **1**.

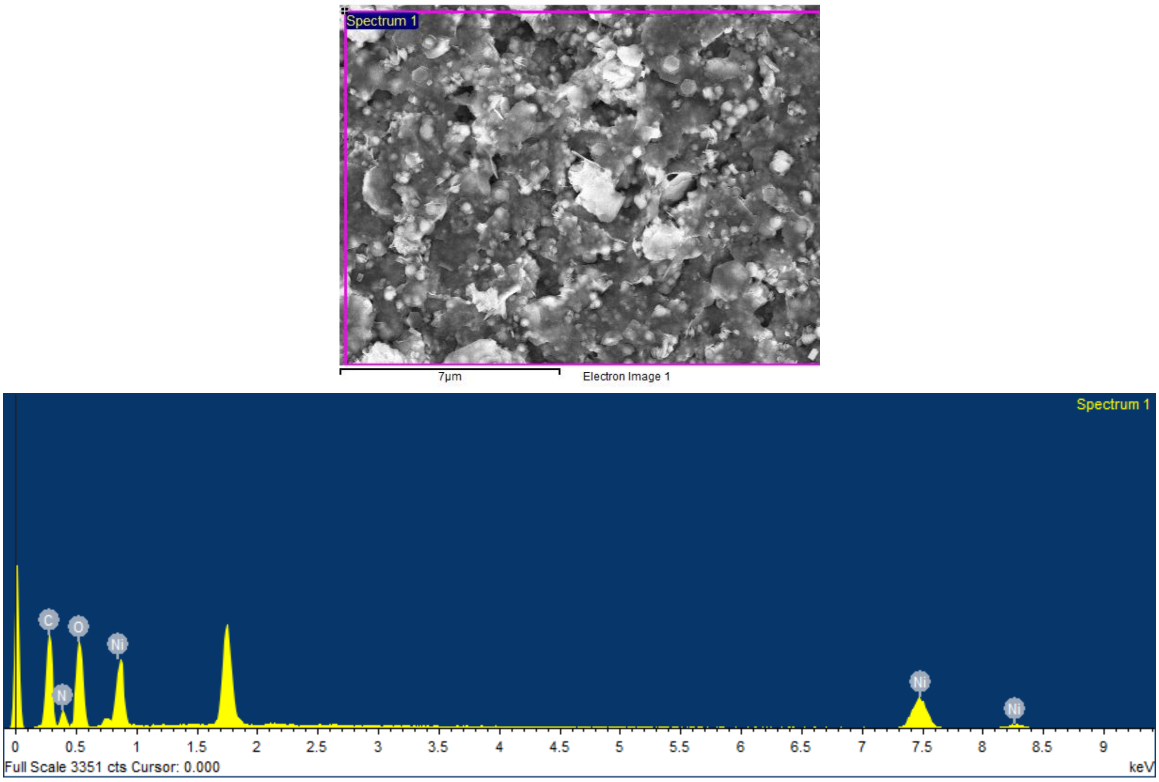


Figure S3.A2: Multiple particles wide area EDX spectrum of compound **1**.

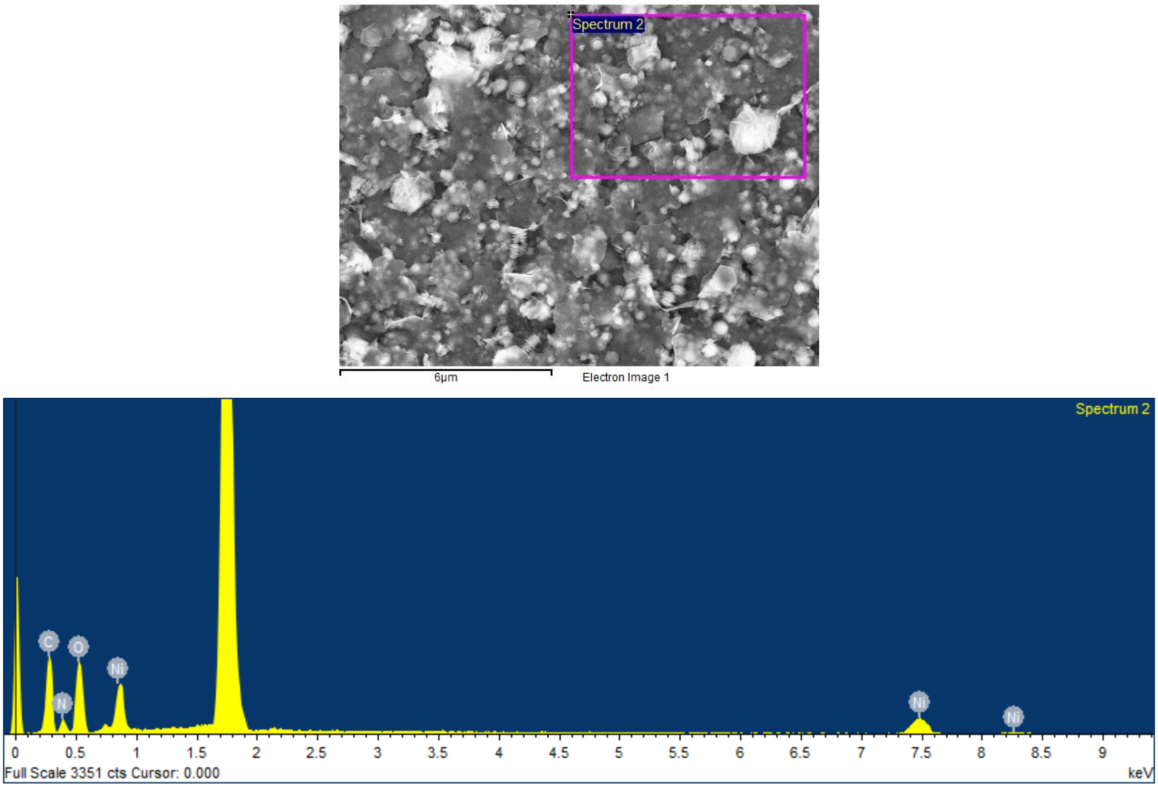


Figure S3.A3: Multiple particles wide area EDX spectrum of compound **1**.

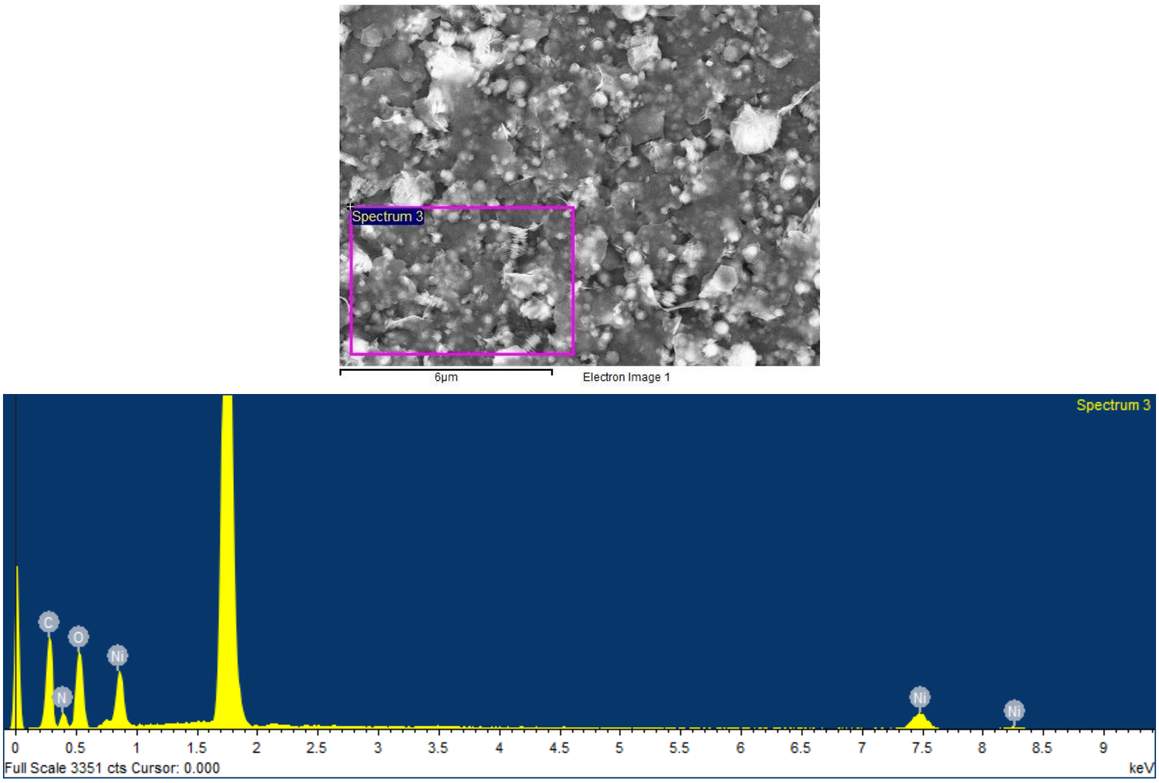


Figure S3.A4: Multiple particles wide area EDX spectrum of compound **1**.

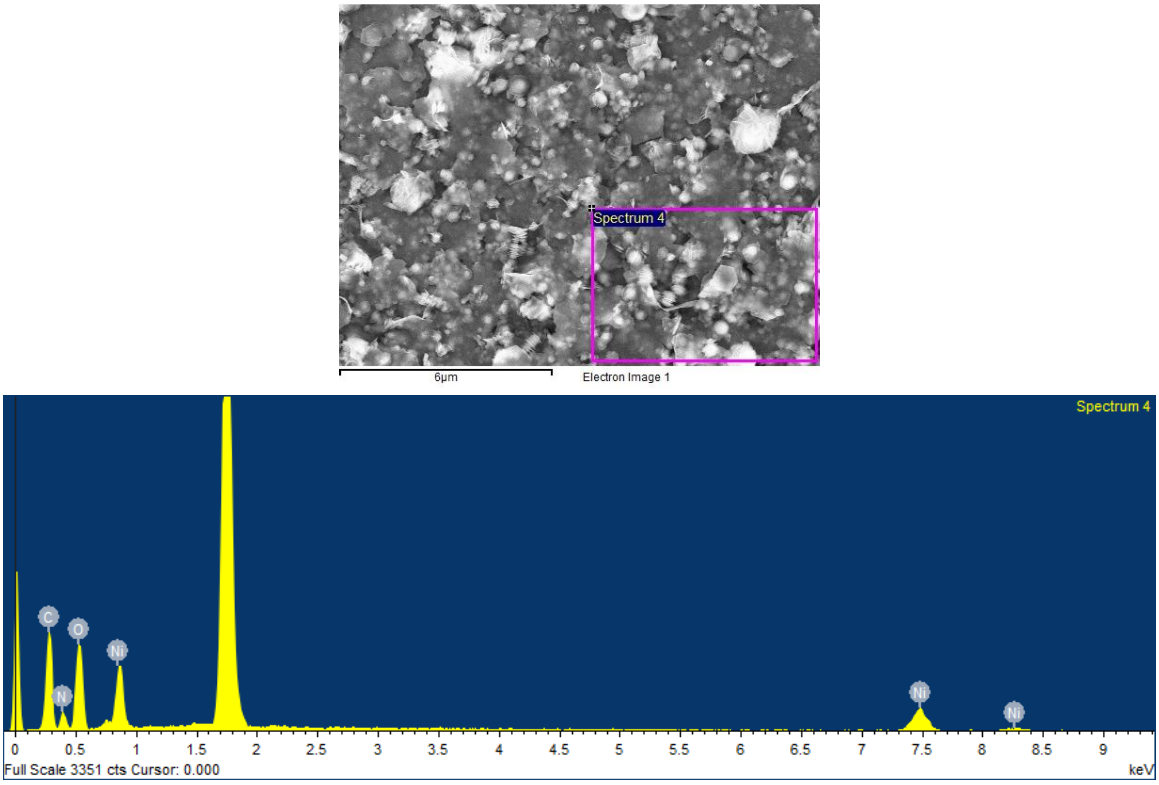


Figure S3.A5: Multiple particles wide area EDX spectrum of compound **1**.

