

Electronic Supplementary Information (ESI) for:

Ni(salphen)-based metal-organic framework for the synthesis of cyclic carbonates by cycloaddition of CO₂ to epoxides

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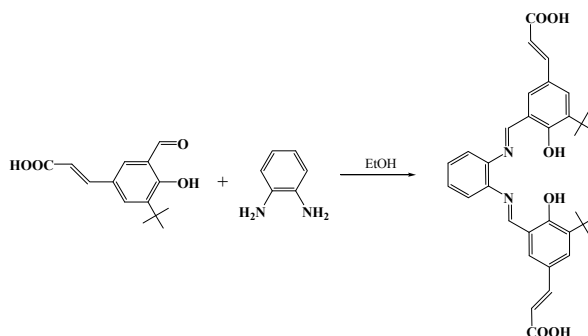
1. Materials and general procedures

All solvents were purchased from Alfa or TCI and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40 kV, 40 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 17.7 s/step and a step size of 0.02° (2θ). Thermogravimetric analyses (TGA) were performed on a Q600 SDT instrument under a flow of N₂ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ between ambient temperature and 800°C . Nitrogen and carbon dioxide adsorption experiments were performed with Quantachrome AS-1 MP. Liquid nitrogen was used as coolants to achieve cryogenic temperatures (77 K). The experiments were conducted using ultrahigh-purity N₂ (99.999%), and CO₂ (99.998%). The N₂ sorption isotherms were collected using a pressure range from 10^{-6} atm to 1 atm at 77 K. The CO₂ sorption isotherm was performed at 273 K, using a pressure range of 0.1–1 atm. Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. ¹H NMR and ¹³C NMR were done on a Bruker Model AM-400 (400 MHz) spectrometer. Infrared (IR) spectra were measured from a KBr pellets on a Nicolet Model Nexus 470 FT-IR spectrometer in the range of $4000\text{--}400 \text{ cm}^{-1}$. Gas chromatography-mass spectroscopy (GC-MS) spectrometry was recorded on Shimadzu Model GCMSQP5050A system that was equipped with a $0.25 \text{ mm} \times 30 \text{ m}$ DB-WAX capillary column.

Single crystal X-ray diffraction data for MOF **1** were collected on a Rigaku Mercury CCD diffractometer operated at 90 kV and 50 mA using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The empirical absorption corrections were performed using the CrystalClear program.¹ The structure was solved by direct methods and refined on F^2 by full-matrix least squares technique using the SHELXTL-97 program package.² SQUEEZE subroutine of the PLATON software suite³ was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL file was used to further refine the structure. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The coordinated water H atoms were not added using a riding model since the four water oxygen atoms in this structure have anomalously large U_{eq} and U_{ii} values. Note that the contributions of these eight water H atoms have been included in the overall formula, formula weight, density, $F(000)$ calculations reported in Table S1 and in the CIF. Crystal data and details of the data collection are given in Table S1, while the selected bond distances and angles are presented in Table S2.

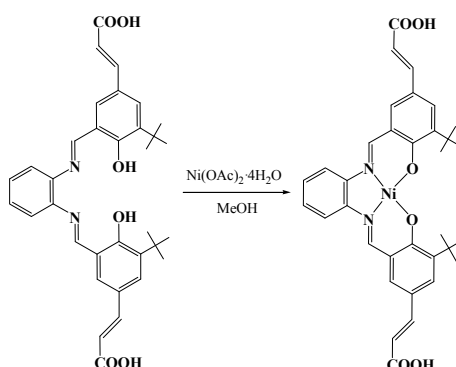
2. Synthesis of ligand Ni-H₂L and MOF 1

2.1 Synthesis of H₄L



(E)-3-(3-tert-butyl-5-formyl-4-hydroxyphenyl)acrylic acid (H₂tbfha) was synthesized according to the published procedure.⁴ A solution of H₂tbfha (0.981 g, 4 mmol) in EtOH (50 mL) was added dropwise to a solution of *o*-phenylenediamine (0.216 g, 2 mmol) in EtOH (50 mL) at 60°C and then the reaction mixture was stirred at 60°C for 2 h. The orange powder precipitate of H₄L was collected by filtration, washed with EtOH and THF, and dried under reduced pressure (0.95 g, 85%). ¹H NMR (DMSO-*d*₆): δ 1.33 (s, 18H), 6.28 (d, 2H), 7.39-7.51(m, 10H), 8.34(s, 2H); ¹³C NMR(DMSO): 29.63, 35.21, 116.55, 118.64, 123.20, 125.77, 128.55, 129.15, 131.97, 133.84, 141.62, 145.73, 164.99, 166.83, 171.20