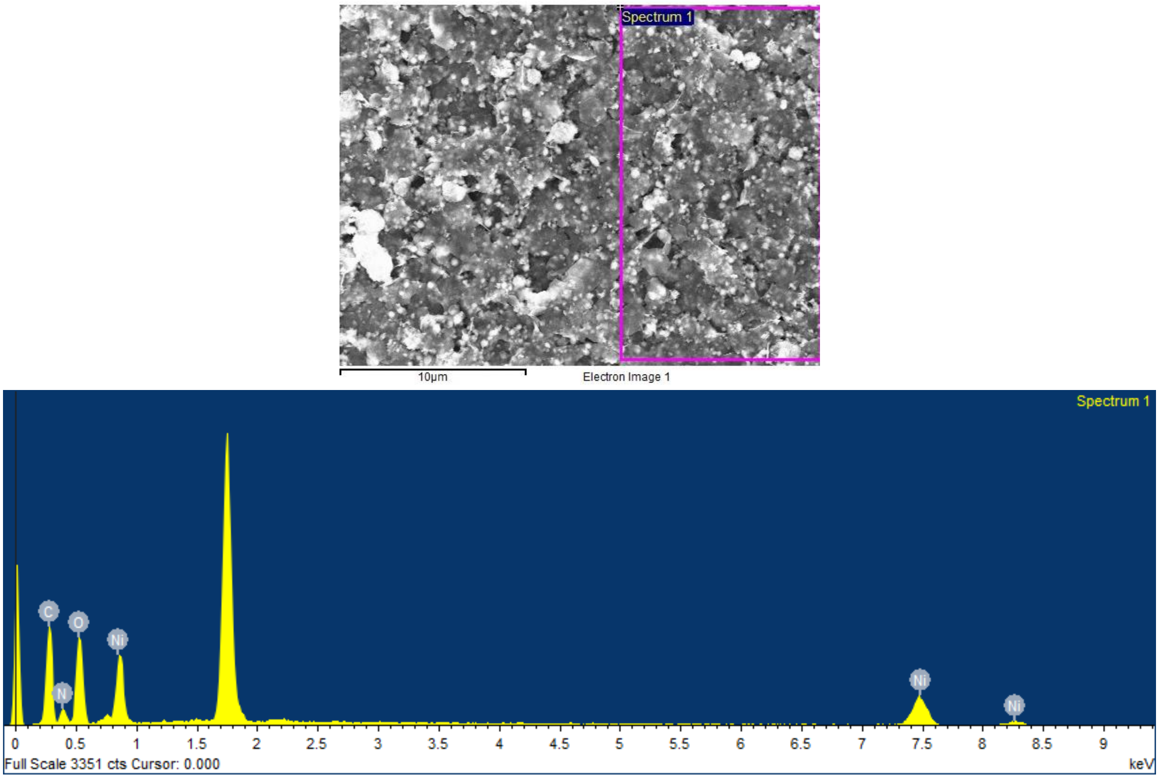


Figure S3.A6: Multiple particles wide area EDX spectrum of compound **1**.

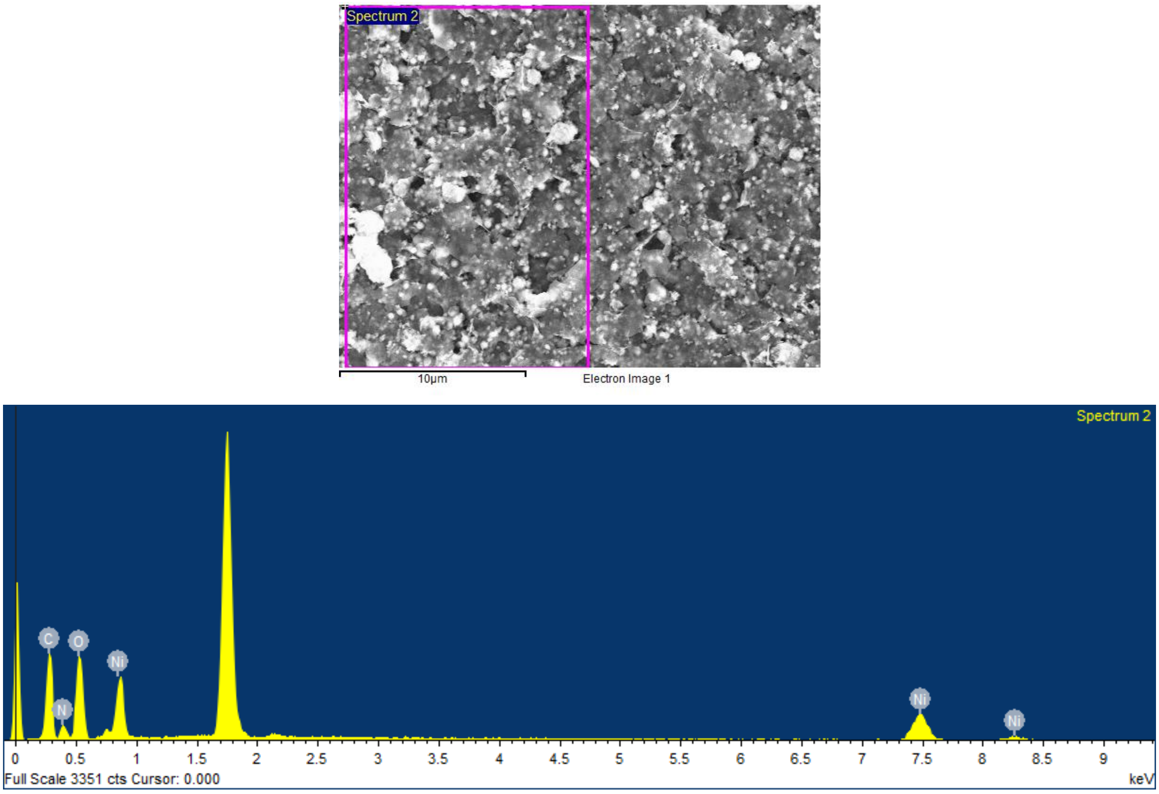


Figure S3.A7: Multiple particles wide area EDX spectrum of compound **1**.

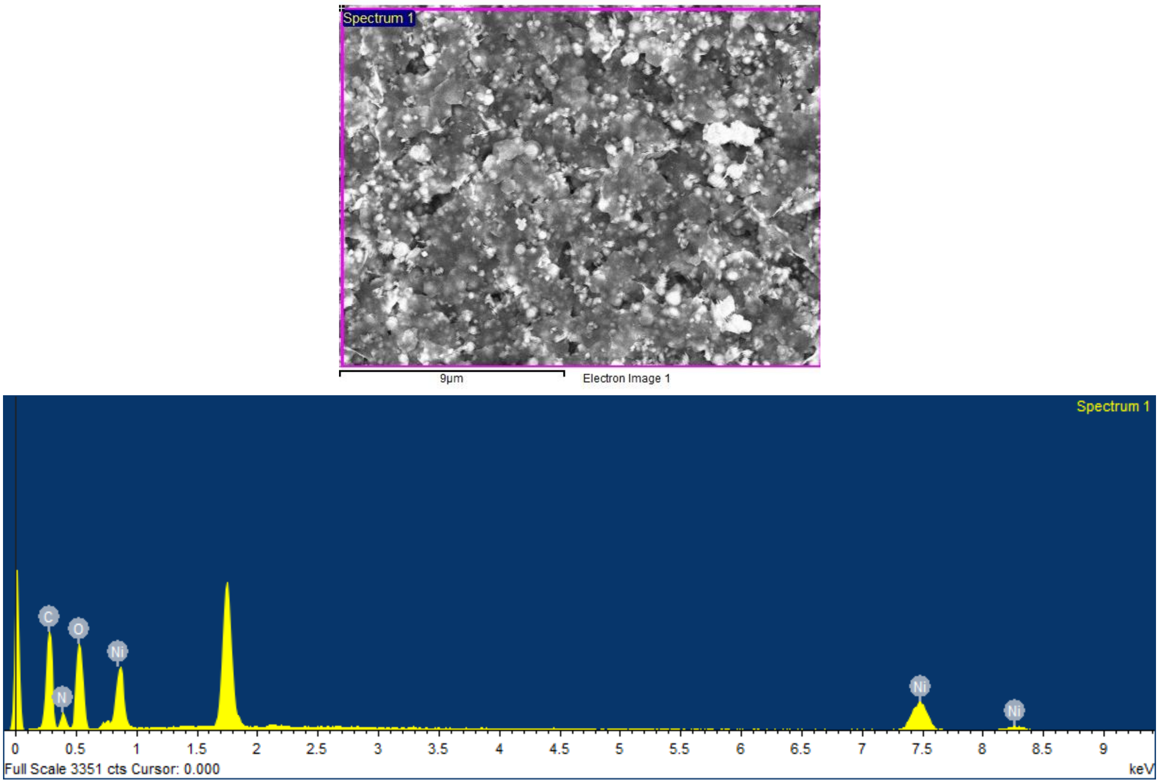


Figure S3.A8: Multiple particles wide area EDX spectrum of compound **1**.

Batch-B:

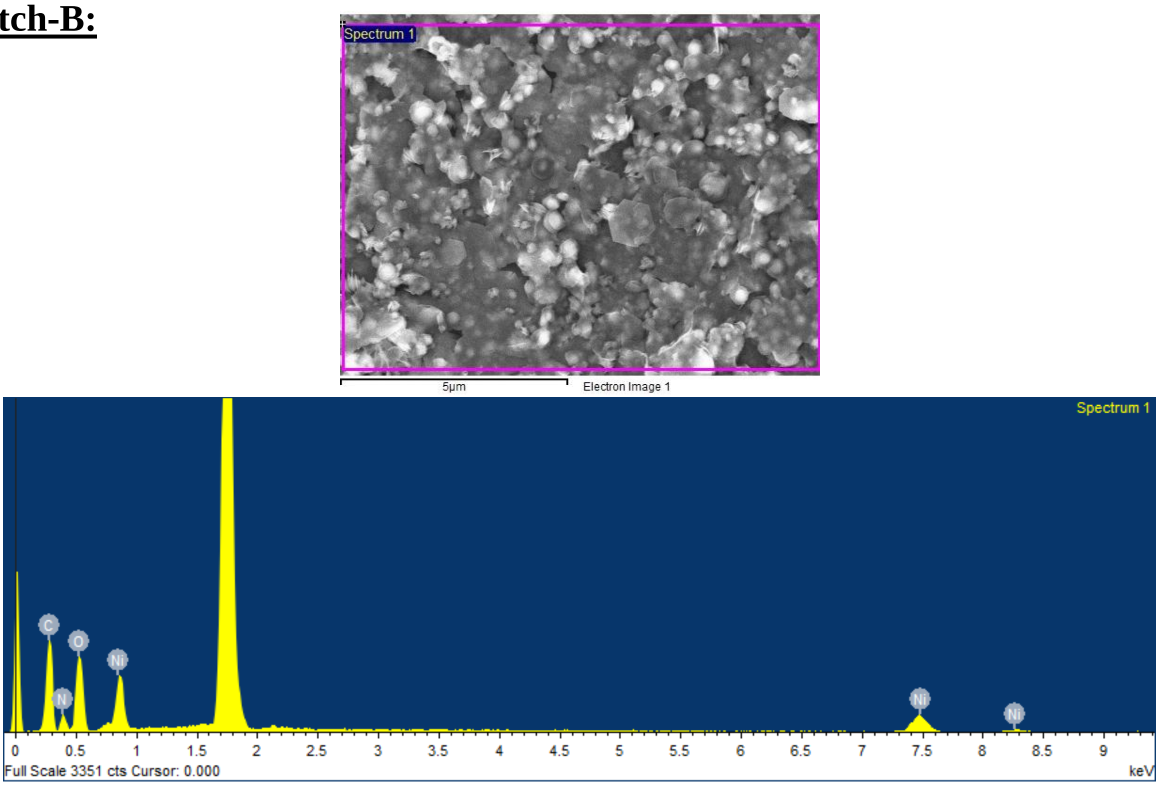


Figure S3.B1: Multiple particles wide area EDX spectrum of compound **1**.

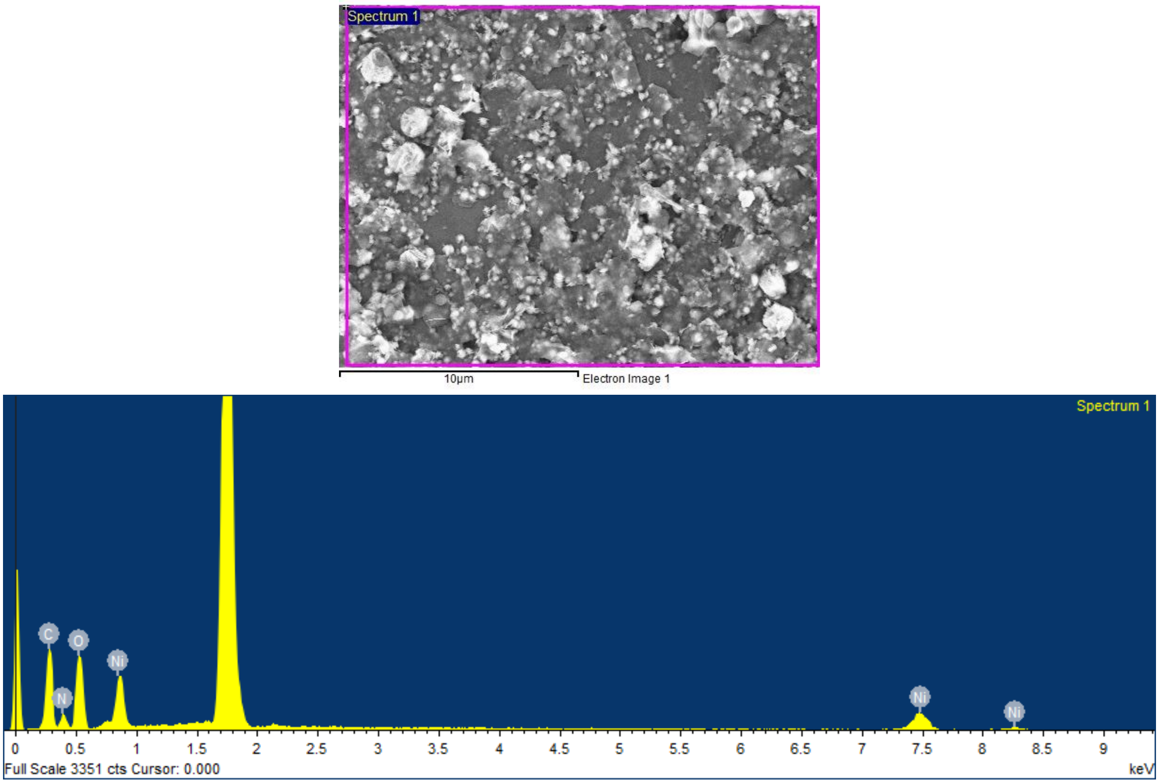


Figure S3.B2: Multiple particles wide area EDX spectrum of compound **1**.

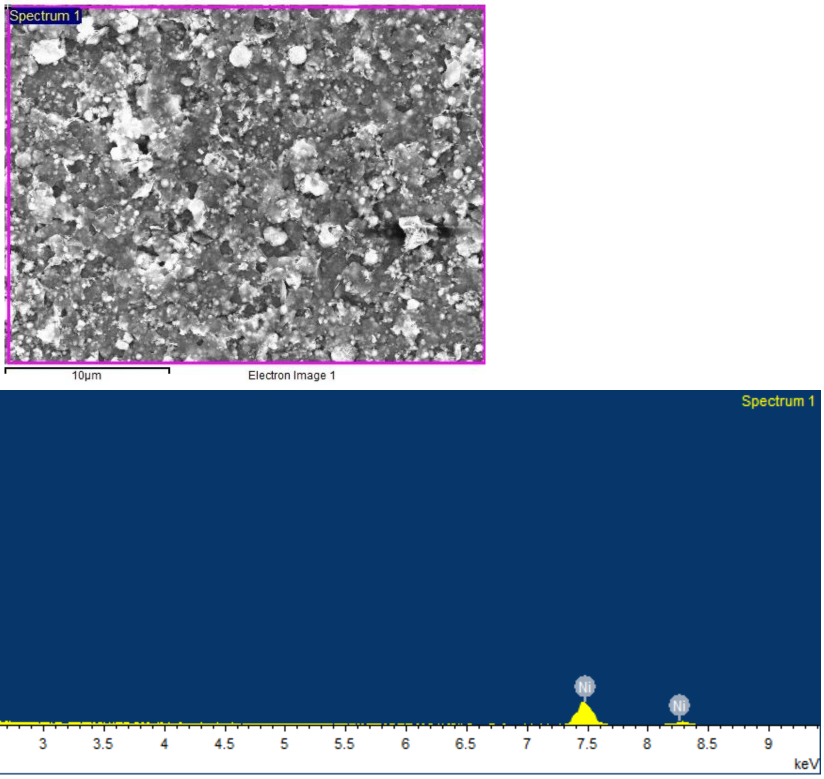


Figure S3.B3: Multiple particles wide area EDX spectrum of compound **1**.

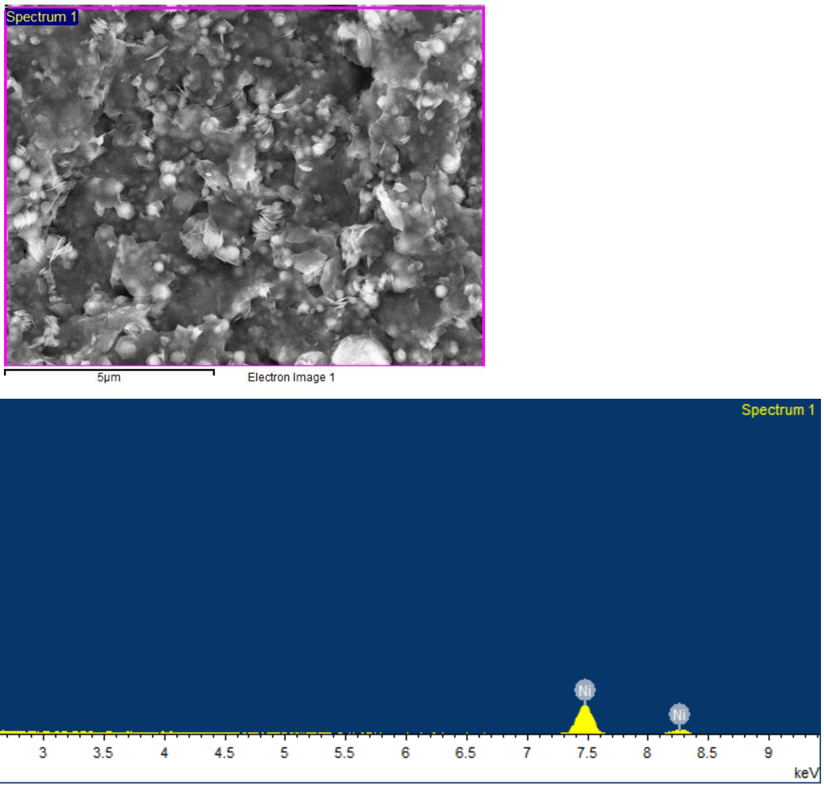


Figure S3.B4: Multiple particles wide area EDX spectrum of compound **1**.