2.2 Synthesis of Ni-H₂L



A solution of Ni(OAc)₂·4H₂O (0.25 g, 1 mmol) in DMF (20 mL) was added dropwise to a solution of H₄L (0.56 g, 1 mmol) in DMF (20 mL). The reaction mixture was stirred at room temperature for 3h. Addition of EtOH to above red solution resulted in precipitation of a red powder of Ni-H₂L, which was collected by filtration, washed with EtOH and dried under reduced pressure (0.47g, 76%). Anal (%). Calcd for C₃₄H₃₄N₂NiO₆: C, 65.30; H, 5.48; N, 4.48. Found: C, 64.75; H, 5.40; N, 4.52. IR (KBr Pellet, *v*/cm⁻¹): 3481, 2949, 2866, 26655, 2576, 1674, 1592, 1534, 1436, 1387, 1338, 1271, 1203, 1163, 1037, 978, 949, 854, 786, 728, 621, 568, 475.

2.3 Synthesis of MOF 1

A solution of CdCl₂ (1.9 mg, 0.01 mmol), Ni-H₂L (6.3 mg, 0.01 mmol), DMF (3 mL), and H₂O (1 mL) in a capped vial was heated at 80°C for four days. Red block-like crystals of **1** were filtered, washed with EtOH and Et₂O and dried at room temperature. The products can be best formulated as [Cd₂(L-Ni)₂(H₂O)₄]·3DMF on the basis of microanalysis, TGA and single-crystal diffraction. Anal (%). Calcd for C₇₇H₉₃Cd₂N₇Ni₂O₁₉: C, 52.46; H, 5.32; N, 5.56. Found: C, 53.06; H, 5.51; N,

5.24. IR (KBr Pellet, ν/cm^{-1}): 3439, 2945, 1665, 1609, 1532, 1383, 1334, 1245, 1205, 1163, 1098, 977, 862, 784, 751, 664, 625, 567.

2.4 General Procedure for Coupling Reaction of CO₂ with Epoxide

A 10-mL stainless steel reactor was charged with epoxide (10.0 mmol), catalyst and ammonium salt (amount indicated in the text), and then CO₂ (2 MPa). The mixture was heated with stirring at a constant temperature for a reaction time. The reactor was then cooled in an ice bath for 30 min, and excess CO₂ was released carefully. The catalyst was recovered by centrifugation and the filtrate was analyzed by a GC-MS spectrometer (using 1,3,5-trimethylbenzene as an internal standard).

Table S1. Crystal data and structure refinements for **1**

Compound	1
Empirical formula	C ₇₇ H ₉₃ Cd ₂ N ₇ Ni ₂ O ₁₉
Formula weight	1762.81
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
	$a = 16.348(3) \text{ \AA}$ $\alpha = 89.29(3)^\circ$
	$b = 16.635(3) \text{ \AA}$ $\beta = 87.12(3)^\circ$
	$c = 20.293(4) \text{ \AA}$ $\gamma = 68.48(3)^\circ$
Volume (Å ³)	5127.4(17)
<i>Z</i>	2
Density (calcd. g/cm ³)	1.142
Absorption coeff. (mm ⁻¹)	0.816
F(000)	1816
Crystal size (mm)	0.20 × 0.20 × 0.20
Crystal color & shape	brown block
θ range data collection	3.02 to 25.00
Limiting indices	-18 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 19, -24 ≤ <i>l</i> ≤ 24
Reflections collected	38898
unique	17511 [<i>R</i> _(int) = 0.0534]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	17511 / 115 / 830
Goodness-of-fit on <i>F</i> ²	0.947
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0810, <i>wR</i> ₂ = 0.2369
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1333, <i>wR</i> ₂ = 0.2650