Batch-C:

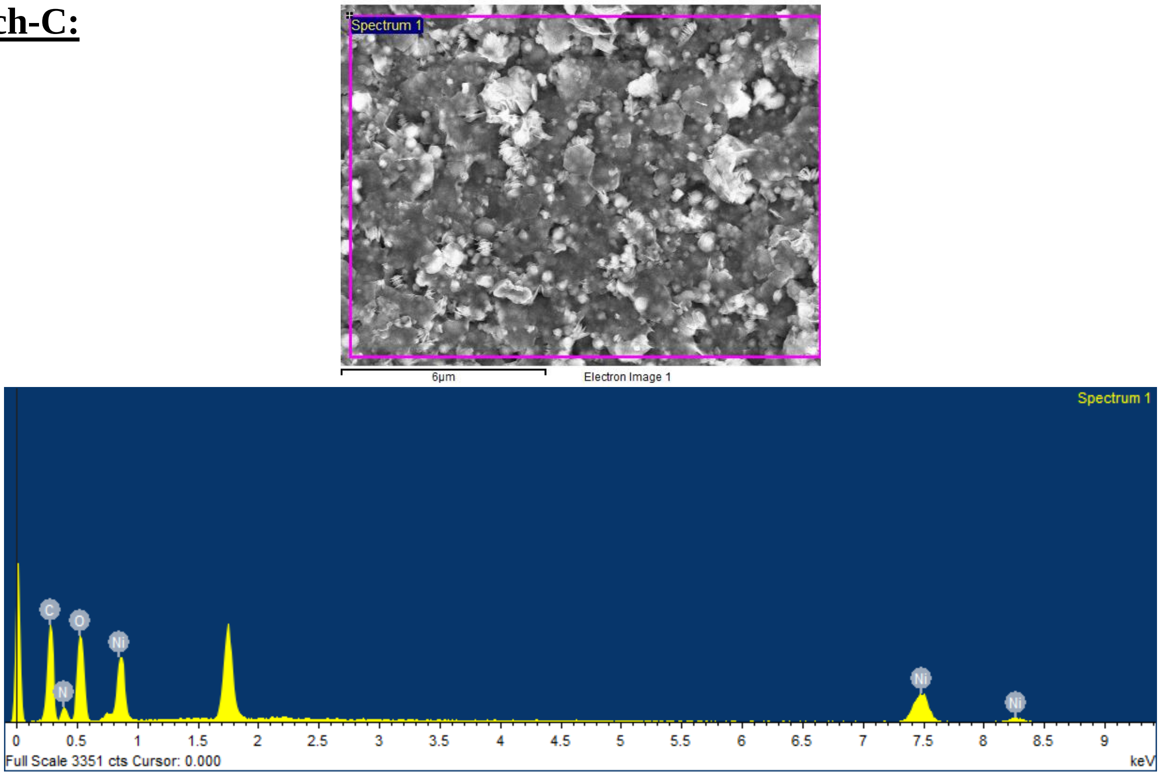


Figure S3.C1: Multiple particles wide area EDX spectrum of compound **1**.

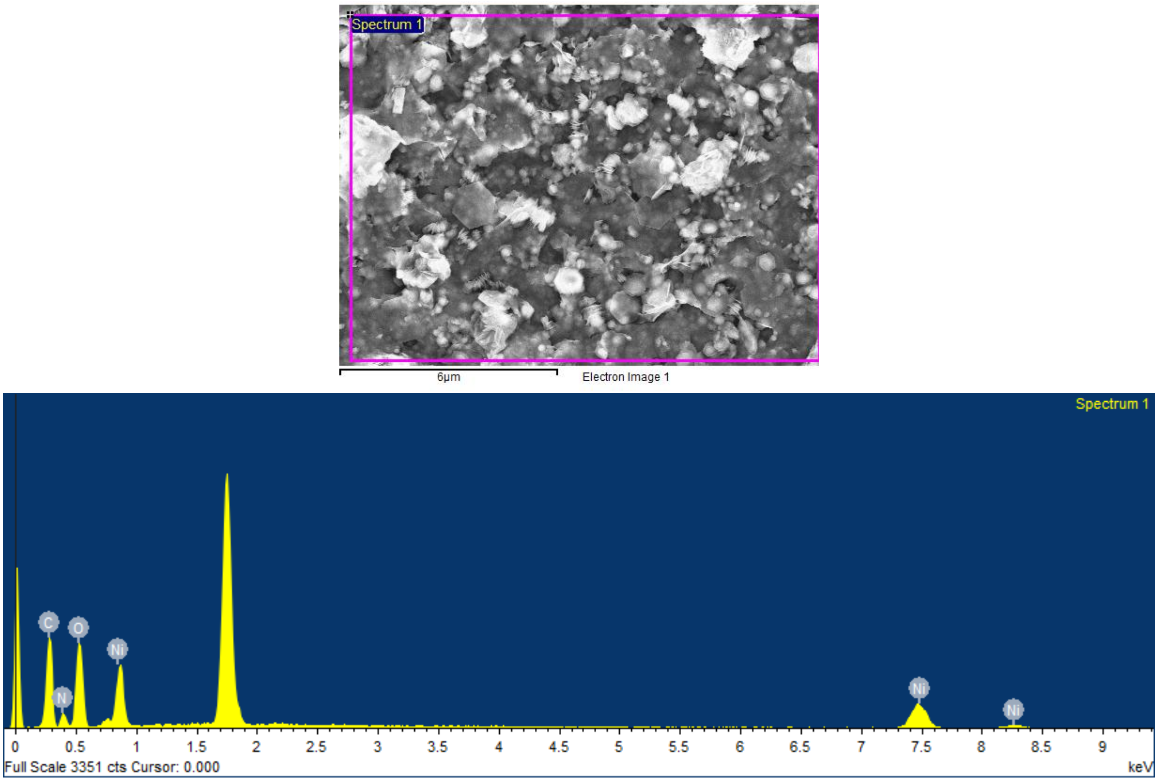


Figure S3.C2: Multiple particles wide area EDX spectrum of compound **1**.

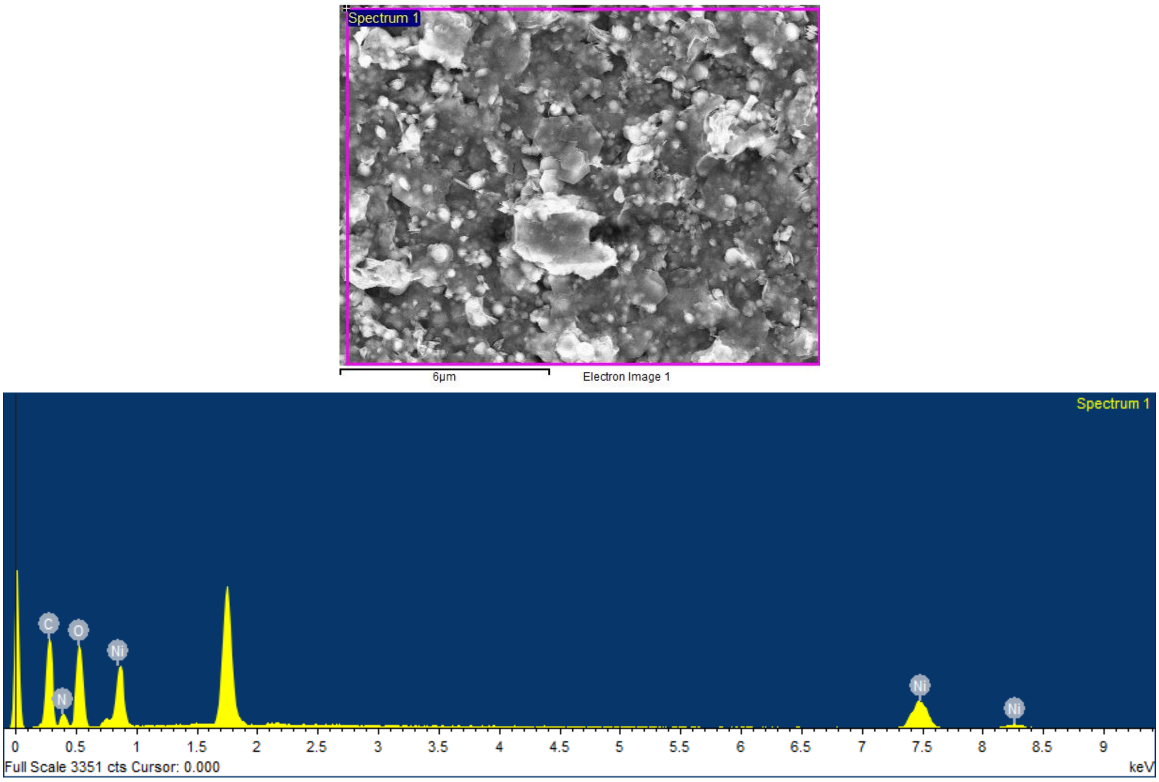


Figure S3.C3: Multiple particles wide area EDX spectrum of compound **1**.

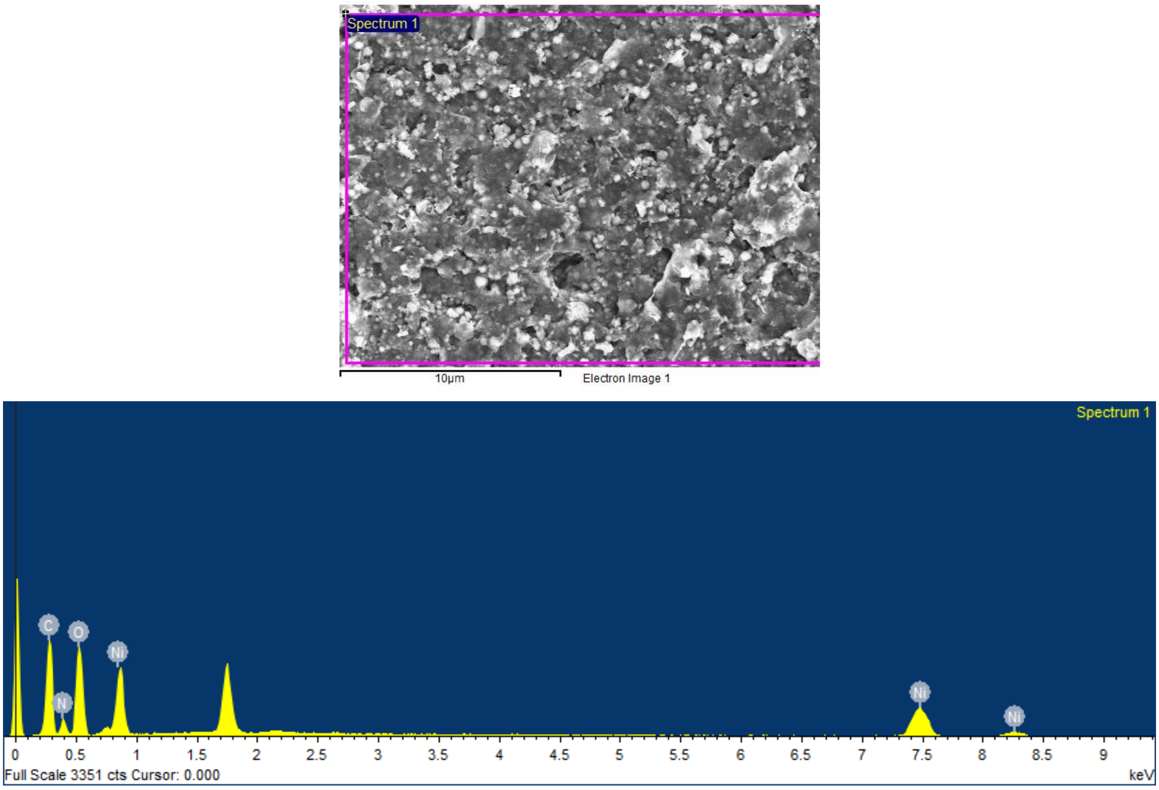


Figure S3.C4: Multiple particles wide area EDX spectrum of compound **1**.

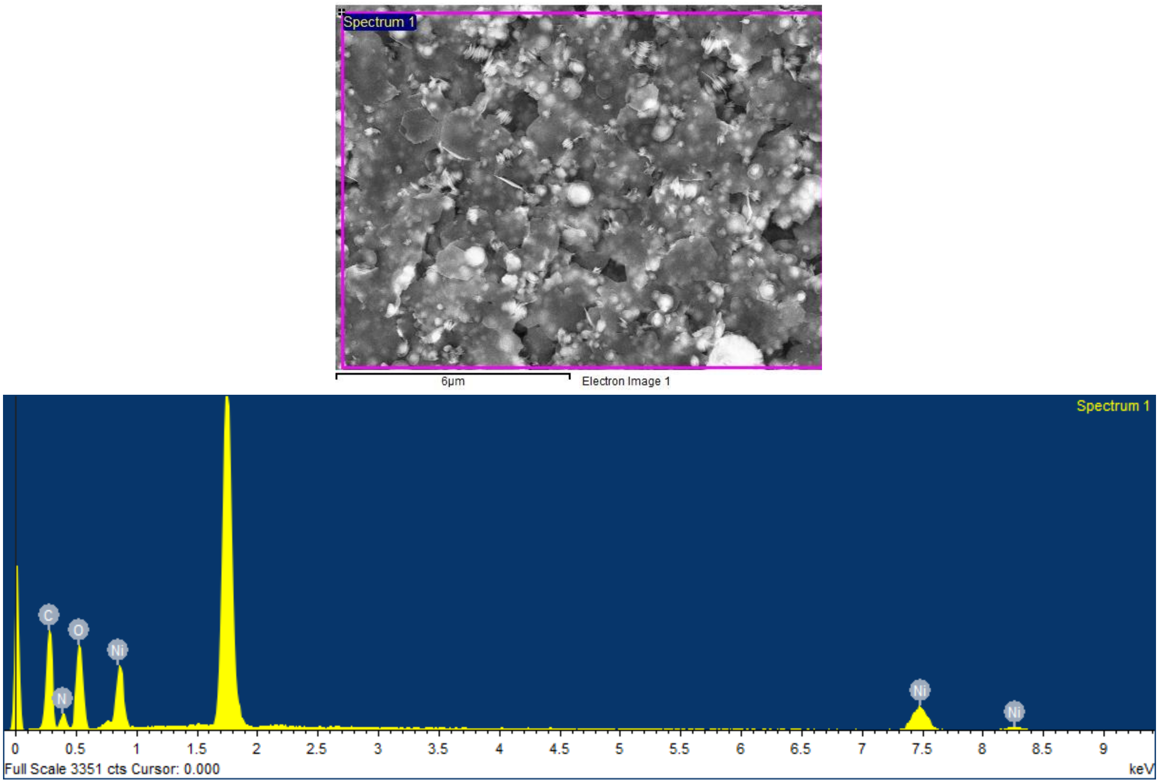


Figure S3.C5: Multiple particles wide area EDX spectrum of compound **1**.

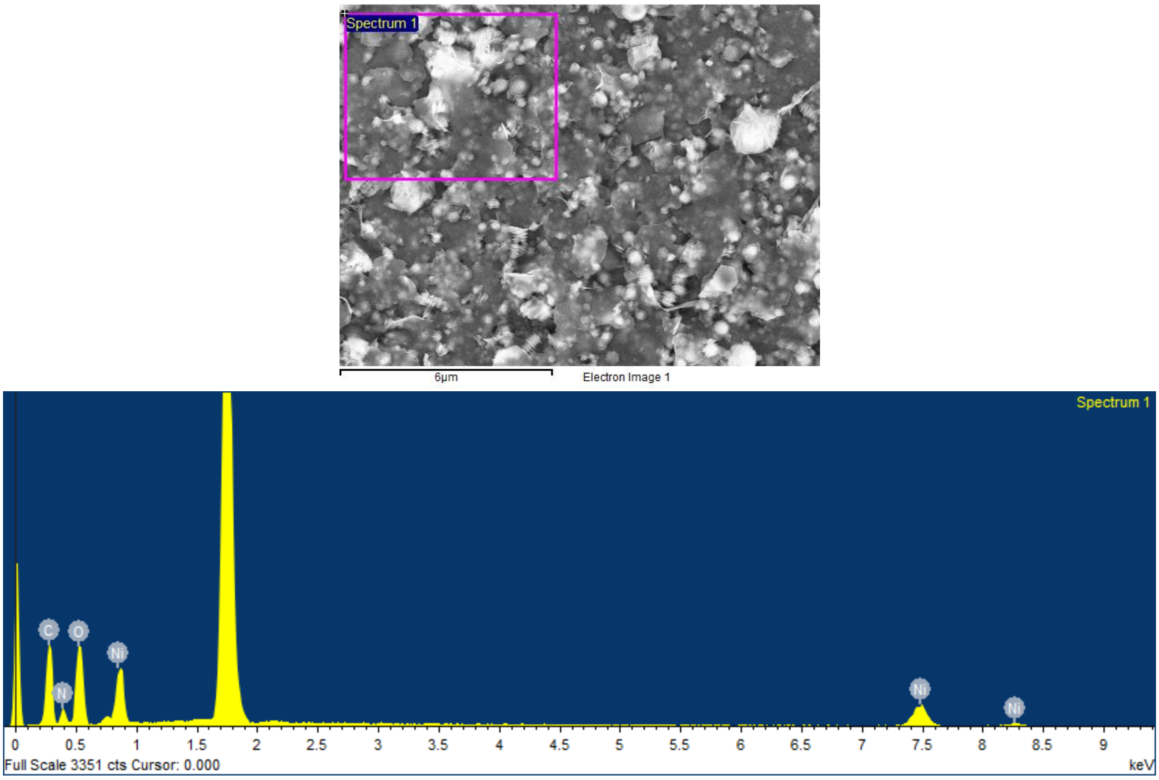


Figure S3.C6: Multiple particles wide area EDX spectrum of compound **1**.

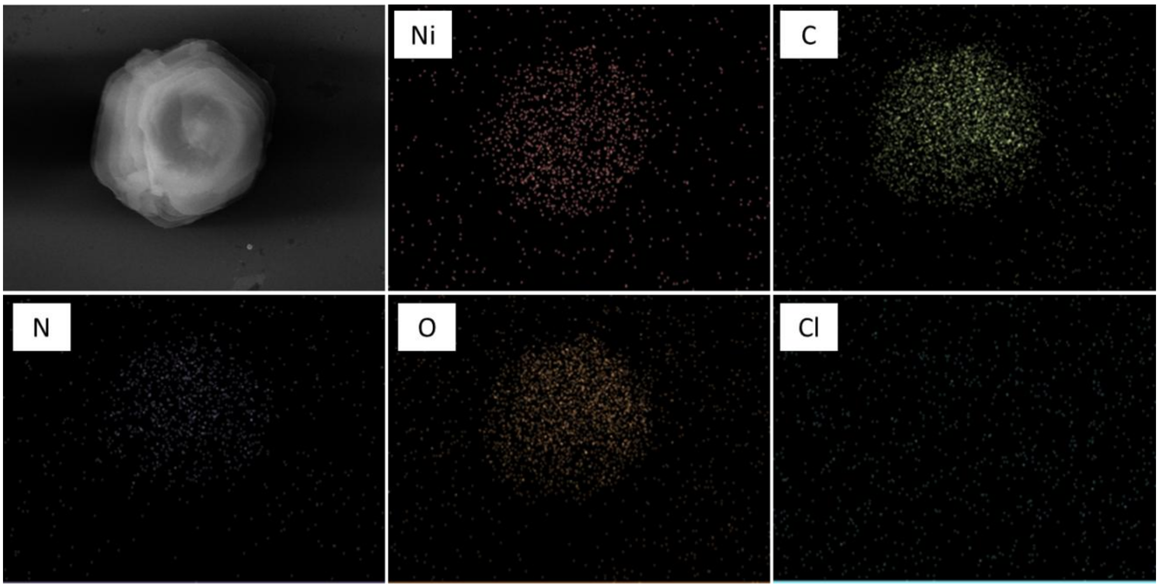


Figure S4: EDX elemental mapping images of hexagonal particle of compound **1** confirming homogenous distribution of Ni, C, N, O in compound **1**. The mapping profiles confirm the absence of Cl$^-$ anions in compound **1**.

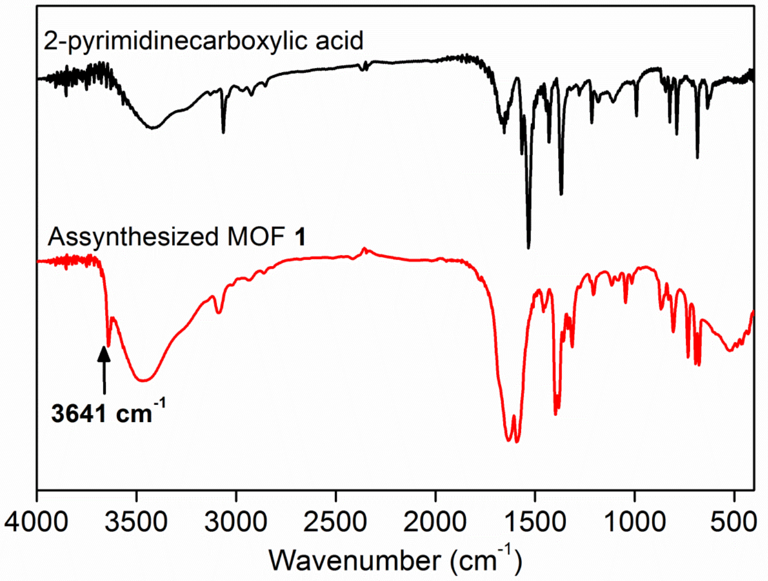


Figure S5: FT-IR spectra ofstarting material 2-pyrimidinecarboxylic acid, as-synthesized MOF**1**.

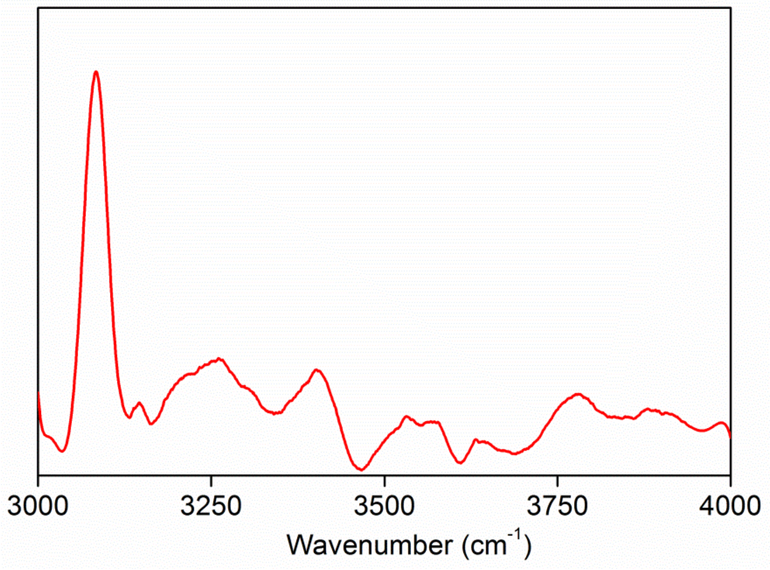


Figure S6: Raman spectra of assynthesized MOF **1**.