Table S2. Selected bond lengths [Å] and angles [°] for **1^a**

Bond lengths			
Cd(1)-O(10)	2.281(7)	Cd(2)-O(12)#2	2.355(6)
Cd(1)-O(2W)	2.248(12)	Cd(2)-O(5)	2.364(6)
Cd(1)-O(10)	2.281(6)	Cd(2)-O(11)#3	2.582(11)
Cd(1)-O(3)	2.292(6)	Cd(2)-O(12)#2	2.355(7)
Cd(1)-O(4)	2.349(5)	Ni(1)-O(2)	1.837(4)
Cd(1)-O(1W)	2.403(16)	Ni(1)-N(1)	1.843(5)
Cd(1)-O(9)	2.546(7)	Ni(1)-N(2)	1.842(4)
Cd(2)-O(4W)	2.181(8)	Ni(1)-O(1)	1.853(4)
Cd(2)-O(11)#2	2.286(8)	Ni(2)-O(7)	1.831(4)
Cd(2)-O(6)	2.316(9)	Ni(2)-O(8)	1.839(5)
Cd(2)-O(3W)	2.360(13)	Ni(2)-N(4)	1.850(5)
Cd(1)-O(10)#1	2.234(10)	Ni(2)-N(3)	1.868(6)
Bond angles			
O(2W)-Cd(1)-O(10)#1	91.3(5)	O(11)#2-Cd(2)-O(3W)	123.9(5)
O(2W)-Cd(1)-O(10)	92.8(4)	O(6)-Cd(2)-O(3W)	96.7(4)
O(10)#1-Cd(1)-O(10)	69.6(4)	O(4W)-Cd(2)-O(12)#2	90.3(3)
O(2W)-Cd(1)-O(3)	93.2(4)	O(11)#2-Cd(2)-O(12)#2	51.7(3)
O(10)#1-Cd(1)-O(3)	147.7(2)	O(6)-Cd(2)-O(12)#2	129.7(3)
O(10)-Cd(1)-O(3)	142.0(3)	O(3W)-Cd(2)-O(12)#2	84.9(4)
O(2W)-Cd(1)-O(4)	95.2(3)	O(4W)-Cd(2)-O(5)	89.0(3)
O(10)#1-Cd(1)-O(4)	91.4(3)	O(11)#2-Cd(2)-O(5)	137.3(3)
O(10)-Cd(1)-O(4)	159.6(3)	O(6)-Cd(2)-O(5)	52.1(3)
O(3)-Cd(1)-O(4)	56.3(2)	O(3W)-Cd(2)-O(5)	82.8(4)
O(2W)-Cd(1)-O(10)#1	91.3(5)	O(12)#2-Cd(2)-O(5)	167.6(3)
O(2W)-Cd(1)-O(1W)	174.9(4)	O(4W)-Cd(2)-O(11)#3	81.9(4)
O(10)#1-Cd(1)-O(1W)	89.8(5)	O(11)#2-Cd(2)-O(11)#3	68.7(5)
O(10)-Cd(1)-O(1W)	83.0(4)	O(6)-Cd(2)-O(11)#3	89.6(3)
O(3)-Cd(1)-O(1W)	88.5(4)	O(3W)-Cd(2)-O(11)#3	165.8(6)
O(4)-Cd(1)-O(1W)	89.7(4)	O(12)#2-Cd(2)-O(11)#3	101.0(3)
O(2W)-Cd(1)-O(9)	85.2(3)	O(5)-Cd(2)-O(11)#3	91.2(3)
O(10)#1-Cd(1)-O(9)	120.9(3)	O(4W)-Cd(2)-C(66)#2	109.1(4)
O(10)-Cd(1)-O(9)	51.8(3)	O(11)#2-Cd(2)-C(66)#2	25.5(3)
O(3)-Cd(1)-O(9)	91.3(2)	O(6)-Cd(2)-C(66)#2	109.0(4)
O(4)-Cd(1)-O(9)	147.7(3)	O(3W)-Cd(2)-C(66)#2	104.4(5)
O(1W)-Cd(1)-O(9)	90.0(5)	O(12)#2-Cd(2)-C(66)#2	26.3(3)
O(2W)-Cd(1)-C(26)	96.4(3)	O(5)-Cd(2)-C(66)#2	160.9(4)
O(10)#1-Cd(1)-C(26)	119.0(3)	O(11)#3-Cd(2)-C(66)#2	85.5(3)
O(10)-Cd(1)-C(26)	167.2(4)	O(4W)-Cd(2)-C(33)	115.2(4)
O(3)-Cd(1)-C(26)	28.7(2)	O(11)#2-Cd(2)-C(33)	112.9(4)
O(4)-Cd(1)-C(26)	27.7(2)	O(6)-Cd(2)-C(33)	25.3(3)
O(1W)-Cd(1)-C(26)	87.3(4)	O(3W)-Cd(2)-C(33)	90.2(3)
O(9)-Cd(1)-C(26)	120.0(3)	O(12)#2-Cd(2)-C(33)	153.5(4)