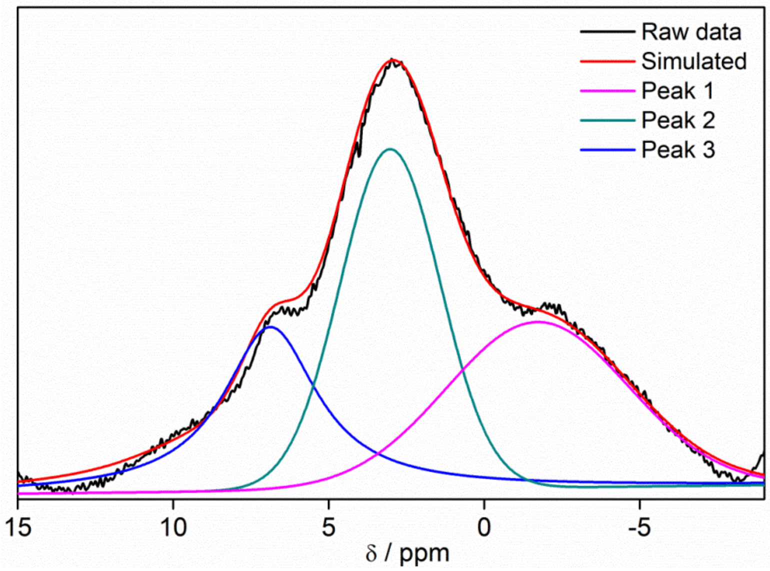


Figure S7: Solid-state ^{1}H-NMR (ss-^{1}HNMR) of compound **1** at room temperature with curve fitting.

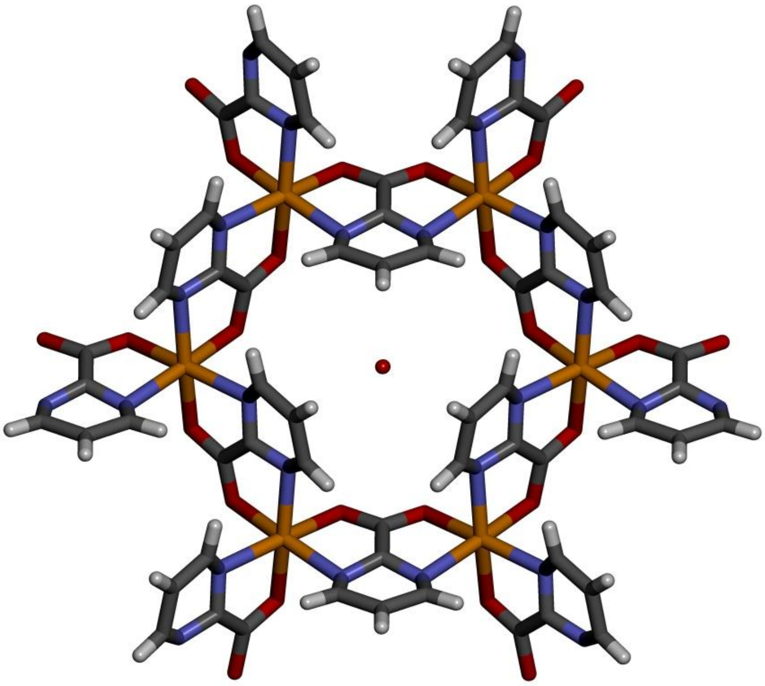


Figure S8: Alternate arrangement of aromatic rings and carboxylate groups lining 1D hexagonal channel in compound **1** along *c* axis.

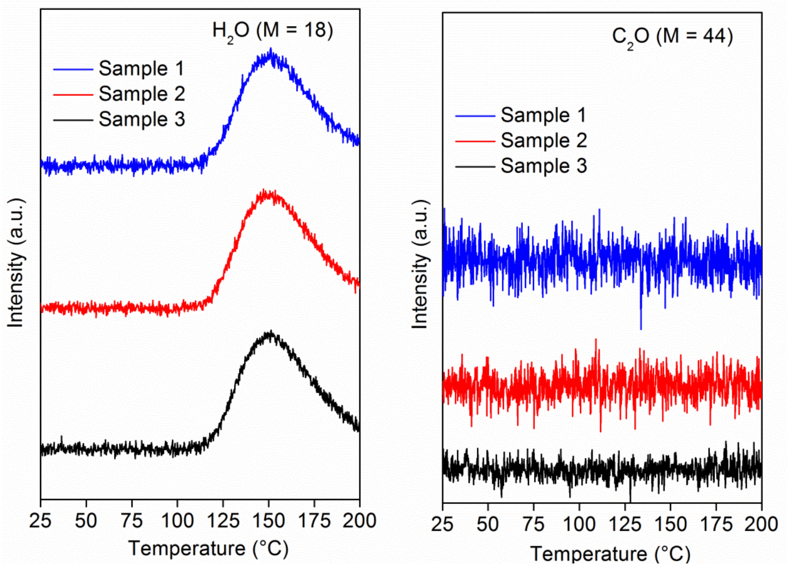


Figure S9: Temperature programmed desorption mass spectrometry analysis of air exposed MOF **1**. The profiles validate the absence of bicarbonate anions.

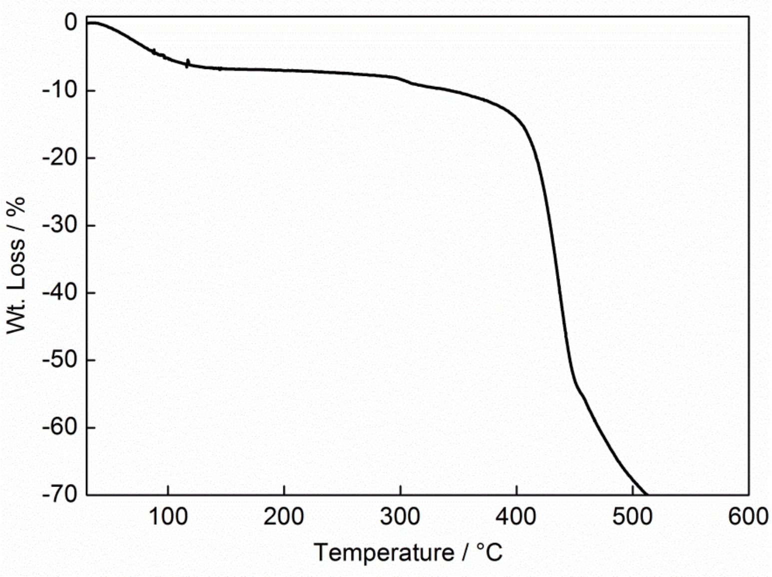


Figure S10: Thermogravimetric (TGA) analysis of compound **1**.

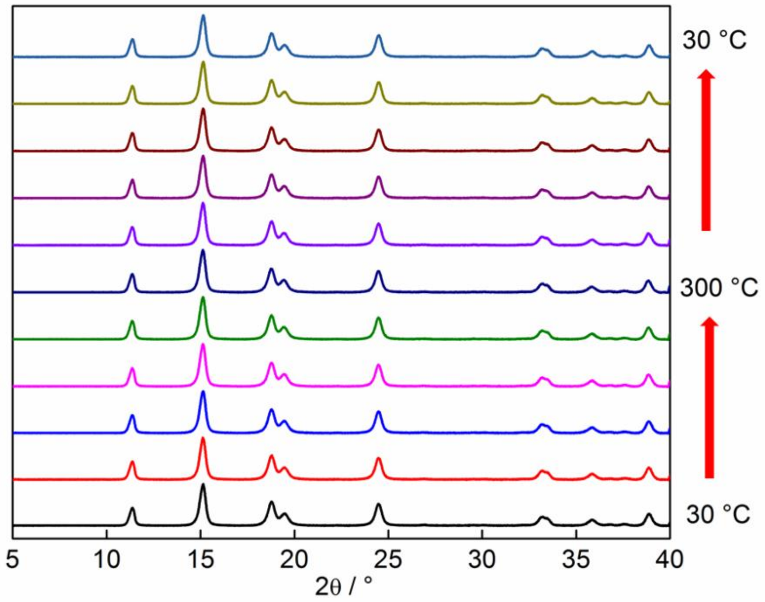


Figure S11: Variable temperature PXRD patterns of compound **1**during heating and cooling cycles.

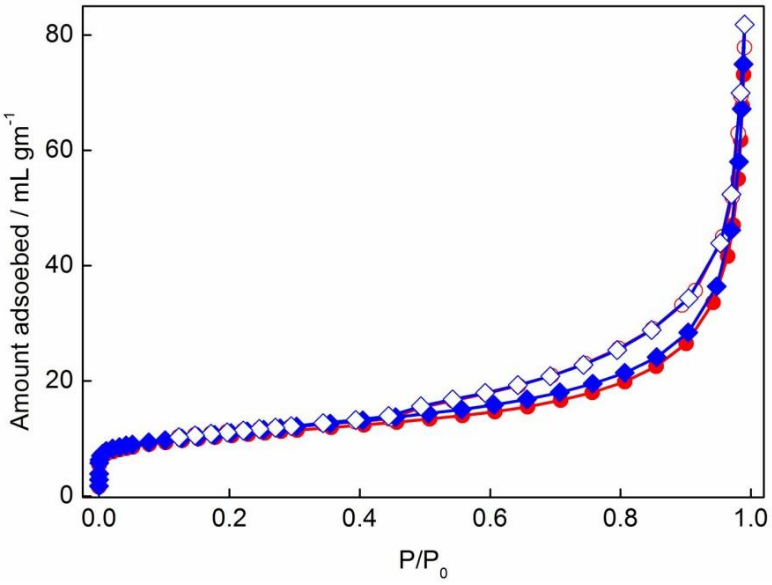


Figure S12: N_2adsorption isotherms at 77 K for assynthesized and 1N NaOH treated compound **1**.

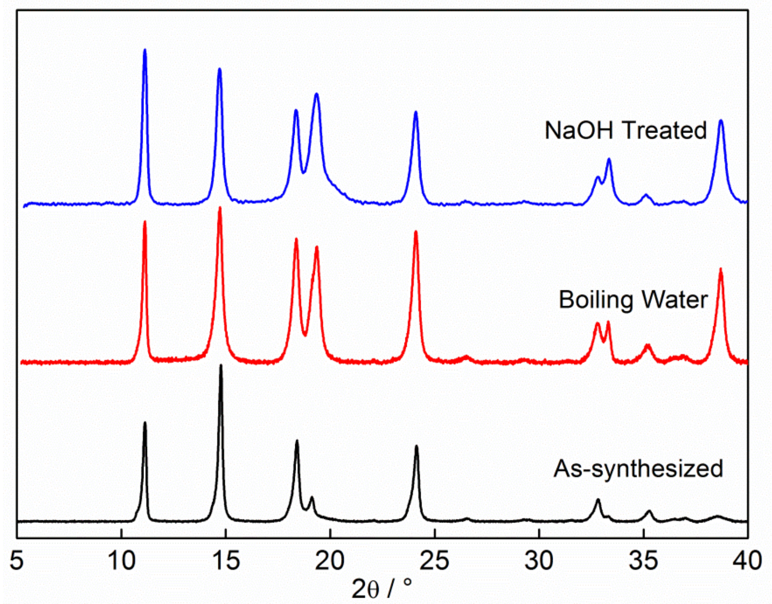


Figure S13: PXRD patterns of as-synthesized MOF **1**, boiling water treated MOF, NaOH treated MOF.