O(4W)-Cd(2)-O(11)#2	122.7(4)	O(5)-Cd(2)-C(33)	26.7(3)
O(4W)-Cd(2)-O(6)	140.0(3)	O(11)#3-Cd(2)-C(33)	90.0(3)
O(11)#2-Cd(2)-O(6)	89.2(3)	C(66)#2-Cd(2)-C(33)	134.3(4)
O(4W)-Cd(2)-O(3W)	85.2(6)	O(2)-Ni(1)-N(2)	94.5(2)
O(2)-Ni(1)-N(1)	179.4(2)	O(7)-Ni(2)-N(4)	175.9(2)
N(2)-Ni(1)-N(1)	84.9(2)	O(8)-Ni(2)-N(4)	95.5(2)
O(2)-Ni(1)-O(1)	86.28(18)	O(7)-Ni(2)-N(3)	94.1(2)
N(2)-Ni(1)-O(1)	178.7(2)	O(8)-Ni(2)-N(3)	172.6(2)
N(1)-Ni(1)-O(1)	94.4(2)	N(4)-Ni(2)-N(3)	85.7(3)
O(7)-Ni(2)-O(8)	85.2(2)		

^a Symmetry mode for **1**: #1 -x+1, -y+2, -z; #2 x+1, y, z+2; #3 -x+2, -y+1, -z; #4 x-1, y, z-2.

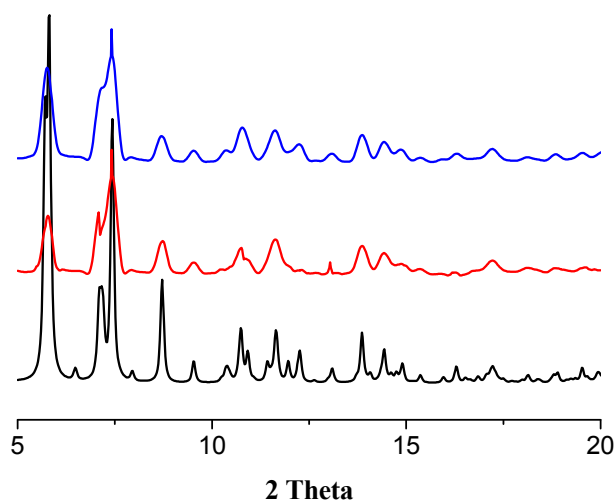


Fig. S1 Powder X-ray diffraction patterns of **1**, black: simulated patterns from single-crystal structure; red: as-synthesized pristine sample; blue: after 3 run catalysis.

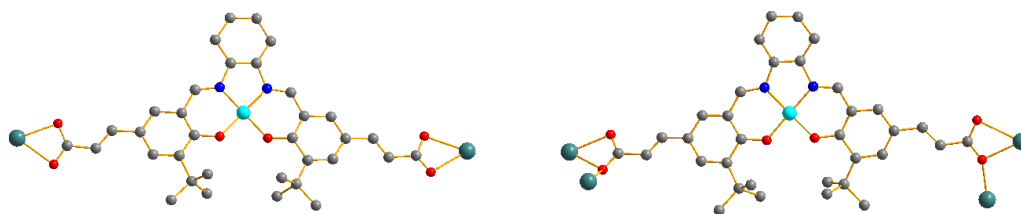


Fig. S2 Coordination modes of NiL units.

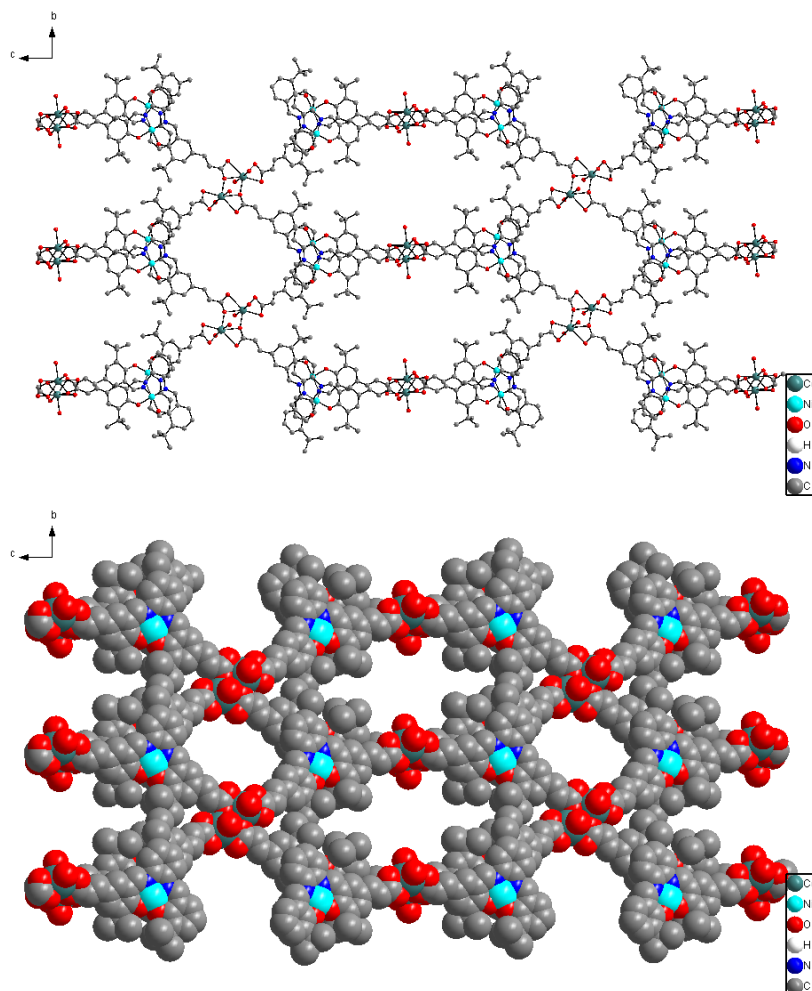


Fig. S3 2D network of along *a*-axis.

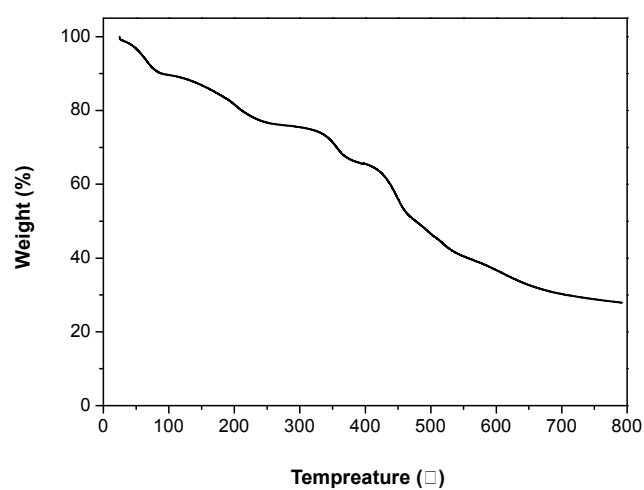


Fig. S4 Thermogravimetric analysis (TGA) curve for **1**. The sample was heated to 800 °C at the heating rate of 10 °C /min.

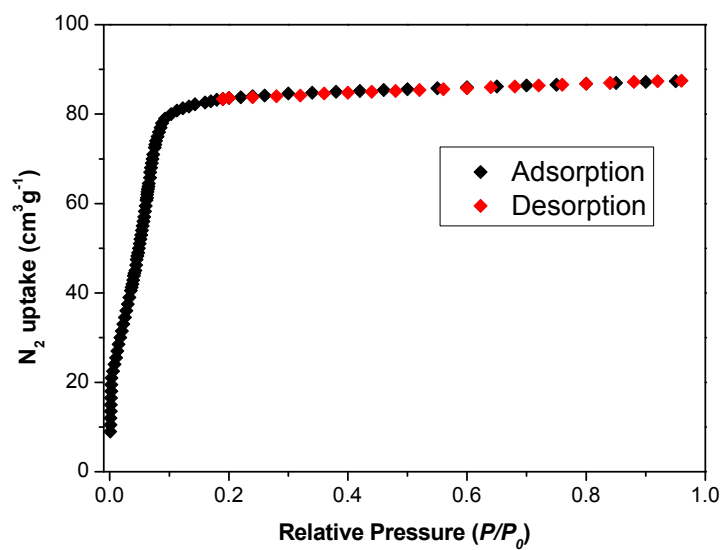


Fig. S5 Nitrogen adsorption isotherm of MOF 1 at 77K.