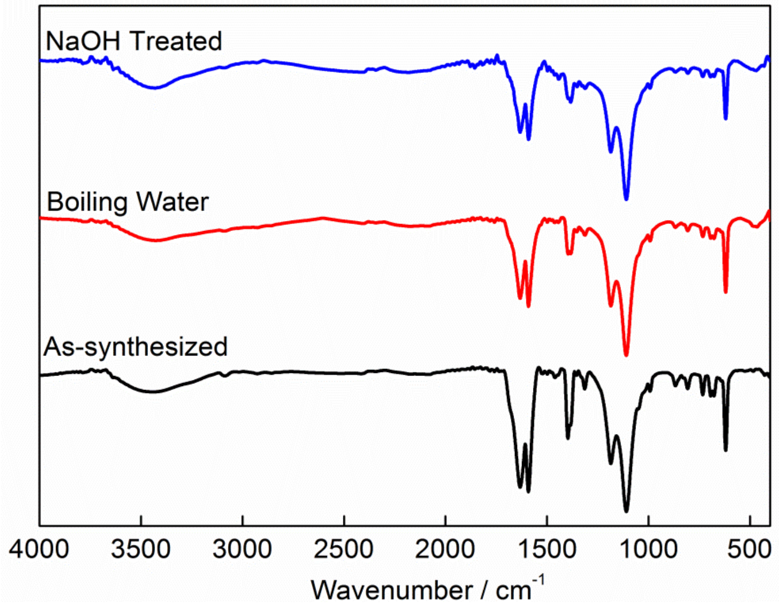


Figure S14: FT-IR spectra of as-synthesized MOF **1**, boiling water treated MOF, NaOH treated MOF.

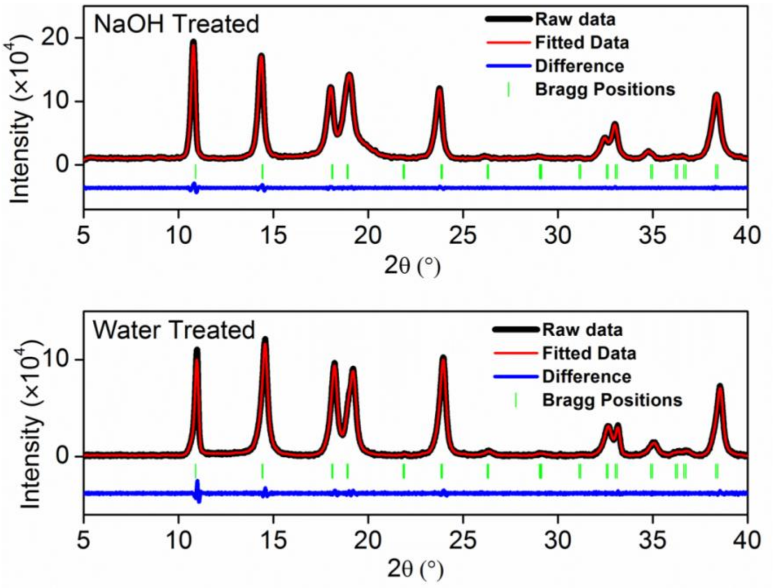


Figure S15: Rietveld-refined PXRD patterns of boiling water and NaOH treated compound **1**.

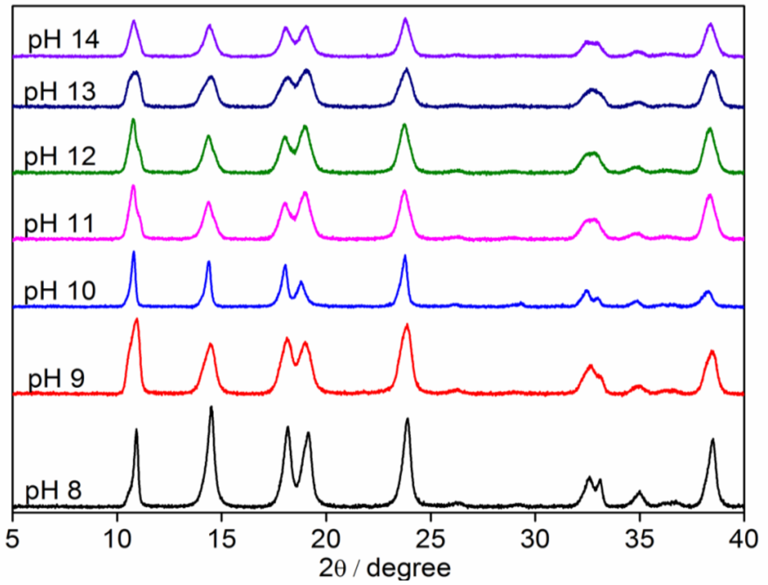


Figure S16: Overlapping PXRD patterns of compound **1** treated with solutions of different pH.

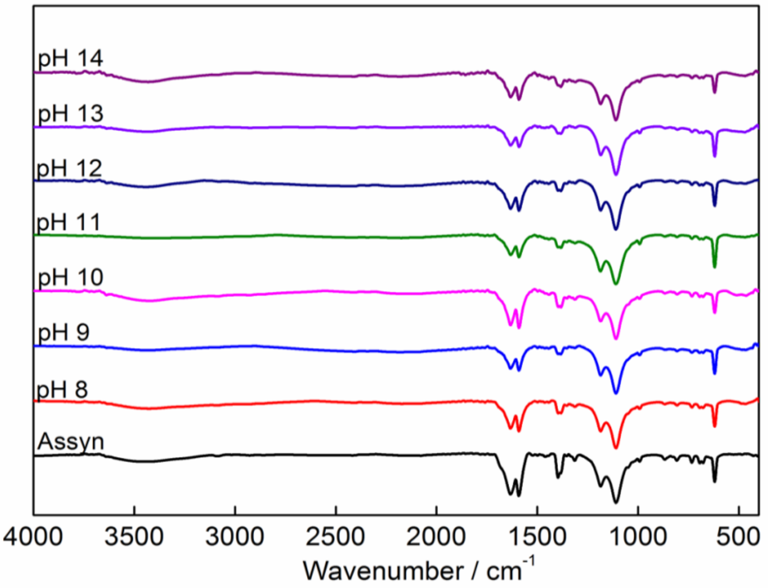
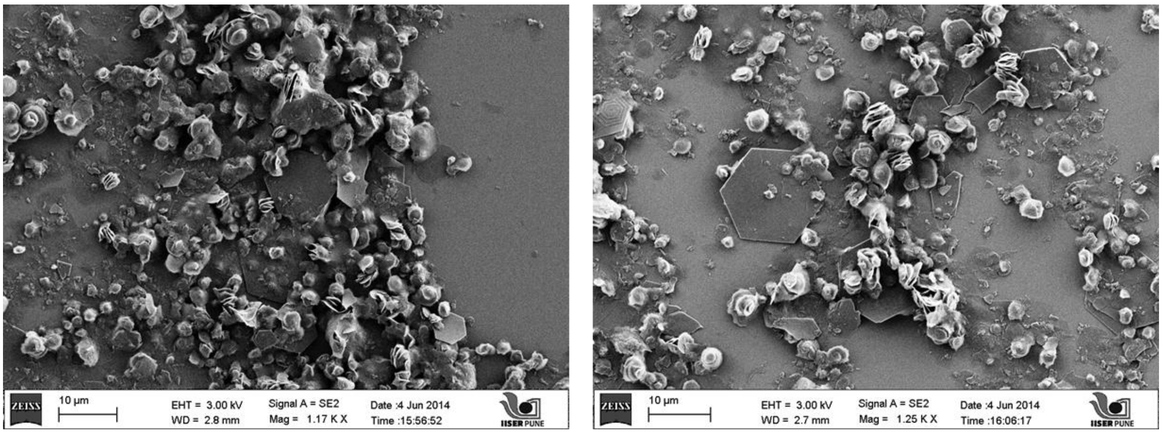


Figure S17: Overlapping FT-IR patterns of compound **1** treated with solutions of different pH.



Before Treatment

After treatment

Figure S18: Comparison between SEM images of assynthesized and NaOH treated samples of compound **1**.

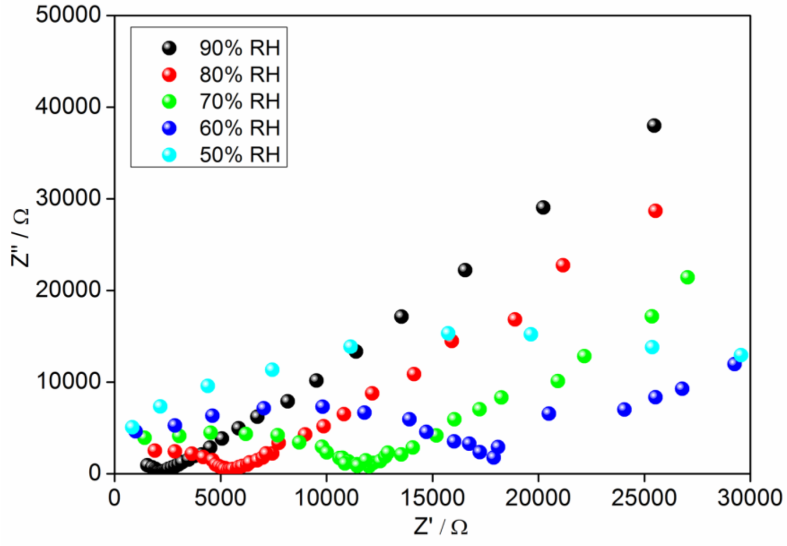


Figure S19: Humidity dependence of Nyquist plots of compound **1**.

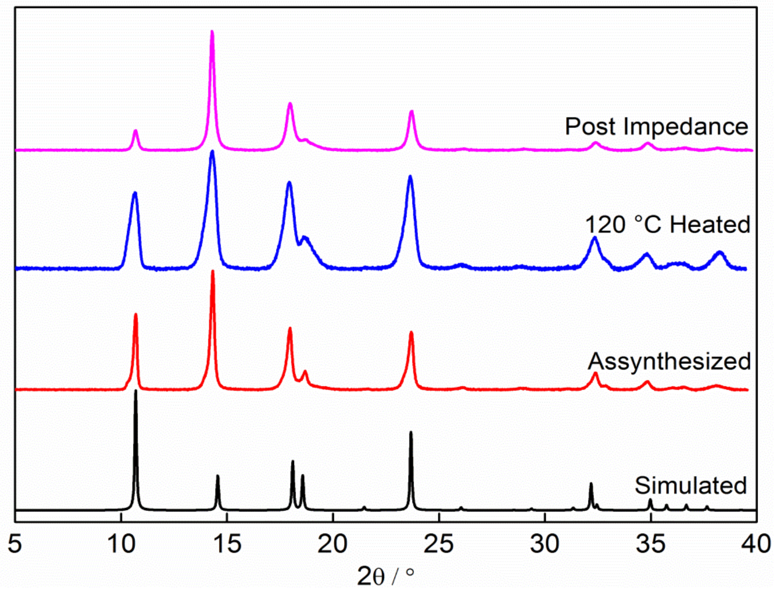


Figure S20: Overlapping PXRD spectra of assynthesized compound **1**, compound **1** heated at 120 °C and after impedance analysis.