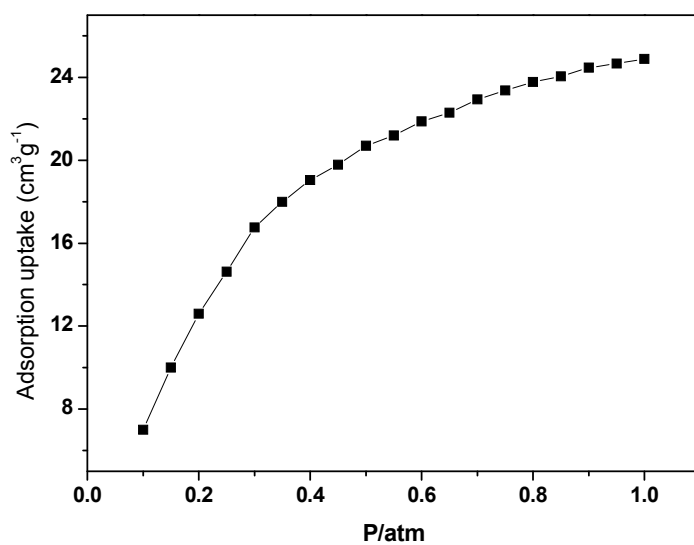


Fig. S6 Carbon dioxide adsorption isotherm for MOF 1 at 273 K.

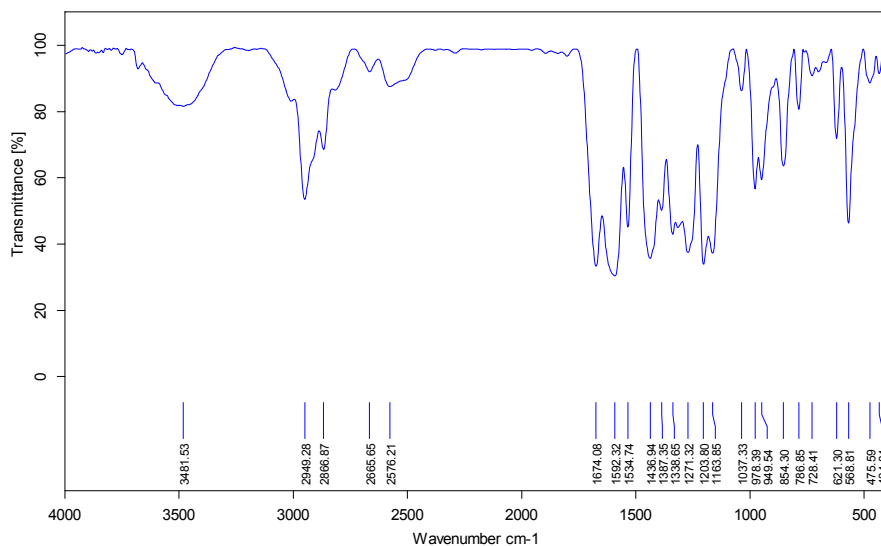


Fig. S7 IR spectrum of ligand Ni-H₂L

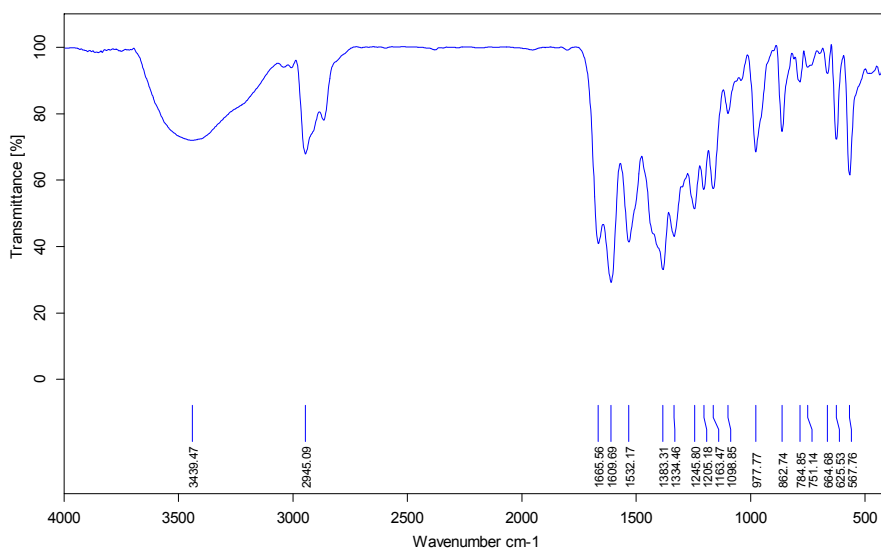


Fig. S8 IR spectrum of ligand MOF 1

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3. A. L. Spek, (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
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