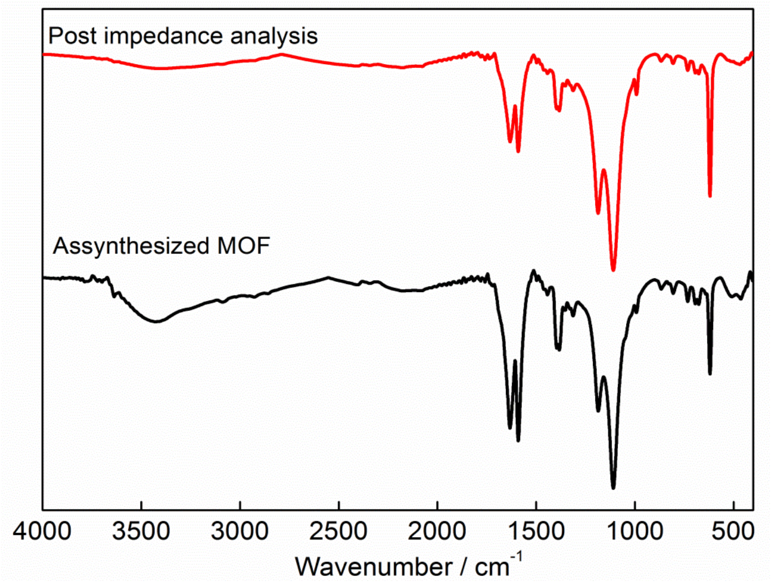


Figure S21: FT-IR spectra of assynthesized MOF**1**, and after impedance analysis.

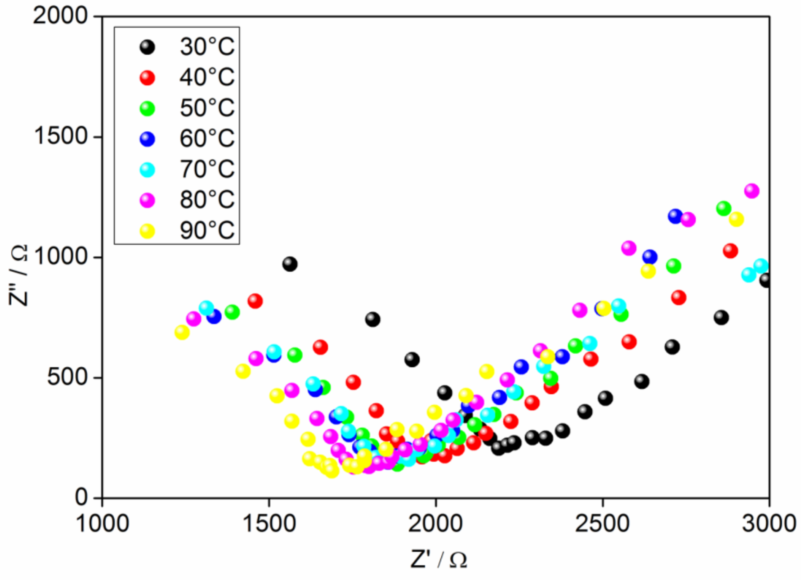


Figure S22: Temperature dependence of Nyquist plots of compound **1**.

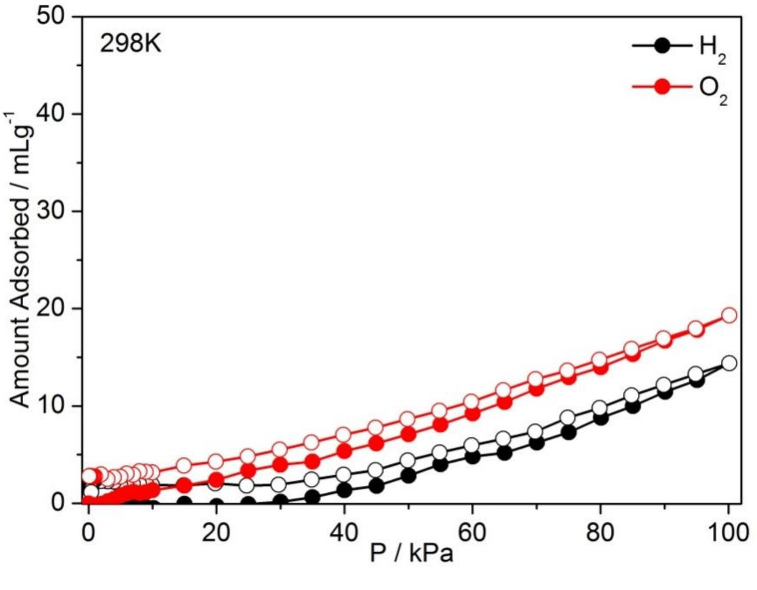


Figure S23: H_2 and O_2 adsorption isotherms at 298 K for compound **1**.

X-ray crystal structure analysis for compound 1.

The software Fullprof Suite (March 2014) was used for Rietveld refinement.[5] The space group *P*31*m* in its trigonal representation was used as the basis. The background was refined using a six coefficients polynomial function using a combination of Thompson-Cox-Hastings pseudo-Voigt and axial divergence asymmetry peak shape functions. The instrumental broadening, displacement and zero error were refined using LaB_6 standard. During the refinement lattice parameters, peak shape, background, preferred orientation and displacement were simultaneously refined.[6] The atomic positions were successively added to the refinement after the convergence. The atomic positions were refined starting with heavier atoms. Further, the anisotropic temperature factors U for the atoms were refined.

Lattice type	P
Space group name	P 3 1 m
Space group number	157

Lattice parameters
a = 9.33000 Å
c = 6.05500 Å
α = 90.0000 (°)
β = 120.0000 (°)
V = 456.465593 Å^3
R_{wp}= 3.2
R_p = 3.9
χ^2 = 1.3

Table S1. Structure parameters of compound **1**.

Number	Atom	Name	Site	X	Y	Z	g	B (Å^2)	U (Å^2)
1	Ni	Ni1	2b	0.66667	0.33333	0.445	1	2.779	0.035
2	N	N	6d	0.8651	0.316	0.5847	2	2.924	0.037
3	O	O1	6d	0.8592	0.5049	0.185	1	3.533	0.045
4	C	C1	3c	1	0.445	0.5243	1.218	3.322	0.042
5	C	C2	6d	0.8518	0.2636	0.7912	1.218	5.809	0.074
6	H	H2	6d	0.7494	0.1864	0.8492	1.218	7.185	0.091
7	C	C3	3c	1	0.2948	0.8976	1.218	7.46	0.094
8	H	H3	3c	1	0.2416	1.0297	1.218	9.317	0.118
9	C	C4	3c	1	0.535	0.3072	1.218	1.904	0.024
10	O	O2	1a	1	0	0.97813	2	2.809	0.352
11	O	O3	1a	1	0	0.5877	2	2.155	0.357

Table S2. Bond distance table of compound **1**.

Number	Atom1	Atom2	Cyclicity	Length	Number	Atom1	Atom2	Cyclicity	Length
1	Ni	N	cyclic	2.12	27	N	C1	cyclic	1.29
2	Ni	O1	cyclic	2.33	28	N	C2	cyclic	1.33
3	Ni	N	cyclic	2.11	29	O1	C4	cyclic	1.41
4	Ni	O1	cyclic	2.32	30	C1	C4	cyclic	1.56
5	Ni	N	cyclic	2.11	31	C1	N	cyclic	1.29
6	Ni	O1	cyclic	2.32	32	C2	H2	acyclic	0.931
7	N	C1	cyclic	1.29	33	C2	C3	cyclic	1.417
8	N	C2	cyclic	1.33	34	C3	H3	acyclic	0.941
9	O1	C4	cyclic	1.41	35	C3	C2	cyclic	1.417
10	C1	C4	cyclic	1.56	36	C4	O1	cyclic	1.41
11	C1	N	cyclic	1.29	37	N	C2	cyclic	1.33
12	C2	H2	acyclic	0.931	38	C2	H2	acyclic	0.931
13	C2	C3	cyclic	1.417	39	N	C1	cyclic	1.29
14	C3	H3	acyclic	0.941	40	N	C2	cyclic	1.326
15	C3	C2	cyclic	1.417	41	O1	C4	cyclic	1.41
16	C4	O1	cyclic	1.41	42	C1	C4	cyclic	1.56
17	N	C2	cyclic	1.33	43	C1	N	cyclic	1.29
18	N	Ni	cyclic	2.11	44	C2	H2	acyclic	0.931
19	O1	Ni	cyclic	2.32	45	C2	C3	cyclic	1.417
20	C2	H2	acyclic	0.931	46	C3	H3	acyclic	0.941
21	Ni	N	cyclic	2.11	47	C3	C2	cyclic	1.417
22	Ni	O1	cyclic	2.32	48	C4	O1	cyclic	1.41
23	Ni	N	acyclic	2.11	49	N	C2	cyclic	1.326
24	Ni	N	acyclic	2.11	50	N	Ni	cyclic	2.11
25	Ni	O1	acyclic	2.32	51	O1	Ni	cyclic	2.32
26	Ni	O1	acyclic	2.32					

Table S3: ICP-AES analysis data of the supernatant of the solution in which compound **1** was dipped for 8h and 24h.

Description	Time	Ni content in ppm	% retention	% degradation
Compound **1** dipped in 1N NaOH	8 hours	0.262	99.70	0.30
Compound **1** dipped in 1N NaOH	24 hours	0.27	99.69	0.31

References:

1. J. Suarez-Varela, A. J. Mota, H. Aouryaghal, J. Cano, A. Ro-driguez-Dieguez, D. Luneau and E. Colacio, *Inorg. Chem.*, 2008, **47**, 8143.
2. T. Roisnel and J. Rodríguez-Carvajal, *Mater. Sci. Forum,* 2001, **378-381**, 118.
3. M. M. Shirolkar, C. Hao, X. Dong, T. Guo, L. Zhang, M. Li, H. Wang, *Nanoscale,* 2014, **6**, 4735.
4. K. Momma and F. Izumi, *J. Appl. Crystallography,* 2011, **44**, 1272.
5. Rodriguez, C. J. A Rietveld and pattern matching analysis program; Laboratoire Leon Brillouin, CEA-CNRS, France (FULLPROF (March 2014)).
6. Rodríguez Carvajal, J. Study of MicroStructural effects by powder diffraction using the Program FULLPROF, 2003.